Harmonic Vibrational Effects on Isotropic Hyperfine Coupling Constants

Molecular Hydrogen in Interstellar Ice and

Atomic Relaxation in Doped Silicon

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Abstract

Harmonic vibrational effects on isotropic hyperfine coupling constants, molecular hydrogen in interstellar ice and atomic relaxation in doped silicon.

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Three separate topics are presented covering the temperature dependence of isotropic hyperfine coupling constants, an anharmonic analysis of molecular hydrogen in interstellar ice and the microscopic structure of doped crystalline silicon lattices.

The temperature dependence and vibrational effects of isotropic hyperfine coupling constants are studied using the *ab-initio* density functional methods BLYP and B3LYP with the common double and triple zeta basis sets 6-31G(d,p) and 6-311G(d,p). Harmonic oscillator wavefunction averages for all normal modes of a molecule are accounted for and the temperature dependence is developed from the Boltzmann distribution.

An ab-initio study of the atomic displacements and microscopic structure of phosphorus and arsenic in doped silicon is carried out. The structures and relative displacements are estimated using SCF, DFT and MP2 methods with STO-3G, 3-21G, 3-21G(d,p) and 6-31G(d,p) basis sets with a 13 atom silicon molecular cluster. The calculations are carried out on clusters using empirical parameters for Si-Si and Si-H bond lengths in addition to fully optimised clusters.

Following the discovery of a species thought to be molecular hydrogen in interstellar clouds by IR spectroscopy, *ab-initio* density functional B3LYP calculations are performed to back up experimental and semi-empirical studies of molecular hydrogen in amorphous ice. Anharmonic calculations are carried out on hydrogen molecule adsorbed onto ice and trapped in a cage. The issue of species other than molecular hydrogen and surface transport of hydrogen is addressed.
Statement of Originality

The work described in this thesis is based on work conducted by the author in the Department of Chemistry at the University of Leicester mainly during the period between October 1994 and March 1997

All work in this thesis is original unless otherwise acknowledged in the text or by references and is not being submitted for another degree in this or any other university.

Signed

[Signature]

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Abbreviations and Other Information Applicable Throughout Text.

Hfcc : HyperFine Coupling Constant.
Eqbm : Equilibrium.
Eq. : Equilibrium.
Aiso : Isotropic hyperfine coupling constant.
Vib. : Vibrational contribution.
Tot. : Total.
Freq. : Frequency.

Distances are measured in angstroms (Å).
Hfcc values are in Gauss (G) or a.u.
Hfcc thermal gradients are in units of milligauss per kelvin (mG/K).
Normal mode frequencies are specified as inverse centimetres (cm⁻¹).

All calculations were performed using the GAUSSIAN-94 suite of programs from Gaussian Inc. using a silicon graphics platform (Challenge-XL mainframe, 512MB R4400)
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Chapter 1

Introduction
Introduction

All ab-initio techniques of quantum chemical analysis rely on solving the molecular Hamiltonian for a many-particle system. Solution of the equation for the two particle system composing the hydrogen atom is relatively straightforward and may be found in any standard textbook on the subject [1]. The introduction of another particle such as an electron into the system complicates matters somewhat, the resultant system being a three body one, which is known from the field of celestial orbital mechanics to have no elementary closed solution which has lead to many approximate techniques such as perturbation theory which attempt a solution with differing degrees of success.

In practice the many-particle differential equation is solved using an iterative self consistent field technique with the wavefunctions of the various bound states of the system built up from one electron orbitals that are derived from the analytic solutions for the hydrogen atom. The Hartree-Fock method, the simplest of the various ab-initio techniques, introduces electron-electron repulsion in terms of the interaction of an electron with the averaged fields of the other electrons in the system.

Other methods such as the Møller-Plesset methods use perturbation theory to account for electron correlation, a technique stemming from celestial orbital mechanics, involving the expansion of an unknown problem in terms of a known solvable problem. A newer technique which is halfway between ab-initio and semi-empirical is the density functional family of methods which have their origins in studies of electron gases. DFT methods rely on the theorem of Kohn and Sham who proved that the exchange and correlation energy can be represented exactly as functionals of the electron density (other techniques use wavefunction operators).
The exact solution of the many particle system is out of reach to current mathematics, but considerable research has been directed toward approximations. A commonly employed technique is the Born-Oppenheimer approximation[2] which notes that due to the relative mass of a nucleon to that of an electron, the electrons for all purposes react instantaneously to any change in the nucleon positions which allows separation of the nuclear and electronic energy surfaces. While this simplifies calculations somewhat, it does have an adverse effect of not accounting for contributions arising from nuclear motion to calculated observables which as will be shown in chapter 2 in some cases are not negligible.

This chapter briefly details HF and DFT theory in addition to vibrational mechanics and isotropic hyperfine coupling constants which are of importance to this thesis but is not intended as a full mathematical exposition of the methodologies involved as the functional computer code is now generally standardised in packages such as GAUSSIAN-94 for the basic procedures required (energy calculations, geometry optimisation and normal mode analysis).

**Hartree-Fock theory**

The behaviour of electrons in a molecular system can be described by the many particle Schrödinger equation which is a second order differential equation. The simple form of the equation is deceptive as it is impossible to solve analytically for all but the simplest systems such as hydrogen. A major problem encountered in the solution of the equation is that of finding a suitable state function.

The self consistent field method [3] is the basis of nearly all quantum molecular techniques for solving the Schrödinger equation and stems from Eckart’s theorem which is probably better known as the variation theorem. The variation theorem states that given a
normalisable state function \( \phi \) that is an approximation of the true state function \( \psi \), the expectation of the energy using the trial functions \( \varepsilon \) will be greater than or equal to the true energy \( E \).

\[
H \psi = E \psi \quad [1.1]
\]

\[
\varepsilon = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \geq E \quad [1.2]
\]

If parametised state functions are employed as the trial functions then the condition that the true energy of the bound state that is desired is a lower bound to any trial guesses at the parameters provides a method for the solution of the Schrödinger equation.

The trial state functions must obey certain conditions such as normalisability [1.3], orthogonality[1.4], zero amplitude at the boundary and they must be antisymmetric [1.5] (i.e. the interchange of any two parameters results in the sign of the function being inverted, a requirement due to the fermionic characteristics of electrons).

\[
\int \phi_i \phi_i^* d\tau = 1 \quad [1.3]
\]

\[
\int \phi_i \phi_j^* d\tau = 0 \quad [1.4]
\]

\[
\phi(r_1,...,r_i,...,r_j,...,r_n) = -\phi(r_1,...,r_j,...,r_i,...,r_n) \quad [1.5]
\]

In fact the normalisability and orthogonality conditions are not actually required but do simplify calculations and interpretation enormously. The problem of finding a minimum for \( \varepsilon \) by variation of parameters has lead to a vast area of research. The basic principle involves minimising the differential of the expectation energy \( \varepsilon \) with respect to all its variable parameters:

\[
\frac{\partial \varepsilon}{\partial r_1} = 0, \frac{\partial \varepsilon}{\partial r_2} = 0, ..., \frac{\partial \varepsilon}{\partial r_n} = 0 \quad [1.6]
\]

In some cases this can be achieved by an analytic solution and the equations are
known as secular equations. However, the introduction of mathematically complex wavefunctions and large numbers of parameters soon render this method unviable for large systems which leaves the solution in the domain of iterative gradient descent methods.

To provide flexibility, a molecular orbital is built up from a linear combination of functions normally centred on the nuclei of the molecule and has the form:

$$\phi_i = \sum_{i=1}^{N} c_{n_i} \chi_i$$  \hspace{1cm} [1.7]

where the $c$ are the molecular orbital expansion coefficients and the $\chi$ are known as basis functions. The choice of the basis functions for most computations today is the gaussian function [1.8] because of its ease of handling with the complex mathematics involved rather than the older Slater type functions [1.9] which are much harder to work with.

$$g(\alpha, r) = cx^n y^m z^l e^{-ar^2}$$  \hspace{1cm} [1.8]

$$e(\alpha, r) = cx^n y^m z^l e^{-\alpha |r|}$$  \hspace{1cm} [1.9]

$C$ is a constant factor, $n$, $m$, $l$ are positive non-zero integers which have a relationship to the total angular momentum of the system, $\alpha$ is an expansion factor and $r$ is the radial distance from a given atomic centre.

There are two main differences between the two types of function, one of which is particularly applicable to spin density calculations which form a large part of this thesis. The Slater type functions have an exponential fall-off rather than an asymptotic gaussian fall-off which is much more rapid and more importantly the Slater functions obey a cusp condition at the nucleus which the GTFs do not. In the calculation of hyperfine coupling constants, the description of the nuclear region has been an essential feature for the description of electron density in the core region. In the calculation of hyperfine coupling constants, the description of the core region is essential to the quality of the calculation given the point like...
These molecular orbitals are assembled into determinantal form [1.10, below] which is the most convenient representation that provides for the antisymmetry condition, each orbital having a factor of $\alpha(i)$ or $\beta(i)$ which represents the spin of electron $i$.

$$\psi(r) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(r_i)\alpha(1) & \phi_1(r_i)\beta(1) & \phi_2(r_i)\alpha(1) & \phi_2(r_i)\beta(1) & \phi_{n/2}(r_i)\alpha(1) & \phi_{n/2}(r_i)\beta(1) \\ \phi_1(r_n)\alpha(n) & \phi_1(r_n)\beta(n) & \phi_2(r_n)\alpha(n) & \phi_2(r_n)\beta(n) \end{vmatrix}$$

[1.10]

The above equation represents the closed shell case and applies to the RHF method. The UHF or spin polarised HF method looks similar but allows spin paired electrons to have different spatial orbitals.


$$\sum_{\nu=1}^{N} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{\nu i} = 0$$

[1.11]

where $F$ is the Fock Matrix, $\mu = 1, 2, \ldots N$, $S$ is the overlap matrix and $N$ is the number of electrons in the system. It is at this point that it becomes obvious why an iterative solution must be used to solve this system when the Fock matrix is stated [1.12]:

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda=1}^{N} \sum_{\sigma=1}^{N} \sum_{\lambda=1}^{\text{occupied}} 2 c_{\alpha i} c_{\beta i} \left\{ (\mu \nu | \lambda \sigma) - \frac{1}{2} (\mu \lambda | \nu \sigma) \right\}$$

[1.12]

Where $\mu$, $\nu$, $\lambda$, and $\sigma$ are electrons, $(\mu \nu | \lambda \sigma)$ is the coulomb integral and $(\mu \lambda | \nu \sigma)$ is the exchange integral. Both the Fock matrix and the orbitals are dependent upon the expansion coefficients via a non mathematically separable relationship. Open shell methods in this formalism can regard the $\alpha$ and $\beta$ electrons as two different but related sets of Fock matrices which allows a correct description of many open shell systems but does introduce problems of
spin contamination which require annihilation.

Although this method includes two-electron repulsion integrals which deal with the coulomb repulsion and the exchange interaction, it does not attempt to account for dynamic electron correlation effects which are important for any complete study of a quantum molecular system.

So-called Post SCF methods such as perturbation theory can be used to account for the effects in an approximate way, but one worth mentioning here before DFT methods are dealt with are the techniques based around configuration interaction and multi-configuration SCF which simply stated use a linear combination of the Slater determinants written down earlier in which each determinant represents a particular electronic configuration (i.e. single and double excitations). Big CI based calculations represent the best benchmark calculations available for the solution of the Schrödinger equation, the major problem with them is the vast amount of computer time required for their use. Application to even relatively small organic systems can push the limits of existing computer resources.

*Density functional theory*

Density functional theory takes a different approach to the problems of dealing with electron correlation than previous methods which makes it of particular interest not least because it requires much less computer resources to achieve a result than perturbation or CI based methods.

Kohn and Sham demonstrated that there exists a unique functional that describes the ground state energy and electron density exactly. The problem is that no-one knows what this functional looks like. Current approaches separate the energy into four components;

\[
E = E^{T} + E^{V} + E^{J} + E^{XC}
\]  

[1.13]
E is the kinetic term, E^V is the nuclear-electron attraction term, E^J the electron-electron repulsion term (or Coulomb self-interaction term) and E^{XC} the exchange and correlation term which accounts for exchange energy and dynamic correlation effects. This approach differs from the HF approach by using the electron density directly in the integrals rather than large determinantal wavefunctions with the exception of the kinetic term for which no density based functional is known.

In practice this method does not escape SCF entirely since it still requires an initial fitting of its density field for which SCF orbitals are used. There are a large number of variations on the basic theme of DFT in use, currently the most popular are those due to Becke-Lee-Yang-Parr and Perdew-Wang. These differ mainly in the exchange-correlation functional form employed. E^{XC} can be written as a non specific functional of the \( \alpha \) and \( \beta \) electron densities and their gradient functions [1.14].

\[
E^{XC}(\rho) = \int f(\rho_\alpha (r), \rho_\beta (r), \nabla \rho_\alpha (r), \nabla \rho_\beta (r)) d r 
\]  

[1.14]

Where \( \rho(r) \) is a function for the electron density and \( \nabla \rho(r) \) is the gradient. This functional can be split into two additive parts, the exchange and the correlation parts, each of which itself can either be a local functional (depends on the electron density alone) or a gradient corrected functional (depends on the density and its gradient).

A newer idea that has been developed is the use of Hybrid functionals which briefly stated use a linear combination of the exchange and correlation functionals from various methods (including HF). The coefficients of the combination are determined by fitting to experimental data such as ionisation energies, proton affinities etc. and other benchmark calculation data. Later in this work, the B3LYP hybrid functional is employed for calculation of hyperfine coupling constants in a variety of radicals. This particular functional incorporates components from LDA (Local Density Approximation), HF, B88 (Becke - 1988), VWN3 and
LYP (Lee, Yang and Parr).

DFT methods have taken off in theoretical chemistry due to their success in the calculation molecular parameters and energies. They are known to give good estimation of force fields for vibrational calculations and perform reasonably well at structure calculations. They are of particular use in the field of isotropic hyperfine coupling constants which are sensitive to spin contamination effects, DFT based methods give results that show a very low or zero spin contamination which obviates the need for computationally expensive spin annihilation calculations.

DFT methods do have one drawback however, the integrals for the exchange correlation functional cannot be evaluated analytically which leaves numerical procedures as the only viable option. The integration technique uses a grid of points distributed on a set of radial shells, the quality of the integration depending on the number of points. This can introduce numerical problems and produce results of inadequate quality if the integration grid is not fine enough, but using fine grids increases the CPU resources required.

*Geometry optimisation*

The energy of a molecule is dependent upon its molecular structure, the most well known example being the potential energy curve of a diatomic molecule. A fundamental procedure in molecular mechanics is the determination of a geometry that corresponds to a minimum on the potential surface of the molecule. In a similar way that a stationary or bound state of the system can be found by iteratively solving the Fock equations subject to the variation theorem, the geometry of a molecule may be optimised by attempting to minimise the forces acting upon all atoms.

The force constant matrix (also known as the Hessian) for the molecular assembly
may be calculated as the second derivative of the potential surface with respect to the three spatial co-ordinates (x,y,z) at the atoms of interest. Chain optimisation techniques attempt to descend a 'path' on the force constant surface to a minimum by allowing the atoms to move slightly at each step, with a recalculation of the energy and force constants at each step.

Other modifications of this technique can be used to follow reaction paths and find transition state structures at saddle points on the surface. Although the specifics of the technique used can vary the quality of the optimised structure, especially in difficult cases where there are shallow minima for example, the ultimate control of the quality lies with the calculation of the property surface. A calculation of the normal modes of a molecule at a non stationary geometry will result in negative frequencies being returned. The basis set plays an important role in the determination of the property surface and for any quantitative calculation to be achieved, a high quality basis set must be employed.

Basis sets

As noted earlier, gaussian orbitals are the most commonly employed functions for molecular calculations. A basis set is assembled from atomic orbitals of various angular momenta (i.e. s, p, d functions) which centre on an atom and will later be transformed into molecular orbitals. The main object of the basis set is to provide sufficient spatial flexibility to accurately describe the electron density of a molecule. Early basis sets did not employ polarisation functions such as p and d orbitals. It is now recognised that they are essential in any basis set to provide directional flexibility of the electron density.

A basis set is usually provided as a set of gaussian primitives which are of fixed size in space. The actual basis orbitals of the set are themselves composed of a linear combination of these primitives. A minimal basis set provides only those basis functions required for the
description of the electronic structure of the system. i.e. for carbon it would provide 1s, 2s, 2p_x, 2p_y and 2p_z only.

An extension of this is the split valence basis set which provides one or more functions of differing spatial size for each atomic orbital. A double zeta basis has two functions for each orbital and a triple zeta, three. The 6-31G and 6-311G basis sets are examples. Beyond this, the addition of polarisation functions allows enhanced flexibility over that of the split valence basis set by adding in more angular momentum functions than are required. These are usually indicated after the basis set thus 6-311G(d,p) where the first letter refers to the orbitals added to the heavy atoms and the second to hydrogen atoms.

A further enhancement that can be made is the addition of diffuse functions which are of use in calculations of excited states and anions where the electron density extends outward from the nucleus.

Vibrational motion

Vibrational motion is potentially one of the most important theoretical areas due to its relationship to, and effects upon, spectroscopic observations. Vibrational motion can be studied using techniques such as IR and Raman spectroscopy which rely on absorption and scattering of light respectively, but it causes effects on other observations such as vibrational splitting of electronic energy levels and it is the basic mechanism for thermal modulation of observables (such as hyperfine coupling constants). The definitive reference for molecular vibrations is Cross, Decius and Wilson [5].

The vibrational motion of a nuclear assembly is governed by the interaction of the system with its own energy surface. The most common method of description of this interaction is known as the simple harmonic oscillator model, based upon a spring, which
describes a particle of mass \( m \) moving in a potential field \( V(x) = \frac{1}{2}kx^2 \) where \( k \) is the force constant. This classical mathematical model has the virtue of having an exactly soluble quantum analogue for an \( N \) atom molecule as opposed to a more realistic model for the motion which employs anharmonic potentials for which one usually has to resort to more complex mathematics or even numerical techniques. The exact solutions for the simple one dimensional quantum harmonic oscillator are noted in chapter 2 where a model for the temperature dependence of an observable is developed.

For a diatomic molecule, the classical frequency of its fundamental normal mode can be calculated from

\[
v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]

[1.15]

where \( k \) is the force constant and \( \mu \) is the reduced mass of the molecule, excited state energies can be obtained from the familiar \( E = (n + \frac{1}{2})\hbar v_0 \). From a first principles angle this presents something of a problem since experimentally the force constants are estimated from the above formula using the observed frequencies but we know neither. This situation can be resolved by noting that the force constant is the second differential of the energy surface with respect to space

\[
V(x) = \frac{1}{2}kx^2
\]

[1.16]

and

\[
\frac{d^2}{dx^2}V(x) = k
\]

[1.17]

In the situation of an \( N \) atom molecule this principle can be extended by calculating the diagonalised matrix of the second differential of the energy surface with respect to the \( x, y \) and \( z \) co-ordinates on each atom. This process will give the \( 3N \) independent harmonic force constants from which the \( 3N-6 \) normal mode frequencies can be calculated after removing
three rotation and three translations of the molecule. For a thorough exposition of this topic, see [3]. Although it must be regarded in most practical situations as a mathematical artefact, the motion of the molecule can be decomposed into $3N-6$ (for a non-linear molecule) sets of motion vectors describing the instantaneous displacement of each atom in a particular normal mode away from the energy minimum. This model of the motion finds an application in visualisation of the vibrational process, the normal modes of water probably being the best known example, and more importantly to this work it can also be applied to problems of vibrational averaging as will be addressed in chapter 2.

The effects of anharmonicity are present in all real-world vibrations, for the most part the force field estimations of harmonic analysis especially that of the density functional methods are adequate for most applications. In some cases a treatment of anharmonic effects are required. The analysis of molecular hydrogen in ice (chapter 4) employs anharmonic analysis by two methods to obtain an accurate theoretical estimate of the $\text{H}_2$ stretching frequency. The simplest procedural method is to numerically integrate to obtain a zero point energy, the technique of which is noted in chapter 4. A secondary method also noted in chapter 4 involves the diagonalisation of a matrix of the cross products of basis functions taken from the set of exact solutions of the harmonic oscillator.

**Hyperfine coupling constants**

Hyperfine coupling constants arise from an interaction between the magnetic moments of the unpaired electron density and nuclei. This interaction can be resolved into two parts, an anisotropic interaction which is expressible as a tensor and an isotropic part known as the Fermi-contact interaction which is rotation invariant with respect to an external magnetic field. The isotropic interaction can be expressed (for the hydrogen atom) as,
where \( a_H \) is the Fermi contact parameter, \( g_e, g_0 \) and \( g_H \) are the gyromagnetic ratios of the electron, free space and the proton, \( \beta_H \) is the Bohr magneton for hydrogen and \( \rho_s(r_H) \) is the expectation value of the spin density distribution at the hydrogen nucleus.

The isotropic hyperfine coupling constant can be measured from electron spin resonance data as the separation of peaks in the ESR spectrum. ESR relies on the principle that when an external magnetic field is applied to an atom, the electron will tend to align its spin state to that corresponding to the lowest energy. A transition to a higher energy can be achieved by the absorption of radiation of the correct wavelength which is governed by the condition;

\[
hv = g_e \beta H \tag{1.19}
\]

where \( \beta \) is the Bohr magneton, \( B \) is the external field strength and \( g_e \) is the gyromagnetic ratio for the electron (2.0023). This resonance peak can develop multiplets due to a secondary interaction of the electron spin angular momentum with that of the nucleus (if it has an intrinsic spin) which causes a number of peaks to develop centred on the resonance point. With a nucleus of spin 1/2 such as a proton, two peaks will be observed, with higher nuclear spins, \( 2I+1 \) multiplets will be observed where \( I \) is the nuclear spin.

In orbital terms the isotropic hfcc interaction arises from s orbitals which have the virtue of having a non-zero amplitude at the nucleus. Pure \( \pi \) radicals can give isotropic interaction terms, this is due to the effects of other electronic configurations mixing with the ground state which can lead to a polarisation of the s orbitals and hence an imbalance in the \( \alpha \) and \( \beta \) spin densities. A generally accepted point for any theoretical calculations of isotropic hfcc values is that consideration of electron correlation effects (CI) are essential if accuracy is
to be obtained.

An equivalent way of considering the problem which gives a better visualisation is by considering polarisation effects which give an explanation of the sign of the hfcc. An $\alpha$-spin electron in a half-occupied atomic $p$ orbital will interact, via the exchange interaction, differently with the $\alpha$ and $\beta$ spin electrons of a doubly occupied inner shell $s$ orbital leading to a polarisation of the spins at the nucleus. Although the electron in the $p$ orbital has a node passing through the nucleus, its effect will be experienced by the electrons of the $s$ orbital. The object of chapter 2 is to study the effects of vibrational averaging on the isotropic hyperfine coupling constants for $\alpha$ and $\beta$ protons by averaging the hfcc along the normal co-ordinates using density functional methods.
References


Chapter 2

The Temperature Dependence of Isotropic Hyperfine Coupling Constants
2. The Temperature Dependence of Isotropic HFCC’s.

Introduction

Electron spin resonance (ESR) spectroscopy is a widely used technique for the study of radical and radical-like systems in many areas of physical science from chemistry to semiconductors, yielding data about the structure, bonding, reactivity, environment and electron distribution within the radical. The data is generally presented in the form of hyperfine coupling constants (hfcc), the isotropic or Fermi-contact component and the anisotropic component. Theoretical prediction of the hfcc serves as a valuable counterpart to experimental ESR data, often enabling interpretation and assignment of the data to a structural and/or environmental model when such a correlation is initially unclear from the experimental data alone due to the action of degrading effects.

Usually the theoretical prediction of hfcc’s is limited to calculations performed at the equilibrium geometry of a molecule with respect to some method, or in some cases at an idealised geometry derived from other theoretical calculations or experimental data. While in many cases this approach is sufficient to allow assignment of experimental data, it takes no account of contributory effects that arise from vibrational action and the attendant thermal modulation of these contributions which may be considerable even at the zero point level in some situations.

In this chapter we will be concerned with a theoretical description of the vibrational modulation effects upon the isotropic hyperfine coupling constant for hydrogen and its isotopic variants, deuterium and muonium, in small radicals by employing the harmonic oscillator approximation and accounting for the contributions of all normal modes of the molecule. This will be extended to consider the temperature dependence of the isotropic hfcc in terms of the Boltzmann distribution. Hereafter the term ‘hfcc’ will refer to the isotropic
The Temperature Dependence of Isotropic HFCC's

Overview

The database of literature of both experimental and theoretical studies of radicals and their properties is very large. Some radicals such as the methyl radical have for a long time been known to exhibit a significant temperature dependence effect on the observed hfcc. While this effect is sometimes related in experimental reports, the theoreticians seem to have left it relatively untouched compared to the work performed on estimation of hfcc contributions from molecules at their equilibrium geometry.

It has been assumed for a long time that the temperature dependence phenomenon arises as a consequence of the vibrational contributions of a molecule to the observed hfcc. While the large amount of work on equilibrium contributions shows that most of the observed value can be accounted for without recourse to vibrational contributions, there is always a small discrepancy that can be partially accounted for by, a) deficiencies in the theoretical methods, and b) neglecting zero-point and temperature effects arising from vibrational motion.

The methyl radical was the subject of some of the earliest theoretical studies by Moss [1] and later Schrader [5, 38]. The methyl radical is convenient from both an experimental and theoretical point of view. The radical is planar in its equilibrium configuration (Herzberg [42]) with $C_{3v}$ symmetry possessing a nodal plane in the molecular plane. This nodal plane would, from a simplistic precept, infer that the protons should display no Fermi-contact interaction. McConnell [43] solved the problem of introducing unpaired electron density into the proton $1s$ orbitals in terms of an electron spin polarisation mechanism. This effect alone was not expected to provide a significant contribution from modes executing in the molecular plane turning attention to the out-of-plane bending mode which breaks the symmetry and
allows the protons to sample the delocalised unpaired electron density in the $p$ orbital directly via a hyperconjugation mechanism.

The mathematical approach to the problem of the temperature dependence taken by Moss was to average the hyperfine coupling over the out of plane vibration using a transform of the bending angle into the normal co-ordinates. A Boltzmann average over all harmonic vibrational levels leads to an expression of the form:

$$\frac{hv}{2F} \coth \frac{hv}{2kT}$$

for a given mode where $F$, $v$ and $k$ are the force constant, vibrational frequency for the mode and Boltzmann’s constant respectively.

Subsequent to this Schrader used orbital following techniques and wavefunction averaging over a restricted number of the lower vibrational states in an attempt to quantitatively explain the hyperfine couplings and their thermal gradient. This work employed a semi-empirical approach and required an adjustment to make estimated couplings conform to experiment. The thermal gradient was underestimated by the technique as 1.35mG/K compared to the experimental value of 2.1mG/K.

Although these approaches had some success with the methyl radical, they did not achieve quantitative accuracy but did manage to give a qualitative description of the process. Theoretical deficiencies in the estimation of spin density are an obvious first target for the failure but there other sources of error, some obvious and some more obscure that obfuscate the problem.

The first is the use of a harmonic oscillator approximation. Although the SHO is the basis of current standard vibration analysis (See Cross, Decius and Wilson [61] for a definitive work) and in most cases performs perfectly adequately, it must be remembered that it is a mathematical decomposition of a real problem that in most cases has restricted physical
significance, another example being the use of orbitals to describe electron density. In reality vibrational motion is most likely to behave in a chaotic manner, a recent paper by Shen and Pritchard [4] highlighted this in relation to the problem of estimating the rate constant of the unimolecular rearrangement of methyl isocyanate to methyl cyanide which is very sensitive to the shape of the potential surface along the reaction path.

Since a complete map of the potential surface over all independent variables is impossible currently for all but the simplest molecules, another way to enhance the description of the vibrational motion is to use calculations akin to reaction path calculations where the large amplitude motion (LAM) of a molecule is separated and averages over the remaining small amplitude motions (SAM) are taken at points along this path. Relating this to the methyl radical, when the radical bends, the other motions will be executing at the same time. If we consider the bending motion as sufficiently slow compared to the other vibrations, it can be regarded as the LAM and the remaining five as the SAM’s. Some conceptual work has been done in this area by Barone et. al. [8, 52] from the angle of examining the quadratic environment along the LAM with subsequent perturbation theory to examine anharmonicity.

Secondly, not considering anharmonicity may cause a problem in some cases. This will not be particularly relevant to heavy isotopes and protons in most cases but would be of considerable importance where muonium is concerned as this is very light and samples a large area of the potential surface. This is unlikely to be a point of major concern in the methyl radical.

Finally there is a source of error that is particularly pertinent to the methyl radical calculations. Both Moss and Schrader work from the assumption that the co-ordinate $\theta$ (an angular co-ordinate describing the out of plane angle of the methyl radical) can be regarded as proportional to the normal co-ordinate, which is valid for small $\theta$. The use of an angular co-
ordinate introduces a problem with excited state wavefunctions in that they may have a considerable amplitude over an increasing angular range which could lead to numerical difficulties.

More recently the temperature dependence of the HC\textsubscript{60} and MuC\textsubscript{60} (Mu = Muon) adducts have been studied by Morton \textit{et. al.} [2] using the formulae due to Moss, but with the intent of accounting for the contributions arising from all normal modes. This approach reproduced experimental results reasonably well despite the need to scale the results for known deficiencies in the semi-empirical method used. In actuality, only those modes which would have made a considerable contribution to the hfcc were included, with particular attention concentrated on the wagging, rocking and stretching modes of the attached proton (or muon). This approach of restricting the number of modes considered has been applied elsewhere particularly when a muon is involved since the muon moves so fast its motion can be considered decoupled from the rest of the molecule.

An interesting approach to the problem of accounting for extraneous effects beyond direct equilibrium contributions to the hfcc has been applied by Fortunelli \textit{et. al.} [25, 26] to small organic radicals which can be best described as a transfer of parameters procedure. The technique is to calculate the equilibrium hfcc of an \( \alpha \) or \( \beta \) proton for a small radical such as methyl or ethyl using some method. The ratio of this value with the experimental value is then found. An estimation of the experimental proton hfcc for another similar radical may then be made by multiplying the equilibrium hfcc calculated by the same method by the previously found ratio.

Surprisingly the technique is reasonably good for closely related radicals in the estimation of \( \alpha \) and \( \beta \) proton hfcc, but fails somewhat when applied to \( \gamma \) proton hfcc. The principle behind the procedure is that in similar radicals the extraneous effects will scale
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proportionately with increasing size of similar molecules. This technique is of some interest here as it provides a percentage estimate of the outstanding contributions above the equilibrium, however, it offers no particular insight into the mechanisms at work.

In this chapter the principle of accounting for averages over all normal modes is applied to a variety of small radicals, both organic and inorganic, with various characteristics from the diatomic OH radical to the large bicyclo [2,2,1] hept-2-ene radical using *ab-initio* density functional theory. The thermal variation is developed from a different angle to those previously by creating a large finite sum of Boltzmann weighted wavefunction averages over an ensemble of exited states of a harmonic oscillator. Although the analytic approach using the coth() formulae are perfectly applicable, a simpler approach has been taken to provide a clearer breakdown of the problem and to make more information available during processing.

In the subsequent calculations, the BLYP and B3LYP density functional methods have been selected for calculations of geometry and the proton hfcc's. The common 6-31G(d,p) and 6-311G(d,p) basis sets, which are of double zeta and triple zeta quality with polarisation functions, were employed rather than specialised spin density basis sets such as those due to Chipman[11] because these basis sets are well characterised in a wide variety of calculations from molecular geometry to hfcc calculation and additionally they are coded into the GAUSSIAN-94 package which was used for all calculations.

A recent paper by Batra [7] *et. al.* highlighted the effectiveness of DFT based methods for use in hfcc calculation of organic radicals even when applied at a non-equilibrium geometry such as UHF/3-21G* which was found to be effective. Additional features of DFT methods which makes their application to this sort of problem attractive are their good estimation of force fields in polyatomic molecules for normal mode analysis[13,15] and their estimation of the ground state electron density (at least for diatomic molecules) is very close
to a QCISD reference standard[3]. Other references attest to the abilities of DFT based methods in a variety of settings [14, 18, 19, 40, 41]

Methods

The temperature variation phenomenon has been investigated in terms of the harmonic oscillator approximation in which all normal modes of the molecule are accounted for. The harmonic oscillator approximation is the standard method in use today for the analysis of the vibrational modes of polyatomic molecules since, for every-day use, it is the only mathematically reasonable analytic method available and has the advantage of providing a simplistic conceptual breakdown of a molecular vibration. The harmonic oscillator approximation possesses a Hamiltonian [2.2] for which analytic solutions for the wavefunctions of the various vibrational quantum states can be readily obtained and in addition to this, the zero-point averages of properties over the wavefunctions are expressible as simple equations (e.g. the well known zero-point energies, \((n + \frac{1}{2})hv\) for \(n=0\)).

As has been touched upon in the overview, the general methodology for previous investigations of the effect of vibrational contributions to the observable hfcc, were restricted to consideration of a restricted subset of the normal modes of the molecule, particularly those in which it was assumed that the atom of interest would make a significant contribution, the other modes being ignored on the basis that they make insignificant contributions to the total observable. While this may be justifiable in a number of cases, there are two good reasons not to impose such a restriction in a consideration of the temperature dependence problem;

- The temperature dependence is generally governed by low-frequency modes, whereas there are other modes for which the atom of interest can be regarded as moving with sufficient amplitude to make a significant contribution to the observable which, in the case of
hydrogen and the muon, are generally higher frequency modes (e.g. a decoupled muon stretching mode).

- The sum of the contributions from the other modes in the molecule cannot be guaranteed in all cases to be negligible.

The process of deriving a temperature dependence equation for the hfcc of an atom in a radical can be considered in the following steps.

- Geometry optimisation and calculation of the normal modes and co-ordinates.
- Single point calculation of properties along the normal co-ordinates.
- Curve fitting and computation of property averages.
- Calculation of temperature variance of the property.

Although simple in concept, the analysis of all normal modes of a molecule generates a very large amount of data and involves an enormous number of calculations. In view of this the procedure was automated by the use of AWK, shell scripts and C++ in order to both speed up the data processing steps and to remove the possibility of human error in the data processing.

**Geometry optimisation.**

The geometry optimisation and normal mode calculation were carried out using the same theoretical method and basis set using the standard algorithms provided by GAUSSIAN-94 to locate a minimum energy geometry. Despite evidence that DFT calculations of the hfcc are just as good at a non stationary geometry generated by a computationally cheaper method [7], the same method and basis were used as a pair in all cases for both the optimisation and frequency calculations due to the mathematical point that the normal mode calculations are only valid at a stationary point on the energy surface.
**Single point calculations.**

The variation of the hfcc and potential along a normal co-ordinate was sampled by expanding the molecular geometry along the 3-space vector for the normal co-ordinate in a series of steps to provide at least 4 sample points in either direction along the co-ordinate. At each step a single point calculation was performed using tight cut-offs on the convergence of the SCF integrals (GAUSSIAN option scf=tight, equivalent to a maximum change of $10^{-6}$ in any element of the density matrix) to ensure an accurate and consistent value. The expansion points along the normal co-ordinate were chosen so as to provide:

- An accurate description of the property variation along the normal co-ordinate, particularly around the potential surface minimum (A description of the curvature at the minimum is essential for a harmonic oscillator).
- To provide sufficient points for accurate non-linear regression analysis, while not generating an excess of single point calculations which would massively increase the CPU time required to calculate the samples.

**Curve fitting.**

Because of the finite number of samples taken along a normal co-ordinate, to increase the amount of information available the sample points are fitted to a polynomial equation of the form:

$$a(x) = a_0 + a_1x + a_2x^2 + \ldots + a_nx^n$$  \[2.1\]

by the use of polynomial regression analysis, the details of which can be found in any suitably advanced statistics textbook. In practice the potential and the hfcc samples were fitted to cubic curves, the accuracy of the curve fitting being checked explicitly by backsubstituting.
the sample co-ordinates \( x \) and finding the absolute difference in the computed sample value with the recomputed sample value. An acceptable fit was judged to be one with no difference greater than \( 10^{-5} \) for any sample point. As a further check, the variation of potential along the normal co-ordinate should have a positive \( a_2 \) value, if it is negative, this means that the curve is inverted which is an unacceptable situation. In addition to this, the \( a_0 \) values should all be essentially identical and equal to the value of the property calculated at the equilibrium position.

*Property averages over a harmonic oscillator wavefunction.*

The contributions to an observable arising from the zero point motion of the molecule are estimated as an average over the harmonic oscillator wavefunction. As a consistency check upon the averaging procedure, the averages of the energy are computed as well as the hfcc averages which provides a reasonably sensitive test of the averaging process. The calculated zero point frequency should closely match the harmonic frequencies as calculated initially by GAUSSIAN, the difference being typically less than 5%.

We would not expect an exact match but if a large discrepancy exists here, then it can be assumed that there is a problem with the estimation of the hfcc average. The major source of error in this procedure arises from the sampling procedure used to describe the property variation along a normal co-ordinate. The GAUSSIAN values for the normal mode frequencies are calculated as an analytic derivative whereas a sampling procedure inherently introduces errors relative to this technique.

The harmonic oscillator wavefunctions can be found as analytic solutions to the one-dimensional Schrödinger equation [2.2] for the simple harmonic oscillator (SHO) for a mode \( i \) and a vibrational quantum level \( n \);
The harmonic oscillator wavefunctions are expressed as the product of a Hermite polynomial $H_n(x)$ and an exponential;

$$\psi_{i,n} = A_{i,n} H_n(\xi_i) e^{-\xi_i^2/2} \tag{2.3}$$

Where $A_{i,n}$ is a normalisation factor [eqn. 2.5] and $\xi_i = x_0 \sqrt{\gamma_i}$ is the normal co-ordinate for the normal mode $i$. The factor $\gamma_i$ is given by;

$$\gamma_i = \frac{4\pi^2 \mu_i \nu_{0,i}}{h} \tag{2.4}$$

where $\mu_i$ is the reduced mass and $\nu_{0,i}$ is the fundamental harmonic frequency for mode $i$. The factor $A_{i,n}$ in [2.3] is the normalisation constant which is given by;

$$A_{i,n} = \left( \frac{1}{2^n n! \sqrt{\pi}} \right)^{\xi_i} \tag{2.5}$$

The Hermite polynomials $H_n(\xi)$ are given by the recursion relationship [2.6]. Given the initial polynomials, $H_0(\xi) = 1$ and $H_1(\xi) = 2\xi$, successive polynomials can be derived;

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi) \tag{2.6}$$

Using these wavefunctions, the average of a property represented by a function such as [eqn. 2.1] can be found (a process identical to calculating an observable such as energy);

$$<a>_{i,n} = \int \psi_{i,n}(\xi) a_i(\xi) \psi_{i,n}^* \, dx \tag{2.7}$$

The square of the harmonic oscillator wavefunctions are symmetric about $\xi=0$ which leads to any odd power terms in the polynomial representation [2.1] of a property averaging out to zero over the integral. We can conveniently restrict attention to the polynomial $a_i(x) = a_0 + a_2 x^2$
which, for the ground state \( n=0 \) of mode \( i \), gives an integral of:

\[
\langle a \rangle_{i,0} = \frac{a_{2,i}}{2\gamma_i}
\]  

[2.8]

The wavefunction average of the property for a given mode is a simple function of the polynomial coefficient for \( x^2 \) and \( \gamma \). For the excited vibrational states, \( n=1,2,3,.. \), the relationship is simply:

\[
\langle a \rangle_{i,n} = 2(n + \frac{1}{2})\langle a \rangle_{i,0}
\]  

[2.9]

**Boltzmann averages.**

The statistical distribution of an ensemble of molecules at a temperature \( T \), generally obeys the Boltzmann distribution which describes the partitioning of the molecules between the available states. If there are \( N \) molecules distributed over \( n \) states of energy \( E_n=E_0-E_n \), the Boltzmann distribution for the number of molecules in a given state \( j \) has the form:

\[
n_j = \frac{N e^{-\beta E_j}}{\sum_n e^{-\beta E_n}}
\]  

[2.10]

Dividing both sides by \( N \), we get the probability distribution form:

\[
p_j = \frac{e^{-\beta E_j}}{q}
\]  

[2.11]

where \( q \) is known as the molecular partition function;

\[
q = \sum_n e^{-\beta E_n}
\]  

[2.12]

and \( \beta = \frac{1}{kT} \), \( k \) is the Boltzmann constant and \( T \) is the temperature.

In the case of a harmonic oscillator, the vibrational energy levels are equally spaced and are multiples of each other. In this situation, the partition function \( q \) can be expressed as a geometric progression, for which a sum to infinity may be written, simplifying the equation
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for the probability of occupation of a given level $\varepsilon_j$. From our definition above, $\varepsilon_0=0$, the next state is $\varepsilon = \hbar \nu_{0,1}$ (i.e. $\Delta\varepsilon=\hbar \nu$), we can write $q$ as;

$$q = 1 + (e^{-\beta\varepsilon}) + (e^{-\beta\varepsilon})^2 + \ldots \quad [2.13]$$

The sum of $[2.13]$ to infinity is;

$$q = \frac{1}{1 - e^{-\beta\varepsilon}} \quad [2.14]$$

hence the probability of occupation for a quantum level $j$ becomes;

$$p_j = (1 - e^{-\beta\varepsilon}) e^{-\beta\varepsilon} \quad [2.15]$$

The temperature variation of an observable

Now that we have a model for the distribution of molecules in various vibrational states and a description of the observable average of a property for a given vibrational quantum level corresponding to a particular mode, a representation of the temperature variation of the observable in terms of the probability weighted Boltzmann average of the wavefunction averages of the property at a given temperature may be written. For a given normal mode $i$, the contribution to the total observable at a given temperature $T$ will be;

$$\langle a \rangle_{i,T} = \sum_{n=0}^{\infty} p_{n,i} \langle a \rangle_{n,i} \quad [2.16]$$

(where $n$ is a given quantum state). This can be written as;

$$\langle a \rangle_{i,T} = 2\langle a \rangle_{0,i} \sum_{n=0}^{\infty} (1 - e^{-\beta\varepsilon}) e^{-\beta\varepsilon} (n + \frac{1}{2}) \quad [2.17]$$

from which it follows that the estimated observable of the property $a$ at a given temperature $T$ will be the sum of $[2.17]$ over all normal modes $i$ added to the calculated equilibrium value of the property at the equilibrium geometry;

$$\langle a \rangle_T = a_{eqbm} + \sum_i \langle a \rangle_{i,T} \quad [2.18]$$
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This equation when calculated over a suitably large number of vibrational states gives the same curve form as the previously mentioned formulae employing coth functions.

Results

A variety of radicals have been studied ranging from OH, a simple diatomic through delocalised planar-\(\pi\) radicals such as allyl to the larger flexible bicyclo [2,2,1] hept-2-ene radical. Where temperature dependence data for the radical is available, this is compared to the theoretical prediction from the previously specified model, otherwise the temperature is assumed to be 298K and zero point vibrational contributions are compared to experimental data.

The radicals studied were;

- Hydroxyl and amino radicals, OH and NH\(_2\).
- The formyl radical, HCO.
- The CH\(_2\)CH and CH\(_2\)N radicals.
- The methyl and ammonium cation radicals, CH\(_3^+\) and NH\(_3^+\).
- The allyl radical, CH\(_2\)CHCH\(_2\).
- The bicyclo [2,2,1] hept-2-ene radical.

These radicals represent a cross section of a number of important classes. Diatomics represent the simplest type of radical. From a theoretical angle they exist in a one dimensional potential surface enabling a complete map of their energy space to be constructed. The triatomic HCO radical possesses three independent variables has been recently mapped by Webster[23] using an anharmonic analysis. Beyond the triatomic radicals, complete mapping of the energy and property surface of the molecule becomes an impossibility with current computational power and theoretical approaches dictating a need for alternative techniques.
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such as normal mode analysis.

The methyl radical is the smallest example of a \( \pi \) radical. The vinyl radical is a small delocalised \( \pi \) radical and the allyl radical is an example of an alternate \( \pi \) radical. Radicals possessing a \( \pi \) system are known as rigid or semi-rigid molecules and can exhibit features such as restricted internal rotation. The bicyclo [2,2,1] hept-2-ene radical is an example of a much larger semi-rigid radical, its flexibility being restricted by the cage structure. This radical presents a large number of normal modes, including several at low frequency involving motion of the cage and hence would present a more interesting challenge for a theoretical model.

All hfcc conversions from units of a.u as given by GAUSSIAN-94 into units of gauss have been corrected for the small variations in the spin density at an isolated H nucleus as predicted by a given method / basis combination. From analytic calculations[19], the isolated H nucleus should have a spin density of \( 1/2 \) a.u giving a value of 508G or 1420 MHz, however, the incomplete description of the nuclear potential in any given method leads to a slightly different value. The Fermi-contact values for a free hydrogen atom and their ratio to \( 1/2 \) are presented in table 2.1 below.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis set</th>
<th>Fermi-contact / a.u</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>0.3031690806</td>
<td>1.04994</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>0.3016362195</td>
<td>1.05527</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311++G(3df,3pd)</td>
<td>0.2995990735</td>
<td>1.06245</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>0.3010583208</td>
<td>1.05730</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>0.2970468094</td>
<td>1.07158</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311++G(3df,3pd)</td>
<td>0.2955124323</td>
<td>1.07715</td>
</tr>
</tbody>
</table>

Ratio taken with \( 1/\pi \) (0.318309886)

Where an isotopic substitution has taken place, the hfcc are scaled where stated by the ratio of the magnetic moments for the isotope and a proton. For the deuterium atom this is \( 1/6.51437 \). For a muon it is 3.18335. The Fermi-contact values in units of a.u. presented in tables of the wavefunction averages by mode have not been scaled and are therefore directly
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comparable with values from GAUSSIAN.

The OH radical.

The diatomic radicals are an excellent starting point for the study of the effect of molecular motion upon observables due to the simple one dimensional potential energy surface that the radical exists in. This radical has been studied in the gas phase by Radford[44] who reported a value of -26.7 gauss for the proton hfcc. A radical thought to be hydroxyl has been studied in γ-irradiated ice and liquid water with a proton hfcc of +41.3 gauss [information from ref. 60].

The theoretical calculations are directly identifiable with results in the gas phase, and also to a lesser degree, those in rare-gas matrices. The hfcc of those species in ice or water will be ignored due to the possibility of environmental effects.

Table 2.2 below shows the results of density functional calculations and the zero point vibrational contribution calculated by each method, the hfcc values having been corrected for the spin density of an isolated H atom estimated by a particular method / basis.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Eq / G</th>
<th>Vib / G</th>
<th>Tot / G</th>
<th>Freq</th>
<th>Re-Freq</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-24.21</td>
<td>-0.41</td>
<td>-24.62</td>
<td>3538.08</td>
<td>3541.29</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>-24.01</td>
<td>-0.43</td>
<td>-24.44</td>
<td>3549.63</td>
<td>3553.07</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-22.33</td>
<td>-0.36</td>
<td>-22.69</td>
<td>3569.02</td>
<td>3572.33</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-25.50</td>
<td>-0.44</td>
<td>-25.95</td>
<td>3694.14</td>
<td>3697.66</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>-25.62</td>
<td>-0.47</td>
<td>-26.09</td>
<td>3702.17</td>
<td>3705.76</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-24.05</td>
<td>-0.40</td>
<td>-24.45</td>
<td>3711.50</td>
<td>3715.06</td>
</tr>
</tbody>
</table>

Eq - Equilibrium contribution; Vib - Vibrational contribution; Tot - Total
Freq - GAUSSIAN-94 Harmonic frequency; Re-Freq - Recalculated frequency.

The first noticeable aspect of these results is the small value of the vibrational contribution, a not totally unexpected result since the molecule possesses only one high frequency mode with limited range to sample the property surface. This can be compared to the results for OD and OMu in tables 2.3 and 2.4 where OD shows a smaller contribution and
OMu a much larger one. This isotope effect can be directly attributed to the mass difference between the systems and the way it affects the sampling of the surrounding potential surface.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Eq / G</th>
<th>Vib / G</th>
<th>Tot / G</th>
<th>Freq</th>
<th>Re-Freq</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-24.21</td>
<td>-0.30</td>
<td>-24.51</td>
<td>2575.76</td>
<td>2578.38</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>-24.01</td>
<td>-0.32</td>
<td>-24.32</td>
<td>2584.16</td>
<td>2586.84</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-22.33</td>
<td>-0.27</td>
<td>-22.59</td>
<td>2598.28</td>
<td>2600.89</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-25.50</td>
<td>-0.32</td>
<td>-25.82</td>
<td>2689.37</td>
<td>2691.97</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-25.62</td>
<td>-0.34</td>
<td>-25.96</td>
<td>2695.21</td>
<td>2697.98</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-24.05</td>
<td>-0.29</td>
<td>-24.34</td>
<td>2702.01</td>
<td>2704.79</td>
</tr>
</tbody>
</table>

Eq - Equilibrium contribution; Vib - Vibrational contribution; Tot - Total
Freq - GAUSSIAN-94 Harmonic frequency; Re-Freq - Recalculated frequency.

The majority of the variation of the total hfcc arises from the equilibrium contributions estimated by the various calculations, the closest to experiment being the B3LYP/6-31G(d,p) result for OH. It is at this point that care must be exercised for reasons noted earlier. Is the similarity to experiment because the model describes the system very well, or is it mere co-incidence? The vibrational contributions vary in absolute terms by a relatively small amount, but the equilibrium values vary by a much larger amount. The difference between the smallest and largest basis sets is just over 1.5G, larger than the vibrational contribution. With a variability on this magnitude it is unsurprising that a coincidence with experiment can be found by variation of the method and basis set.

The vibrational contributions follow a similar trend in magnitude to the equilibrium values, the largest basis set giving values significantly lower than the smaller two basis sets. The harmonic frequencies in contrast show an increase with increasing basis set size for both methods. All hfcc have a negative sign. The vibrational contributions in this case are negative, the only source of unpaired electron density to the proton arising from spin polarisation effects.
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Table 2.4 - OMu radical hfcc results in reduced form

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Eq / G</th>
<th>Vib / G</th>
<th>Tot / G</th>
<th>Freq</th>
<th>Re-Freq</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-24.21</td>
<td>-1.19</td>
<td>-25.40</td>
<td>10240.24</td>
<td>10249.80</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>-24.01</td>
<td>-1.27</td>
<td>-25.27</td>
<td>10273.65</td>
<td>10283.30</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-22.33</td>
<td>-1.07</td>
<td>-23.40</td>
<td>10329.77</td>
<td>10339.60</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-25.50</td>
<td>-1.29</td>
<td>-26.79</td>
<td>10691.92</td>
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<tr>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>-25.62</td>
<td>-1.36</td>
<td>-26.98</td>
<td>10715.14</td>
<td>10725.20</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-24.05</td>
<td>-1.15</td>
<td>-25.21</td>
<td>10742.17</td>
<td>10751.80</td>
</tr>
</tbody>
</table>

Eq - Equilibrium contribution; Vib - Vibrational contribution; Tot - Total
Freq - GAUSSIAN-94 Harmonic frequency; Re-Freq - Recalculated frequency.

Procedurally, the wavefunction averaging technique used can be considered to have worked well in all cases as the harmonic frequency recalculated by averaging the potential curve over the analytic wavefunction recovers the frequency given by GAUSSIAN-94 very well, in all cases with a discrepancy of no more than 10cm⁻¹ which implies that the property averages are unlikely to be contaminated by artefacts from this source.

Overall all the proton results are broadly consistent with experiment, the B3LYP method performing slightly better than BLYP, B3LYP/6-311G(d,p) giving a total hfcc closest to experimental. The vibrational contributions push the hfcc toward the experimental value, the values being negative in sign as determined experimentally. As regards temperature dependence, no experimental data is available at this time, but the model shows a practically flat curve as one would intuitively expect from a radical with one high frequency mode where excited states would be unpopulated even at elevated temperatures.

The formyl radical HCO.

The formyl radical is a well known radical that has been observed in the gas phase and can be formed by a number of mechanisms such as flash photolysis of acetaldehyde and by the addition of hydrogen atoms to carbon monoxide. While the H and D isotopomers have been observed[39, 45], MuCO presents difficulties in observation and it is suspected that the MuCO radical may be too short lived to observe or be thermodynamically unstable[23,46]. Recently the MuCO and DCO isotopomers were studied theoretically by Webster[23] using a
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variation-perturbation technique to allow for anharmonicity, finding hfcc's of 370.44 MHz (132.52 G) for HCO, 361.50 MHz (129.33 G) for DCO and 437.75 MHz (156.60 G) for MuCO, the latter two values being reduced hfcc's.

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>Hfcc / G (exp)</th>
<th>C-X Mode 1 / cm⁻¹</th>
<th>C-X Mode 2 / cm⁻¹</th>
<th>C-X Mode 3 / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO (X=H)</td>
<td>136.17 / 137.2</td>
<td>2434.48</td>
<td>1868.17</td>
<td>1080.76</td>
</tr>
<tr>
<td>DCO (X=D)</td>
<td>21.24</td>
<td>1909.77</td>
<td>1794.59</td>
<td>846.50</td>
</tr>
</tbody>
</table>

Table 2.5 - Experimental values for hfcc and vibrational modes of HCO and DCO

Experimentally HCO and DCO are reasonably well characterised with experimental vibrational and hfcc data from several sources being given in table 2.5. The theoretical zero point data for HCO, DCO and MuCO are presented below in tables 2.6, 2.7 and 2.8 respectively. In all tables in this section, mode 1 refers to the symmetric stretching vibration, mode 2 to the asymmetric stretch and mode 3 to the X-C-O bending mode.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Eqbm</th>
<th>Vib</th>
<th>Total</th>
<th>Mode 1</th>
<th>Mode 2</th>
<th>Mode 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>137.00</td>
<td>4.48</td>
<td>141.48</td>
<td>2524.72</td>
<td>1852.25</td>
<td>1090.47</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>135.10</td>
<td>4.84</td>
<td>139.94</td>
<td>2491.46</td>
<td>1847.79</td>
<td>1078.97</td>
</tr>
<tr>
<td>BLYP</td>
<td>Big</td>
<td>135.60</td>
<td>4.77</td>
<td>140.17</td>
<td>2551.06</td>
<td>1848.94</td>
<td>1072.89</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>136.10</td>
<td>4.49</td>
<td>140.59</td>
<td>2651.43</td>
<td>1946.66</td>
<td>1122.74</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>134.40</td>
<td>4.82</td>
<td>139.22</td>
<td>2618.21</td>
<td>1940.91</td>
<td>1111.13</td>
</tr>
</tbody>
</table>

Hfcc values are in Gauss, normal modes in cm⁻¹.

The various calculations of the HCO normal mode frequencies show a significant increase down the table, the B3LYP frequencies being some 100 cm⁻¹ greater than the BLYP values for all three modes. BLYP/6-311G(d,p) reproduces the experimental frequencies very well, the other BLYP results not being too far out of line. Both methods using the 6-311G(d,p) basis give values slightly lower than the other two basis sets, a feature repeated with the total and equilibrium hyperfine coupling constants while the vibrational contribution is the largest for this basis. Comparing these results to the calculated HCO mode frequencies from ref 23, viz 2566.76, 2094.67 and 1132.14 cm⁻¹ which are harmonic mode frequencies, the DFT calculations give values closer to the observed ones but with the B3LYP values straying toward those produced by the variation-perturbation technique used in ref 23.
An interesting feature of the hfcc results is the constancy of the vibrational contributions which vary by no more than 0.3G over all calculations and their large magnitude. The small variations in the values produce a compensation effect on the variation of the equilibrium contribution which leads to a very small variability in the total hfcc. The total hfcc are all over-estimates compared to the experimental, again the 6-311G(d,p) basis performing the best at approximately 139G compared to 137G by experiment.

The equilibrium contributions show a different behaviour to those in the OH radical, here the 6-31G(d,p) basis shows a significantly larger hfcc. The BLYP/6-31G(d,p) eqbm hfcc is 137G which is almost identical to the experimental but when combined with the vibrational contributions gives an overestimate.

The temperature variance model for HCO shows a small variation for all calculations. The model gives a positive temperature dependence with a very small increase of only 0.1 G over a 500K range and a gradient in the linear region (300 - 500K) of 0.51mG/K which given the errors inherent in these approximate methods is negligible. Similarly the MuCO and DCO temperature curves show a very small rise over 500K.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Eqbm</th>
<th>Vib</th>
<th>Total</th>
<th>Mode 1</th>
<th>Mode 2</th>
<th>Mode 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>21.03</td>
<td>0.483</td>
<td>21.51</td>
<td>1903.18</td>
<td>1791.17</td>
<td>845.81</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>20.74</td>
<td>0.523</td>
<td>21.26</td>
<td>1883.20</td>
<td>1781.48</td>
<td>837.56</td>
</tr>
<tr>
<td>BLYP</td>
<td>Big</td>
<td>20.82</td>
<td>0.492</td>
<td>21.31</td>
<td>1918.28</td>
<td>1791.55</td>
<td>833.05</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>20.89</td>
<td>0.484</td>
<td>21.37</td>
<td>2009.55</td>
<td>1871.74</td>
<td>871.39</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>20.63</td>
<td>0.522</td>
<td>21.15</td>
<td>1990.34</td>
<td>1860.07</td>
<td>863.08</td>
</tr>
</tbody>
</table>

Hfcc values are unreduced and in Gauss, normal modes in cm⁻¹. 'Big' refers to a 6-311++G(3df,3pd) basis set.

The DCO results look rather better in comparison to the experimental data. The normal modes for all methods are in reasonable agreement, B3LYP again overestimating by approximately 100 cm⁻¹ and BLYP/6-31G(d,p) giving harmonic frequencies almost spot-on to the experimental.
The hfcc data appears to follow experimental data exceptionally well, however it must be remembered that these values have been scaled by the ratio of the magnetic moments for D and H (6.51437) and hence any errors have been reduced by this factor which is reflected in the much lower variations of the equilibrium hfcc.

The 'reduced' hfcc values for the vibrational contributions of the three isotopomers show the relative differences one would expect with the mass variation in the order DCO (~3G), HCO (~4.5G) and MuCO (~13G).

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Eqbm</th>
<th>Vib</th>
<th>Total</th>
<th>Mode 1</th>
<th>Mode 2</th>
<th>Mode 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>436.11</td>
<td>42.52</td>
<td>478.63</td>
<td>7389.98</td>
<td>2920.90</td>
<td>1855.36</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>430.06</td>
<td>45.68</td>
<td>475.74</td>
<td>7199.37</td>
<td>2887.12</td>
<td>1850.15</td>
</tr>
<tr>
<td>BLYP</td>
<td>Big</td>
<td>431.65</td>
<td>43.32</td>
<td>474.97</td>
<td>7365.45</td>
<td>2869.61</td>
<td>1853.43</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>433.23</td>
<td>42.38</td>
<td>475.61</td>
<td>7365.45</td>
<td>2869.61</td>
<td>1853.43</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>427.86</td>
<td>45.39</td>
<td>473.25</td>
<td>7561.12</td>
<td>2971.63</td>
<td>1944.63</td>
</tr>
</tbody>
</table>

Hfcc values are unreduced and in Gauss, normal modes in cm\(^{-1}\).

The harmonic MuCO normal mode Mu-C frequencies are somewhat different to those predicted in ref 23 (5929.18, 2596.11, 2086.12 cm\(^{-1}\)) which is most likely due to anharmonic contributions not accounted for here which factor significantly in muon modes. The reduced total hfcc values are in accord with the values predicted by Webster, the values predicted by harmonic analysis being smaller by some 6-8G for the density functional calculations. Compare 150G (BLYP/6-31G(d,p)) as the highest value predicted here to 156.62G from Webster’s calculations which are from a perturbation based method with a 6-311G(d,p) basis. Again the differences are partially attributable to the lack of consideration of anharmonic effects in this work and partially to the differences in the theoretical method, perturbation correlation and UHF methods are known to have problems with predicting hfcc values.

Comparing the break down of the current calculations and those of reference [23], there is a significant difference in the various contributions. From ref[23] (in unreduced units), the equilibrium component for MuCO is 387.10G, the harmonic component is...
100.11G and the anharmonic 11.83G. Comparing the BLYP/6-31G(d,p) values of 436.11G (equilibrium) and 42.52G (harmonic) for the current DFT calculations, the equilibrium is much larger and the harmonic contribution smaller. Ignoring the anharmonic component, Webster's value is 487.21G, slightly larger than the DFT calculations at 478.63G which could be attributed to differences in the theoretical method.

A pertinent point to be considered is the breakdown of the individual contributions of each normal to the vibrational contribution. The BLYP/6-311G(d,p) results for the three isotopomers are shown below in table 2.9 in units of a.u.

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>Mode 3</th>
<th>Mode 2</th>
<th>Mode 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO</td>
<td>0.000752</td>
<td>0.000161</td>
<td>0.001962</td>
</tr>
<tr>
<td>DCO</td>
<td>0.000426</td>
<td>0.000532</td>
<td>0.001066</td>
</tr>
<tr>
<td>MuCO</td>
<td>0.000218</td>
<td>0.002780</td>
<td>0.005523</td>
</tr>
</tbody>
</table>

All hfcc in units of a.u. unscaled for free atom corrections.

These values are representative of the trends exhibited by the other calculations for this radical. For HCO, the symmetric stretch makes a large contribution to the proton hfcc. This contribution decreases somewhat for the equivalent D isomer with a large increase for the Mu isomer as would be expected as a result of the differences in the range of motion. The asymmetric stretch makes a much smaller contribution to the hfcc in the case of a proton but there is a noticeable difference where D or Mu is involved, these molecular isomers show a contribution of approximately a half of that from mode 1 whereas the for the proton it is approximately 1/10. For mode 3 the situation is different again, the proton isomer gets a larger contribution, D is relatively unchanged and Mu is much decreased.

The small value of the contribution from mode 2 for a proton and the high value of the deuterium is something of an anomaly but is repeated over all calculations. The change in the phase of the motion of the oxygen and proton atoms will alter the local spin density environment of the proton which in this case appears to lead to a smaller hfcc contribution. The low value of the proton contribution for this mode could be the result of a simple
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balancing effect between positive and negative contributions along the normal mode. The bending mode contribution for a proton is much larger than both the D and Mu. Again this could be due to a simple balancing effect.

The vinyl radical

The vinyl (CH$_2$CH) radical is a simple planar π radical that presents an added dynamic complication in addition to the vibrational molecular motion, namely that of internal rotation. The system can rotate about its central π bond which itself is a thermally controlled process. Experimental data infers that the barrier to rotation about this bond is not excessively large since studies of the radical in liquid ethane show an equivalence of the α and β protons. Techniques exist to account for the effects of simple rotating groups such as the methyl group [32, 33] and the associated quantum tunnelling effect [34] which would be applicable for radicals such as the ethyl radical [30, 31]. Although a parallel of these techniques could be employed in this radical, normal co-ordinates should incorporate a semblance of the rotation in terms of the out of plane vibrations but there will be no account of quantum tunnelling.

Close analogues of the vinyl radical such as the fluorovinyls induce yet another complication of a pyramidalised radical centre which technically would require double oscillator techniques to study. Density functional calculations on fluorovinyl radicals [22] have shown reasonable results.
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Fig 2.1 The vinyl radical

Experimental values for $H(\alpha)$, $H(\beta_1)$ and $H(\beta_2)$ are given in table 2.10 below for the vinyl radical in liquid ethane and a solid rare gas matrix ($H(\beta_1)$ lies cis to the $\alpha$ proton).

<table>
<thead>
<tr>
<th>Radical</th>
<th>Medium</th>
<th>$A_{\text{iso}} H(\alpha)$</th>
<th>$A_{\text{iso}} H(\beta_1)$</th>
<th>$A_{\text{iso}} H(\beta_2)$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH=CH</td>
<td>Liquid ethane</td>
<td>13.4</td>
<td>51</td>
<td>51</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Solid rare gas</td>
<td>16.0</td>
<td>68</td>
<td>34</td>
<td>60</td>
</tr>
</tbody>
</table>

All hfcc in Gauss

In liquid ethane, the observations suggest that the two $\beta$ protons are equivalent which would imply a rapid inversion of the radical at average temperatures, while in contrast the radical in a solid gas matrix shows considerable differentiation of the $\beta$ protons, the larger coupling arising from the proton cis to the $\alpha$ proton. This is an intriguing situation since one would expect spin polarisation and hyperconjugation effects between the $\beta$ protons and the $sp$ hybrid orbital at $C_\alpha$ to affect the proton trans to $H_\alpha$. The solid rare gas matrix, while restricting some aspects of the molecular motion will be more identifiable with theoretical calculations due to the absence of rotation effects.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Equilibrium</th>
<th>Vibrational</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>18.20</td>
<td>0.86</td>
<td>19.06</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>18.34</td>
<td>0.99</td>
<td>19.33</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>16.23</td>
<td>0.73</td>
<td>16.96</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>16.42</td>
<td>0.87</td>
<td>17.30</td>
</tr>
</tbody>
</table>

All values in gauss

The B3LYP method performs slightly better than BLYP on the $\alpha$ proton hfcc. The
vibrational contribution is almost negligible here at < 1G. Table 2.12 shows the vibrational modes and their respective contributions to the three protons as estimated by BLYP/6-31G(d,p). The α proton vibrational hfcc is mainly governed by the highest frequency mode, modes 1 and 2 practically cancelling each other out, and the mid range modes perform likewise leading to a net positive contribution.

<table>
<thead>
<tr>
<th>Frequency / cm⁻¹</th>
<th>Alpha</th>
<th>Beta cis</th>
<th>Beta trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>699.33</td>
<td>0.000168</td>
<td>0.000213</td>
<td>9.45e-5</td>
</tr>
<tr>
<td>764.55</td>
<td>-0.00014</td>
<td>0.000170</td>
<td>-7.11e-5</td>
</tr>
<tr>
<td>882.16</td>
<td>-4.89e-5</td>
<td>0.000264</td>
<td>0.000417</td>
</tr>
<tr>
<td>1030.35</td>
<td>6.96e-5</td>
<td>0.000208</td>
<td>0.000177</td>
</tr>
<tr>
<td>1367.30</td>
<td>9.08e-5</td>
<td>0.000176</td>
<td>0.000254</td>
</tr>
<tr>
<td>1618.10</td>
<td>-2.99e-5</td>
<td>0.000373</td>
<td>0.000324</td>
</tr>
<tr>
<td>2967.91</td>
<td>-1.87e-5</td>
<td>8.44e-5</td>
<td>0.000696</td>
</tr>
<tr>
<td>3070.06</td>
<td>-6.46e-5</td>
<td>0.000431</td>
<td>-3.66e-5</td>
</tr>
<tr>
<td>3168.37</td>
<td>0.000384</td>
<td>-7.78e-5</td>
<td>-5.90e-5</td>
</tr>
</tbody>
</table>

All hfcc values in a.u. unscaled for free atom correction.

The beta protons both show a large contribution arising from the mid range modes, the β-cis proton differs from the trans proton in modes 1, 2, 7 and 8. Again there arises a net positive contribution to the hfcc leading overall to a positive temperature dependence curve. When summed, the beta protons do not drastically differ in their contributions, the cis proton gaining a slightly higher contribution from its vibrational effects.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Equilibrium</th>
<th>Vibrational</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>65.18</td>
<td>3.01</td>
<td>68.19</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>65.87</td>
<td>3.22</td>
<td>69.09</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>63.31</td>
<td>2.85</td>
<td>66.16</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>63.83</td>
<td>3.05</td>
<td>66.87</td>
</tr>
</tbody>
</table>

All values in gauss

The vibrational contributions from the β protons are larger than the α at approximately 3G. The estimated β₁ hfcc is in good agreement with experiment, the BLYP values being closer this time and the B3LYP smaller.

The temperature variance (unshown) is predicted to be positive, the β₁ proton values rising by only 0.1G and β₂ by 0.3G over a 500K temperature range, giving gradients over the
linear section of the curve between 300 and 500K of 0.84 and 1.24 mG/K respectively for BLYP/6-31G(d,p) calculations.

<table>
<thead>
<tr>
<th>Table 2.14 Vinyl radical $A_{\text{me}}H(\beta_2)$ hfcc values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method</strong></td>
</tr>
<tr>
<td>BLYP</td>
</tr>
<tr>
<td>BLYP</td>
</tr>
<tr>
<td>B3LYP</td>
</tr>
<tr>
<td>B3LYP</td>
</tr>
</tbody>
</table>

All values in gauss

The estimated hfcc for the $\beta_2$ proton is larger than the experimental by ~8G in the best case, the vibrational contributions taking the equilibrium away from the experimental. The magnitude of the hfcc in this case is due to the equilibrium contribution which is rather large, however, the most comparable experimental values come from a matrix environment which may introduce interactions that are not accounted for in these isolated case calculations.

**The CH$_2$N Radical**

The CH$_2$N radical is a small planar $\pi$ radical that like HCO possesses a very large proton hyperfine coupling constant.

<table>
<thead>
<tr>
<th>Table 2.15 CH$_2$N hfcc values in various media</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Radical</strong></td>
</tr>
<tr>
<td>CH$_2$N</td>
</tr>
<tr>
<td>Liquid CH$_2$N</td>
</tr>
</tbody>
</table>

All hfcc in Gauss

Experimentally a value of 87.3G is observed for the beta protons. This is much larger than one would expect for an organic radical, for example comparing the vinyl radical values of 51G in solution and a methyl radical of -23G. The DFT calculations reproduce the experimental values very well, B3LYP performing slightly better than BLYP, both basis sets giving very similar values.

<table>
<thead>
<tr>
<th>Table 2.16 CH$_2$N proton hfcc values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method</strong></td>
</tr>
<tr>
<td>BLYP</td>
</tr>
<tr>
<td>BLYP</td>
</tr>
<tr>
<td>B3LYP</td>
</tr>
<tr>
<td>B3LYP</td>
</tr>
</tbody>
</table>

All values in gauss
The vibrational contributions are on the order of 4G which are very similar to the contributions to the β protons in the vinyl radical. The vibrational modes all give similar contributions to the hfcc, table 2.17 details the contributions from all calculations.

Table 2.17 Vibrational contributions to CH\textsubscript{2}N proton hfcc by mode

<table>
<thead>
<tr>
<th>Method / Basis</th>
<th>Frequency (cm\textsuperscript{-1})</th>
<th>Harmonic (au)</th>
<th>Total (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP / 6-31G(d,p)</td>
<td>900.40 / 0.000279</td>
<td>939.04 / 0.000256</td>
<td>932.14 / 0.000266</td>
</tr>
<tr>
<td>BLYP / 6-31G(d,p)</td>
<td>943.48 / 0.000567</td>
<td>990.39 / 0.000522</td>
<td>988.47 / 0.000545</td>
</tr>
<tr>
<td>B3LYP / 6-31G(d,p)</td>
<td>1352.65 / 0.000375</td>
<td>1394.76 / 0.000345</td>
<td>1378.51 / 0.000380</td>
</tr>
<tr>
<td>B3LYP / 6-31G(d,p)</td>
<td>1669.55 / 0.000449</td>
<td>1735.45 / 0.000483</td>
<td>1721.94 / 0.000465</td>
</tr>
<tr>
<td>B3LYP / 6-31G(d,p)</td>
<td>2885.34 / 0.000299</td>
<td>2988.85 / 0.000291</td>
<td>2955.40 / 0.000360</td>
</tr>
<tr>
<td>B3LYP / 6-31G(d,p)</td>
<td>2924.85 / 0.000469</td>
<td>3045.52 / 0.000422</td>
<td>3007.56 / 0.000473</td>
</tr>
</tbody>
</table>

First value in a box is frequency / cm\textsuperscript{-1}, second is hfcc average / a.u. unscaled for free atom correction.

All calculations behave similarly in the relative magnitude of the contributions arising from each mode. The BLYP method gives lower harmonic frequencies but higher hfcc averages than the comparable B3LYP calculation.

The NH\textsubscript{2} Radical

The NH\textsubscript{2} radical can be formally classed as an inorganic π-radical. Experimental values have been obtained [18] of -23.9G for the proton in this system. The DFT calculations compare well with the experimental values, the B3LYP method performing better on the whole.

Table 2.18 NH\textsubscript{2} isotropic hfcc values

<table>
<thead>
<tr>
<th>Method / Basis</th>
<th>Equilibrium</th>
<th>Vibrational</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP 6-31G(d,p)</td>
<td>-22.50</td>
<td>-0.39</td>
<td>-22.89</td>
</tr>
<tr>
<td>BLYP 6-311G(d,p)</td>
<td>-21.97</td>
<td>-0.45</td>
<td>-22.42</td>
</tr>
<tr>
<td>BLYP 6-311++G(3df, 3pd)</td>
<td>-19.22</td>
<td>-0.42</td>
<td>-19.64</td>
</tr>
<tr>
<td>B3LYP 6-31G(d,p)</td>
<td>-24.03</td>
<td>-0.42</td>
<td>-24.55</td>
</tr>
<tr>
<td>B3LYP 6-311G(d,p)</td>
<td>-23.65</td>
<td>-0.48</td>
<td>-24.13</td>
</tr>
<tr>
<td>B3LYP 6-311++G(3df, 3pd)</td>
<td>-21.08</td>
<td>-0.46</td>
<td>-21.54</td>
</tr>
</tbody>
</table>

All values in gauss

The vibrational contributions are small, all under -0.5G and negative. The contributions of each mode are negative and small leading to a negative temperature dependence whose change over 500K is negligible at less than 0.1G as one would expect from the lack of low frequency modes. There is some obvious disagreement among the
various calculations, the BLYP values slightly underestimating experimental and B3LYP slightly overestimating. The 6-311++G(3df,3pd) basis gives a much lower equilibrium hfcc than the other two basis sets as has been observed in previous calculations while all vibrational contributions are approximately equal.

Table 2.19 ND$_2$ reduced isotropic hfcc values

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Equilibrium</th>
<th>Vibrational</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-22.50</td>
<td>-0.29</td>
<td>-22.79</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>-21.97</td>
<td>-0.33</td>
<td>-22.30</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-19.22</td>
<td>-0.31</td>
<td>-19.53</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-24.03</td>
<td>-0.31</td>
<td>-24.35</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>-23.65</td>
<td>-0.35</td>
<td>-24.00</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-21.08</td>
<td>-0.34</td>
<td>-21.41</td>
</tr>
</tbody>
</table>

All values in gauss

Table 2.19 above shows the hfcc calculations for ND$_2$ as the reduced values. The vibrational contributions are smaller than those for the equivalent proton isotopomer following expectations due to the mass difference.

The contributions of each mode for NH$_2$ are shown in table 2.20 below for all calculations.

Table 2.20 NH$_2$ Contributions by mode

<table>
<thead>
<tr>
<th>Mode</th>
<th>BLYP 6-31G(d,p)</th>
<th>BLYP 6-311G(d,p)</th>
<th>BLYP 6-311++G(3df,3pd)</th>
<th>B3LYP 6-31G(d,p)</th>
<th>B3LYP 6-311G(d,p)</th>
<th>B3LYP 6-311++G(3df,3pd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bending</td>
<td>-6.09e-5</td>
<td>-5.20e-5</td>
<td>-7.34e-5</td>
<td>-7.14e-5</td>
<td>-6.10e-5</td>
<td>-8.09e-5</td>
</tr>
<tr>
<td>Antisymmetric</td>
<td>-7.99e-5</td>
<td>-1.00e-4</td>
<td>-7.97e-5</td>
<td>-8.40e-5</td>
<td>-1.10e-4</td>
<td>-8.62e-5</td>
</tr>
<tr>
<td>Symmetric</td>
<td>-9.14e-5</td>
<td>-1.10e-4</td>
<td>-9.56e-5</td>
<td>-9.51e-5</td>
<td>-1.20e-4</td>
<td>-1.0e-4</td>
</tr>
</tbody>
</table>

All values in a.u. unscaled for free atom correction.

Although the values are very small, all calculations show an increase in the magnitude of the contributions with increasing frequency. The 6-311G(d,p) basis gives very large contributions for the two stretching modes compared to the other two basis sets.

The Allyl Radical

The allyl radical is the simplest example of an alternate planar $\pi$ radical which displays the effects of an alternating proton hfcc along the conjugated $\pi$ system, an effect which arises from spin polarisation transfer along this system.
The Temperature Dependence of Isotropic HFCC's

Fig 2.2 - The Allyl Radical

Experimental values for the three proton environments are shown below in table 2.21 and 2.22 along with some closely related radicals at various temperatures.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Medium</th>
<th>$A_{\text{iso}}$H($\alpha$)</th>
<th>$A_{\text{iso}}$H($\beta$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_2\text{CHCH}_2$</td>
<td>Liquid propene</td>
<td>-13.92</td>
<td>-14.83</td>
<td>16</td>
</tr>
<tr>
<td>$\text{CH}_2\text{C}^{13}\text{CHCH}_2$</td>
<td>Liquid propene</td>
<td>-13.97</td>
<td>-14.87</td>
<td>16</td>
</tr>
<tr>
<td>$^{13}\text{CH}_2\text{C}^{13}\text{CHCH}_2$</td>
<td>Liquid propene</td>
<td>-13.92</td>
<td>-14.83</td>
<td>16</td>
</tr>
</tbody>
</table>

All hfcc in Gauss

$\alpha$ is the proton trans to the $\beta$ proton

Hfcc measured at 315K

The difference in the proton hfcc between the various $^{13}$C substituted allyl isotopomers is practically nil, however there is a small effect when the substitution is made at the $C_3$ position. Comparing these values to the related 1,1dimethylallyl radicals in table 2.22, the $\beta$ proton hfcc is only slightly affected by the structural change relative to the allyl radical.

Table 2.22 Experimental CH$_2$CHCH$_2$ and related hfcc values at two temperatures

<table>
<thead>
<tr>
<th>Radical</th>
<th>Medium</th>
<th>$A_{\text{iso}}$H / Mu</th>
<th>$A_{\text{iso}}$H / Mu</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_2\text{CHCH}_2$</td>
<td>-</td>
<td>4.06 (143K)</td>
<td>4.53 (503K)</td>
<td>Beta proton</td>
<td>9</td>
</tr>
<tr>
<td>$\text{Me}-\text{C}=\text{CHCH}_2$</td>
<td>-</td>
<td>3.56 (153K)</td>
<td>4.04 (356K)</td>
<td>Beta proton</td>
<td>9</td>
</tr>
<tr>
<td>$\text{Me}-\text{C}=\text{C}^{13}\text{MuCH}_2$</td>
<td>-</td>
<td>4.01 (210K)</td>
<td>4.26 (288K)</td>
<td>Beta muon</td>
<td>9</td>
</tr>
<tr>
<td>$\text{Me}-\text{C}=\text{CC}^{13}\text{Mu}$</td>
<td>-</td>
<td>28.44 (210K)</td>
<td>25.97 (288K)</td>
<td>Beta muon</td>
<td>9</td>
</tr>
<tr>
<td>$\text{MuCHCHCHCl}$</td>
<td>Allyl chloride</td>
<td>36.63(197K)</td>
<td>33.33(298K)</td>
<td>Muon coupling</td>
<td>10</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CH}^{13}\text{MuCHCl}$</td>
<td>Allyl chloride</td>
<td>39.85(197K)</td>
<td>35.46(298K)</td>
<td>Muon coupling</td>
<td>10</td>
</tr>
<tr>
<td>$\text{CH}_2\text{Cl}$</td>
<td>Allyl chloride</td>
<td>7.87(175K)</td>
<td>9.30(298K)</td>
<td>CH$_2$Cl protons</td>
<td>10</td>
</tr>
</tbody>
</table>

All hfcc in Gauss

$A_{\text{iso}}$ H / Mu represent the isotropic hyperfine coupling constant of the appropriate atom as specified in the comment column.

The muonium hfcc are reduced values.

Theoretical calculations have been performed on the allyl radical and its $\beta$-muonium substituted isotopomer using BLYP/6-31G(d,p) and B3LYP/6-31G(d,p).
The β-H hfcc are overestimated by all methods upon inclusion of vibrational contributions which are considerable for this proton at > 1G. The B3LYP equilibrium hfcc values are higher than the BLYP by almost 2G. The reduced vibrational contributions for the muon show a small increase over their proton counterparts giving zero point isotope effects of 1.05 (BLYP) and 1.07 (B3LYP) respectively. These values are close to an isotope effect reported in ref [9] of 1.04 which was obtained by extrapolation of experimental data to zero temperature. The breakdown by mode of the contributions are shown in table 2.24 below.

### Table 2.23 CH₂CH₃ β proton and muon hfcc values

<table>
<thead>
<tr>
<th>Radical</th>
<th>Method</th>
<th>Basis</th>
<th>Equilibrium</th>
<th>Vibrational</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CH₃</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>3.26</td>
<td>1.17</td>
<td>4.43</td>
</tr>
<tr>
<td>CH₂CH₃</td>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>5.13</td>
<td>1.25</td>
<td>6.37</td>
</tr>
</tbody>
</table>

Table 2.23 CH₂CH₃ β proton and muon hfcc values

<table>
<thead>
<tr>
<th>Mode</th>
<th>CH₂CH₃</th>
<th>BLYP (6-31G(d,p))</th>
<th>CH₂CH₃</th>
<th>B3LYP (6-31G(d,p))</th>
<th>CH₂CH₃</th>
<th>Muon (6-31G(d,p))</th>
<th>CH₂CH₃</th>
<th>Muon (6-31G(d,p))</th>
<th>CH₂CH₃</th>
<th>Muon (6-31G(d,p))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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<td></td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>418.59</td>
<td>4.28e-6</td>
<td>520.50</td>
<td>6.55e-6</td>
<td>535.35</td>
<td>3.67e-6</td>
<td>534.42</td>
<td>6.03e-6</td>
<td>535.35</td>
<td>3.67e-6</td>
</tr>
<tr>
<td>2</td>
<td>987.51</td>
<td>7.09e-5</td>
<td>1011.95</td>
<td>6.15e-6</td>
<td>1296.14</td>
<td>6.77e-6</td>
<td>1043.75</td>
<td>6.46e-6</td>
<td>1296.14</td>
<td>6.77e-6</td>
</tr>
<tr>
<td>3</td>
<td>1206.63</td>
<td>4.96e-6</td>
<td>1206.63</td>
<td>4.96e-6</td>
<td>1315.84</td>
<td>7.52e-5</td>
<td>1217.89</td>
<td>5.73e-5</td>
<td>1315.84</td>
<td>7.52e-5</td>
</tr>
<tr>
<td>4</td>
<td>1469.70</td>
<td>1.30e-5</td>
<td>1469.70</td>
<td>1.30e-5</td>
<td>1503.09</td>
<td>1.61e-5</td>
<td>1278.57</td>
<td>1.07e-5</td>
<td>1503.09</td>
<td>1.61e-5</td>
</tr>
<tr>
<td>5</td>
<td>1499.76</td>
<td>1.54e-6</td>
<td>1499.76</td>
<td>1.54e-6</td>
<td>1538.03</td>
<td>4.49e-6</td>
<td>1430.50</td>
<td>1.59e-5</td>
<td>1538.03</td>
<td>4.49e-6</td>
</tr>
<tr>
<td>6</td>
<td>2540.88</td>
<td>0.000165</td>
<td>2540.88</td>
<td>0.000165</td>
<td>2613.74</td>
<td>0.000266</td>
<td>1528.63</td>
<td>1.09e-5</td>
<td>2613.74</td>
<td>0.000266</td>
</tr>
<tr>
<td>7</td>
<td>3077.68</td>
<td>1.04e-6</td>
<td>3077.68</td>
<td>1.04e-6</td>
<td>3156.53</td>
<td>1.80e-6</td>
<td>1535.71</td>
<td>4.36e-6</td>
<td>3156.53</td>
<td>1.80e-6</td>
</tr>
<tr>
<td>8</td>
<td>3083.70</td>
<td>2.39e-6</td>
<td>3083.70</td>
<td>2.39e-6</td>
<td>3162.73</td>
<td>4.58e-6</td>
<td>3146.91</td>
<td>1.53e-5</td>
<td>3162.73</td>
<td>4.58e-6</td>
</tr>
<tr>
<td>9</td>
<td>3174.14</td>
<td>3.62e-6</td>
<td>3174.14</td>
<td>3.62e-6</td>
<td>3256.29</td>
<td>6.59e-6</td>
<td>3156.81</td>
<td>2.86e-6</td>
<td>3256.29</td>
<td>6.59e-6</td>
</tr>
<tr>
<td>10</td>
<td>3175.08</td>
<td>4.37e-6</td>
<td>3175.08</td>
<td>4.37e-6</td>
<td>3257.15</td>
<td>5.85e-6</td>
<td>3163.16</td>
<td>5.88e-6</td>
<td>3257.15</td>
<td>5.85e-6</td>
</tr>
<tr>
<td>11</td>
<td>3706.47</td>
<td>6.49e-5</td>
<td>3706.47</td>
<td>6.49e-5</td>
<td>3795.37</td>
<td>0.000106</td>
<td>3256.47</td>
<td>5.02e-6</td>
<td>3795.37</td>
<td>0.000106</td>
</tr>
<tr>
<td>12</td>
<td>8801.63</td>
<td>2.56e-5</td>
<td>8801.63</td>
<td>2.56e-5</td>
<td>9047.35</td>
<td>5.17e-5</td>
<td>3258.92</td>
<td>6.08e-6</td>
<td>9047.35</td>
<td>5.17e-5</td>
</tr>
</tbody>
</table>

First value in a box is frequency in cm⁻¹ and the second is the hfcc in a.u.

A large number of the modes give very small contributions to the hfcc and are negligible. The hfcc appears to be determined by only one or two modes at most. Mode 3 makes a contribution for both muon and proton isotopomers, this mode represents an out of plane vibration of the α protons mainly, the β proton moving very slightly out of plane. When a muon is present at the β position there arises an additional but much smaller contribution from mode 12 which represents an in plane motion alone. Interestingly the frequencies of mode 3 are identical for the two isotopomers a situation that probably occurs because of the
The Temperature Dependence of Isotropic HFCC's

non-participation of the β atom in the mode, i.e. the β atom is essentially stationary while everything else moves.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Method</th>
<th>Basis</th>
<th>Equilibrium</th>
<th>Vibrational</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CH₂</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-14.52</td>
<td>0.30</td>
<td>-14.22</td>
</tr>
<tr>
<td>CH₂CH₂</td>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-16.45</td>
<td>0.17</td>
<td>-16.28</td>
</tr>
<tr>
<td>CH₂CMuCH₂</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-14.53</td>
<td>0.26</td>
<td>-14.26</td>
</tr>
<tr>
<td>CH₂CMuCH₂</td>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-16.45</td>
<td>0.086</td>
<td>-16.36</td>
</tr>
</tbody>
</table>

All hfcc in Gauss

The calculations for the α protons show an approximate 1G difference between the α₁ and α₂ protons in the order expected from the experimental values, with the signs being reproduced as expected. The vibrational averaging calculations give a net positive value for the zero-point contributions in both cases, the majority of this arising from the modes at 749.65 and 772.84 cm⁻¹ (values from BLYP/6-31G(d,p) calculations) for the α protons which represent out of plane motion of these protons. It should be noted at this juncture that there are other modes which represent very similar motions of the α protons that give much smaller contributions which infers that this one particular mode gives a significant contribution due to the way the positive and negative contributions to the hfcc balance along the normal coordinate.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Method</th>
<th>Basis</th>
<th>Equilibrium</th>
<th>Vibrational</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CH₂</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-15.19</td>
<td>0.41</td>
<td>-14.78</td>
</tr>
<tr>
<td>CH₂CH₂</td>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-17.19</td>
<td>0.27</td>
<td>-16.92</td>
</tr>
<tr>
<td>CH₂CMuCH₂</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-15.19</td>
<td>0.35</td>
<td>-14.84</td>
</tr>
<tr>
<td>CH₂CMuCH₂</td>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-17.19</td>
<td>0.19</td>
<td>-17.00</td>
</tr>
</tbody>
</table>

All hfcc in Gauss

Experimental results from the chlorine substituted allyl radical indicate that there is a positive temperature dependence for the protons in the CH₂Cl unit which lie at a β position in MuCH₂CHCH₂Cl while in contrast a negative dependence for the muon at the β position in both radicals. The experimental data from the allyl radical and its dimethyl counterparts show a positive temperature dependence for the β proton and muon. In the case of Me₂CCCH₂Mu, the muon shows a negative temperature dependence similar to the allyl chloride. The structure
of these radicals are quite different, the allyl chloride and Me₂CCCH₂Mu are not planar π radicals whereas the Me₂CCHCH₂ radical has retained the essential character of the planar allyl unit in the vicinity of the radical centre, consequently these two structures show very different hfcc, the non planar radicals showing very large β hyperfine coupling constants.

By assuming a linear temperature dependence in the region of the experimental results (~140K - 500K), the values of \( \frac{\partial A_{	ext{int}}}{\partial T} \) may be compared. This will give an approximate indication of how well the theoretical calculations have reproduced the gradient which is a vital factor for the thermal variance. Although this is not strictly a correct way to calculate the gradients, it will serve as a comparison since the experimental data is sparse and unsuitable for calculating the correct gradient at a given temperature.

Table 2.27 Experimental temperature gradients for various radicals

<table>
<thead>
<tr>
<th>Radical</th>
<th>Hfcc (Temp)</th>
<th>Hfcc (Temp)</th>
<th>Gradient G/K</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CHCH₂</td>
<td>4.06 (143K)</td>
<td>4.53 (503K)</td>
<td>0.00131</td>
<td>Beta proton</td>
</tr>
<tr>
<td>Me₂C=CHCH₂</td>
<td>3.56 (153K)</td>
<td>4.04 (356K)</td>
<td>0.00236</td>
<td>Beta proton</td>
</tr>
<tr>
<td>Me₂C=CMuCH₂</td>
<td>4.01 (210K)</td>
<td>4.26 (288K)</td>
<td>0.00321</td>
<td>Beta muon</td>
</tr>
<tr>
<td>Me₂C=CCH₂Mu</td>
<td>28.44 (210K)</td>
<td>25.97 (288K)</td>
<td>-0.0317</td>
<td>Beta muon</td>
</tr>
<tr>
<td>MuCH₂CHCH₂Cl</td>
<td>36.63 (197K)</td>
<td>33.33 (298K)</td>
<td>-0.0327</td>
<td>Muon coupling</td>
</tr>
<tr>
<td>CH₂CMuCH₂Cl</td>
<td>39.85 (197K)</td>
<td>35.46 (298K)</td>
<td>-0.0435</td>
<td>Muon coupling</td>
</tr>
<tr>
<td>CH₂MuCH₂Cl</td>
<td>7.87 (175K)</td>
<td>9.30 (298K)</td>
<td>0.0116</td>
<td>CH₂Cl protons</td>
</tr>
</tbody>
</table>

All hfcc in gauss

Table 2.27 above compares experimental gradients, care must be exercised when comparing gradients by this method since the magnitude will be shallower when the points are closer together and closer to low temperatures. There is no muonated radical data available for the allyl radical, however the 1,1 dimethylallyl radical shows a small increase of approximately 1 mG/K on substitution of the muon. Comparing the allyl and its protic dimethyl companion, there is again a 1 mG/K increase in the gradient.

Table 2.28 Beta proton temperature gradients for allyl radical and muonated allyl radical

<table>
<thead>
<tr>
<th>Radical</th>
<th>Hfcc (Temp)</th>
<th>Hfcc (Temp)</th>
<th>Gradient G/K</th>
<th>Method</th>
<th>Basis</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CHCH₂</td>
<td>4.67 (140K)</td>
<td>5.26 (500K)</td>
<td>0.00164</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>Beta proton</td>
</tr>
<tr>
<td>CH₂CHCH₂</td>
<td>6.38 (140K)</td>
<td>6.93 (500K)</td>
<td>0.00143</td>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>Beta proton</td>
</tr>
<tr>
<td>CH₂CMuCH₂</td>
<td>4.91 (140K)</td>
<td>5.50 (500K)</td>
<td>0.00164</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>Beta muon</td>
</tr>
<tr>
<td>CH₂CMuCH₂</td>
<td>6.80 (140K)</td>
<td>7.33 (500K)</td>
<td>0.00137</td>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>Beta muon</td>
</tr>
</tbody>
</table>

All hfcc in gauss
Table 2.28 shows the gradient of the temperature dependence curve as an approximation between 140K and 500K. Even though there is a difference in the vibrational contributions for the muon and proton, the gradient of the curve does not show any significant change for the BLYP result. By comparison of the allyl and dimethyl allyl gradients in table 2.27 we would expect to see approximately 1 mG/K increase in the gradient on substitution of a muon.

The B3LYP result actually shows a decrease in the gradient on muonation which is a rather worrying situation. Referring to table 2.24, the contributions by mode between the two radicals for B3LYP. The contributions from mode 3 are smaller in both cases by $3 \times 10^{-6}$ a.u.

for the muon radical, the difference between the two radicals at the zero point level being made up by a higher frequency mode, however this difference at the zero point level would only account for approximately 0.005G

A possible source of this error is the Boltzmann model of population of the harmonic oscillator states which would tend to leave contributions from high frequency modes such as those in the muonated allyl radical relatively unchanged with temperature due to the population weighting.

Generally, for the allyl radical the theoretical calculations overestimate the hfcc compared to the experimental, moreso by the B3LYP method than the BLYP and the gradient of the temperature curve for the muon substituted radical is underestimated. The gradient for the allyl radical is reasonably well reproduced compared to the experimental but the model is very lacking in its description of the muonated radical.

The ammonium cation radical

This radical is a planar radical that is isoelectronic with the methyl radical and
structurally very similar. The two radicals are of interest to compare as the vibrational effects upon their observables will be very similar. Calculations have been performed for NH$_3^+$ and ND$_3^+$ using BLYP over 6-31G(d,p), 6-311G(d,p) and 6-311++G(3df,3pd) basis sets which are presented in table 2.30.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Method</th>
<th>Basis</th>
<th>$A_{iso}$</th>
<th>$A_{vib}$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3^+$</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-26.05</td>
<td>1.19</td>
<td>-24.86</td>
</tr>
<tr>
<td>NH$_3^+$</td>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>-26.25</td>
<td>1.33</td>
<td>-24.92</td>
</tr>
<tr>
<td>NH$_3^+$</td>
<td>BLYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-23.74</td>
<td>1.07</td>
<td>-22.67</td>
</tr>
<tr>
<td>ND$_3^+$</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-26.05</td>
<td>0.92</td>
<td>-25.13</td>
</tr>
<tr>
<td>ND$_3^+$</td>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>-26.25</td>
<td>1.03</td>
<td>-25.22</td>
</tr>
<tr>
<td>ND$_3^+$</td>
<td>BLYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-23.74</td>
<td>0.87</td>
<td>-22.87</td>
</tr>
</tbody>
</table>

The equivalent results for the deuterated molecule show the expected decrease in the vibrational contribution which leads to a larger negative coupling constant (N.B the deuterated values are reduced). The harmonic normal modes for these molecules possess only one out-of-plane mode which is the lowest lying frequency. For NH$_3^+$ and ND$_3^+$ using BLYP/6-31G(d,p) these are 857.64cm$^{-1}$ and 658.26cm$^{-1}$ respectively which make the major
contribution to the hfcc in both cases, the other modes all making negligible contributions in total.

The predictions of the gradient of the temperature dependencies are positive and small, the variation of the hfcc for NH$_3^+$ over 300K-500K by BLYP/6-31G(d,p) being 0.222G giving a gradient of 1.1mG/K assuming linearity over that range. The equivalent gradient for the deuterated molecule is 1.4mG/K.

The contributions of the six modes are shown below in table 2.31. The out of plane mode contributes the majority of the hfcc, the in plane modes making relatively negligible contributions. A noticeable feature is the positive contribution of the out of plane mode and the negative contributions of the in plane modes. The negative contributions in total account for -1.92e-4 a.u. (-0.322G scaled for free atom hfcc) for NH$_3$/6-31G(d,p) and the lowest frequency mode alone contributes 1.509G (scaled). The total vibrational hfcc contribution is 21% lower than the value would be of the in-plane modes were not accounted for. Given the small magnitudes involved, this is a substantial proportion. This point is particularly applicable to the methyl radical since early studies of the temperature dependence focused only on the lowest frequency mode.

<table>
<thead>
<tr>
<th></th>
<th>6-31G(d,p) (NH$_3$)</th>
<th>6-311G(d,p)</th>
<th>6-311++G(3df,3pd)</th>
<th>6-31G(d,p) (ND$_3$)</th>
<th>6-311G(d,p)</th>
<th>6-311++G(3df,3pd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>857.64 / 9.01e-4</td>
<td>853.35 / 9.84e-4</td>
<td>857.83 / 8.85e-4</td>
<td>658.26 / 6.92e-4</td>
<td>654.20 / 7.55e-4</td>
<td>658.40 / 6.82e-4</td>
<td></td>
</tr>
<tr>
<td>1497.50 / -5.51e-5</td>
<td>1493.92 / -2.98e-5</td>
<td>1492.82 / -1.01e-5</td>
<td>1096.23 / 3.96e-5</td>
<td>1093.69 / -2.09e-5</td>
<td>1092.99 / -4.02e-5</td>
<td></td>
</tr>
<tr>
<td>1497.70 / -2.55e-5</td>
<td>1494.06 / -1.34e-5</td>
<td>1492.96 / -2.66e-5</td>
<td>1096.36 / -1.82e-5</td>
<td>1093.78 / -9.28e-6</td>
<td>1093.08 / -1.93e-5</td>
<td></td>
</tr>
<tr>
<td>3260.44 / -2.10e-5</td>
<td>3255.11 / -4.02e-5</td>
<td>3254.24 / -3.20e-5</td>
<td>2306.37 / -1.48e-5</td>
<td>2302.60 / -2.86e-5</td>
<td>2301.98 / -2.28e-5</td>
<td></td>
</tr>
<tr>
<td>3445.83 / -6.66e-5</td>
<td>3424.89 / -8.33e-5</td>
<td>3423.99 / -7.40e-5</td>
<td>2555.73 / -5.02e-5</td>
<td>2540.01 / -6.26e-5</td>
<td>2539.09 / -5.58e-5</td>
<td></td>
</tr>
<tr>
<td>3445.93 / -2.50e-5</td>
<td>3424.95 / -3.04e-5</td>
<td>3424.06 / -1.30e-5</td>
<td>2555.77 / -2.08e-5</td>
<td>2540.01 / -2.47e-5</td>
<td>2539.10 / -2.66e-5</td>
<td></td>
</tr>
</tbody>
</table>

First value is frequency / cm$^{-1}$ and second value is hfcc average / a.u.
Note that the hfcc averages have not been scaled by free atom hfcc values.

**The methyl radical.**

The methyl radical has been the subject of much research over the years including vibrational and temperature dependence research. These calculations centre on the basic
methyl radical rather than the substituted versions such as the fluoromethyl radical which present a problem of a double minima in the bending mode [20, 21]. Various experimental hfcc are given in table 2.32 for the radical in different environments, the value in liquid methane being the most often quoted value at -23.0G. Experimentally the gradient of the temperature dependence curve [5, 6] is 2.1mG/K. The values of the hfcc at 4K in liquid methane and argon are almost identical, the liquid methane value being a little smaller. Liquid hydrogen at 4K shows a value a little higher than that for argon. The data shows a minimal temperature effect between 4K and 97K in liquid methane which in linear terms would give a gradient of 0.75mG/K.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Medium/Medium</th>
<th>$\Delta_{\text{isoH}}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>Liquid methane / 97K</td>
<td>(-)23.04</td>
<td>5</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>Liquid methane / 4K</td>
<td>(-)22.97</td>
<td>5*</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>Argon / 4K</td>
<td>(-)23.06</td>
<td>5*</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>Hydrogen / 4K</td>
<td>(-)23.21</td>
<td>5*</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>Water / 273K</td>
<td>(-)22.67</td>
<td>6</td>
</tr>
<tr>
<td>CD$_3$</td>
<td>Liquid methane / 97K</td>
<td>(-)33.576</td>
<td>5</td>
</tr>
</tbody>
</table>

All hfcc in Gauss

*These are secondarily quoted from another reference cited in ref 5.
This reference does not give a negative sign for the hfcc usually reported elsewhere

With a gradient of 2.1mG/K, the methyl radical shows a reasonably strong temperature dependence. The theoretical calculations of this gradient, taken as an approximation between 300K and 500K assuming linearity over this range are shown in table 2.33. The gradient is overestimated by all calculations but there is a trend toward a smaller gradient with increasing basis set size shown by both methods, the BLYP/6-311++G(3df,3pd) basis giving a gradient of 3.70mG/K. The B3LYP method gives very similar but slightly larger gradients for an equivalent basis. In comparison with table 2.34 showing the total hfcc with zero point corrections, its is unfortunate that the 6-311++G(3df,3pd) basis underestimates the equilibrium hfcc by a large amount, however, given the number of sources of error affecting the gradient it is a reasonable result to obtain a value within a few mG/K.
The theoretical gradients presented below show a decrease with an increase in the frequency of the lowest mode, an effect that occurs due to the increasing separation of the second excited state with increasing fundamental frequency. Comparing the BLYP and B3LYP results for the first two basis sets, the B3LYP gradients are higher even though the frequency of mode 1 is higher than its BLYP counterpart. The explanation of this small anomaly lies with the higher wavefunction averages of the B3LYP method.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Gradient</th>
<th>Mode 1</th>
<th>Mode 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>6.11</td>
<td>458.60</td>
<td>1385.34</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>5.13</td>
<td>503.26</td>
<td>1369.32</td>
</tr>
<tr>
<td>BLYP</td>
<td>6-311++G(3df,3pd)</td>
<td>3.70</td>
<td>543.63</td>
<td>1373.51</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>6.34</td>
<td>461.67</td>
<td>1420.49</td>
</tr>
<tr>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>5.33</td>
<td>505.07</td>
<td>1430.24</td>
</tr>
</tbody>
</table>

Table 2.33 Gradients of methyl radical temperature curve and the two lowest freq. modes

Gradients expressed as mG/K between 300 and 500K scaled by free atom hfcc ratio (see earlier)
Modes 2 and 3 are almost doubly degenerate, lowest frequency shown

Calculations of the equilibrium hfcc and zero point contributions for CH₃ differ in their success somewhat, as is shown in table 2.34 below. The closest calculation to the experimental result is B3LYP/6-311G(d,p). As has been seen in other calculations, the equilibrium values vary somewhat, in this case by upto 7G, the largest basis set giving the smallest value and correspondingly giving the smallest zero point contribution for both CH₃ and CD₃. The vibrational contributions are opposite in sign to the equilibrium hfcc making a positive contribution to the hfcc and leading to a positive temperature dependence, an effect originating from loss of symmetry in the π system which would obviate spin polarisation effects.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Method</th>
<th>Basis</th>
<th>Equilibrium</th>
<th>Vibrational</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-24.12</td>
<td>2.18</td>
<td>-21.94</td>
</tr>
<tr>
<td>CH₃</td>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>-22.64</td>
<td>2.05</td>
<td>-20.59</td>
</tr>
<tr>
<td>CH₃</td>
<td>BLYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-19.78</td>
<td>1.60</td>
<td>-18.19</td>
</tr>
<tr>
<td>CH₃</td>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-26.19</td>
<td>2.24</td>
<td>-23.95</td>
</tr>
<tr>
<td>CH₃</td>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>-24.69</td>
<td>2.10</td>
<td>-22.59</td>
</tr>
<tr>
<td>CD₃</td>
<td>BLYP</td>
<td>6-31G(d,p)</td>
<td>-24.12</td>
<td>1.71</td>
<td>-22.41</td>
</tr>
<tr>
<td>CD₃</td>
<td>BLYP</td>
<td>6-311G(d,p)</td>
<td>-22.64</td>
<td>1.60</td>
<td>-21.03</td>
</tr>
<tr>
<td>CD₃</td>
<td>BLYP</td>
<td>6-311++G(3df,3pd)</td>
<td>-19.78</td>
<td>1.25</td>
<td>-18.54</td>
</tr>
<tr>
<td>CD₃</td>
<td>B3LYP</td>
<td>6-31G(d,p)</td>
<td>-26.19</td>
<td>1.75</td>
<td>-24.43</td>
</tr>
<tr>
<td>CD₃</td>
<td>B3LYP</td>
<td>6-311G(d,p)</td>
<td>-24.69</td>
<td>1.65</td>
<td>-23.05</td>
</tr>
</tbody>
</table>

Table 2.34 Calculated CH₃ and CD₃ hfcc values

All hfcc in Gauss
Deuterated values in reduced form (CD₃ observed is -23.295G reduced)
The BLYP values for the total hfcc underestimate the observed hfcc for both CH₃ and CD₃, the effect being less noticeable for CD₃ in unreduced form due to the scaling. The B3LYP values for the total hfcc are reasonably close to observed hfcc, however, if the trend observed with increasing basis set size for BLYP is followed, the B3LYP/6-311++G(3df,3pd) calculation would underestimate the observed CH₃ hfcc.

The vibrational contributions broken down by mode follow essentially the same pattern as NH₃. Table 2.35 below shows data only for CH₃.

<table>
<thead>
<tr>
<th>Mode</th>
<th>BLYP / 6-31G(d,p)</th>
<th>BLYP / 6-311G(d,p)</th>
<th>BLYP / 6-311++G(3df,3pd)</th>
<th>B3LYP / 6-31G(d,p)</th>
<th>B3LYP / 6-311G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>458.60 / 1.53e-3</td>
<td>503.26 / 1.46e-3</td>
<td>543.63 / 1.19e-3</td>
<td>461.67 / 1.59e-3</td>
<td>505.07 / 1.51e-3</td>
</tr>
<tr>
<td></td>
<td>1385.34 / -1.20e-4</td>
<td>1369.32 / -4.83e-5</td>
<td>1373.51 / -1.69e-5</td>
<td>1420.49 / -1.30e-4</td>
<td>1403.24 / -1.46e-5</td>
</tr>
<tr>
<td></td>
<td>1385.48 / -2.18e-5</td>
<td>1369.33 / -1.20e-5</td>
<td>1373.54 / -8.88e-5</td>
<td>1420.56 / -2.30e-5</td>
<td>1403.25 / -5.99e-5</td>
</tr>
<tr>
<td></td>
<td>3059.14 / -1.58e-5</td>
<td>3034.90 / -5.13e-5</td>
<td>3042.15 / -3.94e-5</td>
<td>3131.58 / -1.97e-5</td>
<td>3103.95 / -5.45e-5</td>
</tr>
<tr>
<td></td>
<td>3236.12 / -5.10e-6</td>
<td>3208.26 / -1.30e-4</td>
<td>3215.59 / -9.76e-5</td>
<td>3313.34 / -6.77e-6</td>
<td>3282.95 / -3.81e-6</td>
</tr>
<tr>
<td></td>
<td>3236.23 / -7.06e-5</td>
<td>3208.31 / -3.55e-6</td>
<td>3215.61 / -5.37e-6</td>
<td>3313.46 / -7.59e-5</td>
<td>3282.95 / -1.40e-4</td>
</tr>
</tbody>
</table>

First value is frequency / cm⁻¹ and second value is hfcc average / a.u. Note that the hfcc averages have not been scaled by free atom hfcc values.

Here the molecule presents higher vibrational averages than those in the ^NH₃ radical. Referring to the BLYP/6-31G(d,p) data, the lowest mode contributes 2.56G alone, the remaining in-plane modes contribute a total of -0.39G. The in-plane modes result in the loss of ~15% of the magnitude of the contribution from the lowest mode, compare NH₃(BLYP / 6-31G(d,p)) value of ~21%.

Although the in-plane modes certainly modify the vibrational contributions by a non-negligible amount, the dominant effect in the methyl and NH₃ radicals still lies with the out of plane mode. Quantitative accuracy has not been achieved although the results are encouraging.

*The bicyclo [2,2,1] hept-2-ene (norbornene) radical.*
This is an example of a large flexible cage radical that possesses no actual π system beyond that at the radical centre and a more complex vibrational structure than the radicals considered previously with a larger number of low frequency modes that mainly originate from the cage structure. This compound exhibits various phases from plastic to crystalline dependent on temperature. From a theoretical angle this could present a problem due to the possibility of environmental interactions in the various phases, however, experimental data indicates that the effect of the solvent upon the hfcc is very small [28], the hfcc varying by less than 1% (see table 2.36). The EXO and ENDO positions are marked in fig 2.3 above to clarify the α and β locations, however in the parent molecule the connecting C-C bond is a double bond.

A muon or a proton can add to this double bond forming a radical with an α centre that is neither sp² or sp³ hybridised, the muon affording two different isomers that show different hyperfine frequencies (table 2.36). The protic radical also shows distinctive hfcc at the EXO and ENDO positions due to an asymmetric orbital at the α position.

Experimental temperature dependence data [27, 28] for the ENDO and EXO muonic radicals show that both curves present a negative temperature dependence which for a muon at the EXO position is much more pronounced than that of the ENDO and that they both follow an approximately linear trend over a temperature range of 150 - 300 K. Ref [28] notes
a similar data set to ref [27] but notes that the EXO temperature dependence data is dependent on the thermal history of the sample and that no discontinuities are shown over the liquid-plastic phase transition.

Ref [28] gives the gradient of the EXO temperature dependence curve as -0.10 MHz/K (-35.7 mG/K) and shows an ENDO curve with almost constant gradient. Ref[27] gives no numerical values for the gradients but shows a graph for which the EXO line is very close to that of [28] but with an ENDO line showing a slightly more pronounced negative gradient but still very small in comparison to the EXO.

Table 2.36 Hyperfine frequencies of muonated norbornene radical at 300K in various solvents

<table>
<thead>
<tr>
<th>Position</th>
<th>Solvent (a)</th>
<th>Solvent (b)</th>
<th>Solvent (c)</th>
<th>Solvent (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXO</td>
<td>410.20 (146.75)</td>
<td>409.4 (146.46)</td>
<td>409.7 (146.57)</td>
<td>409.0 (146.32)</td>
</tr>
<tr>
<td>ENDO</td>
<td>256.45 (91.74)</td>
<td>256.8 (91.87)</td>
<td>256.4 (91.73)</td>
<td>255.0 (91.23)</td>
</tr>
</tbody>
</table>

Data from ref [28]. First value is hfcc in MHz, bracketed in gauss. Values are unreduced.
(a) Pure norbornene, (b) 2M norbornene in ethanol
(c) 2M norbornene in norbornane, (d) 2M norbornene in cyclohexane

Kawamura et al. [29] studied the protic radical in cyclohexane and found hfcc of 41.7G at the EXO position, 25.6G at the ENDO and (-)20.6G at the alpha position measured at 147K.

Theoretical calculations have been performed here using BLYP/6-31G(d,p) accounting for the vibrational modulation effects of all normal modes upon the protic radical in addition to the ENDO and EXO muon substituted radicals. The radicals posses a number of low frequency modes (table 2.37) that are mainly due to cage flexions which have a substantial bearing on the temperature dependence of this radical.
The molecule possesses a considerable number of normal modes, the first few of which make the major vibrational contributions. The addition of a muon at either the EXO or ENDO position makes no major impact on these low frequency modes, however in both cases the higher frequency modes are increased with respect to the protic radical. There is no significant difference between the EXO and ENDO modes except at high frequency,
The Temperature Dependence of Isotropic HFCC’s particularly those in which the muon participates dominantly, the highest frequency mode making a significant contribution to the hfcc which will effectively act as a constant contribution to the temperature dependence due to the high energy of this mode.

The hfcc calculations are shown below in table 2.38 for $\alpha$, $\beta_{\text{ENDO}}$ and $\beta_{\text{EXO}}$ for the three radicals.

Table 2.38 BLYP/6-31G(d,p) hfcc calculations for bicyclo [2,2,1] hept-2-ene

<table>
<thead>
<tr>
<th>Radical / Position</th>
<th>Equilibrium</th>
<th>Vibrational</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protic / Alpha</td>
<td>-20.31</td>
<td>1.80</td>
<td>-18.51</td>
</tr>
<tr>
<td>Protic / Endo</td>
<td>26.62</td>
<td>1.10</td>
<td>27.72</td>
</tr>
<tr>
<td>Protic / Exo</td>
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<td>45.87</td>
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<td>-18.64</td>
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<tr>
<td>Exo muon / Endo</td>
<td>26.62</td>
<td>1.95</td>
<td>28.57</td>
</tr>
<tr>
<td>Exo muon / Exo</td>
<td>44.45</td>
<td>5.73</td>
<td>50.18 (150.74)</td>
</tr>
<tr>
<td>Endo muon / Alpha</td>
<td>-20.31</td>
<td>1.35</td>
<td>-18.96</td>
</tr>
<tr>
<td>Endo muon / Endo</td>
<td>26.62</td>
<td>3.44</td>
<td>30.06 (95.69)</td>
</tr>
<tr>
<td>Endo muon / Exo</td>
<td>44.45</td>
<td>0.48</td>
<td>44.93</td>
</tr>
</tbody>
</table>

**Emboldened text refer to muon substituted positions.**

All hfcc in gauss, muon values in reduced form except for bracketed values which are scaled for muon magnetic moment

As would be expected, the vibrational contributions from those positions substituted with a muon are much increased relative to their proton counterparts and it can be seen that the presence of the muon causes a slight effect on the vibrational contributions from the surrounding $\alpha$ and $\beta$ protons, an exo muon causing an increase at the endo position and a small decrease at the $\alpha$ position. The endo muon again causes a decrease at the $\alpha$ position and a large decrease in the vibrational contribution from the exo position (1.42G Vs 0.48G).

These variations in the hfcc at positions other than those muon substituted are interesting in light of the usual assumption that the majorly contributing muon modes are essentially decoupled from all other modes. Although the muon for most purposes can be regarded as decoupled, the above results show that the small perturbations to the other modes can have a significant effect.

For the protic radical, the total hfcc are reasonably close to the experimental values, all positions being overestimated slightly. The muon hfcc estimations are again reasonably close, the exo muon being overestimated by ~13G and the endo muon by ~4G relative to the
experimental for the radical in pure norbornene at 300K, which considering the neglect of the inherent anharmonicity of muon stretching modes is not an unreasonable result. The large difference in the hfcc for the endo and exo positions is likely to arise from the asymmetry of the orbital at the alpha position which will interact more strongly with the exo atom leading to a higher spin density at this position.

Since absolute comparisons of the hfcc are suspect due to the sensitivity of the equilibrium contribution to the method and basis set, a better comparison to experimental results would be the ratio of ENDO and EXO hfcc between ESR and μSR data (after ref[28]). Table 2.39 below shows the ESR/μSR and ENDO/EXO ratios for both experimental data (from [27] and [28]) and the above calculations. There is no essential difference between the calculated values taken at 147K (as were the experimental) and 0K.

The ratios of the calculated hfcc are slightly lower than the experimental but nevertheless in very good agreement. The ESR/μSR ratio is a direct indication of the isotope effect. An exact correlation would not be expected due to the lack of consideration of anharmonic effects in the muon modes which can make a considerable contribution (see HCO section earlier). The endo/exo ratio is very close to the experimental value which is good indication that the relative differences in the calculation are small even if the absolute differences are large.

The temperature variance calculations are more successful for this molecule than previous molecules. The comparison of the curves for the reduced hfcc at the α, β_{endo} and β_{exo} positions are shown in Figs 2.4, 2.5 and 2.6 below respectively.
The calculations are successful at predicting the negative temperature dependence of the \( \beta \) positions despite the zero point contribution being positive. This is a very good result as it directly shows that the model is allowing enhanced contributions from modes with a negative contribution as the temperature rises and overall giving a good description of the temperature dependence process, however as has been noted before and below, the model has significant problems dealing with the temperature dependence of the muon.

The alpha position shows a positive temperature dependence with gradients at the linear section between 300K and 500K of 4.95mG/K (protic radical and endo muon) and...
4.80mG/K for the exo muon radical. There is little difference between the comparable proton equivalent hfcc at this position, the substitution of a muon at the endo position having the largest effect increasing the magnitude of the reduced hfcc by -0.5G. In the protic radical the $\alpha$ hfcc is dominated by modes 2,3,4 and 5 which contribute 1.497G. The remaining modes contribute 0.306G in total. On muon substitutions at the endo and exo position, the majority of the contributions at the $\alpha$ position arise from modes 2,4 and 5 (contributions above 1.0e-4 a.u.).

The endo position shows a negative temperature dependence with a similar gradients in the linear section of -2.1mG/K (protic), -2.0mG/K (exo substituted) and -2.6mG/K (endo substituted radical). Experimentally the gradient of the endo muon hfcc is almost non existent compared to the exo muon hfcc. In the endo substituted radical, the endo position temperature dependence the largest contribution arises from mode 2 which is the only one above 1.0e-4 a.u.
a.u., the other modes at the low frequency end are on the order of $10^{-5}$ a.u and all negative. These negative modes dominate the temperature dependence leading to a negative gradient.

The exo positions show a little more variation across the radicals. The linear gradients here are again negative with values -5.5mG/K (protic), -8.7mG/K (endo substituted) and -4.3mG/K (exo substituted). Experimentally the gradient of the exo position with a muon at this location is -0.1MHz/K (-35.77mG/K) which is drastically underestimated by the theoretical calculations which was also seen to a lesser degree for the allyl radical. The exo position in the exo substituted radical is dominated by modes 2, 4 and 5 which are all negative in sign. The majority of the remaining modes contribute negatively to the hfcc, but there are some positive contributions such as from mode 1 which makes a contribution on the order of $2.4e-5$ a.u. These positive contributions arising from very low frequency modes could lead partially to the drastic underestimate of the thermal gradient but as has been mentioned earlier as they will gain significant magnitude at high temperatures.

*Summary and Conclusions.*
Calculations have been performed in an attempt to access the effects of including vibrational modifications to hyperfine coupling constants by accounting for the contributions arising from all normal modes and the estimation of the temperature variance of the observable in terms of the Boltzmann population model using two common density functional methods and commonly employed standard basis sets.

Success has been a mixed affair. In some cases almost quantitative accuracy has been achieved while in others there are significant problems. In all cases of calculation of the thermal gradient, qualitative accuracy has been achieved with the gradient being calculated in the correct direction.

A number of important points have arisen from the calculations;

- A major source of variation in the hfcc values arises from the equilibrium calculation which can differ wildly with theoretical method and basis set.
- The vibrational contribution in some cases is not negligible.
- The vibrational contributions for a given molecule are very similar over different basis sets and methods, but proportionately vary just as much as equilibrium hfcc values.
- The gradient of the linear section of the temperature dependence curve is not well described by the harmonic oscillator model, an effect most likely due partially to the harmonic oscillator approximation and partially to the description of the normal modes by the method and basis set.
- The sign of the temperature dependence is correctly described by the model.
- The model correctly describes the qualitative differences in the vibrational contributions for different isotopes when expressed in reduced form.
- The model fails to describe the difference in the gradient of the temperature dependence for different isotopes, particularly the muon.
• The isotope effect is reproduced reasonably well for the bicyclo [2,2,1] hept-2-ene radical.

The large variations in the equilibrium hfcc contributions present a problem for any attempt at direct comparison with experimental data. This is a problem that lies with the theoretical method and basis set and given that the values can in some cases almost reproduce experimental hfcc, this can lead to a game of 'pick and choose the calculation'. A possibility not explored here is the use of spin-density optimised basis sets which would improve the hfcc situation. A distinct advantage of using standard basis sets is that they have a large database of information available against which to judge performance.

There exist other options for vibrational analysis such as the use of different vibrational co-ordinate systems [58] (i.e. distinguished co-ordinates) which may present a better option in some cases and the use of LAM path based analysis which was touched upon earlier. Anharmonic effects would present an advantageous addition to the model improving the frequencies and vibrational wavefunctions available especially where muons and known anharmonic proton modes are involved.

It is clear that there are processes involved that are not accounted for by the model as is evidenced by the incorrect description of the thermal gradient for a muon. The most likely source of error in this case lies with a combination of the Boltzmann model and the harmonic analysis but given possibilities such as vibrating molecules acting as chaotic systems, any method such as harmonic and anharmonic analysis will be an approximation. A possibility that lies in the future is the complete mapping of the electronic and vibrational space of a molecule to obtain theoretical observables that are not dependent on a mathematical decomposition of the problem as normal mode approaches are, either by the use of analytic techniques or a Monte-Carlo based statistical approach. This style of approach would obviate
the effects of any possible breakdown of the Born-Oppenheimer approximation which remains as an unlikely but possible problem with the muon.

In the more immediate present, this work could be extended to include studies of the behaviour of different functionals, in particular Perdew-Wang'91 which is a gradient corrected functional and CI based techniques as a benchmark. Spin density basis sets such as those due to Chipman would be an advantageous step as would anharmonic analysis.

A major problem with the application of this technique is the enormous number of calculations involved. An interesting possibility would be to try an estimate the wavefunction average of a mode on the basis of a very small molecular displacement along the normal mode and make an approximate estimate of those modes that do not appear significant thus decreasing the number of calculations required.

Ab-initio studies of radical systems with the inclusion of vibrational effects is a viable possibility with the use of density functional methods, although as molecular size increases the number of calculations involved drastically increases making its application useful only in the most difficult cases. More quantification of the technique is needed to determine its behaviour and more research to resolve the light isotope difficulties.
References


[61] Cross, Decius and Wilson, 'Molecular Vibrations', 1955.
Chapter 3

The Microscopic Structure of c-Si
Introduction

Most modern electronic components are based upon the modification of the semiconducting properties of silicon that can be brought about by introducing impurities such as phosphorus and boron along with a passivating agent, usually hydrogen, into the lattice. It is of no surprise therefore that the study of the lattice defects caused by the presence of these impurities have been, and continue to be a subject of much interest in condensed-matter physics and theoretical chemistry. The physical structure of acceptor (e.g. B, Al) and donor (e.g. P, As) complexes has been the subject of some debate due to the difficulty of obtaining direct information, however, many studies both from a theoretical and an experimental angle have settled on the structures shown in Fig 3.1a and 3.1b for hydrogen passivated acceptor and donor complexes respectively.

Evidence has come from direct methods such as ion-channelling and x-ray diffraction that have pointed to crystal structures possessing a unit-cell symmetry of group \( C_{3v} \). The behaviour of IR [10] spectra under stress back up these observations. Theoretical studies aimed at estimation of the vibrational frequencies of the hydrogen units have been shown to be in good agreement with experiment, however, while it is generally agreed that the physical structure is as shown in Fig 3.1a and 3.1b, the relaxation characteristics of the defect atoms with respect to the unperturbed lattice are less well resolved with conflicting results from the various theoretical methods and defect models being reported.

Study of the defect sites in lattices from a theoretical angle presents a problem in that the lattice symmetry is broken by the presence of the impurities which makes the application of techniques from solid-state physics impossible. There are two main approaches to the problem of modelling these systems, the cluster approach and the supercell approach. In the
cluster approach, the system is modelled from the point of view of a defect situated in an infinite host lattice with dangling bonds on the cluster surface being passivated with hydrogen. Although ideally the lattice should be as large as possible, in practice a balance has to be struck between the size of the lattice and the available computational resources, however, it must be noted that a cluster that is too small may lead to artefacts in the results arising from surface effects.

In the supercell approach, the lattice is modelled by replicated cells containing the defect site. While this approach has the advantage of creating a more realistic lattice structure, the supercell must be as large as possible to reduce the possibility of artificial interactions between the defects which again raises the problem of computational resources.

In this section we examine the physical structure and relaxation characteristics of a hydrogen passivated silicon-donor complex employing an Si$_{13}$XH$_{25}$ cluster model for X=P and As dopants (Fig 3.2). The silicon cluster and an analogous carbon cluster with a nitrogen impurity are examined using SCF, MP2 and B3LYP based methods with the standard 3-21g, 3-21g(d,p) and 6-31g(d,p) basis sets. In addition to these calculations, the use of complete optimisation of the cluster parameters within certain symmetry constraints are compared against the use of experimentally determined parameters within the same constraints.

![Fig 3.1a](image1.png) ![Fig 3.1b](image2.png)
Calculation Methods

The impurity complex was modelled using a Si$_{13}$HXH$_{24}$ (X=P, As) cluster with the unshown dangling surface bonds on the silicon atoms saturated with hydrogen as shown in Fig's 3.2a and 3.2b. The choice of this particular configuration satisfies two important properties, (a) the retention of the C$_{3v}$ unit-cell symmetry observed experimentally by x-ray techniques and (b) the presence of sufficient host atoms to provide a good approximation of the defect environment. The cluster extends the simplistic structure shown in Fig's 3.1a and 3.1b by providing a more realistic cage environment for the passivating hydrogen.

Two different sets of calculations were performed in order to address the question of the use of empirical parameters to construct the cluster geometry. In both cases the clusters were restricted to C$_{3v}$ symmetry, all angles were set to tetrahedral (as occurs in an unperturbed silicon lattice) and all Si-Si bond lengths were set to be equal and kept so during any initial geometry optimisation. Additionally the surface hydrogen's were grouped into different symmetry environments and each group allowed to optimise individually, the SiH$_3$ units attached to atom X$_2$ were oriented to a minimum energy position. This procedure would remove most of the arbitrary forces imposed by a particular basis set.

The most comprehensive set of calculations used full geometry optimisation of the cluster within the symmetry restrictions laid down above. A smaller set of calculations were

![Fig 3.2a](image1.png)  ![Fig 3.2b](image2.png)

(a) Si$_{14}$H$_{24}$ cluster. X$_1$ and X$_2$ = Si  
(b) Si$_{13}$HXH$_{24}$ cluster. X$_2$ = P or As
performed on empirical clusters in which the Si-Si bond length was set to an average experimental value of 2.38 Å and all surface hydrogen bond lengths set to 1.48 Å in an attempt to judge the effects of using a geometry representing a non-stationary point on the energy surface of a particular method and basis set.

A key question that arises in the use of any approximation is that of validity. If a particular cluster configuration is a valid approximation of the ideal infinite lattice, then there should be no appreciable forces acting on the atoms internal to the cluster. Hence if the exterior atoms of the cluster are fixed in some position, determined by geometry optimisation, upon relaxation (the interior atoms are allowed to move subject to any symmetry constraints) there should be no significant displacement of these atoms relative to their original positions.

To this end, calculations were performed using a variety of theoretical methods and basis sets on the cluster displayed in fig 3.2a in which the cluster was re-optimised (its geometry being either determined by a previous optimisation or by the use of empirical parameters) with all atoms fixed except \(X_1\) and \(X_2\) which were allowed to move along the \(z\) axis of the cluster (the \(z\) axis is co-incident with the \(C_3\) axis). On the basis that atom \(X_1\) was chosen to be at zero \(z\) co-ordinate and the negative \(z\) direction was toward the cage structure, the displacements were calculated, a positive displacement indicating relaxation toward the cage.

This procedure was chosen to reveal any excessive forces present in the cluster that may arise as a result of surface effects due to finite cluster size and deficiencies in the electronic description of the system without resorting to harmonic force-constant calculations that for the MP2 method can be excessively resource hungry.

Once the suitability of the cluster had been established, the next stage was to perform the same calculation as above on the cluster in Fig 3.2b where \(X_2\) is P or As and a passivating hydrogen is introduced at the anti-bonding site of atom \(X_1\) which is silicon. The displacement
of the atoms $X_1$, $X_2$ from the positions in the unperturbed cluster were calculated again with clusters based on optimised and empirical geometries.

For the purposes of comparison, a similar set of calculations were performed for an analogous carbon cluster with a nitrogen impurity, in the empirical case using a C-C bond length of 1.5445Å and a C-H bond length of 1.091Å. Identical restrictions on the symmetry of this cluster were imposed to those imposed on the silicon cluster.

These calculations wherever possible were performed using combinations of SCF, B3LYP and MP2 methods with the common basis sets, STO-3G, 3-21G, 3-21G(d,p) and 6-31G(d,p) in order to gain an overall view of the predictions made with regard to the geometry and relaxation characteristics of the cluster, the particular basis sets being chosen to represent those commonly used in quantum chemistry, STO-3G being included merely as a benchmark as it is inadequate in a practical setting. Due to constraints on computer resources, some MP2 results are missing, however, for SCF and B3LYP methods a complete set exists for all clusters.

The various methods differ mainly in their inclusion of electron correlation effects, SCF is the common HF method which treats an electron as moving in an averaged field of all other electrons, MP2 is second order Møller-Plessett perturbation theory which includes some electron correlation effects and B3LYP is one of many variations of the more recent density functional theory(DFT).

The DFT methods are of interest not least due to the fact that they express an exact ground state wavefunction for a many-electron system which makes them of particular use in the estimation of electron density based observables such as spin-densities. The B3LYP method selected is Becke's three parameter hybrid method that uses the gradient corrected correlation-exchange functional of Lee, Yang and Parr.
Results

Cluster geometry.

Table 3.1 shows the various optimised bond lengths for the cluster in fig 3.2a in addition to the mean averaged Si-H bond lengths for the three surface hydrogen environments.

STO-3G basis underestimated Si-Si and SI-H bond lengths for all three methods, the other basis sets performing somewhat better. An interesting artefact of the results occurs between 3-21G and 3-21G(d,p) results, the latter basis showing a shorter bond length which may be attributed to the extra flexibility afforded by polarisation functions. Progression to the 6-31G(d,p) basis shows a lengthening of the bond distance by about 0.03 Å.

Table 3.1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SCF</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
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</tr>
<tr>
<td>r_{Si-Si}</td>
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<tr>
<td>r_{Si-H(AVG)}</td>
<td>1.4805</td>
<td>1.5055</td>
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</table>

A table of optimised bond lengths(Å) for the pure silicon cluster.

The SCF and B3LYP Si-Si distances for the two largest basis sets compare very well, the MP2 values being significantly smaller a trend not reflected in the Si-H distances where the B3LYP values are slightly larger.

The Si-Si variances with basis set may be attributed in part to variations in the description of the electronic structure of the Si atom by the basis which would lead directly to variations in bond distance estimation. Overall agreement with the experimental values is reasonable, especially for the Si-H distances. The Si-Si values differ somewhat showing a marked dependence on the basis set.

The coincidence of the SCF and B3LYP Si-Si/3-21G(d,p) distances with the experimental value of 2.351 Å [16] can be regarded as fortuitous in light of the other results. It
is of slight concern that the B3LYP and MP2 values do not agree given that both methods include electron correlation effects (both by different mathematical techniques) which suggests that one method may be liable to producing artefacts. Turning attention to the carbon analogue of the silicon cluster (fig 3.2a), the optimised structural parameters are shown in table 3.2 below.

The results for the carbon cluster show much less variability than those for the silicon cluster, the C-H distances being estimated to better than 0.01Å for all methods and basis sets. The estimation of the C-C distance is subject to a little more variation, all methods and basis sets overestimating slightly with the exception of MP2/6-31G(d,p) which estimates this parameter very closely. The SCF method performs reasonably well, the overestimate being less than 0.01Å for all basis sets while the MP2 method starts with a large overestimate of 0.034Å with STO-3G but for 6-31G(d,p) estimates it very well. B3LYP on the other hand performs somewhat worse than the other methods, its best estimate being 0.023Å with a 6-31G(d,p) basis.

For both the silicon and carbon clusters, the SCF/6-31G(d,p) combination performs very well for the purpose of estimating structural parameters. B3LYP/6-31G(d,p) performs reasonably well and is a good compromise where computational resources are restricted and consideration of electron correlation is important for subsequent calculations. Some of the variations could arguably be attributed to the finite size of the cluster and some variance from experiment is to be expected on this basis alone which would tend to cast a new interpretation of the MP2 results as a co-incidence. In addition, this the basis set does not account for a mathematical approximation of any particular method which contributes to the variations. The next point to be addressed is that of the suitability of the cluster for calculations involving relaxation of the internal atoms X₁ and X₂ of the cluster in fig 3.2a.
As has been noted previously, if the cluster was a perfect representation of an infinite lattice, there should be no appreciable displacement of internal atoms ($X_1$ and $X_2$ in Fig 3.2a) upon relaxation, and further any displacement should preserve the bond length between the displacing atoms.

This issue is of particular relevance when addressing relaxation calculations performed upon a cluster whose geometry does not lie at a minimum energy with respect to the particular method and basis being used since the existence of significant non-zero energy gradients at that particular geometry may lead to anomalous motion due to the optimisation alone. Calculations on the cluster with empirical Si-Si and Si-H bond lengths were performed using an older Si-Si value of 2.38Å instead of a more modern value of 2.351Å [16].

The older value, although closer to the optimised B3LYP and SCF 6-31G(d,p) results does not particularly detract from the fundamental purpose of the exercise since one would expect to see much lower atomic displacements for SCF and B3LYP 6-31G(d,p) calculations than in the MP2 / 6-31G(d,p) data if the cluster geometry has a major effect on the atomic relaxation’s.

Table 3.3 below shows the relaxation distances and the bond lengths between $X_1$ and $X_2$ for the silicon cluster, the results for the optimised cluster appearing first and those for the cluster with empirical parameters following. A positive $\Delta$ value indicates movement toward the cage structure in Fig 3.2a.

The results obtained are encouraging, especially for the empirical cluster where the largest validity concerns lie. The three methods broadly agree on a number of points;

1. The $X_1$-$X_2$ distance is slightly shorter in the relaxed position than the Si-Si distance employed elsewhere in the cluster, but not by a significant amount, a feature observed in both the empirical and optimised clusters.
2. The displacements of the relaxing atoms are small, below 0.02Å.

3. The displacements of both atoms are away from the cage structure.

<table>
<thead>
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<th>Parameter</th>
<th>SCF</th>
<th>B3LYP</th>
<th>MP2</th>
</tr>
</thead>
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<td>ΔX_1</td>
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<td>-0.0123</td>
<td>-0.0129</td>
</tr>
<tr>
<td>ΔX_2</td>
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<td>-0.0038</td>
<td>-0.0109</td>
</tr>
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<td>X_{1-X_2}</td>
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<td>2.3772</td>
<td>2.3502</td>
</tr>
<tr>
<td>R_{Si-Si}</td>
<td>2.2554</td>
<td>2.3857</td>
<td>2.3522</td>
</tr>
<tr>
<td>ΔX_{1}</td>
<td>-0.0204</td>
<td>-0.0122</td>
<td>-0.0106</td>
</tr>
<tr>
<td>ΔX_{2}</td>
<td>-0.0134</td>
<td>-0.0040</td>
<td>-0.0096</td>
</tr>
<tr>
<td>X_{1-X_2}</td>
<td>2.3730</td>
<td>2.3718</td>
<td>2.3790</td>
</tr>
</tbody>
</table>

Relaxation distances (Å) for pure silicon cluster (See fig 3.2a).

The first set of results are for the optimised cluster.

The **emboldened** results are the optimised Si-Si bond lengths from table 3.1

The second set in *italics* are for the empirical parameter cluster.

Although with values so small, no practical conclusions can be drawn, the results across all calculations are not drastically dissimilar from each other. A noticeable feature is that there is very good agreement between the displacements observed in the empirical cluster to those in the optimised cluster. Although there is only one result for the MP2 calculations on the empirical cluster, this value is similar to the other empirical cluster STO-3G results but more encouragingly, the displacements estimated for the 3-21G and 3-21G(d,p) basis are very similar between the two clusters which lends strong evidence that the cluster geometry does not drastically affect the displacements (the 3-21G(d,p) Si-Si value is 2.35Å for SCF and B3LYP).

The SCF and B3LYP results follow each other closely both for displacements and the corresponding bond distance (X_1-X_2) the values not being too dissimilar to the Si-Si value used elsewhere in the cluster. The MP2 results differ slightly estimating smaller displacements and bond length for those basis sets where polarisation functions are included, the bond length being smaller by almost 0.02Å.

From the above results, the cluster employed gives no reason for major concerns over the validity of the configuration for use in relaxation calculations. The imposed symmetry constraints, surface effects and theoretical deficiencies do not appear to contribute majorly to
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internal forces and more interestingly, the displacements do not appear to be majorly sensitive to small differences in the geometry of the system as is evidenced by the nearly identical displacement distances shown by the empirical cluster.

As a parallel, the same calculations were performed on the carbon cluster the results for which are displayed in table 3.4 below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SCF</th>
<th>B3LYP</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>STO-3G</td>
<td>3-21G</td>
<td>6-31G(d,p)</td>
</tr>
<tr>
<td>ΔX₁</td>
<td>-0.0060</td>
<td>-0.0090</td>
<td>-0.0090</td>
</tr>
<tr>
<td>ΔX₂</td>
<td>-0.0097</td>
<td>-0.0071</td>
<td>-0.0044</td>
</tr>
<tr>
<td>rₓ₁₋ₓ₂</td>
<td>1.5620</td>
<td>1.5599</td>
<td>1.5514</td>
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<tr>
<td>rₓ₁₋ₓ₂</td>
<td>1.5583</td>
<td>1.5528</td>
<td>1.5560</td>
</tr>
<tr>
<td>ΔX₁</td>
<td>-0.0069</td>
<td>-0.0100</td>
<td>-0.0102</td>
</tr>
<tr>
<td>ΔX₂</td>
<td>-0.0104</td>
<td>-0.0096</td>
<td>-0.0061</td>
</tr>
<tr>
<td>rₓ₁₋ₓ₂</td>
<td>1.5480</td>
<td>1.5431</td>
<td>1.5404</td>
</tr>
</tbody>
</table>

Relaxation distances(Å) for pure carbon cluster.
The first set of results are for the optimised cluster.
The **boldened** results are the optimised C-C bond lengths from table 3.2
The second set in *italics* are for the empirical parameter cluster.

The observations noted for the silicon cluster are backed up by similar calculations on the analogous pure carbon cluster. Again a very close agreement between the atomic relaxations of the optimised and empirical cluster is observed for equivalent basis sets with a small displacement of the atoms (with the exception of ΔX₂(MP2/6-31G(d,p)) which is anomalously large at -0.0303Å). The data from these calculations reiterate the point that the displacements mainly originate from surface and basis set effects.

All displacements are negative as before but they are smaller in magnitude than in the Si cluster, the exception being ΔX₂(MP2/6-31G(d,p)) which is conspicuously large at -0.0303Å putting it out of line with the other values. The smaller magnitude of the displacements may originate from a better description of the electronic structure of the carbon atom which would lead to better estimation of the bond distances.

Examination of the X₁-X₂ distances reveals another anomaly in that the MP2/6-31G(d,p) value is more than 0.02Å longer than the optimised C-C bond distance for the cluster which directly follows from the displacement parameters. This point is of some
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concern and in addition to the point noted for the silicon cluster could pose problems with using MP2 methods on these clusters.

The parallels between the carbon and silicon cluster suggest that while there are some minor residual forces in the cluster, these mostly due to structural effects, the differences in displacement magnitude between the C and Si clusters possibly arising from the differences in the electronic structure of the two clusters. The differences between the various basis sets for a given method can be attributed to the flexibility of the given basis. Interestingly electron correlation effects do not appear to impact much on the results as is shown by the similarities between the three methods with the exception of MP2/6-31G(d,p).

The phosphorus substituted cluster.

The results of the relaxation calculations for the phosphorus substituted cluster are shown in table 3.5 below for both the optimised and empirical clusters.

An immediately noticeable feature of the results is the variation of the $\Delta P$ values for both clusters predicted by the various calculations. The SCF results are all negative in sign whereas the inclusion of electron correlation effects in the other two sets gives different behaviour. The first two basis sets give positive displacements, while the other two which include polarisation functions give negative displacements. In addition to this, restricting attention to the 3-21G(d,p) and 6-31G(d,p) basis sets, both clusters show significant variation in the magnitude of the displacement. B3LYP predicts the smallest displacement, the value being not much larger than the relaxation noted in the unsubstituted cluster. The MP2 value is a little larger at twice the magnitude, with the SCF value being some 6.5 times larger at -0.0807Å.

An increase in the size of the basis in all cases leads to an increase in the magnitude of the displacement but the inclusion of electron correlation lowers the magnitude. The $\Delta P$
values for the empirical cluster follow those of the optimised cluster closely especially for the 6-31G(d,p) basis except for the STO-3G basis. On the basis of the results, although there may be a small displacement of the P atom, the change is small and given the magnitudes predicted it is likely that it originates from internal forces due to structural factors. There is a point that the P atom is slightly smaller than the Si atom in terms of its covalent radius (P=1.10Å, Si=1.18Å) and on this basis a small effect may be anticipated however this does not take into account electronic factors.

In contrast, the ΔSi values are very different. All calculations show a large positive displacement of the Si atom (X_i) into the cage structure on the order of 0.5Å which places the Si atom almost co-planar with the three basal Si atoms of the cage structure, a feature observed in other calculations on similar systems. The ΔSi values for the 3-21G(d,p) and 6-31G(d,p) basis sets show similar trends across the three methods as were noted for ΔP values, B3LYP shows the smallest displacements, SCF the largest. Additionally ΔSi increases from STO-3G to 3-21G, the same being repeated for 3-21G(d,p) to 6-31G(d,p). The empirical cluster results show different behaviour, the ΔSi values decreasing steadily from STO-3G to 6-31G(d,p), the 3-21G values in this case not appearing to be out of place. Although this puts the two sets of results at some variance with each other, the 6-31G(d,p) values for SCF and B3LYP are very close to their optimised counterparts in both cases which correlates with the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>STO-3G</th>
<th>3-21G</th>
<th>6-31G(d,p)</th>
<th>STO-3G</th>
<th>3-21G</th>
<th>6-31G(d,p)</th>
<th>STO-3G</th>
<th>3-21G</th>
<th>6-31G(d,p)</th>
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<tbody>
<tr>
<td>AP</td>
<td>-0.0387</td>
<td>-0.0126</td>
<td>-0.0649</td>
<td>-0.0807</td>
<td>+0.0349</td>
<td>+0.0721</td>
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<td>-0.0124</td>
<td>+0.0002</td>
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<tr>
<td>ΔSi</td>
<td>0.5408</td>
<td>0.6134</td>
<td>0.5549</td>
<td>0.5802</td>
<td>0.4915</td>
<td>0.5767</td>
<td>0.4802</td>
<td>0.5144</td>
<td>0.5767</td>
</tr>
<tr>
<td>ΔSi-H</td>
<td>1.4087</td>
<td>1.5272</td>
<td>1.5230</td>
<td>1.5117</td>
<td>1.4693</td>
<td>1.5639</td>
<td>1.5680</td>
<td>1.5549</td>
<td>1.5435</td>
</tr>
<tr>
<td>ΔSi-p</td>
<td>2.8349</td>
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<td>2.8988</td>
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<td>2.9358</td>
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<td>ΔP</td>
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<td>-0.0798</td>
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<tr>
<td>ΔSi</td>
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<td>0.6066</td>
<td>0.5927</td>
<td>0.5754</td>
<td>0.5600</td>
<td>0.5378</td>
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<td>0.6255</td>
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<td>ΔSi-H</td>
<td>1.4013</td>
<td>1.5274</td>
<td>1.5158</td>
<td>1.5101</td>
<td>1.4644</td>
<td>1.5660</td>
<td>1.5548</td>
<td>1.5547</td>
<td>1.4375</td>
</tr>
<tr>
<td>ΔSi-p</td>
<td>3.1432</td>
<td>2.9969</td>
<td>3.0604</td>
<td>3.0358</td>
<td>2.9472</td>
<td>2.8663</td>
<td>2.9280</td>
<td>2.9037</td>
<td>3.0323</td>
</tr>
</tbody>
</table>

Relaxation distances(Å) for phosphorus substituted silicon cluster.

The first set of results are for the optimised cluster.

The second set in italics are for the empirical parameter cluster.

SCF giving the smallest Si-H bond distance and B3LYP the largest, the difference being
0.43Å at the 6-31G(d,p) level.

In contrast to the Si-H distances, the Si-P lengths are somewhat more variable. As has been noted above, the empirical and optimised clusters agree quite closely at the 6-31G(d,p) level, however, for the other basis sets there are fairly large discrepancies. The MP2 and B3LYP methods with 6-31G(d,p) basis estimate the Si-P distance at 2.91Å while SCF/6-31G(d,p) gives a larger value of 3.03Å, the SCF values being larger for all basis sets than those of the other two methods, again a point noted in the ΔSi and ΔP values for this cluster.

The estimated Si-H distances are somewhat larger than the experimentally observed values of ~1.48Å, the inclusion of electron correlation effects increasing this distance but making the displacements of the P and Si atoms smaller compared to SCF. This offsets a tendency for the bond distances and displacements to increase with increasing basis set size. The correlation’s between the predictions of the B3LYP and MP2 methods, both of which include for some electron correlation effects suggest that the SCF results may be slightly out of line when dealing with a substituted cluster despite the close correlation’s with observed parameters noted in the first calculations.

The displacements are broadly consistent with other theoretical studies of this style of complex, ref. [7] reports a small displacement of 0.09Å for the P atom and 0.63Å for the Si atom within a P substituted Si supercell using HF calculations. Ref. [9] reports 0.66 and 0.18Å, ref. [12]; 0.819(Si) and 0.177(P) for a 7 atom Si cluster, 0.739(Si) and 0.187(P) for a 34 atom Si cluster both by a semi-empirical PRDDO method, 0.832(Si) and 0.020(P) for HF/STO-3G and 0.780(Si) and 0.030(P) for HF/SV (Split valence). Ref. [8] reports 0.74(Si) and 0.54(P) from a similar cluster to this work using MNDO method. Finally ref. [11] reports 0.557(Si) and 0.096(P) using a 64 atom supercell approach and density functional methods.

The displacements calculated in ref. [11] are very close to the current results, the main feature of most calculations seeming to show a very small displacement of the P atom away
from the cage structure and a large displacement of the Si atom into the ‘cage’ structure.

For the next set of calculations, the phosphorus atom was replaced with an arsenic atom which is again acts as a donor in silicon and the same set of calculations were performed, the aim being to compare the displacement parameters and the bond lengths with that of the previous cluster in light of the introduction of a larger atom into the cluster.
The microscopic structure of silicon-donor complexes in c-Si

The arsenic substituted cluster.

Table 3.6

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SCF</th>
<th>B3LYP</th>
<th>MP2</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>STO-3G</td>
<td>3-21G</td>
<td>6-31G(d,p)</td>
</tr>
<tr>
<td>ΔAs</td>
<td>0.0247</td>
<td>0.0959</td>
<td>0.0226</td>
</tr>
<tr>
<td>rSi-H</td>
<td>1.4087</td>
<td>1.5276</td>
<td>1.5268</td>
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<td>rSi-As</td>
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</tr>
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<td>ΔAs</td>
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</tr>
<tr>
<td>ΔSi</td>
<td>0.6697</td>
<td>0.6426</td>
<td>0.6185</td>
</tr>
<tr>
<td>rSi-H</td>
<td>1.4129</td>
<td>1.5271</td>
<td>1.5189</td>
</tr>
<tr>
<td>rSi-As</td>
<td>3.1082</td>
<td>2.9244</td>
<td>2.9864</td>
</tr>
</tbody>
</table>

Relaxation distances (Å) for arsenic substituted silicon cluster.

The first set of results are for the optimised cluster.
The second set in italics are for the empirical parameter cluster.

The above results show a much different pattern to those of the phosphorus cluster. While the ΔSi values are still approximately in agreement, but a little larger, the ΔAs values however are somewhat different to their ΔP counterparts. The SCF values are consistent between the empirical and optimised clusters as are the B3LYP results, remaining consistent with previous observations, however, the agreement ends when comparing the SCF values to the two other methods. The SCF values are much smaller in magnitude than the other two sets, the ΔAs(SCF/6-31G(d,p)) value being negative in comparison to a reasonably large positive value for the other two methods. The B3LYP and MP2 results are in good agreement with each other both for the ΔSi and ΔAs values.

The Si-H distances are almost identical for all calculations to those estimated for the previous cluster while the Si-As distances are shortened slightly in comparison by approximately 0.02 Å. The bond distances given by the three methods follow the trends noted previously, the smallest Si-H distance given by SCF to the largest by B3LYP and the contrary situation for Si-As distances.
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The nitrogen substituted carbon cluster.

Equivalent calculations to above were performed on a carbon cluster of identical configuration to that of fig 3.2b with a nitrogen impurity at position X₂ and a hydrogen passivating agent at the anti-bonding position of a carbon atom at position X₁. The results of these calculations are shown below in table 3.7.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SCF</th>
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<td>2.1471</td>
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<tr>
<td>r&lt;sub&gt;C-N&lt;/sub&gt;</td>
<td>2.1182</td>
<td>2.1270</td>
<td>2.1246</td>
</tr>
</tbody>
</table>

Relaxation distances (Å) for nitrogen substituted carbon cluster.

The first set of results are for the optimised cluster.
The second set in *italics* are for the empirical parameter cluster.

The results, although different to those of the previous two clusters are not too far removed in their characteristics. A significantly larger displacement of the nitrogen atom is observed than was noted for the P or As atoms, and the direction is away from the cage structure. This is counterbalanced somewhat by a smaller movement of the C atom into the base region of the cage.

The empirical and optimised results show a broad agreement with each other, the SCF sets being almost identical but the B3LYP and the two MP2 results show a slightly smaller C-N distance for the empirical case while the C-H distances are in good agreement for all calculations. The C-H distances estimated by B3LYP and MP2 are very similar to each other, the MP2 being slightly shorter, but both sets are longer than those for the SCF method.
Summary and Analysis

Initial calculations on the unsubstituted clusters to determine geometry and suitability of the cluster gave encouraging results, throughout the calculations the most consistent results were obtained using 6-31G(d,p) basis sets. The SCF calculations reproduced the observed structural parameters of a silicon cluster very well, the other two methods performing competitively, B3LYP/6-31G(d,p) overestimating the Si-H distance by 0.02Å and MP2/6-31G(d,p) underestimating the Si-Si distance by 0.033Å.

No calculation shows any cause for concern as regards cluster suitability, all displacements of free atoms in the cluster being under 0.02Å and the Si-Si distance for the free atoms being maintained to within similar tolerances which lie well within the accepted accuracy limits of 0.05Å for structural calculations by any of the three methods. Surprisingly, the use of an empirically derived geometry which represents a non-stationary point on the energy surface of a particular method did not affect the relaxation calculations when compared to it's equivalent optimised cluster indicating a low sensitivity to small changes in the structure. The majority of the relaxation demonstrated by the unsubstituted cluster most likely stems from residual surface effects due to finite size and residual forces due to deficiencies in the basis set and the imposition of symmetry.

In subsequent discussion, attention will be restricted to the 6-31G(d,p) basis set except where specified since these give the most consistent sets of results between the three methods, the differences in the results from calculations based on the other basis sets serving as a comparison.

On substitution of phosphorus into the cluster, no significant relaxation beyond that inherent to the cluster was observed for B3LYP or MP2, SCF on the other-hand showed a large displacement, the converse situation occurring when arsenic is substituted, for which SCF predicts a small negative displacement, the other two methods predicting a larger
positive displacement that significantly exceed the expected residual displacement in the cluster.

The silicon displacements for the P and As clusters are on the order of 0.5 Å and 0.6 Å respectively. The three methods used show some variability of the ΔSi values, in the P cluster the B3LYP value was lowest at 0.5147 Å, MP2 midway and SCF the largest at 0.5802 Å, the differences between them being 0.031 Å and 0.035 Å respectively while for the As cluster, the SCF and MP2 values were almost equivalent at 0.6130 Å and higher than the B3LYP by only 0.031 Å. the relaxation of the Si atom places it nearly co-planar with the bottom three atoms of the cage structure.

The upshot of the displacements is that the distance between the relaxing atoms increases to the point where it is doubtful that a bond in the classical sense exists. The Si-H distances are slightly longer than the experimentally observed value, B3LYP predicting the longest bonds at ~1.55 Å for both clusters, MP2 midway and SCF the shortest bonds at ~1.51 Å.

The length of the Si-P and Si-As bonds may be rationalised in terms of two effects, firstly, the passivating hydrogen will feed electrons into the anti-bonding orbital of the Si atom to which it is attached, thus weakening the Si-X bond. Additionally to this, the P or As in its normal oxidation state is three co-ordinate, another bonding site becoming available via a co-ordination bond which is somewhat weaker and hence longer than a normal co-valent bond.

The slight displacement of the P atom away from the cage structure may be due to residual forces, however, it is possible that there may be a small contributory effect from a smaller Si-P bond (by virtue of the smaller covalent radii of P as compared to Si) that would tend to pull the P atom toward the bottom three Si-H₃ units. By the same simple rationale, the As atom has a larger covalent radius than Si which would explain the displacement of the As
atom toward the cage as a result of the longer Si-As bonds. 

These processes do not however explain the rather large change of position of the Si atom. As noted above, the passivating hydrogen feeds electrons into the Si antibonding orbital which would tend to lengthen an already long bond which would also tend to push the Si atom away from the heteroatom if the latter was unable to move. The upward movement would also push the passivating hydrogen atom upwards in the cage in an attempt to maintain an energetically competitive Si-H bond length.

The same arguments can be applied to the carbon cluster, the nitrogen in the cluster can easily form 3 bonds to the base CH$_3$ units and given that the average C-N bond (1.47Å in (CH$_3$)$_3$N) for this co-ordination of nitrogen is smaller than a C-C bond (1.54Å), this would rationalise the negative movement of the N atom, and explain the smaller movement of the free C atom into the cage.

Conclusions

The calculations have shown that the microscopic structure of the defect sites in both silicon and carbon lattices can be well represented by a finite cluster and the displacements rationalised in terms of normal chemical bonding arguments, the calculations agreeing well with other work based on similar systems modelled by cluster and supercell methods.

The differences in reported relaxation distances and directions have been shown to be very dependent on the basis set and theoretical method used on a system, however it has been established that the inclusion of electron correlation effects are desirable in these calculations, the best evidence being the agreement of the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) results.

Despite some discrepancies in the MP2 results relative to the other values, the agreement between the two methods is an excellent result given that they are based upon two different mathematical techniques for the representation of electron correlation effects. A
possible source of problems with MP2 arises from the need to start geometry optimisations reasonably close to the equilibrium structure due to problems that can occur when attempting to calculate large corrections to a property such as the energy. SCF methods, while excellent in many applications for structural calculations have demonstrated significant disagreement with the other two methods for relaxation calculations. Generally the B3LYP method with a 6-31G(d,p) basis performs very well for the assigned task.

**Future Work**

The point of the vibrational motion of the lattice and particularly the passivating hydrogen atom has not been addressed in this particular research which, given the importance of this particular observable would be the next logical step. Further desirable extensions would be to complete the MP2 empirical geometry cluster results and possibly add a new set of calculations using QCISD / 6-31G(d,p) basis.

Given the dependence of the results on the basis set and method, a more important continuation would be to perform the same calculations on both a larger cluster and various supercells, and include analysis of semiconductor band-gaps in these systems.
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References


Chapter 4

Hydrogen and Ice in Interstellar Clouds
4. Hydrogen and Ice in Interstellar Clouds

Introduction

A large part of modern astronomy is based around spectroscopic composition analysis of the vast fields of gas and dust that pervade the interstellar medium. It is known that most of the more complex molecules tend to congregate in the dense cool regions such as the Horsehead nebula in Orion which is an example of a dark nebula, the cold dust grains providing an ideal environment for deposition or nucleation. Observation of these regions by a combination of IR, microwave, radio and other techniques has provided understanding of the physics of very small particles in the interstellar environment in addition to knowledge of the composition of these regions. The list of detected compounds ranges from the earliest molecules to be detected, which were CH, CN and CH+, from their very strong absorption characteristics showing up in the optical spectra of stars, to ever more complex molecules such as HCN, NH3 and HC11N.

Molecules such as H2 generally have to be observed by their emission characteristics, which are spectacularly demonstrated by emission nebulae. Hydrogen when ionised by radiation from a star whose wavelength is equal to or below the H2 Lyman continuum limit of 91.2nm, fluoresces, emitting radiation mainly as Balmer lines which lie in the Hα region leading to a characteristic redness. This emission occurs in a region of space around the star known as the H(II) region which terminates when the density of photons capable of causing ionisation falls off, leaving the H(I) region in which the 21cm emission line of H2 arising from forbidden transitions between the hyperfine levels of the ground state. While this technique is useful where the interstellar medium is relatively tenuous or translucent to radiation, a problem occurs in the dark dense regions due to optical extinction factors, molecular hydrogen generally only being observable in regions of clouds that are disturbed or
exposed to intense radiation, which does not offer much hope for the detection of H\(_2\) trapped in interstellar ices in all sorts of astrophysical environments.

Recently [1] a line at 4141cm\(^{-1}\) was detected in IR spectra of WL5, a protostar in the \(\rho\)-Ophiuchus cloud complex and has lead to speculation that it originates from molecular hydrogen in the condensed phase which is a result of considerable importance since H\(_2\) is the most abundant species in the clouds and plays the dominant role in models of interstellar chemistry. While under normal conditions molecular hydrogen is invisible in the IR due to symmetry arguments, only a small electronic perturbation to one of the atoms is required to break the symmetry and allow observable IR intensity to be developed. The observed line lies very close to the experimentally observed vibration frequency of gaseous molecular hydrogen, 4161cm\(^{-1}\), as determined by Herzberg[2] from the quadrupole spectrum of hydrogen and later by Stoicheff[3] from Raman spectra. While it is generally thought that the perturbations arising from intermolecular interactions in gaseous molecular hydrogen are too weak to produce observable intensity in the IR, it is known that condensed H\(_2\) in a matrices such as ice and argon can be detected, experimental evidence tending to favour a model of hydrogen in association with ice.

There are two pertinent questions that can be asked at this point;

1. What environment does the observed hydrogen exist in?
2. How does the hydrogen get there?

A simple model of a dust grain in a cloud consists of the nucleus (a dust grain) which is surrounded by an ice mantle. Ice in an interstellar environment is believed to be of a type known as amorphous, which has a characteristic low density, highly disrupted structure and is formed by slow deposition of water at low temperatures (< 70K), in addition to this it is also known to occur in association with other compounds such as methanol, carbon monoxide and
ammonia[11]. While there are endless possible environments that could be proposed for the hydrogen, they can be broadly divided into those for which it is inside the matrix, and those outside, however, the situation is complicated by the disrupted structure of amorphous ice for which one could envisage pockets and microchannels inside the matrix which are a halfway house between a surface and a confining cavity.

Experimental evidence from work by Sandford and Allamandola[11] on H$_2$ composites with interstellar ice analogues rich in H$_2$O shows a band at 4137cm$^{-1}$ which is identifiable as the Q$_\text{t}(1)$ pure vibrational transition of ortho-hydrogen (V=0,J=1 to V=1,J=1) and it was suggested that the 4141cm$^{-1}$ line was due to this transition. This was followed by a suggestion from Hixson, Buch[10] et al. that the 4141cm$^{-1}$ line was due to the Q$_\text{t}(0)$ vibrational transition of para-hydrogen (V=0,J=0 to V=1,J=0) which they located in the region 4138-4145cm$^{-1}$, based on arguments that the Q$_\text{t}(1)$ transition is unlikely to be seen due to a number of reasons including evidence that H$_2$ in both liquid water and ice behaves as an almost free rotor and secondly, ortho-hydrogen is almost completely converted to para-hydrogen, even at temperatures as low as 10K, over a short timescale the conversion being catalysed by paramagnetic species such as oxygen.

Although there is a known difference in the binding energies of ortho and para-hydrogen[9] onto the surface of ice, this does not help with the environment of the trapped species. Dissly, Allen and Anicich[12] show that hydrogen in co-deposited ice matrices does not escape below 30K and can still be detected in the matrix at temperatures of 70K which implies that the hydrogen is reasonably well ‘trapped’. Earlier work by Hixson, Buch[10] et al. with surface absorbed H$_2$ on amorphous D$_2$O ice showed a Q$_\text{t}(0)$ transition due to ortho-hydrogen at 4140cm$^{-1}$. This was interpreted in terms of interactions with dangling OD bonds on the surface and more importantly was assigned to hydrogen bound to an ‘exposed’ oxygen
atom in a deep binding site. This would at first appear to be at variance with a model in which the hydrogen is trapped, however in an amorphous ice, the sponge like structure would imply that the ‘surface’ composes most of the volume of the ice. In the paper by Dissly[12] et al., the suggestion is made that a significant population of the $H_2$ in interstellar ice is controlled by the thermodynamic behaviour of molecules in surface binding sites.

This turns attention to the subject of incorporation of the $H_2$ into the ice. It has been suggested that hydrogen, *in-situ*, could be produced by a number of means, including chemical and UV photoprocessing of $H_2O[11]$, with co-deposition of hydrogen during accretion of the ice mantle of a dust grain being another viable possibility. As for surface bound hydrogen, the formation of a mantle of pure hydrogen beyond a mono-layer is unlikely[12] at the estimated cloud temperatures due to a very sharp drop-off in the binding energy for the second layer, the critical temperature for bi-layer formation being in the region of $T<4K$. The proposal by Dissly *et. al.* that $H_2$ could be controlled by thermodynamic considerations of surface binding sites is particularly attractive given the observation by Hixson *et. al.* of the 4140cm$^{-1}$ band for $H_2 / D_2O$ composites. While there are volatility considerations for surface bound hydrogen, Dissly *et. al.* noted that hydrogen will have a tendency to migrate across a surface at low temperature, heading for the deeper low energy binding sites, which has been echoed by Hixson *et. al.* in terms of a semi-empirical study on a cluster of 450 water molecules.

To sum up, the issue of the 4141cm$^{-1}$ band observed from WL5 in $\rho$-Ophiuchus is far from resolved, experimental evidence would seem to suggest that the band could arise from the $Q_{1}(0)$ transition of a surface bound $H_2$ molecule, but due to a lack of detailed knowledge of the internal structure of amorphous gas-ice co-deposits, the environment may be a large closed cavity, the surface of a micro-channel in the ice or a deep, almost cavity like binding
site on the surface.

In view of this, ab-initio calculations have been performed on hydrogen in the presence of a number of different simple perturbing environments including cationic(Li$^+$), anionic(F$^-$) and neutral(HF, H$_2$O). In particular a cluster of water molecules in an idealised configuration was used to study the effect of placing the hydrogen in a closed cage of water molecules and positions on the exterior of the cluster. The vibrational frequency of the hydrogen in each case has been calculated by the use of both harmonic and anharmonic potentials. All calculations were carried out using GAUSSIAN-94 on either a 512MB 150MHz SGI-Challenge XL or a 200MHz 96MB Challenge-S system.

**Methods and Results**

The approach taken to the analysis of H$_2$ in the various environments was to first to evaluate the capability of various theoretical methods and basis sets to reproduce the observed vibration frequency of free H$_2$ before applying it to other environments, since if this is incapable of being reproduced then there is little hope for any kind of accurate analysis of any other system. The study was then extended to complexes of H$_2$ with Li$^+$, F, HF, H$_2$O and finally, the cluster of 12 H$_2$O molecules. The basic technique for analysis of the H$_2$ frequency was to calculate a set of samples of the energy surface along the normal co-ordinate of the hydrogen molecule and to employ Hermite polynomials (detailed in chapter 1) for harmonic analysis, and to employ two different methods for the anharmonic analysis.

The calculated harmonic frequency of free H$_2$ is close to 4400cm$^{-1}$ which is more than 200cm$^{-1}$ higher than the observed value of 4161cm$^{-1}$ which indicates a large anharmonic component. A pertinent question to ask is, will an environmental interaction with H$_2$ affect the potential energy curve to the extent that it will cause a change in the observed frequency?
This possibility has been raised by Ashcroft[6] with reference to the anomalous behaviour of \( \text{H}_2 \) under high pressure, but later discounted by Loubeyre[7] et al. for that particular case, however the possibility exists that there environments where the interaction is much larger, for example in association with other molecules such as water[13,14].

**The free hydrogen molecule**

The results for the harmonic and anharmonic analysis of free \( \text{H}_2 \) are presented in Table 4.1 Although 3-21G(d,p) was never intended for use as a basis set, its inclusion is merely for comparison purposes.

It is immediately clear from the data that the 3-21G(d,p) basis is inadequate in all methods for description of the harmonic frequency while the larger and more flexible 6-311G(d,p) and 6-311++G(3df,3pd) basis perform much better. It can be seen that the configuration interaction method involving all single and double excitations (QCISD), which for \( \text{H}_2 \) is a complete CI, is clearly the best method, the anharmonic frequency differing from the experimental by only 5.7 cm\(^{-1}\). A currently insurmountable problem with CI based methods is the large amount of computational resources required for their use for anything beyond a small system.

The Møller-Plesset perturbation methods, while less compute intensive than CI perform less well, requiring extension to the fourth order to obtain reasonable correlation with experiment which offsets any advantage gained. The density functional method, in this case Becke’s three parameter hybrid with the correlation functional of Lee, Yang and Parr (B3LYP), provides the best compromise between resource usage and accuracy, the experimental values being reproduced to within 1\% and consequently was selected for use in subsequent calculations in view of the need to examine larger systems.
As an additional point not shown in table 4.1, the B3LYP method with the 6-311G(d,p) basis gives an anharmonic frequency of 4198.2 cm\(^{-1}\) which is closely comparable to the result for 6-311++G(3df,3pd), from which we can conclude that the results for the larger basis are not spurious and consequently we can expect all remaining calculations to estimate frequencies that are slightly too high but hopefully all within 1% of experiment or thereof.

<table>
<thead>
<tr>
<th>Method</th>
<th>3-21G(d,p) Harmonic</th>
<th>6-311G(d,p) Harmonic</th>
<th>6-311G++(3df, 3pd) Harmonic</th>
<th>6-311G++(3df, 3pd) Anharmonic</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF</td>
<td>4629.8</td>
<td>4596.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B3LYP</td>
<td>4464.8</td>
<td>4423.8</td>
<td>4410.3</td>
<td>4191.5</td>
</tr>
<tr>
<td>MP2</td>
<td>4596.6</td>
<td>4533.5</td>
<td>4517.6</td>
<td>4342.3</td>
</tr>
<tr>
<td>MP3</td>
<td>-</td>
<td>-</td>
<td>4467.4</td>
<td>4251.5</td>
</tr>
<tr>
<td>MP4(SDQ)</td>
<td>-</td>
<td>-</td>
<td>4457.5</td>
<td>4198.9</td>
</tr>
<tr>
<td>QCISD</td>
<td>4490.5</td>
<td>4424.6</td>
<td>4402.2</td>
<td>4166.7</td>
</tr>
</tbody>
</table>

Calculated frequencies / cm\(^{-1}\) for H\(_2\) across various basis sets and methods. The experimental frequency is 4161 cm\(^{-1}\) and the estimated experimental harmonic frequency is 4400 cm\(^{-1}\).

**Table 4.1**

**Anharmonic analysis**

The harmonic frequencies were taken from GAUSSIAN-94 which employs the standard technique for calculation of the normal modes based on diagonalisation of the force constant matrix for the molecule which is outlined in chapter 1.

The anharmonic frequencies were determined from the energy surface sampled along the normal co-ordinate of the hydrogen molecule. The surface samples were taken over a range such that the resultant function was of the form of the familiar Morse function. Due to the non-expressability of this function as a simple polynomial, the curve was fitted to four separate polynomial functions of up to the fourth order \((r-r_e)^4\), each overlapped and subject to the constraints that the differentials and magnitudes of two bordered curves must be equal across their respective boundaries. The first region covered the steepest part of the curve with a negative gradient that spanned from \(r-r_e=-0.05\text{Å}\) to \(-0.8\text{Å}\), the second region spanned the
equilibrium position about \( r_e \), the third covered the steepest positive slope, upto \( \sim 3 \AA \), and the fourth covered the dissociation zone.

In practice it was found that the fourth region was reproduced correctly at large internuclear distances only by the CI based method, and clipping this region at various points, or even ignoring it totally, did not affect the accuracy of the estimation of the \( \text{Q}_1(0) \) transition which occurs between the two lowest levels and hence this region was removed.

To ensure validity of results, two different but equivalent methods were used to obtain the zero point energy and the first excited vibrational state for the anharmonic oscillator. The calculated levels were compared to those predicted and observed for \( \text{H}_2 \) by Stoicheff[3].

The first method was to perform a direct numerical solution of the 1-D Schrödinger equation for an arbitrary potential field. If we re-write the Schrödinger equation in terms of a dimensionless variable \( z \) which is simply some convenient scaling, in this case \( \alpha = \frac{8\pi^2 m}{\hbar^2} \) where \( m \) is the mass of the system;

\[
-\frac{d^2}{dz^2} \psi + \alpha(V(z) - E)\psi = 0
\]

and then consider the solution \( \psi \) to be defined on a discrete grid \( (\Delta z) \) rather than a continuous number field we obtain;

\[
\frac{\psi_{j+1} - 2\psi_j + \psi_{j-1}}{(\Delta z)^2} + \alpha(V_j - E)\psi_j = 0
\]

This is a recursion relation in \( \psi \) so that we can rearrange to obtain \( \psi_{j+1} \) in terms of \( \psi_j \) and \( \psi_{j-1} \);

\[
\psi_{j+1} = \left[ 2 - \alpha(\Delta z)^2(\text{E} - V_j) \right] \psi_j - \psi_{j-1}
\]

where \( V_j \) is the sample of the potential field \( V \) at a point \( z=j(\Delta z) \). The initial values \( \psi_0 \) and \( \psi_1 \) are chosen arbitrarily dependent upon the solution required (generally for the oscillator potentials, \( \psi_0=0 \) and \( \psi_1=0.00001 \) or less) and the value of \( \alpha\text{E} \), the eigenvalue for the required
state is 'guessed'. In practice a convergence technique was used that scanned for a value of $E$ that corresponded to a bound state of the system by brute-force, the initial guess being provided by the harmonic oscillator approximation. This technique gave 14 excited states before dissociation, of which the first 7 were in excellent agreement with Stoicheff's[3] values.

The second method for calculation of anharmonic frequencies involved using the first 30 harmonic oscillator wavefunctions to construct a basis set from which a matrix of all possible interactions between the four segment potential field function and the basis set was constructed. This matrix was diagonalised to obtain a set of eigenvalues corresponding to the bound states of the potential field. The first seven states calculated were in excellent agreement with Stoicheff, however beyond that the states were unsuitable due to inadequacies in the description of the higher states by an incomplete basis set. Given that the transition we are interested in estimating is the $Q_1(0)$ transition that occurs between the two lowest lying states, the above methods are more than adequate for the task at hand.

**Small Hydrogen Complexes.**

The calculations presented in this sub-section are related to the question of the effect of a perturbing environment upon the observable vibration frequency of hydrogen. Complexes of $\text{H}_2$ with Li$, \text{F}, \text{HF}$ and $\text{H}_2\text{O}$ were constructed (See Fig 4.1) and were, in each case, optimised using the B3LYP density functional method with a 6-311++G(3df, 3pd) basis. The calculated geometric parameters are presented in Table 4.2 with all distances in Å and angles in degrees. The harmonic and anharmonic vibration frequencies for $\text{H}_2$ in each of the above complexes were estimated. The suffix (NC) in Table 4.2 indicates that the frequencies were estimated by sampling along the normal co-ordinate of the complex corresponding to
The basic molecules.

Complex A  Complex B
F

Complex C

Complex D

Fig. 4.1 Optimised structures and geometry's for small complexes of hydrogen obtained using B3LYP method with 6-311G++(3df, 3pd) basis set. Bond lengths in Å and angles in degrees.

The calculated frequencies for the various complexes are presented in Table 4.3, as can be seen the difference between the calculated H₂ frequency in the H₂-HF complex employing the normal co-ordinate samples and the H-H axis samples is only 2 cm⁻¹. The data for complex A show that the H₂ bond length is longer that for free H₂ which indicates that the interaction with F⁻ is of considerable magnitude. The calculated harmonic vibration frequency for the complexed H₂ is 3263.3 cm⁻¹ as compared to 4410.3 cm⁻¹ for free H₂ which is a reduction that is consistent with a longer bond length. The intermolecular distance in this complex is smaller than in the other complexes which could be interpreted as of some form of weak bonding occurring between the components, possibly electrons feeding into the anti-bonding orbitals of hydrogen, lengthening the bond and

Table 4.2

<table>
<thead>
<tr>
<th></th>
<th>Free Molecule</th>
<th>Complex A</th>
<th>Complex B</th>
<th>Complex C</th>
<th>Complex D</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ Bond Length</td>
<td>0.7427</td>
<td>0.8106</td>
<td>0.7520</td>
<td>0.7432</td>
<td>0.7443</td>
</tr>
<tr>
<td>HF Bond Length</td>
<td>0.9220</td>
<td>-</td>
<td>-</td>
<td>0.9222</td>
<td>-</td>
</tr>
<tr>
<td>H₂O Bond Length</td>
<td>0.9611</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.9612</td>
</tr>
<tr>
<td>H₂O Bond Angle</td>
<td>105.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>105.10</td>
</tr>
<tr>
<td>Other Distance</td>
<td>-</td>
<td>1.6068</td>
<td>2.0223</td>
<td>2.7741</td>
<td>2.7059</td>
</tr>
</tbody>
</table>

Summary of geometric parameters of the complexes shown in Fig 1. Bond lengths in Å and angles in degrees.

*The 'Other Distance' refers to the intermolecular distance.
causing a polarisation effect which could conceivably lead to a favourable ion-dipole interaction. Given the reduction in harmonic frequency, this case of interaction is regarded as too extreme for further consideration.

The opposing complex, H$_2$ with Li$^+$, complex B, does not show the extreme interaction of F. Its geometric configuration is a T shape with an intermolecular distance of 1.987Å as compared to 1.607Å for the F complex. The configuration arises from the interaction of the lithium ion with the quadrupolar moment (sigma bond electrons) of the H$_2$ molecule. As with F a lengthening of the H$_2$ bond is observed, in this case the effect can be interpreted as loss of electrons from the σ-bond of the hydrogen to the ion, thus weakening the bond. This is reflected in the reduced harmonic (4285.6cm$^{-1}$) and anharmonic (4084cm$^{-1}$) frequencies of the hydrogen as compared to the free molecule.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Harmonic Frequency$^*$</th>
<th>Anharmonic Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>4410.3 (0)</td>
<td>4191.5</td>
</tr>
<tr>
<td>Li$^+$ - H$_2$ (NC)</td>
<td>4285.6 (44.1)</td>
<td>4084.8</td>
</tr>
<tr>
<td>HF - H$_2$</td>
<td>4403.5 (3.1)</td>
<td>4214.6</td>
</tr>
<tr>
<td>HF - H$_2$ (NC)</td>
<td>4403.5 (3.1)</td>
<td>4216.5</td>
</tr>
<tr>
<td>H$_2$O - H$_2$ (NC)</td>
<td>4383.9 (14.9)</td>
<td>4186.6</td>
</tr>
</tbody>
</table>

Frequencies (cm$^{-1}$) and intensities (KM / mole) for various H$_2$ complexes. (NC) Refers to frequency analysis along the normal co-ordinate.
$^*$ The value in brackets is the intensity as given by the harmonic analysis in GAUSSIAN.

The remaining two complexes C and D form examples of neutral molecular interactions. The HF-H$_2$ interaction causes an effect that is much smaller than the ion interactions, the H$_2$ bond length being changed by less than 0.0005Å, with the harmonic frequency being only slightly reduced. The effect of interest in this system is the slight perturbation of the electronic symmetry of the hydrogen molecule that is induced by the effects of the HF dipole. This small effect is enough to allow weak transitions, rendering the
H$_2$ visible in the IR. In order to examine the effect of the vibrational motion upon the H$_2$ frequency, the frequencies of the hydrogen were calculated by the two methods outlined earlier, the first being to simply freeze the HF atomic positions at their equilibrium values and sample the potential surface of the H$_2$ as it extends along its bond axis, effectively regarding the molecule as a free diatomic oscillator, while the second technique involved extending the assembly of atoms in the complex along the normal co-ordinate vectors for the particular normal mode that can be identified with the H$_2$ stretching mode.

The difference between the two different methods is small, approximately 2cm$^{-1}$ for the anharmonic frequencies. The reductions in the harmonic frequency on accounting for anharmonicity show that the HF-H$_2$ cluster has a difference of approximately 200cm$^{-1}$ whereas free hydrogen shows a 220cm$^{-1}$ difference. The small reduction in the harmonic frequency of H$_2$-HF is compensated for by a slight change in the anharmonic components of the energy surface which lead to an increase in the anharmonic frequency, essentially the vibration has become more harmonic by approximately 20cm$^{-1}$, making the observable anharmonic frequency for H$_2$ in the complex closer to that of free H$_2$.

A similar complex is H$_2$O-H$_2$, which is of direct relevance to the problem at hand. The structure of this complex can be rationalised in terms of the lone pair on the oxygen[8], the complex being stabilised by the interaction of an induced dipole in H$_2$ interacting with the oxygen lone pair. In comparison to the HF complex, there is a larger drop in the harmonic frequency for this complex (24.6cm$^{-1}$) compared to free H$_2$, however the anharmonic frequency is only 4.9cm$^{-1}$ smaller than that for the free molecule. This difference in behaviour can be attributed to a stronger interaction between O and H$_2$ than F and H$_2$ which is partially supported by the shorter intermolecular bond distance of 2.71Å for the H$_2$O-H$_2$ complex as compared to 2.77Å in HF-H$_2$. 
In a neutral complex $X-H_2$, the larger the interaction between the components, the greater the reduction in the harmonic stretching frequency compared to free $H_2$, however, the anharmonicity will be reduced, making the vibration more harmonic compared to free $H_2$ thus tending to cancel the effect out.

The behaviour of the frequencies is in accord with that observed for the HF-H$_2$ complex so that a 'rule-of-thumb' could be proposed;

This, in essence would imply that the observed stretching frequency of H$_2$ in a neutral complex will be counter-intuitively similar to that of free H$_2$ even if the interaction is relatively large. This adds justification to the assignment of the 4141 cm$^{-1}$ interstellar line to molecular hydrogen, and it adds the possibility that the observed species is occurring in association with other molecules.

**H$_2$ and Ice.**

In the next set of results, the effect of an idealised ice structure consisting of 12 water molecules upon the H$_2$ frequency is considered. In the ideal structure, the O-O distances were set to 2.76 Å and the O-H distances to 0.98 Å. The cluster [Fig 4.2] was constructed so as to have a plane of symmetry passing through its centre which enabled determination of the optimum position for an introduced H$_2$ molecule more easily than for a non-symmetric system. In addition to this, for reasons of resource usage, the basis set was reduced from the 6-311++G(3df,3pd) used in previous calculations to a 6-311G(d,p) basis on the H$_2$ molecule.

<table>
<thead>
<tr>
<th>Species</th>
<th>Basis Set</th>
<th>Harmonic Freq.</th>
<th>Anharmonic Freq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ (NC)</td>
<td>6-311G**</td>
<td>4419.2 (0)</td>
<td>4198.2</td>
</tr>
<tr>
<td>H$_2$ (NC)</td>
<td>6-311G++(3df, 3pd)</td>
<td>4410.3 (0)</td>
<td>4191.5</td>
</tr>
<tr>
<td>H$_2$ absorbed in [ICE] (NC) Fig 4.2(a)</td>
<td>6-311G**[3-21G**]</td>
<td>4414.8 (6.0)</td>
<td>4182.8</td>
</tr>
<tr>
<td>H$_2$ adsorbed on [ICE] (NC) Fig 4.2(b)</td>
<td>6-311G** [3-21G**]</td>
<td>4221.3 (273.6)</td>
<td>4063.9</td>
</tr>
</tbody>
</table>

Harmonic and anharmonic frequencies (cm$^{-1}$) for the H$_2$ stretching vibration of the absorbed and adsorbed models along the normal co-ordinate (NC). Calculations done using B3LYP. A 3-21G** basis set was used on the water molecules in the ice structure.
and a 3-21G(d,p) on the water molecules. As was mentioned previously, the effect on the predicted H$_2$ frequency on changing from a 6-311++G(3df,3pd) basis to 6-311G(d,p) is small, the actual figures are presented in Table 4.4. The use of 3-21G(d,p) basis on the water molecules is justifiable given that the predicted structural parameters are generally acceptable and that we are not estimating molecular properties for which 3-21G(d,p) is arguably unsuitable.

Since there are so many possible configurations of the water molecule structure, to create an environment for every possible binding site of the H$_2$ molecule would be impossible, in view of which the structure was used to study two extremum environments for the hydrogen. The first was the case in which H$_2$ was adsorbed onto the surface of the structure (Fig 4.2a), and the second where the hydrogen was absorbed into the structure, trapped inside a cell (Fig 4.2b). The actual positions shown for the hydrogen are the minimum energy positions for that configuration.

Examination of the data for the adsorbed case shows a harmonic frequency for H$_2$ of 4221.3 cm$^{-1}$ which is much lower than the free H$_2$ frequency of 4419.2 cm$^{-1}$ for the same basis. It is also lower than the frequency of H$_2$ in the presence of a single water molecule. A possible origin for this effect is coupling of the H$_2$ mode to a mode of the cluster, however, given that the nearest cluster modes are the OH stretching frequencies which are 400 - 500 cm$^{-1}$ lower than H$_2$, a strong coupling would not be expected. When the anharmonic effects are included, the H$_2$ frequency falls by approximately 250 cm$^{-1}$ relative to free H$_2$ suggesting that the hydrogen in this environment is more anharmonic than free H$_2$. On the face of it, this would appear not to support an assignment of the interstellar line to surface-bound hydrogen, however, it has to be remembered that in real amorphous ice there are many different configurations of the water molecules at the surface.
The computational and experimental study of deuterated ice and hydrogen by Hixson et al. in which a semi-empirical study of 450 water molecules was performed, the observed band at 4141 cm\(^{-1}\) arising from molecular hydrogen was proposed to originate from deep binding sites in which the hydrogen was electrostatically bound to an oxygen atom. While these results do not oppose that conclusion, in fact they support it on the basis of the exposed oxygen being a good binding site, all the minimum energy configurations for the hydrogen (Fig 4.2a) being centred upon an oxygen, they do indicate that there would have to be compensating effects that would effectively 'raise' the anharmonic frequency of the hydrogen in the binding site (i.e. make it more harmonic).

The other extremum environment is that in which the hydrogen molecule is trapped inside a lattice cell (Fig 4.2b), the absorbed model. From Table 4.1 it can be seen that the anharmonic frequency for this situation gives a value very close to that of free H\(_2\). In such an environment, from a simple perspective one might expect to see a compression effect on the H\(_2\) exerted by the surrounding cage which would lead to an increase in the observed frequency (Badgers[5] rule, simple correlation of frequency and force constant suggests frequency increases with external pressure), however, there are other considerations such as interactions with the oxygen atoms comprising the cage.

In terms of the earlier conjecture, in the above situation we would expect that the
interaction would tend to have an opposing effect (on inclusion of anharmonic effects) to any increase in frequency produced by pressure effects leading to the possibility that one may balance the other out. The calculated anharmonic frequency for H\textsubscript{2} in a cage is only 15 cm\textsuperscript{-1} lower than that of free H\textsubscript{2} for the same basis set, which when compared to the interstellar line which is 20 cm\textsuperscript{-1} lower than free H\textsubscript{2} appears to be a good result. This gives a strong implication that the binding site of the observed hydrogen is either inside the lattice or, more likely, a relatively closed-in binding site (such as could be formed by strategically removing some water molecules from the cluster in Fig 4.2 to give one as in Fig 4.3).

**Hydrogen Mobility In Ice.**

The previous results indicating the possibility of hydrogen trapped inside the lattice, although unlikely given the experimental and theoretical evidence in favour of surface based binding sites, does beg the question, can the hydrogen become trapped in the lattice or released from it as a dynamic process? This essentially asks can the hydrogen diffuse through solid ice? To address this possibility, a hydrogen molecule was moved along an axis passing along the cluster symmetry plane, passing through the centre of the face of the ice cell. The energy profile (ignoring zero-point contributions) along this co-ordinate is plotted in Fig 4.

![Image of hydrogen molecule](image.png)

**Fig 4.3**

An open arrangement, with one less water molecule than those in Fig 4.2.

The base axis is the displacement from the equilibrium position of the hydrogen molecule,
positive being toward the face. The peak of the barrier is \(-24\text{KJ mol}^{-1}\) and the thermal energy at the estimated cluster temperature in space (10K) is approximately \(0.1\text{KJ mol}^{-1}\). Zero-point

![Profile of energy for H2 moving across a face in O12H24 cluster](image)

Fig 4.4
B3LYP energy profile as H\(_2\) moves across the cluster from an OHO bond to a face.

analysis of the potential for a particle with the mass of hydrogen moving within it gives 5

![Fig 4.5](image)
Fig 4.5
The track of the hydrogen molecule in Fig 4.
(a) 1Å from minimum energy.
(b) Minimum energy position.
(c) Outside cell face.

states before there is an appreciable probability of quantum tunnelling effects. This is a fortunate result as a probability of diffusion would indicate that the hydrogen would be able to diffuse both in and out, the equilibrium only being determined by the relative binding energies.
Conclusions

The calculations presented have led to a conjecture that molecular interactions with hydrogen will tend to render the normal mode of hydrogen visible in the IR and will also tend to cause the observable vibrational frequency of the mode to be closer to that of free hydrogen than would be intuitively expected, however, this is shown not to hold well for hydrogen adsorbed onto an ice cluster. While there is evidence to support an abstract notion of a compensation effect as conjectured, further analysis of this effect is required, possibly looking at the linear (first and third order) components of the potential field in which the hydrogen lies and attempting to elucidate the effect that these have on the electronic symmetry (and consequently the harmonic and anharmonic frequencies) of the hydrogen molecule.

The presented calculations appear to support experimental evidence for the assignment of the observed interstellar line at 4141 cm$^{-1}$ as hydrogen lying in a deep binding site in association with an 'exposed' oxygen atom, the interaction interpretable as an electrostatic interaction with the lone pair on the oxygen. The calculations suggest that a relatively small cage could accommodate the hydrogen, rendering it IR visible with a frequency close to that of free hydrogen. This suggests that hydrogen could conceivably occur in the interstellar ice trapped in small pockets in addition to surface based sites and still show IR activity.

As regards future directions, the effect of broken cages or larger cages upon the hydrogen frequency could be studied from an ab-initio perspective as this would provide a greater insight into the possibilities noted above. In addition to this more information regarding the effects of other molecules in the lattice such as methanol and ammonia as these could conceivably produce hydrogen binding sites with different properties to those of water.
Hydrogen and Ice in Interstellar Clouds

References


