Simulating hyperfine coupling constants of muoniated radicals using density functional theory calculations

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Abstract

In this work we consider potential benefits, and limitations of linking *ab initio* Density Functional Theory (DFT) methods with existing µSR data analysis codes. This is motivated by the desire to provide users of the µSR technique with additional tools to help them better understand and interpret their data. The DFT method may be considered as complementary to the µSR technique. It is essential for interpreting muonium chemistry type experiments, where it provides the experimenter with an indication of the appropriate field regions where resonances are likely to be found, and can also help assign resonances to nuclei and identify the muonium binding sites during data analysis. A link between data analysis and DFT simulation codes is therefore likely to be highly beneficial in making efficient use of beamtime.

The support for this work provided by the European Commission under the 7ᵗʰ Framework Programme through the 'Research Infrastructures' action of the 'Capacities' Program, NMI3-II Grant Number 283883, is gratefully acknowledged.

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1   Introduction

This document investigates the feasibility of linking DFT codes with existing µSR data analysis software, providing a resource for the "inexperienced" user to predict isotropic hyperfine coupling constants (hfcc) in simple organic systems. The term "inexperienced" implies that the user has minimal knowledge of the strengths and weaknesses of the methodology used in the DFT technique.

Ideally, the algorithm would work something like this: the user would select an appropriate/reliable functional and basis set (model chemistry) for their structure(s) (there might be help in the form of an 'expert system' to define the problem) and run the simulation to obtain the muon and nuclear hfcc with minimum user input. However, before we can consider DFT methods as a 'black box' for obtaining this type of information, we need to understand both the limitations on the accuracy of the results (and how this might be improved), and the impact on the results that an inappropriately defined problem might have. This work seeks to understand these limitations by testing the methodology on a simple, well characterised, prototype system.

Due to its simplicity, and the availability of muon and proton hfcc temperature dependence data, the cyclohexadienyl muoniated radical was chosen as a prototype system. We begin by evaluating some choice model chemistries and methodologies, and using these to predict isotropic hfcc, and move on to develop a methodology for zero-point energy (ZPE) correction.

1.1   Quantum mechanical model

DFT can be used to investigate solid-state systems and atomic/molecular systems. Here, we are interested in the latter, and the best comprehensive review of DFT for this context is by Parr and Yang, in 'Density functional theory for atoms and molecules' [1]. However, Koch's 'A chemist's guide to density functional theory' offers an arguably more palatable overview (from a chemists perspective) of the technique [2]. Here, we offer only a very brief introduction, and readers are urged to consult the above texts for a more detailed account of the technique.

DFT is based on two theorems proved by Hohenberg and Kohn in the mid 1960's [3,4]. They state that a description of molecular system is provided by its electron density, $\rho(r)$ and as such, all properties of the ground state system are functionals of $\rho(r)$. The implications of these theorems reduce the problem of calculating the electronic wave function in 3N dimensional space (which is the case in Hartree Fock, Configuration Interaction, and perturbation theory calculations) to calculating the electron density in 3D space using a single set of atomic coordinates. The Kohn-Sham Hamiltonian is expressed by:

$$\widehat{H}_{KS} = -\frac{1}{2}\nabla^2 + v_H + v_{XC} + v_{ext} \tag{1}$$

Where $-\frac{1}{2}\nabla^2$ and v_H are the kinetic energy and the electron-electron repulsion energy, respectively and v_{XC} is the exchange correlation energy and v_{ext} is the external potential. The $\rho(r)$ of a system can be obtained by summing over the individual single-electron wave functions

$$\rho(r) = \sum_{\mu} |\chi_\mu|^2 \tag{2}$$

The single-electron wave functions can be expanded using a plane wave basis (representing the orbital in Fourier space) and solved using the Kohn-Sham equations [5]. In most DFT codes, the ionic potential is removed and replaced by a pseudo-potential term, restricting the wave function and potential to within a core radius. This approach may make the calculation more computationally efficient. However, a large number of plane waves are typically required to converge the properties of interest (over 100 per atom), particularly for the compact $2p$ orbitals of hydrogen atoms. The elegance of the technique lies in the fact that a single determinant describes the electron density - all of the complexity is bundled into the exchange-correlation functional. Unfortunately though, this simplicity is rather a double edged sword. Limitations arising from errors in the standard density-functionals, namely the delocalisation error and fractional charges, and the static electron correlation error and fractional spins have been discussed in the Science paper by Cohen *et al*. [6]. They highlight the following problem: for a calculation on a system involving a single electron, an artificial energy arises from the density of the electron interacting with the electron itself, this is known as a self-interaction error (SIE). This should, in theory be fairly easy to correct for, by evaluating the self-interaction terms and removing them. However, the manifestation in many electron systems is extremely difficult to quantify, and as yet, no method has managed. In a similar way, errors are also produced for the spin-spin interaction.

The Projector Augmented-Wave (PAW) method was invented by Peter Blöchl in 1994 [7] to calculate the electronic properties of materials within a DFT framework. The method is well suited to problems in the solid state and builds upon the advantages gained from pseudo-potential calculations, providing the correct nodal behaviour in valence electron wave functions while providing a description of full all-electron wave functions and density. The main advantage in this context is that since it deals with a full valence electron wave function, an accurate description of the electron spin density at the nucleus is provided. Full details of this type of calculation can be found in Blöchl's review [7]. It was successfully applied to muoniated ethanal by Probert and Fisher where they simulated both zero-temperature and thermally averaged values for the hfcc's [46]. There are a few packages that implement the PAW method, including Quantum ESPRESSO, CASTEP and GPAW.

1.2   Basis sets

The Basis Set is described by a set of functions which are used to describe the molecular orbitals within a system. We can express the MOs of a system as a linear combination of atomic orbitals (LCAO). The main strength of this LCAO approach is that it well suited to molecular systems, containing any number of atoms. It is possible to implement a greater number of AOs in the approach, e.g., to describe hydrogen, we can use more than one s AO, and also include some p and d AOs. A larger number of AOs will provide an increased flexibility of the MO, therefore improving the accuracy of the calculated properties. There are two main types of these basis functions, Slater Type orbitals (STO) [8] and Gaussian Type Orbitals (GTO) [9].

Basis sets differ in the number of component functions used. The *minimal basis set* employs a single Slater function or its Gaussian counterpart for each occupied atomic orbital in the ground state. For example, hydrogen would be described by a single s–function and carbon would be described by two s–functions and a set of 3 p–functions. The most popular *minimal basis set* is the STO–nG, where n is the number of Gaussian functions. The STO-3G is a *single zeta* (SZ) basis set; implementing three primitives per function. The valence orbitals play a greater role in chemical bonding than core orbitals, as such a more sophisticated basis set is required in order to better model valence orbitals. Basis sets can be improved by increasing the number of basis functions per atom. Split valence basis sets do just this, and can be expressed as *a-bcdG*, where *a* represents the number of primitives used for inner shells and *bcd* are the number of primitives used in the valence shell. Doubling, tripling or quadrupling all the basis functions give what are referred to as *double zeta* (DZ), *triple zeta* (TZ) and *quadruple zeta* (QZ), respectively. A popular example is the 6-31G basis set; a DZ basis set, in which the core orbitals are described by six primitive GTO and the valence orbitals are represented by two functions, with the first composed of three primitive GTO, while the second consists of a single GTO.

Split valence basis sets can be further improved through the addition of polarisation and diffuse functions. Polarisation functions have higher values of angular momentum than those present on a particular orbital on an atom in the ground state. For example, the p–orbital introduces polarisation to the s–orbital, and the d–orbital adds polarisations to the p–orbital. This polarisation allows the shape orbital to be modified so as to better cover a bonding region between two atoms. The molecular orbital (MO) of anions and excited states have a tendency to be more spatially diffuse than ground state MO's. To account for this, basis sets are augmented with diffuse functions which essentially increase the size of the orbital. An infinite number of basis functions would be required to perfectly

describe an orbital. In reality, the number of functions present within a basis set is limited. An error is therefore inherent in the description of the orbital; this is known as the Basis Set Limit.

Increasing the complexity of the system, i.e. increasing the number of electrons present, increases the computational expense. Heavier elements such as transition metals and elements from the lower end of the Periodic Table have large numbers of core electrons, and thus require a large number of basis functions to describe them. In a chemical sense, these electrons are fairly unimportant, since it's the valence electrons that are involved in chemical bonding. However, if these core electrons were excluded from the calculation, the valence electrons would be inadequately described - due to a poor description of electron–electron repulsion. So, in chemical systems that contain heavy elements the user can describe them in one of two ways: by treating all the electrons implicitly, resulting in huge computational expense (the calculation will take forever to finish - most high performance computer facilities impose a run time, typically five to seven days; the job automatically terminates after this time has been exceeded); or alternatively, the valence electrons can be treated explicitly and the core electrons may be replaced by an analytical function known as an Effective Core Potential (ECP) [10,11]. From a computational perspective this is a much more efficient approach, and is common practice in modelling systems involving heavier elements. For calculating magnetic properties however, the literature advises using small ECP [12].

Calculating magnetic properties requires a basis set with a high level of flexibility in the core region, and basis sets such as the EPR-II and EPR-III offer this flexibility, particularly in conjunction with the B3LYP functional [41]. EPR-II is a double zeta basis set has a single set of polarisation functions, with an enhanced *s* function, while the triple-zeta EPR-III basis set includes diffuse functions, double *d*-polarisations and a single set of *f*-polarisations.

1.3   Practical considerations

There are numerous software packages that facilitate calculation of hfcc's. Packages such as Gaussian [13] and Vienna Ab initio Simulation Package (VASP) [14] require licences, restricting their accessibility. There are also open source packages available, examples include Quantum ESPRESSO [15], GAMESS [16], Amsterdam Density Functional (ADF) [17], ORCA [18], GPAW [19], and CASTEP [20], all are very well maintained. However, whichever package is chosen, access to a high performance computer facility (such as the SCARF facility [21], open to all STFC departments and Diamond) is essential. Recent advances have seen electronic structure algorithms being reformulated for Graphical Processing Units (GPU), making DFT calculations on large systems (10^3 atoms) feasible. In any case, overcoming a steep learning curve is required to compile the input file for the calculation, and specialist 'first principles' knowledge required to extract meaningful results.

The input of a typical DFT calculation (see Appendix) requires specification of the number and types of atoms present in the molecule, their atomic coordinates, the charge, and multiplicity of the molecule, and definition of model chemistry (theoretical method and basis set). Armed with these parameters, the structure of a molecule and its properties, such as hfcc can be calculated. In order to predict the magnitude of the hfcc, it is crucial to have an accurate description of the spin density at nuclear positions (requiring an accurate optimised structure!). This is reliant on a suitable choice of basis set, and given that each has a limited atomic palette (see The Basis Set Exchange - https://bse.pnl.gov/bse/portal) and suitability for particular applications, this will be the first of many

difficulties that a novice user would encounter. Typically, it would be advisable to consult the literature to ensure the suitability of a choice, as some methods are clearly more adept at simulating hyperfine parameters than others; however, given that most systems that would be used in the linked software would likely be small and organic in nature; there is scope to provide guidance on choice of model chemistry used within the software. Since most software packages (with the exception of ADF) do not allow the muon to be modelled explicitly within the initial geometry optimisation calculation, a proton is frequently used in the muons' place. Clearly, the difference in mass between the muon and the proton must be accounted for, as must the effects of any dynamics or solvation present. These factors add complexity to the calculation, and mean a complicated model must be used to account for them [22]. Again, to help the user, it may be possible to include such models as part of an integrated software package, provided one has the time and computer power.

So far, we have dealt with the input of a typical calculation, but one question which quickly arises when starting out in this field is how to get the structure in the first place. Input structures can be obtained from crystal structure databases such as the Cambridge Structural Database (CSD). Alternatively, they can be drawn from scratch using appropriate visualisation software. Again, there are a plethora of software packages available; Gaussview, CACHe (Scigress Explorer), HyperChem, MOLEKEL, Chem3D, and gOpenMol all offer compatibility with Gaussian. No one package is *better* than another, the choice comes down to personal preference, and more importantly, if it's free.

1.4   μSR theoretical background

In this paper we are particularly concerned about the use of DFT methods to calculate muon-electron and nuclear-electron hfcc's to assist the interpretation of Avoided Level Crossing (ALC) μSR experiments.

During thermalisation, a large proportion of muons that are implanted into organic species capture an electron to form muonium, Mu or μ^+e^-. The spins of the muon and the electron interact through the hfcc. Muonium can rapidly react with centres of unsaturation (double or triple bonds) to form a paramagnetic species known as a muoniated radical [23, 24]. The classic addition involves the formation of a simple covalent bond, with one electron being supplied from muonium, and one electron being supplied from the C=C bond (Figure 1). Pictorially, this leaves an unpaired electron on the beta-carbon atom, but in reality the unpaired electron is often distributed throughout the molecule.
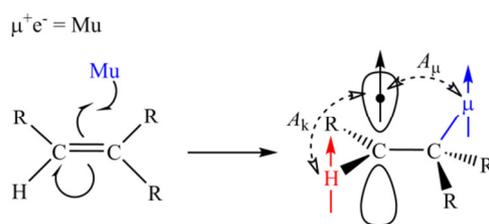

Figure 1. *Schematic showing muonium addition, producing a muoniated radical.*

Depending on the circumstance, the hfcc can have isotropic and anisotropic components. Vacuum muonium can be described by a $1s$ hydrogenic like wavefunction in which the electron spin, $\vec{S}_e$, and the muon spin, $\vec{S}_\mu$, is described entirely by the isotropic hfcc, A. Blundell's review [25] demonstrates that inclusion of the Zeeman terms into the Hamiltonian gives:

$$H_0 = -\gamma_\mu \vec{S}_\mu \cdot \vec{B} + \gamma_\mu \vec{S}_\mu \cdot \vec{B} + A\vec{S}_\mu \cdot \vec{S}_e \qquad (3)$$

and that if this two-spin system is defined by Pauli spin matrices, four energy eigenvalues follow [25]:

$$E_{|\uparrow_\mu \downarrow_e\rangle} = E_1 = \frac{\hbar}{4}\left[A + 2B(\gamma_e - \gamma_\mu)\right] \qquad (4)$$

$$E_{|\uparrow_\mu \downarrow_e\rangle + |\downarrow_\mu \uparrow_e\rangle} = E_2 = -\frac{\hbar}{4}\left[A - 2\sqrt{A^2 + B^2(\gamma_e + \gamma_\mu)^2}\right] \qquad (5)$$

$$E_{|\downarrow_\mu \downarrow_e\rangle} = E_3 = -\frac{\hbar}{4}\left[A - 2B(\gamma_e - \gamma_\mu)\right] \qquad (6)$$

$$E_{|\uparrow_\mu \downarrow_e\rangle - |\downarrow_\mu \uparrow_e\rangle} = E_4 = -\frac{\hbar}{4}\left[A + 2\sqrt{A^2 + B^2(\gamma_e + \gamma_\mu)^2}\right] \qquad (7)$$

The Breit-Rabi diagram in Figure 2 shows that in the absence of a magnetic field the system has two energy levels, a lower energy singly degenerate $\frac{1}{4}A$ state and a higher energy triply degenerate $-\frac{3}{4}A$ state, these are separated by an energy equal to the hfcc. The degeneracy of the triplet state is lifted when a magnetic field is applied, and we now have a system with four distinct energy levels (see Figure 2). At high magnetic fields, these energy levels can begin to converge on one another, becoming nearly degenerate. In the case of vacuum muonium levels 1 and 2 converge at about 16.4 Tesla (A=4.46 GHz).
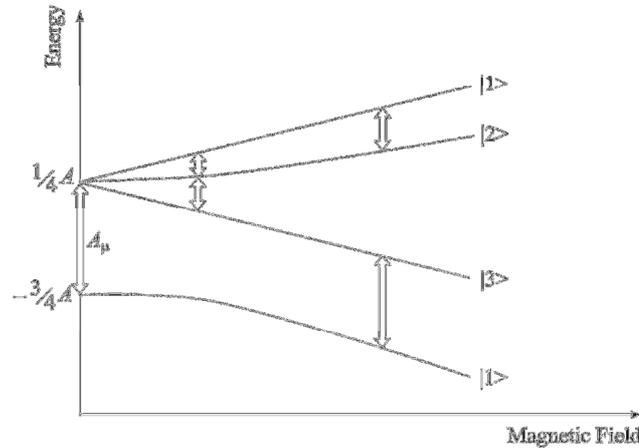

Figure 2. *Breit-Rabi diagram for isotropic muonium.*

The anisotropic component of the hfcc is due to the magnetic dipole interaction between the unpaired electron and the nucleus. The full Hamiltonian ($H_{full}=H_0+H_{\mu,aniso}+H_{nuclei}$) for a three spin system including axial asymmetry, and perpendicular dipolar parameters, D_i ($i=\mu,k$) (describe the anisotropy of the system) has been described in detail by Roduner [26] and more recently in a review by Nuccio *et al*. [27].

1.4.1   Transverse field-µSR

Application of a transverse magnetic field (TF) is one method that is used to gain access to the muon hfcc. In low magnetic fields, the muon polarisation can be distributed between all spin states, making the hfcc inaccessible. In higher magnetic fields, or in the region more commonly known as the Paschen-Back regime, the Zeeman energy begins to dominate, and only differences between levels E_1 and E_2, and between E_3 and E_4 can be observed (see Figure 2). These precession frequencies are described by [28]:

$$f_{12} = \frac{1}{2}A + \frac{1}{2}(\gamma_e - \gamma_\mu)B - \frac{1}{2}A\sqrt{1 + \left(\frac{2B(\gamma_e + \gamma_\mu)}{A}\right)^2} \tag{8}$$

$$f_{34} = \frac{1}{2}A + \frac{1}{2}(\gamma_e - \gamma_\mu)B + \frac{1}{2}A\sqrt{1 + \left(\frac{2B(\gamma_e + \gamma_\mu)}{A}\right)^2} \tag{9}$$

Following Fourier transformation, the frequency spectrum of such a system is characterised by a strong diamagnetic peak, resulting from μ^+ precessing at its Larmor frequency, and a pair of resonances placed symmetrically about this diamagnetic signal. It is the sum of these two frequencies that defines the muon hfcc. Since the wave function of the unpaired electron in a muoniated radical is often spread over the molecule, the magnitude of the hfcc is always characteristic of the muon binding site. In a TF–µSR experiment, a pair of precession frequencies corresponding to each binding site is present. Figure 3 shows such a spectrum for the muoniated cyclohexadienyl radical, with a pair of signals at 208.52 MHz and 305.48 MHz corresponding to a muon hfcc of 513.86 MHz, at 305 K (Figure 3, right). Curiously, the feature it split, and this probably merits further investigation.
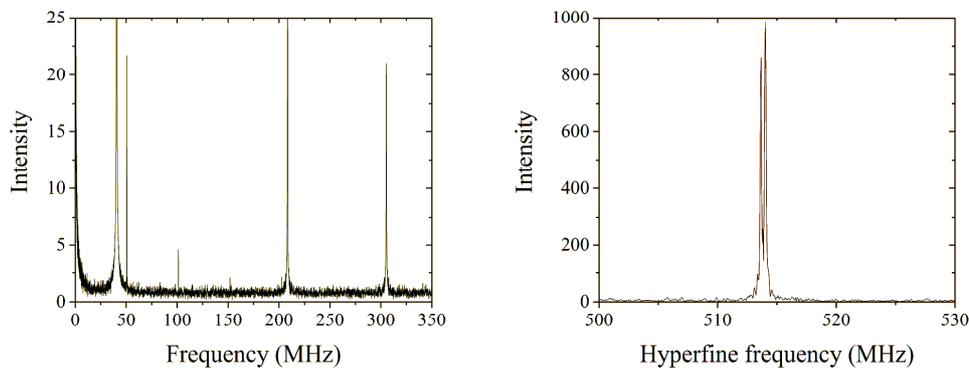

Figure 3. *(Left) TF-µSR spectrum from muoniated benzene at 305 K in a magnetic field of 3 kG. The spectral feature at 40.67 MHz (truncated) is from muons in the diamagnetic environment, the pair of signals at 208.52 MHz and 305.48 MHz are from the muoniated cyclohexadienyl radical. (Right) Correlated spectrum indicating a hfcc of 513.86 MHz for the muoniated cyclohexadienyl radical at 305 K (unpublished data).*

1.4.2   Avoided level crossing-µSR

The technique of Avoided Level Crossing (ALC)–µSR is capable of revealing both muon and nuclear hfcc's, but it is often easier to initially perform a TF–µSR experiment to identify the muon hfcc,

before using ALC to identify any nuclear couplings. The technique involves consideration of anisotropic contributions to the hfcc, and also additional spin–active nuclei. Anisotropy is usually present in muoniated radicals in the solid phase, and averages to zero in liquid and gaseous phases where the reorientation rate of the molecule becomes larger than the dipolar interaction. The spin of the muon, the unpaired electron, and any other spin active nuclei form a quantised system characterised by a series of discrete energy levels. At characteristic magnetic fields determined by the chemical system, two energy levels in the system can become nearly energy degenerate and are able to interact through the isotropic and anisotropic components of the hfcc. During this interaction the muon spins may oscillate between the two energy states, and thus, as the resonance is scanned, a reduction in the muon polarisation is observed (see Figure 3). The magnitude of the muon-electron, A_μ and nuclear-electron, A_k are characteristic of the muon binding site, and give rise to ALC resonances whose position are dependent upon their magnitude. The selection rule |ΔM=0, 1 and 2| (Δ_0, Δ_1 and Δ_2 resonances, respectively) determine the type of resonance, where M represents the sum of z components of the muon, electron, and nuclear spins.
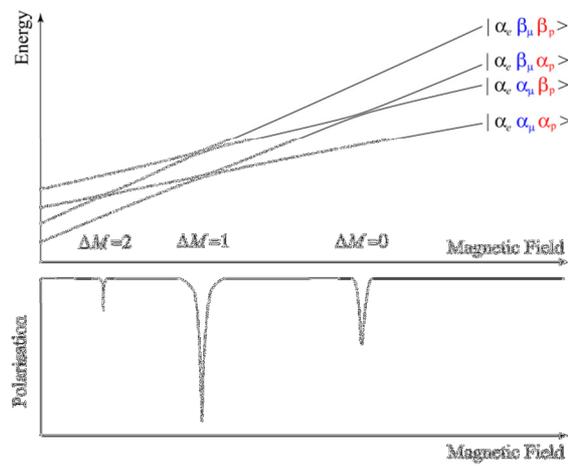

Figure 3. *Breit-Rabi diagram at high magnetic field showing the energy levels of a three spin system, indicating the three types of avoided level crossing.*

The field at which Δ_0 resonances appear is given by:

$$B_{res}^{\Delta_0} = \frac{1}{2}\left(\frac{A_\mu - A_k}{\gamma_\mu - \gamma_k} - \frac{A_\mu + A_k}{\gamma_e}\right) \tag{10}$$

γ_μ, γ_k and γ_e represent the gyromagnetic ratios of the muon, proton and electron, respectively.

The Δ_1 resonance field position can be predicted by:

$$B_{res}^{\Delta_1} = \frac{1}{2}\left(\frac{A_{e\mu}}{\gamma_\mu} - \frac{A_{e\mu}}{\gamma_e}\right) \tag{11}$$

The position of the the ALC resonance is dictated by the magnitudes of the isotropic hfcc's, while the dipolar parameters are responsible for the lineshape and width [24, 26, 27].
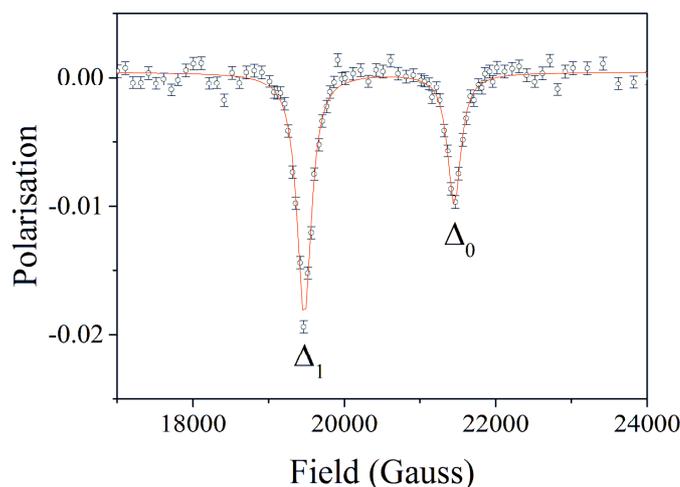
Figure 4. *ALC-μSR spectrum of the muoniated cyclohexadienyl radical at 210 K (unpublished data).*

Figure 4 shows the Δ_1 (1.9471 Tesla) and Δ_0 (2.1453 Tesla) resonances of the cyclohexadienyl radical at 210 K. Calculating the muon and nuclear hfcc therefore enables an estimation of the resonance positions, prior knowledge of which has the potential to save valuable beamtime by allowing the the experimenter to scan only the necessary field regions. The experimenter is also able to assign resonances to nuclei and identify the muon binding site through comparison of the measured and simulated hfcc. However, an understanding of the accuracy to which these values can be calculated is required to avoid discrepancies in assignment. The choice of theoretical method and basis set goes a long way to "reliably" predicting the magnitude of the hfcc, and is strongly affected by the model used in the optimisation to obtain the structure, and in the model chosen for the calculation of hfcc's (they need not be the same model). Some may appear to work well for predicting the properties of basic organic radicals, but this is often due to a fortuitous cancellation of errors. The upshot of this is that when the same method applied to radicals containing many electron atoms, the simulation gives values which are far from realistic.

The choice of model chemistry is often derived through validation against a training set of molecules, and using the results to produce a scale factor. Much work has been done in the areas of simulating Nuclear Magnetic Resonance (NMR) [29] and Electron Paramagnetic Resonance (EPR) [30, 31, 32] using DFT; these studies prove useful in providing information on suitable model chemistries. However, for calculating the hfcc's of muoniated radicals, a reliable method of accounting for the isotope effect is required to bring results from even the best model chemistry close to those of experiment. Hudson and Chafetz demonstrate this for the cyclohexadienyl muoniated radical [33].

2   Developing a model for the muoniated cyclohexadienyl radical

2.1   Evaluating popular DFT methods

The review from Improta and Barone [22] discusses the validity of various quantum mechanical models for calculating hfcc's. Their survey compared simulated spin densities of the methyl radical using empirical, semi-empirical, and non-empirical quantum mechanical calculations. The results

clearly demonstrate the need to include electron correlation in order to provide semi-quantitative agreement with experimental observations. The effectiveness of semi-empirical, Hartree-Fock, and DFT methods have also been evaluated in the work of Batra *et al*. [32], where a selection of small organic molecules were selected as prototype systems. However, the cyclohexadienyl muoniated radical was one of the first to be studied using the μSR technique [34], and is now considered a classic prototype system in muoniated radical chemistry [24, 35]. We therefore use this system to evaluate the effectiveness of various theoretical models, starting simple and building in complexity.

When muonium reacts with an unsaturated C=C bond in benzene, the muoniated cyclohexadienyl radical is formed, with the unpaired electron density delocalised throughout the ring (Figure 5). It is therefore possible to observe the muon-electron, A_μ hyperfine coupling, as well as the *ipso* nuclear-electron coupling. *Ortho*, *meta* and *para* couplings are possible in theory, but their distance from the muon makes them difficult to observe. Yu *et al*. reported TF and ALC μSR measurements of the cyclohexadienyl muoniated radical at 293 K, with hfcc's of $A_\mu = 514.807$ MHz for the muon and $A_k = 126.133$ MHz for the *ipso* proton [36]. Here, we compare this data (calculated from least squares fitting) with values from static gas phase calculations at 300 K obtained using a selection of popular functionals (HF, TPSS [37], B3LYP [38], PBE [39] and PBE0 [40]) all in combination with the EPR-III [41] basis set (Table 1). All of the calculations use a proton in place of the muon, and we account for the larger gyromagnetic ratio of the muon relative to the proton, by scaling A_μ values by a factor of 3.183. However, since the structure was geometry optimised as a protonated radical, the C–μ and the C–H (*ipso*) bond lengths are unrepresentative of a muoniated radical. Consequently, the magnitudes of A_μ and A_k (*ipso*) appear to be significantly underestimated. The most computational inexpensive model, HF/EPR-III provides the best overall agreement; underestimating A_μ by 18.5 MHz (3.6 % error), and overestimating A_k by 29.8 MHz (23.6 % error) compared to the experimental values. Practically, in the setting of an ALC type experiment, this corresponds to a 686 Gauss and 2601 Gauss difference in the magnetic field positions of the Δ_1 and Δ_0 resonances, respectively. This magnitude of error is too large for the calculations to be considered useful, especially when considering application to more complicated systems where numerous radical species are possible, and the aim of the calculation is facilitate identification of the radical structure.
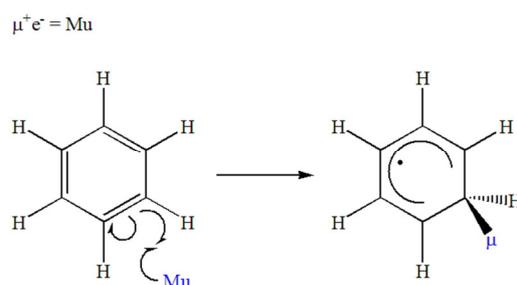
Figure 5. *muonium addition to benzene.*

	A_μ (MHz)	$\Delta_1 B_{res}$ (Gauss)	A_k *ipso* (MHz)	$\Delta_0 B_{res}$ (Gauss)
Exp.[a]	514.8	19088	126.1	20798
HF	496.3	18402 (686)	155.9	18197 (2601)
TPSS	477.1	17692 (1396)	149.9	17495 (3303)
B3LYP	479.7	17785 (1303)	150.7	17587 (3211)
PBE	485.5	18001 (1087)	152.5	17801 (2997)
PBEO	473.7	17563 (1525)	148.8	17368 (3430)

mp2	370.7	13746 (5342)	116.5	13593 (7205)

Table 1: *Comparison of experimentally determined and simulated A_μ and ipso A_k hyperfine coupling constants of the cyclohexadienyl muoniated radical at 293 K. Values in parentheses represent the difference from the experimental value. Calculations use a selection of functionals with the EPR-III basis set, for geometry optimisation and the single point energy calculation that generated the hfcc.*

Table 2 is purely illustrative; to show how changing the description of the orbitals with different basis sets can affect the magnitude of the A_μ.

	A_μ (MHz)	$\Delta_1 B_{res}$ (Gauss)	A_k *ipso* (MHz)	$\Delta_0 B_{res}$ (Gauss)
Exp.[a]	514.8	19088	126.1	20798
STO-3G	364.8	13527 (5561)	114.6	13376 (7422)
3-21 G	391.0	14497 (4591)	122.8	14336 (6462)
6-31 G	473.4	17552 (1536)	148.7	17356 (3442)
6-31 G**	449.0	16648 (2440)	140.8	16476 (4322)
6-311 G**	439.4	16293 (2795)	138.0	16111 (4687)
EPR-II	462.8	17161 (1927)	145.4	16970 (3828)
EPR-III	479.7	17785 (1303)	150.7	17587 (3211)

[a] *Calculated from a least-squares fit of data in reference [36].*

Table 2: *Comparison of experimentally determined and simulated A_μ and ipso A_k hyperfine coupling constants of the cyclohexadienyl muoniated radical at 293 K. Values in parentheses represent the difference from the experimental value. Calculations use the unrestricted B3LYP functional in combination with a selection of basis sets, for geometry optimisation and the single point energy calculation that generated the hfcc.*

2.2   Considering the isotope effect

The hfcc is extremely sensitive to the isotope effect. Compared to a hydrogenated radical, the magnitude of A_μ in a muoniated radical has been reported to be as much as 30–40 % greater (at 300 K) [42]. An unfortunate caveat of the DFT methodology is that nuclei are treated as point charges, and the nuclear quantum effect is not included. In many calculations previously reported for muoniated radical systems, a scale factor is used to lengthen the muon bond post optimisation, and a single point energy calculation is then used to calculate magnetic properties [36, 43, 44]. Lopes de Magalhãeš and Ramos used a Morse potential to calculate the average interatomic distances of C–H and C–μ (1.141 A and 1.197A, respectively) [45]. To identify any additional isotope induced perturbations they increased the C–μ bond length by 4.9 %, fixing it at this length while they re-optimised the structure. Interestingly, they found that the *ipso* C–H bond length in the resulting structure was 0.3 % shorter. In order to test the validity of this simple method, the cyclohexadienyl hydrogenated radical was re-optimised, with a C–H bond (corresponding to the C–μ) lengthened by 4.9 % and fixed during the subsequent minimisation using the uB3LYP/EPR-III model chemistry. As before, the resulting A_μ value was scaled by 3.183. The method overestimates A_μ by 10.3 MHz (2 % error) at 300 K, which in the ALC spectrum would correspond to an overestimation of the Δ_1 resonance position by 196 Gauss. In an ALC experiment running at 300 K, the Δ_1 resonance can be characterised by scanning from 1.84 Tesla to 2.2 Tesla with a 20 Gauss step size. If however, this was an unknown system, and we only have the calculated hfcc, the resonance could be found by scanning the region coarsely in a relatively small amount of time. For example, with 50 Gauss steps, counting 4 MeV/point and assuming a count rate of 90 MeV/hr, it would take approximately 40 minutes to scan the area between 1.89 Tesla to 1.96 Tesla to identify the resonance. The region could then be probed in more detail to fully characterise the resonance lineshape. On the face of it, a 2 % error would be acceptable to use the method to aid experiment.

	A_μ (MHz)	$\Delta_1 B_{res}$ (Gauss)	A_k ipso (MHz)	$\Delta_0 B_{res}$ (Gauss)
Exp.[a]	514.8	19088	126.1	20798
B3LYP/EPR-III	525.1	19284 (196)	141.6	20514 (284)

[a] *Calculated from a least-squares fit of data in reference [36].*

Table 3: *Comparison of experimentally determined and simulated A_μ and ipso A_k of the cyclohexadienyl muoniated radical at 293 K. Calculations employ a selection of functionals in combination with the EPR-III basis set. Following the geometry optimisation, the C–μ bond distance was increased by 4.9 % and the structure re-optimised, to account for the isotope effect [43].*

The model predicts the magnitude of A_μ at 300 K with a 2 % error, but is only useful to us if it can predict A_k couplings with a similar level of accuracy. We found that the *ipso* A_k coupling was similarly overestimated, by 15.5 MHz using the B3LYP/EPR-III level of theory. However, the errors of A_μ and A_k propagate through equation 10, meaning that the the Δ_0 resonance is predicted to be 284 Gauss lower than the experimental resonance position. Just as discussed for the Δ_1 resonance, despite this error these DFT results provide a valuable tool for the resonance search; however, the error is likely to make an unambiguous assignment of a spectrum measured for a more complex molecular system difficult. Couplings for the *ortho, meta*, and *para* protons can be easily calculated in our muoniated cyclohexadienyl radical system, but experimental data associated with these is more difficult to come by. It would be interesting to see if these were systematically overestimated by this method; in which case a simple scale factor could be added to each. It is very likely however, that the method produced these values in a fortuitous cancellation of errors, and the method is unlikely hold true in more complicated systems. For systems where multiple muonium addition sites exist, the task of structural assignment becomes problematic, and the locations of Δ_1 resonances (A_k couplings) become integral to the task. However, the more addition sites, the weaker the intensity of Δ_0 and Δ_1 resonances from each radical, and in polar systems the systematic overestimation of A_k couplings would no longer hold.

2.3 Vibrational averaging

In order to reliably predict the magnitude of both A_μ and A_k couplings, it is therefore necessary to apply zero-point vibrational corrections for comparing with high temperature data. However, validating the method relies on having hfcc temperature dependence data down to low temperatures, as close to 0 K as possible. Previous attempts at calculating the temperature dependence of the hfcc using a Boltzmann average of vibrational and rotational modes proved relatively unsuccessful [46].

Before proposing a methodology for ZPE vibrational averaging, a little more background information if required. The structure of a hypothetical molecule, ABC can be described by the geometric locations of nuclei A, B and C. For any given structure or electronic state, ABC has a specific energy. The Born-Oppenheimer approximation allows the motions of the nuclei and electrons to be separated – the nuclei are much heavier than the electrons, so they move much more slowly. However, it is when dealing with small nuclei, such as the muon, that the approximation begins to fail. In any case, the Born-Oppenheimer energy of a molecule is obtained by determining the electronic wave function for a set of fixed nuclear positions. The Potential Energy Surface (PES) describes the relationship between the locations of A, B and C and the energy. During a geometry optimisation, atoms A, B, and C are arranged so as to minimise the energy, giving the equilibrium geometry. The nuclei of the molecule are not static, but rather vibrating about their equilibrium positions. A molecule composed

of n atoms will have $3n-6$ fundamental modes of vibration (or $3n-5$ for linear molecules). If we plot the total energy of ABC as a function of one of the displacements described by a normal mode, the A–B stretch for example, we get a one dimensional Morse like PES. ABC does not reside at the bottom of this curve, but instead occupies one of the vibrational energy levels. If we have a group of ABC molecules, the energy levels are populated according to the temperature and the inter-level spacing ($E_n = (n + \frac{1}{2})hv_0$). When discussing isotope effects, we are only really concerned with the vibrational contributions – namely the zero-point and temperature dependant vibrational contributions. The ZPE is the difference in energy between the vibrational ground state and the lowest energy point on the Born-Oppenheimer PES, the energy of which is equal to $(n + \frac{1}{2})hv_0$. Vibrational effects have been largely ignored when calculating hfcc for larger radical species [47, 48], and also for smaller organic radical species in some cases [49].

For our prototype system, the muoniated cyclohexadienyl radical, this so called local mode approach applies a vibrational correction to the C–H(μ) degrees of freedom. Similar approaches have previously been demonstrated for a series of cycloalkanes in a paper by Yang and Hudson [29] and more recently by Hudson and Chafetz in their study of the isotropic perturbations induced in the cyclohexadienyl muoniated radical [33]. In the latter example, the authors calculated the average isotropic hfcc across the C–μ stretching, as well as the in plane and out of plane bending motions. Here, we apply and test a similar methodology to the muoniated cyclohexadienyl radical using a combination of a variety of functionals and basis-sets. The results of these ZPE vibrational corrections can be compared to the low temperature experimental data collected by Fleming $et\ al.$ [35] (see Figure 6). Notably, the authors did not record a full data set extending back to T=0. Instead, we have a limited experimental dataset from 313 K to 170 K. Using the liquid state data and extrapolating back to T=0 gives a hfcc of 537.2 ($\pm$1.2) MHz, but this is a non-ideal representation of benzene at T=0. Benzene has a freezing point of 278.65 K, meaning only six of the data points are in the solid state (Figure 6). Extrapolating the solid state data gives an A_0=553.0 ($\pm$1.6) MHz. However, this is not without its problems either; here we assume A_μ continues to have linear temperature dependence down to T=0 K. Fleming's data indicates a splitting of the ΔM=1 resonance below ~180 K, suggesting the possibility of multiple cyclohexadienyl radical environments, and possibly a non-linear A_μ temperature dependence [35]. Preliminary low temperature data on the muoniated cyclohexadienyl radical from a recent ISIS experiment [50] confirm this splitting, and the full analysis should reveal the nature of the A_μ temperature dependence. Fleming $et\ al.$ also included limited temperature dependant hfcc data for H_{ipso}, with three data points reported in the solid state [35] (Figure 6). This A_k data (x 3.183) is extrapolated to T=0 (426.4 MHz), and used with the extrapolated solid state A_μ data to give an experimental quantum factor, 1.297 which we can use for internal calibration.
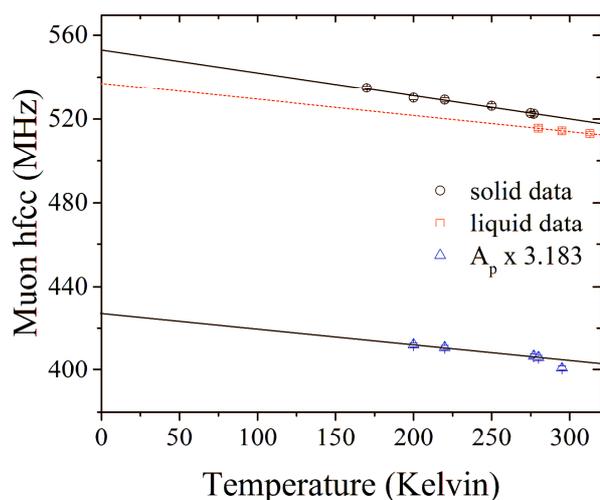
Figure 6. *A_μ temperature dependence for the [C₆H₆μ]* `*` *radical, using data compiled from [35].*

2.3.1 C-µ stretching vibration

The cyclohexadienyl radical was first geometry optimised, imposing C_{2v} symmetry. The optimised structure was taken as input for two further calculations. The first of which was a single-point energy calculation where the muonium isotope was specified (in Gaussian this is done by invoking the *freq=(readisotopes)* keyword), this generated the *3N-6* normal modes of vibration for the muoniated cyclohexadienyl radical that will be used later in the averaging process. The second calculation involved displacing one of the equivalent C–H bonds along its stretching path (corresponding to a mode at 2096 cm^{-1} in [C$_6$H$_7$]$^\bullet$ and 8398 cm^{-1} in [MuC$_6$H$_6$]$^\bullet$), from 0.6 Å to 3.6 Å in 0.1 Å increments. This may be done manually. In this case, the optimised structure is opened in a molecular viewing package, and modified structures associated with each incremental bond change are saved as input files for subsequent energy and hfcc calculations. It is possible to input all these structures into a single input file (using the Gaussian –Link1-- command) and have Gaussian calculate the properties associated with each structure in an iterative manor, writing the results in a single output file. The advantage of this method is that both the energy and the hfcc can be computed together. The resulting energy (reported in Hartrees) can be easily extracted from the output file to a new parameter file (using the command-line utility *grep*). Alternatively, for a more automated approach, Gaussian offers an option to scan the energy of a parameter such as bond length or bond angle in what is known as a rigid PES scan. In order to do this however, the molecular structure must be specified as a Z-matrix[1]. For a rigid PES scan calculation, Gaussian requires an initial value of the parameter, the number of steps, and the step size. Results for each increment can be easily extracted from the output file using, for example, Gaussian Output Tools (GOT - http://gaussot.sourceforge.net/). The energy values can be converted into a more convenient unit of energy such as cm^{-1}, plotted against the corresponding stretch displacement, and fitted by a Morse potential [51]:

$$U_M(r) = D_e\left(1 - e^{-\alpha(R-R_e)}\right)^2 \tag{12}$$

---

[1] The atoms in a molecule are listed in such a way so the position of the first atom is treated as the origin, the position of the second atom is defined by a distance from the first. The position of the third atom is defined by its distance from either the first or the second and the angle made from the three atoms. The position of the forth atom is defined by a bond distance, a bond angle and a torsional bond angle from the previous three atoms. The parameters are listed at the end of the file

Figure 7 (left) shows the Morse potential fit to a C–H displacement, and offers a good fit around the base of the PES (chi^2=0.9946). The Wei four-parameter potential [52](Figure 7 (right)) however, provides a better fit around the PES minima (chi^2=0.9983).

$$U_M(r) = D_e \left(\frac{1 - e^{-a(c-1)(R-R_e)}}{1 - ce^{-a(c-1)(R-R_e)}} \right)^2, |c| < 1 \qquad (13)$$

However, we are only interested in the area around the PES minima, and while a polynomial provides an inadequate fit of energy across the entire displacement, it does give an excellent fit across the area of interest, the PES minima (chi^2=0.9999), see figure 8.
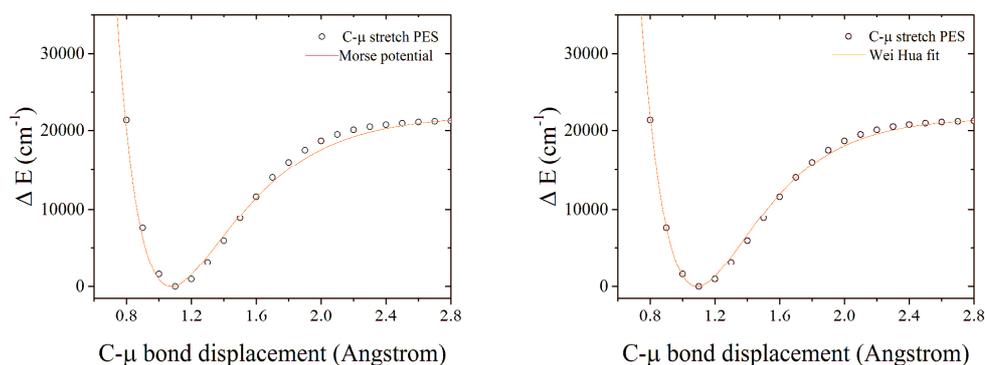

Figure 7. *(Left) Morse potential fit to the C-H bond displacement simulated for the C_6H_7 radical using a B3LYP/EPR-III model chemistry. (Right) Wei Hua four parameter fit to the C-H bond displacement simulated for the C_6H_7 radical using the uB3LYP/EPR-III model chemistry.*

Although we are clearly dealing with an anharmonic potential, the harmonic approximation does provide an adequate description of the PES for low vibrational energy levels. The ZPE can therefore be found from $\frac{h\nu_0}{2}$, for the C–μ stretching vibration at the B3LYP/EPR-III level of theory, this corresponds to 4199.24 cm^{-1} (illustrated by a blue line in Figure 8). At low and ambient temperatures, only the v=0 level is populated, although if dealing with higher temperatures, a Boltzmann distribution could be used to average the populated energy levels. C–H vibrates approximately harmonically (around the minimum of the PES) about the equilibrium bond distance of 1.10293 Å (at the B3LYP/EPR-III level of theory). The ground state wave function in a harmonic oscillator can be modelled as a Gaussian distribution centred about the equilibrium bond position, the one plotted in Figure 8 has been normalised for the purpose of illustration.
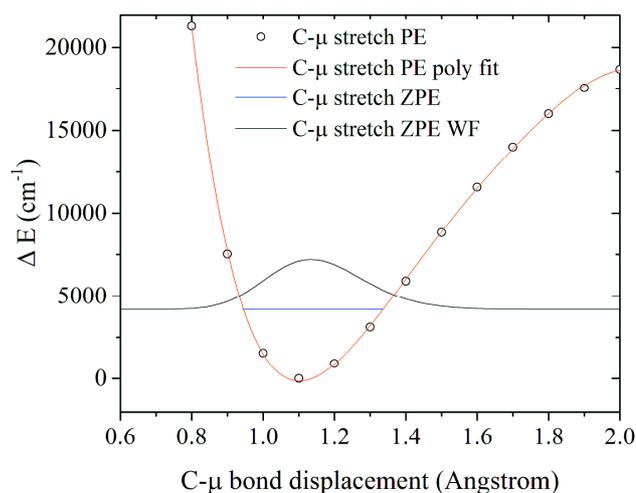
Figure 8. *5th order polynomial fit (red line) to the C-μ bond displacement simulated for the C_6H_7 radical using the B3LYP/EPR-III model chemistry. Blue line indicates the ZPE level for the C-μ stretching vibration, black line indicates the simulated ZPE wave function, normalised to the plot.*
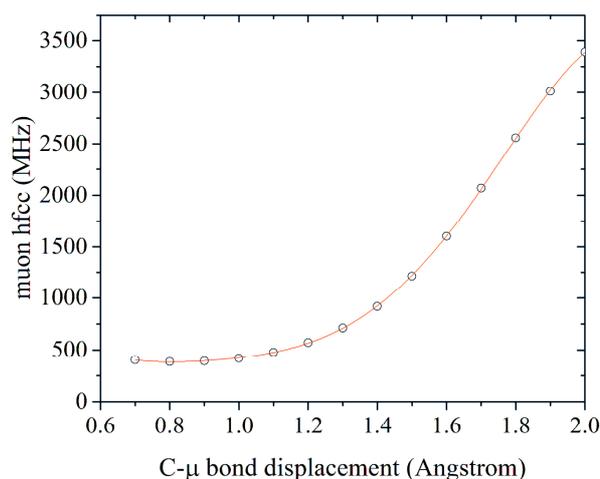

Figure 9. *Muon hfcc as a function of C-H bond displacement simulated for the C_6H_7 radical using the B3LYP/EPR-III model chemistry.*

The hfcc's were plotted against the displacement values and the results plotted and fitted with an appropriate function (data from the uB3LYP/EPR-III calculations shown in Figure 9 was fitted with a five parameter logistic regression). The hfcc function was then evaluated at the same values of displacement as the normalised square of the wave function, and products of the two determined. The ratio of these products, versus the equilibrium hfcc were calculated, and summed over all the evaluated values to obtain the value *P*:

$$P = \sum_{i=1}^{N} \frac{A_i \varphi_i^2}{A_0 \varphi_0^2} \quad (14)$$

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The ratio P, and the value produced by summing the normalised square of the wave function were taken to produce the quantum factor, QF:

$$QF = \frac{P}{\sum_{i=1}^{N} \varphi_i^2} \qquad (15)$$

The quantum factor was multiplied by the value corresponding to the equilibrium hfcc, A_0 to give the vibrational zero-point corrected hfcc for the stretching mode of vibration:

$$A_{ZPE} = QF A_0 \qquad (16)$$

The procedure was repeated at several levels of theory each using a structure that was geometry optimised at the B3LYP/EPR-III level of theory (Table 4).

	$A_{\mu 0}$ (MHz)	Quantum Factor	A_μ ZPE corrected (MHz)
B3LYP/6-31G	469.55	1.225	575.32
B3LYP/6-311++G**	442.64	1.222	540.73
B3LYP/cc-pVQZ	456.12	1.224	558.34
B3LYP/EPR-II	471.50	1.234	581.60
B3LYP/EPR-III	476.35	1.209	576.00
PBE0/EPR-III	461.67	1.214	560.77
PBE0/cc-pVQZ	442.79	1.212	536.84

Table 4: *Comparison of zero-point vibrationally corrected muon hfcc's for the C-µ stretch, using a combination of functionals and basis sets. In each case the structure was initially optimised at the B3LYP/EPR-III level of theory.*

Due to the method used to simulate the PES for the stretching vibration in this work, the equilibrium bond distance, R_0=1.10301 Å (calculated at the optimised level of theory, B3LYP/EPR-III), is not directly sampled in either the energy or hfcc calculations. Therefore, the values used for $A_{\mu 0}$ in Table 4 are obtained from the fits of hfcc's at each level of theory. $A_{\mu 0}$ calculated at the B3LYP/EPR-III level of theory when calculated during the geometry optimisation has a value of 479.7 MHz (see Table 2). We have therefore unwittingly introduced a 0.69 % error before starting the averaging procedure.

2.3.2   C-µ bending vibrations

The muon is also involved in in-plane and out-of-plane bending motions (torsional motions may well need to be taken into account for less rigid molecules). Vibrations involving the muon in a muoniated radical are, to a large extent, vibrationally isolated - motions involve only the muon. Closer inspection of these vibrations from the simulations shows that for the muoniated cyclohexadienyl radical they are not bending motions in a classical sense (forming an arch with fixed C-µ bond length), but rather translations of the muon in and out of plane of the molecule, which gives a varying bond length (see Figure 10). As such, simulation of their energy was achieved by introducing a ghost or dummy atom, and specifying the change in position (bond length) of the muon with reference to this. Notably, it would be possible to automate the process of calculating energy and hfcc in the same way as used for the stretching vibration. Figures 11 and 12 show the simulated energies and muon hfcc's for the *in* and *out* of plane bending motions using the B3LYP/EPR-III level of theory. Notably, the PES

describing these vibrational modes are harmonic, so a symmetric wave function is easily justifiable. The hfcc's sampled across the so called bending coordinate display a much smaller variation compared to the stretching vibration, with a mean of around 500 MHz for both modes. Table 5 and 6 show the couplings and the vibrationally corrected couplings at the selected levels of theory. $A_{\mu 0}$ values for each of the modes were obtained by evaluating the hfcc fitting functions at the equilibrium bond distance, at each level of theory. Unfortunately, this systematic error is magnified when accounting for the difference in the gyromagnetic ratio, resulting in ~3 MHz difference in $A_{\mu 0}$ at the B3LYP/6-31G and PBEO/cc-pVQZ levels of theory.
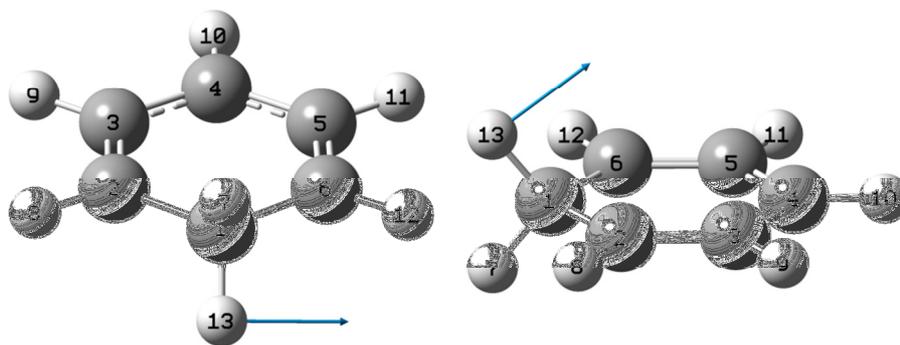

Figure 10. *(Left) in plane bending and (Right) out of plane bending motions of the vibrationally isolated muon.*
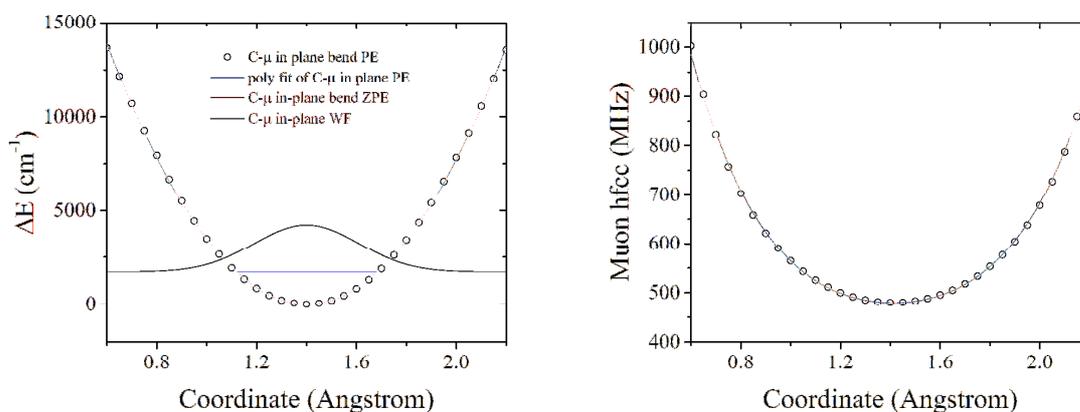

Figure 11. *(Left) PES, and (right) muon hfcc as a function of the in-plane bending motion, simulated for the C_6H_7 radical using the uB3LYP/EPR-III model chemistry. Bending motion reproduced through displacement of H from a ghost atom.*

Figure 12. *(Left) PES, and (right) muon hfcc as a function of the out-of-plane bending motion, simulated for the C_6H_7 radical using the uB3LYP/EPR-III model chemistry. Bending motion reproduced through displacement of H from a ghost atom.*
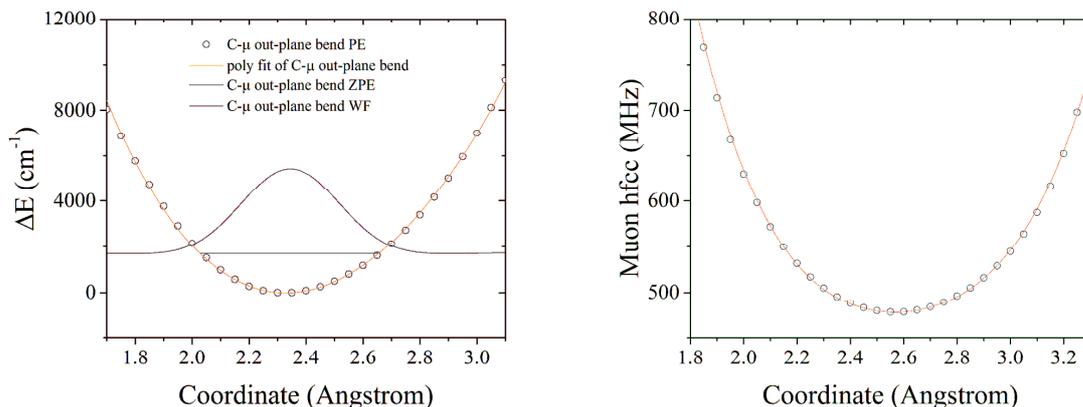
	$A_{\mu0}$ (MHz)	Quantum Factor	A_μ ZPE corrected (MHz)
B3LYP/6-31G	480.41	1.041	500.06
B3LYP/6-311++G**	444.63	1.041	462.91
B3LYP/cc-pVQZ	458.55	1.041	477.46
B3LYP/EPR-II	478.72	1.041	498.81
B3LYP/EPR-III	479.71	1.041	499.51
PBEO/EPR-III	462.73	1.039	480.56
PBEO/cc-pVQZ	442.56	1.038	459.59

Table 5: *Comparison of zero-point vibrationally corrected muon hfcc's for the C-µ in-plane bending ode, using a combination of functionals and basis sets. In each case the structure was initially optimised at the B3LYP/EPR-III level of theory.*

	$A_{\mu0}$ (MHz)	Quantum Factor	A_μ ZPE corrected (MHz)
B3LYP/6-31G	483.22	1.023	493.31
B3LYP/6-311++G**	445.53	1.027	456.66
B3LYP/cc-pVQZ	458.45	1.027	470.96
B3LYP/EPR-II	478.64	1.028	491.90
B3LYP/EPR-III	479.62	1.027	492.66
PBEO/EPR-III	462.63	1.025	474.25
PBEO/cc-pVQZ	445.14	1.022	454.78

Table 6: *Comparison of zero-point vibrationally corrected muon hfcc's for the C-µ out-of-plane bending mode, using a combination of functionals and basis sets. In each case the structure was initially optimised at the B3LYP/EPR-III level of theory.*

2.3.3 Averaging vibrational contributions for comparison with experimental data

An overall ZPE corrected hfcc, A_{TOT} can be calculated by assigning a fractional weighting to the stretching and bending contributions. Here, this was done using the vibrational frequency according to equations 17 and 18.

$$A_{TOT} = \sum_{i=1}^{N} f_i\, A_{ZPE(i)} \tag{17}$$

where A_i is the ZPE vibrationally averaged hfcc and f_i is the fractional weighting for vibrational normal modes considered

$$f_i = \frac{v_i}{\sum_{i=1}^{N} v_i} \tag{18}$$

where v is the vibrational frequency of each of the vibrational normal modes considered.

	A_μ ZPE corrected (MHz)
Exp.	**553(2)**
B3LYP/6-31G	539.66
B3LYP/6-311++G**	504.44
B3LYP/cc-pVQZ	520.58
B3LYP/EPR-II	543.12
B3LYP/EPR-III	540.17
PBEO/EPR-III	523.77
PBEO/cc-pVQZ	501.45

Table 7: *Comparison of the overall ZPE corrected muon hfcc's with the experimental value obtained by extrapolating to zero K [35].*
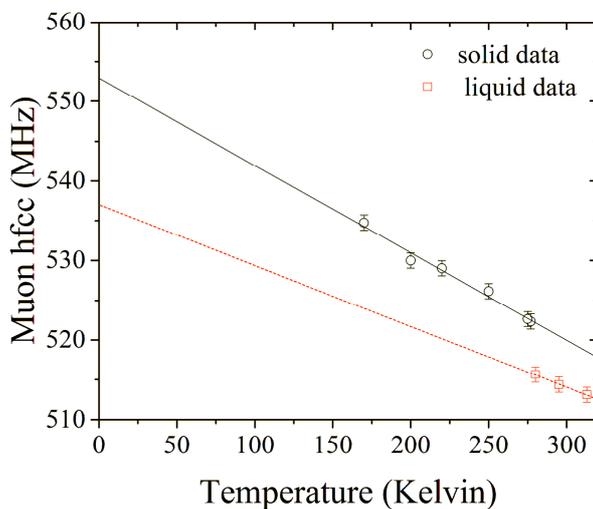

Figure 13. *A_μ temperature dependence for the $[C_6H_6\mu]^\bullet$ radical, using data compiled from [35].*

The overall averages (Table 7) are compared to the experimental data extrapolated back to T=0 K (A_μ = 553 ($\pm$ 1.63) MHz) collected by Fleming *et al* [35]. Comparing DFT results for A_{TOT} to this value suggests a systematic underestimation, with the B3LYP functional in combination with the 6-31G, EPR-II, and EPR-III basis sets giving the best agreement (differences of 13.34 MHz, 9.88 MHz, and 12.83 MHz, respectively). None of the simulated A_{TOT} values are within experimental error, leading to a~300–500 Gauss shift in the predicted Δ_1 resonance field position. Other combinations of the

B3LYP and PBEO functionals with different basis sets led to relatively large underestimations of A_{TOT}. Fortunately, there is plenty of scope for optimising the procedure. The first and most obvious modification would be the choice of model chemistry used for both the initial geometry optimisation and for subsequent calculation of the hfcc's. Improta and Barone noted that small changes in the equilibrium structure have large effects on the hfcc, and that these effects are particularly pronounced in π–character radicals, such as our current example [22]. If the planarity of the molecule is shifted, this can allow s-atomic orbital coefficients to contribute further to the singly occupied molecular orbital (SOMO), this directly affects the spin density at the nucleus. A worthwhile investigation would be to use a semi-empirical methodology to geometry optimise the structure. Any subsequent calculations of A are likely to be higher in magnitude, which could bring A_{TOT} closer to the experimental 553 MHz.

Another area for improvement is the description of the wave function, which was found to significantly affect the magnitude of both A_μ and A_k, so it is possible that results could be further improved by optimising it's description. In the muoniated cyclohexadienyl radical, and indeed for other semi-rigid molecules, a harmonic model should provide an adequate description of the wave function, an optimised version may be required to expand the applicability of the model to a greater variety of systems. There are studies which focussed specifically on simulating ground and low lying excited state vibrational wave functions, using variation-perturbation approaches [53, 54]. Other studies involving muoniated radicals have included a second-order perturbation of principle anharmonicities, and the authors claimed that this markedly improved the accuracy of the method [22].

2.3.4 Nuclear couplings

It is also important that our model accurately reproduces the magnitude of any nuclear couplings. We have already mentioned the limited data available for the H_{Ipso} hfcc which was measured by Fleming *et al*. [35] (see Figure 14). Here, we use the data in the context of the nuclear coupling, and with the minimum number of points available to fit in the solid state, a value of 133.97 ($\pm$ 0.13) MHz is obtained through extrapolation to T = 0 K. Similar issues exist with this extrapolation, as did for extrapolating A_u data. Here though, we have the smallest dataset possible to base such an extrapolation. We are again assuming a linear temperature dependence back to T=0 K, and there are issues relating to the splitting of the Δ_0 resonance below 180 K [35]. However, this is the only data we know to be available at the current time.
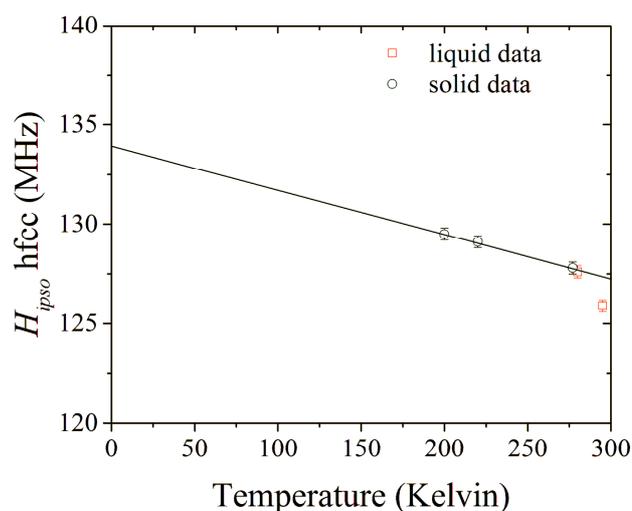
Figure 14. *A_k temperature dependence for the $[C_6H_6\mu]^\bullet$ radical, using data compiled from [35].*

Unlike the C-μ vibrational modes, the C-H_{ipso} modes are not vibrationally isolated. For example, the C-H_{ipso} stretching vibration also involves a translational motion of the muon, in a similar way to the C-μ out of plane bend, and the out of plane C-H_{ipso} involves ring torsions that result in the displacement of all atoms in the molecule. Gaussian does report a breakdown of the atomic displacements in Cartesian space for each molecular vibration along with associated force constants. It would be desirable to have access to a program that transforms these parameters into an input file to calculate the energy and hfcc's across the molecular displacement for any given normal mode, in a similar way to an intrinsic reaction coordinate (IRC) type calculation. To our knowledge, there is no such program that currently exists. Such a tool would also provide access to some of the more complex low energy torsional modes (see Figure 15) that are more energetically accessible at low temperatures within bulk benzene. Such an analysis may become necessary to make our model applicable to a wider variety of molecular systems. Currently though, from a practical perspective it is not possible to exactly simulate these normal modes, and we have to approximate them in isolation. Fortunately, due to the symmetry of the molecule, energy and hfcc data relating to C-H_{ipso} normal modes is the same as for C-μ modes. The difference is how we deal with the data; for C-H_{ipso}, there is no need to correct for the gyromagnetic ratio like we did for the C-μ modes. Data relating to these vibrations is reported in Tables 8, 9 and 10. As before, values for A_{k0} shown in the tables were obtained by evaluating the hfcc fitting function at the equilibrium position for each vibration. As such, small discrepancies can be observed for the values for A_{k0} reported in the tables.
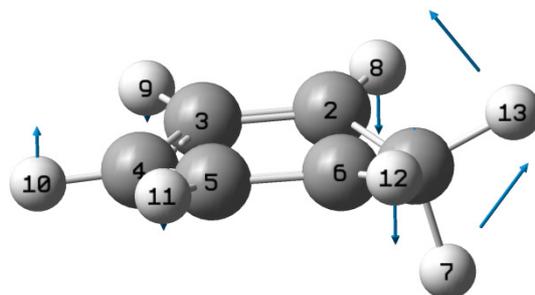

Figure 15. *The lowest energy torsional mode in the muoniated cyclohexadienyl radical.*

	A_{k0} (MHz)	Quantum Factor	$A_{k\ ipso}$ ZPE corrected (MHz)
B3LYP/6-31G	146.81	1.036	152.03
B3LYP/EPR-II	147.46	1.037	152.94
B3LYP/EPR-III	149.00	1.036	155.09

Table 8: *Comparison of zero-point vibrationally corrected muon hfcc's for the C-H$_{ipso}$ stretch, using a combination of functionals and basis sets. In each case the structure was initially optimised at the B3LYP/EPR-III level of theory.*

	A_{k0} (MHz)	Quantum Factor	$A_{k\ ipso}$ ZPE corrected (MHz)
B3LYP/6-31G	150.91	1.041	157.09
B3LYP/EPR-II	150.39	1.042	156.70
B3LYP/EPR-III	150.70	1.041	156.91

Table 9: *Comparison of zero-point vibrationally corrected muon hfcc's for the C-H$_{ipso}$ in-plane bending mode, using a combination of functionals and basis sets. In each case the structure was initially optimised at the B3LYP/EPR-III level of theory.*

	A_{k0} (MHz)	Quantum Factor	$A_{k\ ipso}$ ZPE corrected (MHz)
B3LYP/6-31G	151.80	1.023	155.28
B3LYP/EPR-II	150.36	1.028	154.53
B3LYP/EPR-III	150.67	1.027	154.76

Table 10: *Comparison of zero-point vibrationally corrected muon hfcc's for the C-H$_{ipso}$ out-of-plane bending mode, using a combination of functionals and basis sets. In each case the structure was initially optimised at the B3LYP/EPR-III level of theory.*

Contributions from the stretching and bending modes are accounted for using equations 17 and 18; results are shown in Table 11.

	$A_{k\ ipso}$ ZPE corrected (MHz)
Exp.	**134 (2)**
B3LYP/6-31G	154.18
B3LYP/EPR-II	154.70
B3LYP/EPR-III	155.48

Table 11: *Comparison of the overall ZPE corrected H$_{ipso}$ hfcc's with the experimental value obtained by extrapolating A$_p$ data to zero K [35].*

$A_{k\ TOT}$ for the *Ipso* proton is systematically overestimated by ~14 % for all selected methods. Practically, if the simulated data was the only information known about A_μ and A_k before starting an ALC type experiment, the hunt for the Δ_1 resonance would start ~1200 Gauss away from the resonance. Clearly this isn't good enough to be considered useful. Starting with an overall value for A_{k0} which is closer to the experimental value of 134 MHz would go some way to improving the accuracy of the method.

3 Conclusions

3.1 Outcome of the study of the cyclohexadienyl radical

A common danger with this type of study is to evaluate a property of a system using lots of different functionals/basis sets, and stop once a match is found with the experimental value. In such instances, the match is often coincidental, due to a cancellation of errors. The result is a model that gives a good match for the prototype system, but fails when applied to other more complicated systems. The simple methodology developed in section 2.3 can predict the magnitudes of A_μ in the muoniated cyclohexadienyl radical to a reasonable level of accuracy when using the B3LYP functional in combination with the well-known 6-31G, EPR-II, or EPR-III basis sets, giving a systematic underestimation of $\sim$2 %. Results for the H_{ipso} are less promising, with a systematic overestimation of A_k by $\sim$14 % by all methods tested. In its current state, any of these selected levels of theory could be used to identifying A_μ and locate Δ_1 resonances in ALC type experiments. However, further development is required in order for the technique to be considered useful for predicting A_k and locating Δ_0 ALC resonances.

The procedure used to ZPE correct the muon and nuclear hfcc is as follows:

1. Calculate the PES for a static bond displacement (stretch, bend, torsional) and fit the energy vs. static displacement with an appropriate function
2. Determine the ZPE for the muoniated species
3. Simulate the wave function for the ZPE level
4. Normalise the square of the wave function and sum over all values evaluated
5. Calculate the hfcc for each displacement value, fit with an appropriate function and evaluate at the same values as the wave function
6. Calculate the product of the normalised square of the wave function with corresponding values for A_μ
7. Calculate the ratio of each of the above products with the equilibrium hfcc and sum the results
8. Calculate the ratio of the above summed value with the sum of the normalised square of the wave function to obtain the *QF*
9. Repeat for other modes of vibration (bend, torsional) and average
10. Combine the *QF* for all modes to give an overall *QF* and multiply by A_0 to obtain the ZPE averaged hfcc

3.2 Recommendations for further work

Although, on the face of it, the results we have presented are less than perfect, there is plenty of scope to optimise the methodology. With a little development, there is certainly potential for this to be a valuable tool for the muon user community. In particular, there are two areas which if modified would improve the accuracy of the method. Firstly, the overall value for $A_{\mu 0}$ (for the stretching and bending vibrations) should be as close to the experimental 426 MHz as possible. An alternative level of theory, such as the semi-empirical PM3 method for the initial geometry optimisation could provide a better starting structure on which to perform the averaging procedure. Secondly, in order to simulate the muon and proton couplings with any real accuracy, the overall *QF* should be close to the experimentally determined value of 1.3.

Once the method has been optimised, it can be properly benchmarked. However, further experimental data are required for the low temperature region of the muoniated cyclohexadienyl radical in order to confirm the assumed linear temperature dependence down to T=0 K. The next step would be to test the methodology on a similar radical system with known hfcc temperature dependence data. Unfortunately, we are not aware of any low temperature dependence data for muon and proton hfcc's having been published for any similar muoniated radical systems. Therefore, further down the line, we recommend extending the experimental dataset – additional TF and LF-ALC studies on a similar set of molecules. If the model doesn't hold true on the extended experimental dataset, there is merit for including some of the low energy torsional modes into the averaging procedure, and including the effects of neighbouring benzene molecules. For this, however, programs like CASTEP (using plane waves) or CRYSTAL (using Gaussian type orbitals) hold the key, these periodic potential DFT codes are much better suited for investigating how the lattice might affect the hfcc.

We anticipate this methodology becoming very time consuming for more complicated systems than our benzene prototype, particularly in linear systems which are more torsionally active. However, automation offers the potential of reducing this rather laborious task into something which could be managed by a novice user. As computing power continues to grow over the coming years, it is not out of the question to imagine a ZPE average over all $3N$-6 vibrational modes in fairly complex radical systems to be done in a routine manner by a desktop machine in the muon instrument cabin.

Note Added in Proof

Since completing this programme of work, we have discovered that an alternative approach of taking a product of the QFs for different muon zero point modes produces a much better value for the overall QF in comparison with the weighted average method suggested in the previous section. For the calculations reported here, averaged over the various models, this method gives the value $QF = 1.220(8) \times 1.040(1) \times 1.026(2) = 1.30(1)$, in perfect agreement with experiment; it is notable that the estimate of QF does not depend significantly on the model used. Thus the main problem left to address is the DFT overestimate of $A_{\mu 0}$ shown in Table 11. It seems here that the estimate of the molecular structure provided by DFT is not reliable enough for accurate estimation of absolute hfcc. However, semi-empirical methods can easily provide more reliable structures and a hybrid method [55,56,57] using PM3 for the molecular geometry and DFT for the electronic spin distribution looks very promising in this regard, giving a value of 430 MHz for $A_{\mu 0}$ at the B3LYP/cc-pVDZ level with an overall QF value of 1.30, so that $A_{\mu} = 559$ MHz, all these values being in excellent agreement with experiment. This method is now being applied to a range of systems currently being investigated by μSR (including an extended temperature study of the cyclohexadienyl radical) and a full report will follow in due course [57].

4   Appendix

%chk=H.chk
%mem=1GB
%nprocshared=2
opt freq uB3LYP/6-31G

Geometry optimisation and frequency calculation of muoniated cyclohexadienyl radical

```
0 2
C           0.00000000    0.00000000    1.35870848
C           0.00000000    1.20809735    0.66121314
C           0.00000000    1.20809735   -0.73377752
C           0.00000000   -0.00000000   -1.43127286
C           0.00000000   -1.20809735   -0.73377752
C           0.00000000   -1.20809735    0.66121314
H           0.86313355   -0.00000000    1.99108533
H           0.00000000    2.16038781    1.21101830
H           0.00000000    2.16038781   -1.28358268
H           0.00000000   -0.00000000   -2.53088316
H           0.00000000   -2.16038781   -1.28358268
H           0.00000000   -2.16038781    1.21101830
H          -0.86313355   -0.00000000    1.99108533
```

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