Acetylene

5.1 Introduction

Acetylene is an important yet simple molecule which has been studied and used in many areas of chemistry. Despite its widespread use, predicting and measuring the molecular properties of this molecule has proven to be a challenging task. In particular, the determination of the quadrupole moment has been a controversial exercise with a series of measurements, obtained over a number of years, found to span a broad range [1]. Moreover, different estimates for this property have been obtained via *identical* experimental methods, thereby leading to considerable confusion in the literature as to the most reliable measurement; a concise summary of these attempts and the experimental techniques utilised to measure the quadrupole moment has been presented recently by Coonan and Ritchie [1]. Due to the lack of a permanent electric dipole moment, the only direct routes to the determination of Θ have been the Cotton-Mouton effect [2] and field-gradient induced birefringence experiments [3, 4]. The microwave Zeeman effect [5] could in principle be carried out on the mono-deuterated form, HCCD, to deduce the quadrupole moment, along the lines of the recent work on CH_2CD_2 [6], but it appears that this has not been performed, although Θ for HCCH has been estimated from the rotational transitions of the HCCH-HCl complex [7]. Experimental measurements of electrical properties of acetylene have recently been carried out in this department and estimates of the quadrupole moment [8] and polarizability anisotropy [9] have been obtained. Given that the experimental determination of most of these electrical properties is inherently difficult, *ab initio* techniques may be successfully applied to assess both the reliability of the experimental measurements and perhaps guide the experimentalists towards more accurate experiments. Naturally, this is a cooperative process where critical and careful evaluation of both experimental and theoretical methods is required.

In order to provide reliable theoretical estimates that may be used for such predictive purposes, it is essential that the *ab initio* property calculations for the molecule are accurate and all effects that influence the measured property are included in the theoretical treatment. From a theoretical perspective, multiply-bonded linear systems pose problems for *ab initio* techniques, with accurate modelling of electrical properties requiring carefully constructed basis sets that include functions of the appropriate symmetry [10-12].

A number of accurate self-consistent field (SCF) and high-level correlated studies have been performed on acetylene and are summarised elsewhere [13]. Most of these have neglected the effects of rotational-vibrational motion. A single investigation providing an estimate of the zero-point vibrational correction (ZPVC) to the quadrupole moment [14] has been published and, unfortunately, an incorrect expression was used for calculating the property vibrational average in that work. Considering the number of theoretical studies on this molecule and the speculation surrounding the magnitude of vibrational contributions, it is indeed surprising that no further attempts have been made to include these potentially important effects. Therefore, a detailed study of the vibrational contributions to the quadrupole moment, Θ, dipole polarizability, α, and polarizability anisotropy, $\Delta\alpha$, of acetylene is presented in this Chapter. A number of different basis sets have been investigated in combination with a broad range of electron correlation treatments, with particular emphasis placed on the theoretical estimation of the quadrupole moment. In addition to computing accurate electrical properties and ZPVCs, the versatility of the least-squares derivative method described in Chapter 3 is demonstrated by calculating pure vibrational polarizabilities [15] via the perturbation theory method of Bishop and Kirtman [16-18] and examining the effect of isotopic substitution by computing electrical properties for perdeuteroacetylene, DCCD. Thermal effects and predictions of properties in rotational-vibrational states are also investigated to assess the influence of temperature on the measured properties. Throughout the present Chapter, theoretical results are critically compared with available experimental results since it is hoped that studies of this kind may help to stimulate further experimental work in this fruitful area of research. As was the case for the previous Chapter, this work has already been published in full detail [13] and a reprint of that work is included in Appendix V. Reference is made, where appropriate, to the details in that work, but the bulk of the results and discussion are included in this Chapter as they underpin the results presented in subsequent Chapters, and are central to the main theme of this thesis.

5.2 Computational methods

Full details of the construction method and basis sets used in the present Chapter have been published [13] (see Appendix V) along with the finite-field and finite-field gradient method, convergence criteria and gradient tolerances for the least-squares property derivatives procedure. The general theoretical procedure used to determine the expectation values of properties in particular vibrational states has also been discussed in Chapters 2 and 3. The basis sets utilised in the present Chapter include the TZP2(f, d) basis set, represented as [$5s4p3d1f/3s2p1d$] for heavy atoms/hydrogen, the TZP2(f) [$5s4p3d1f/3s2p$] and the smaller DZP2(f) [$4s3p2d1f/2s2p$] molecular basis sets. The TZP2(f, d) set was designed for accurate prediction of polarizabilities and quadrupole moments and contains carefully optimized polarization and diffuse functions for obtaining these properties. The TZP2(f) basis set, constructed from TZP2(f, d) through removal of d-type functions from hydrogen, was utilised mainly for property derivative calculations. The smaller [$4s3p2d1f/2s2p$] basis set for property derivative calculations was constructed by contracting one of the d-type polarization functions from TZP2(f) and combining the polarization and diffuse functions with the double-zeta (DZ) substrate of Thakkar *et al.* [19].

In the vibrational averaging studies, grids of 69 displaced geometries were generated about the optimized geometries and these were used to determine all the required non-zero energy and property derivatives. Of these geometries, 38 were symmetry-unique and therefore only those were required for the calculation of the energy and property derivatives, with energies, dipole and quadrupole moments and the polarizability tensors for the symmetry-related geometries obtained from appropriate symmetry transformations of the properties calculated at the unique geometries [20]. A step size of $\Delta q_i = 0.10$ in the dimensionless normal coordinates was used to generate standard cubic grids, with an additional geometry derived from a (+Δq_3, +Δq_4, +Δq_5) triple displacement that contributes to the calculation of the ϕ_{345} and P_{345} energy and property derivatives. From equation (2.34) in Chapter 2 it is clear that only derivatives of the form P_i, P_{ii}, P_{iii}, P_{ijj}, P_{ijk}, P_{iiii} and P_{iijj} are required for the calculation of the expectation values of the properties and the anharmonic constants. However, due to the doubly degenerate bending modes, extra property derivatives of the form $P_{t_a t_a t'_a t'_a}$ and $P_{t_a t_a t'_b t'_b}$ are also required for acetylene. Displacements were therefore taken along six of the total of seven normal modes since the $P_{4a4a5a5a}$ and $P_{4a4a5b5b}$ property derivatives are required. If only the A terms of equations (2.39) and (2.40) are required, it would be possible to use only five modes for the calculations thus saving the calculation of properties at eight geometries.

5.3 Results and discussion

5.3.1 Zero-point vibrational corrections

Zero-point vibrational corrections (ZPVCs) to the electrical properties obtained with a number of basis sets have been reported and discussed in detail elsewhere [13] (see Appendix V). An adequate description of the quadrupole moment and the fourth (trans-bending) vibrational mode requires the presence of f-type functions on the carbon atoms. Polarizabilities and the corresponding ZPVCs were found to be relatively unaffected by the f-type functions. For these reasons, only the results from the DZP2(f) and TZP2(f) basis sets have been summarised in Table 5.1. Interestingly, the smaller DZP2(f) set appears to perform very well, yielding vibrational corrections in excellent accord with TZP2(f) results. Although the uncorrected DZP2(f) properties may be inferior to TZP2(f) values, and this is especially true for $\Delta\alpha$, the current results would tend to suggest that smaller well-polarized sets should be able to provide accurate ZPVCs for many molecules.

The averaged relative correction to the vibrationless quadrupole moment is −0.8% and −1.8% at the SCF and MP2 levels respectively, which contrasts with the ZPVC reported by Lindh and Liu [14], where an incorrect expression was used to calculate the vibrational average; their reported value of −0.492 au (−10%) is much too large. Those authors combined theoretical CASSCF quadrupole moment derivatives with experimental harmonic frequencies and force constants [21] to compute the A terms in equations (2.39) and (2.40). Recomputing their CASSCF/ANO1 ZPVC using the derivatives and force constants provided in that work leads to a value of −0.146 au, in improved agreement with the present estimates. This value is still too large in magnitude since their calculated P_{11} and P_{22} second derivatives were numerically computed to be $\leq 10^{-3}$ au and subsequently neglected. Inclusion of these derivatives in the present work reduces the magnitude of the ZPVC by 0.003 au. It is believed that the largest remaining discrepancy with the present work arises from the theoretical description of the bending modes; the modes used by Lindh and Liu for the theoretical quadrupole moment derivatives have associated vibrational frequencies that significantly underestimate the experimental results.

Table 5.1.

SCF and MP2 vibrationally averaged properties (in au) for C_2H_2 at the
optimized geometries.[a]

Property	SCF		MP2	
	DZP2(f)	TZP2(f)	DZP2(f)	TZP2(f)
Θ	5.2426	5.2476	4.8559	4.8530
ZPVC	−0.0402	−0.0386	−0.0814	−0.0812
$<\Theta>_0$	5.2024	5.2090	4.7745	4.7718
α_{xx}	18.788	18.891	18.763	18.826
ZPVC	0.321	0.319	0.266	0.270
$<\alpha_{xx}>_0$	19.109	19.210	19.029	19.096
α_{zz}	30.476	30.365	30.754	30.480
ZPVC	0.876	0.871	0.803	0.813
$<\alpha_{zz}>_0$	31.352	31.236	31.557	31.293
α	22.684	22.716	22.760	22.711
ZPVC	0.506	0.503	0.445	0.451
$<\alpha>_0$	23.190	23.219	23.205	23.162
$\Delta\alpha$	11.688	11.474	11.991	11.654
ZPVC	0.555	0.552	0.537	0.543
$<\Delta\alpha>_0$	12.243	12.026	12.528	12.197

[a] Quadrupole moments were calculated with respect to the centre of mass.
Optimized geometries are reported elsewhere [13] (see Appendix V).

At the SCF level, corrections to the vibrationless polarizability and polarizability anisotropy are approximately 2.2% and 4.8% respectively; results at the MP2 level are similar (increases of 2.0% and 4.5% respectively). These differ markedly from the estimates given by Fowler and Diercksen [22] who utilised an r_0 geometry to obtain SCF corrections of +0.5% and +0.2% respectively for α and $\Delta\alpha$. Although the r_0 geometry technique may recover some of the ZPVC, it does not perform in a balanced way for acetylene, producing corrections that substantially underestimate ZPVCs derived from perturbation theory. This is similar to findings from a study of the first-row hydrides [23] where vibrational corrections estimated from property calculations at r_0 and r_z geometries (using an r_e geometry for the uncorrected property) were all found to underestimate more accurate vibrational corrections.

It is illuminating to partition the total vibrationally averaged property, equations (2.34)-(2.49), into contributions from the P_0, A and B terms using coefficients for the vibrational ground state ($v_i = 0$). Examining the contributions to the total ZPVCs summarised in Table 5.2, the dominant contribution arises from the A terms which originate from the second derivatives of the property and from the combination of cubic force constants, harmonic frequencies and first derivatives of the property (see equations (2.39) and (2.40)). For acetylene, the B terms are found to be of lesser importance and could be neglected with minimal loss in accuracy. The B corrections were also found to change sign with different basis sets and appear to be quite sensitive to the description of the vibrational modes, notably the fourth vibrational mode.

Table 5.2.

Contributions to the ZPVCs (in au) for acetylene.[a]

Terms	Θ	α	$\Delta\alpha$
P_e	4.85297	22.71051	11.65486
P_0	−0.00062	−0.00282	−0.00001
A	−0.07839	0.46606	0.54588
B	−0.00220	−0.01224	−0.00247
$<P>_0$	4.77238	23.16433	12.19826

[a] ZPVCs refer to MP2/TZP2(*f*) results at the optimized geometry. Quadrupole moments were calculated at the centre of mass. For an explanation of the terms, see text.

5.3.2 *Pure vibrational polarizabilities*

Utilising the theory and methods of Chapters 2 and 3 for the pure vibrational polarizability, pure vibrational static polarizabilities and polarizability anisotropies are presented in Table 5.3. Agreement with the experimental results reported by Buckingham *et al.* [24] is satisfactory although the reported measurements only include the harmonic contribution to the pure vibrational polarizability (or the $[\mu^2]^{0,0}$ term in the notation of Bishop and Kirtman [16, 17]) since the harmonic approximation was used experimentally for the analysis of the infrared intensities. A similar route was used to obtain the other values reported in the table, the more recent estimates being computed from the integrated intensities reported by Barnes *et al.* [25] ignoring thermal effects, which is the correct procedure for the present purposes. Because of this, α^v reported in Table 5.3 is considerably smaller than the value of 3.8 au reported by Barnes *et al.*, but there is no inconsistency here. That value is entirely consistent with a measurement of the *total* static polarizability of approximately 26.6 au reported by Bogaard and Orr [26] (derived from the dielectric permittivity measurements of Smyth and Zahn [27]) and the dynamic polarizability extrapolated to zero frequency (22.96 au [28], see Table 5.6).

Table 5.3.

Pure vibrational polarizabilities and polarizability anisotropies (in au) at zero frequency.

		DZP2(*f*)	TZP2(*f*)	Experiment
α^v	SCF	2.802	2.800	
	MP2	2.889	2.863	2.8,[a] 3.1(2),[b] 3.02(3)[c]
$\Delta\alpha^v$	SCF	−3.772	−3.774	
	MP2	−3.849	−3.812	−4.0,[a] −4.3(2),[b] −4.10(4)[c]

[a] Experimental results reported by Buckingham *et al.* [24].
[b] From integrated intensities reported by Bishop and Cheung [29].
[c] From integrated intensities reported by Barnes *et al.* [25] (see text for details).

5.3.3 *Vibrational and rotational state dependence*

The computed MP2/TZP2(f) coefficients for equation (2.34) (tabulated in [13]; see Appendix V) have been used to calculate values of the properties in excited vibrational states (Table 5.4). Bending modes (modes 4 and 5) reduce the value of the quadrupole moment while the stretches have the opposite effect and tend to increase Θ. Vibrational states involving the two bending modes are also the lowest in energy and are therefore likely to be populated before energy levels associated with the stretching modes. For the polarizability and polarizability anisotropy, occupation of higher vibrational states is likely to lead to an increase in these properties with respect to the ground vibrational state.

Table 5.4.

Electrical properties (in au) in fundamental and low-lying vibrational states.[a]

State	E	Θ	α	$\Delta\alpha$
00000	0.00	4.7718	23.162	12.198
00010	612.87	4.6696	23.239	12.204
00001	730.33	4.6705	23.205	12.216
00020	1230.39	4.5645	23.292	12.207
00020	1233.52	4.5660	23.304	12.208
00011	1328.07	4.5683	23.284	12.222
00011	1340.55	4.5676	23.276	12.209
00011	1347.52	4.5680	23.280	12.214
01000	1974.35	4.8062	23.293	12.377
00100	3294.84	4.8776	23.407	12.611
10000	3372.85	4.8700	23.414	12.640

[a] Properties from MP2/TZP2(f) calculations at the theoretical optimized geometry. Experimental vibrational state energies, E, [30] are in cm^{-1}.

5.3.4 *Temperature dependence*

Experimental determination of properties in excited vibrational states for non-dipolar molecules is extremely difficult and virtually no data exists for the properties considered here. To provide more realistic predictions and allow for possible experimental verification, thermal corrections to the quadrupole moment, polarizability and polarizability anisotropy have been calculated. Hohm and Kerl [31] have reported temperature dependent polarizabilities for a variety of molecules up to temperatures of 1000 K. Properties in excited vibrational states (Table 5.4) have been combined with calculation of the partition function by direct summation of experimental vibrational energy states [30], to compute thermal averages via equation (2.70) for a number of temperatures between 0 and 1500 K. In Figure 5.1 the differences between the thermally averaged property at a particular temperature, $<P>^T$, and the property in the rotationless vibrational ground state, $<P>_0$, have been presented for the quadrupole moment, polarizability and polarizability anisotropy. Rotational energies were calculated with the rotational constants from Baldacci *et al.* [32]. The effect of rotation on the properties considered is extremely small but may be significant at low temperatures, before excited vibrational states are populated.

Figure 5.2 gives the temperature dependence of the mean polarizability, separating the effects of rotational and vibrational contributions to the property at a given temperature. The rotational contribution to the polarizability increases almost linearly with temperature, but the vibrational contribution dominates at temperatures above 200 K and leads to a more rapid increase in the property.
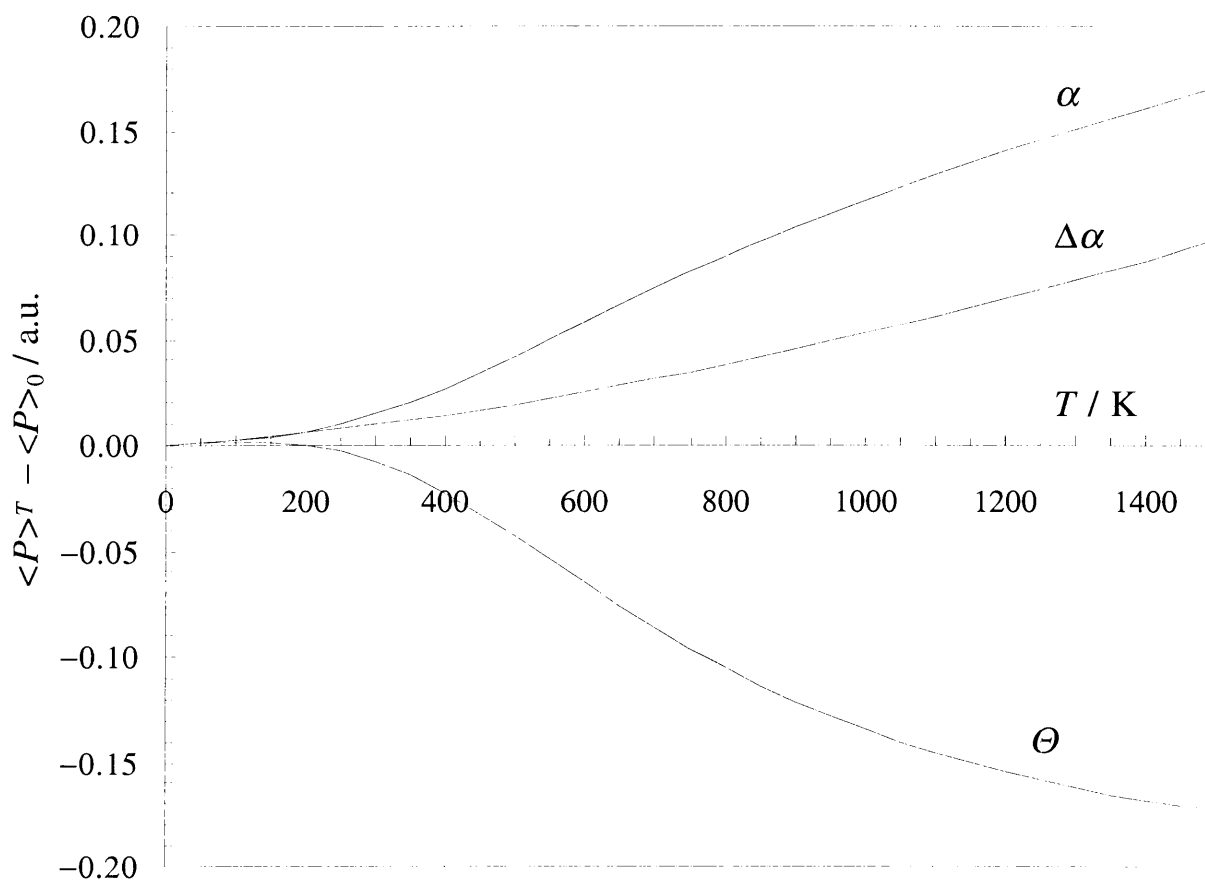
Figure 5.1. MP2/TZP2(*f*) differences between the thermally averaged property for acetylene, $<P>^T$, and the property in the rotationless vibrational ground state, $<P>_0$, for temperatures up to 1500 K.
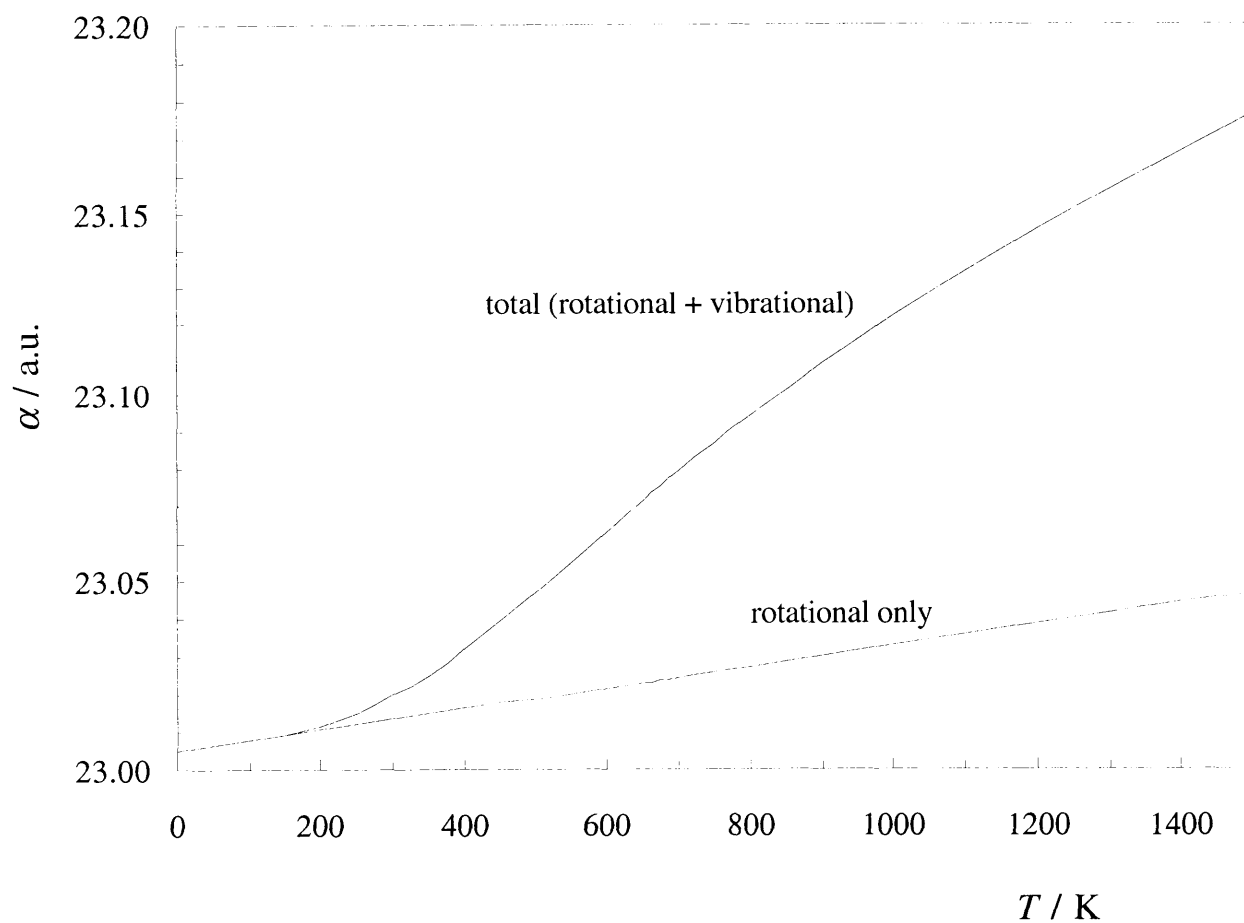
Figure 5.2. MP2/TZP2(*f*) temperature dependence of the mean polarizability for acetylene, decomposed into rotational and combined rotational and vibrational contributions.

5.3.5 *Critical comparison with experiment -* Θ

For the most accurate predictions of vibrationally and thermally averaged electrical properties reported in this and later sections, vibrationless properties have been calculated at the experimental r_e geometry of Strey and Mills [21] and added to the respective ZPVCs evaluated using *theoretical* r_e geometries (stationary points) as described in Chapter 3. While this method is an approximate one, it avoids problems associated with non-stationary points such as imaginary frequencies and projecting out the non-zero gradient term from the potential energy.

Calculated quadrupole moments, using the TZP2(f,d) basis set and a wide variety of different theoretical methods, are compared in Table 5.5. The SCF approximation is particularly poor for this property, severely overestimating the quadrupole moment. Density functional methods improve the situation somewhat, with the local spin-density approximation (DFT-LDA) slightly overestimating more accurate theoretical results, and the non-local corrected Becke-Lee-Yang-Parr (DFT-BLYP) functional also performing quite well but underestimating Θ from superior methods. CISD and MP3 methods do not perform well in calculating this property, both omitting the effect of quadruple substitutions which appear to be important. Methods that include single, double and quadruple and higher substituted determinants such as MP4-SDQ, CCD, QCISD and BD all give similar results, and are all overestimates when compared to BD(T) numbers. The approximate coupled cluster methods ACPF and CEPA-2 do extremely well with MP4 yielding an underestimate, likely to be due to the overestimation of the triples excitation contribution for MP4. Best vibrationless estimates for Θ are obtained using MP4(Feenberg), QCISD(T) and BD(T) methods, all of which are fully complete at fourth-order in a perturbation theory analysis and are partially complete at fifth-order. It is encouraging to find that by repartitioning the perturbation series expansion, MP4(Feenberg) compares favorably with the more expensive methods since MP4 only involves a single n^7 step, for n basis functions, while QCISD(T) and BD(T) involve an iterative n^6 procedure followed by an n^7 step. It would be interesting to see if Feenberg methods also perform equally well for other electrical properties and other molecules.

Many of the theoretical vibrationally averaged estimates for Θ, in Table 5.5, agree well with a recent field-gradient induced birefringence (FGIB) measurement that includes an estimation of the quadrupole hyperpolarizability, $B_{\alpha\beta:\alpha\beta}$.

Table 5.5.

Comparison between vibrationless, vibrationally averaged and thermally averaged (300 K) theoretical quadrupole moments (in au), obtained with the TZP2(f,d) basis set, and experimental results.[a]

Method	Θ	$< \Theta >_0$	$< \Theta >^{300K}$
SCF	5.443	5.404	5.396
DFT-LDA	4.919	4.838	4.830
DFT-BLYP	4.703	4.622	4.614
CISD	4.999	4.918	4.910
MP2	4.797	4.716	4.708
MP3	4.939	4.857	4.849
MP4(SDQ)	4.875	4.794	4.786
MP4	4.787	4.706	4.698
MP4(Feenberg)	4.803	4.722	4.714
CCD	4.881	4.800	4.792
ACPF	4.821	4.740	4.732
CEPA-2	4.817	4.735	4.727
QCISD	4.857	4.776	4.768
QCISD(T)	4.795	4.714	4.706
BD	4.872	4.790	4.782
BD(T)	4.806	4.725	4.717
Experiment	FGIB		4.71(14)[b]
	CME		4.48(13)[c]
	CME		5.57(7)[d]
	CIFIA		4.03(31)[e]

[a] Vibrationless properties were calculated at the experimental r_e of Strey and Mills [21] (r_{CC} = 1.2033 Å, r_{CH} = 1.0605 Å). Vibrational corrections for all correlated wavefunctions and DFT methods are MP2/TZP2(f) corrections, with SCF/TZP2(f) corrections used for the SCF results.

[b] Field-gradient induced birefringence measurement [8] with estimation of quadrupole hyperpolarizability term (see text).

[c] Magnetizability anisotropy (Cotton-Mouton effect) and g value [1].

[d] Magnetizability anisotropy (Cotton-Mouton effect) and g value [33].

[e] Collision-induced far-infrared absorption [34].

For a non-dipolar linear molecule, the molar field-gradient birefringence constant, $_mQ$ is [4, 8]:

$$_mQ = \frac{2N_A}{45\varepsilon_0}\left\{\frac{15}{2}\overline{B} + \frac{\Delta\alpha\Theta}{kT}\right\}$$

Normally the quadrupole hyperpolarizability contribution is obtained directly from experimental measurements of the temperature dependence of $_mQ$ but due to the hazardous nature of acetylene, this was not able to be performed [8]. Subsequently, the contribution of this term has been estimated by using the calculated SCF value of $\overline{B}$ from Maroulis and Thakkar [10], combined with the measured $_mQ$ value from the FGIB experiment of $_mQ = (30.4 \pm 0.9) \times 10^{-26}$ m^5 V^{-1} mol^{-1} at 294 K [8] and using a reported value of $\Delta\alpha$ at 632.8 nm from Bogaard *et al.* [35]. The present best BD(T) theoretical estimate of the quadrupole moment is within 0.3 % of this FGIB estimate with the MP4(Feenberg) and QCISD(T) results also in close agreement. The Cotton-Mouton effect value of Coonan and Ritchie [1] is smaller than the theoretical estimates and the FGIB value, however, when compared to the other Cotton-Mouton estimate by Kling *et al.* [33], the former value appears to be the more reliable of the two. Several interesting points arise from the Cotton-Mouton experimental estimate [1], in particular as a consequence of the temperature range over which the measurements were made: 293 to 442 K. Utilising the temperature dependence of the quadrupole moment obtained in Section 5.3.4 (see Figure 5.1) it is found that as the temperature is increased, the magnitude of Θ decreases. Considering this, it is suggested that the quadrupole moment reported by Coonan and Ritchie [1] is on the correct side of the true value since it is consistent with a decrease of the quadrupole moment with increasing temperature.

5.3.6 *Critical comparison with experiment - α and $\Delta\alpha$.*

Turning to the vibrationally averaged theoretical estimates of α and $\Delta\alpha$, set out in Table 5.6, it is apparent that the TZP2 type basis sets show the most impressive performance due to the more complete set of d-type functions on the carbon atoms. Results for the TZP1 and TZP1(f) basis sets have been presented to clearly highlight the improved performance of the TZP2 type sets for calculating the polarizability and polarizability anisotropy.

Table 5.6.

Comparison of vibrationally averaged mean polarizabilities and polarizability anisotropies (in au) obtained with different basis sets at the experimental r_e geometry.[a]

	Level	TZP1	TZP1(f)	TZP2	TZP2(f)	TZP2(f,d)	Experiment
α	SCF	23.828	23.822	23.914	23.907	23.909	
	MP2	23.024	22.898	23.183	23.036	23.033	
	BD	22.781	22.662	22.942	22.801	22.799	
	BD(T)	23.001	22.852	23.165	23.004	23.005	22.96,[b] 22.95[c]
$\Delta\alpha$	SCF	12.624	12.706	12.525	12.600	12.602	
	MP2	12.106	12.182	12.020	12.080	12.112	
	BD	12.265	12.326	12.167	12.209	12.231	
	BD(T)	12.324	12.404	12.244	12.300	12.313	11.99(4),[d] 11.87(17),[e] 11.5(6),[f] 12.09[g]

[a] Vibrationless properties were calculated using the experimental r_e geometry of Strey and Mills (r_{CC} = 1.2033 Å, r_{CH} = 1.0605 Å) [21]. TZP2(f) ZPVCs from Table 5.1 were then added to the uncorrected properties. For details of the procedure, see text.

[b] Static DOSD estimate [28].

[c] Extrapolation of refractivity data [36] to zero frequency, reported in [28].

[d] $\Delta\alpha(\omega_\sigma)$ obtained from Rayleigh depolarization ratios of Bogaard *et al.* [35] combined with $\alpha(\omega_\sigma)$ from [28], extrapolated to zero frequency using a weighted least-squares fit.

[e] $\Delta\alpha(\omega_\sigma)$ obtained from Rayleigh depolarization ratios of Alms *et al.* [37] combined with $\alpha(\omega_\sigma)$ from [28], extrapolated to zero frequency using a weighted least-squares fit.

[f] $\Delta\alpha(\omega_\sigma)$ obtained from Rayleigh depolarization ratios of Baas and van den Hout [38] combined with $\alpha(\omega_\sigma)$ from [28], extrapolated to zero frequency using a weighted least-squares fit.

[g] Static estimate of $\Delta\alpha$ from molecular beam Stark effect measurements [25].

The inclusion of f-type functions on the carbons decreases the polarizability by a small but significant amount, with the addition of a set of d-type functions on hydrogens having a negligible effect. From Table 5.6, it is evident that SCF methods are completely inadequate for obtaining accurate polarizabilities for acetylene and that some form of electron correlation is required. All basis sets yield overestimates for both α and $\Delta\alpha$ at the SCF level, with the MP2 method providing fortuitously good estimates of α for acetylene that are in close agreement with BD(T) values. This is quite surprising given the relative simplicity of the energy expression for the MP2 method, as compared to the more sophisticated BD and associated coupled-cluster methods, and would lend support to the argument that MP2 methods are capable of excellent results if they are coupled with large basis sets [39]. Interestingly, the $\Delta\alpha$ values for all basis sets display the trend MP2 < BD < BD(T) in contrast to the observed trend for α of BD < BD(T) < MP2. Therefore, although MP2 may provide reasonable estimates of the mean polarizability, its true performance with respect to the Brueckner methods becomes apparent when calculating properties such as $\Delta\alpha$ that depend subtly on a difference between two components of the polarizability tensor. Nevertheless, the differences between MP2, BD and BD(T) are quite small and certainly much smaller than the errors inherent in an experimental determination of $\Delta\alpha$.

Comparing the present most accurate BD(T) vibrationally averaged calculations with experiment in Table 5.6, exceptional agreement is found for the mean polarizability, with TZP1, TZP2(f) and TZP2(f,d) results all within 0.04 au (0.2%) of the DOSD estimate of 22.96 au from Kumar and Meath [28]. Generally, the present theoretical methods perform extremely well. To establish the effect of dispersion SCF/TZP2(f,d) polarizabilities have been calculated at six common laser wavelengths using the pseudo-BD(T) method described in Chapter 3. This is plotted as the solid line in Figure 5.3, where it is compared with the DOSD dispersion curve of Kumar and Meath [28]. Both curves in Figure 5.3 are plotted as cubic polynomials in v^2, although the dispersion in α is virtually linear over this range of frequencies. Ab initio estimates of the lower Cauchy moments (S_{-4} = 111.8 au, S_{-6} = 864.7 au) are in excellent agreement with those reported by Kumar and Meath (S_{-4} = 113.5 au, S_{-6} = 787.2 au), suggesting strongly that the TDHF dispersion of the components of α computed with the TZP2(f,d) basis set is extremely reliable.
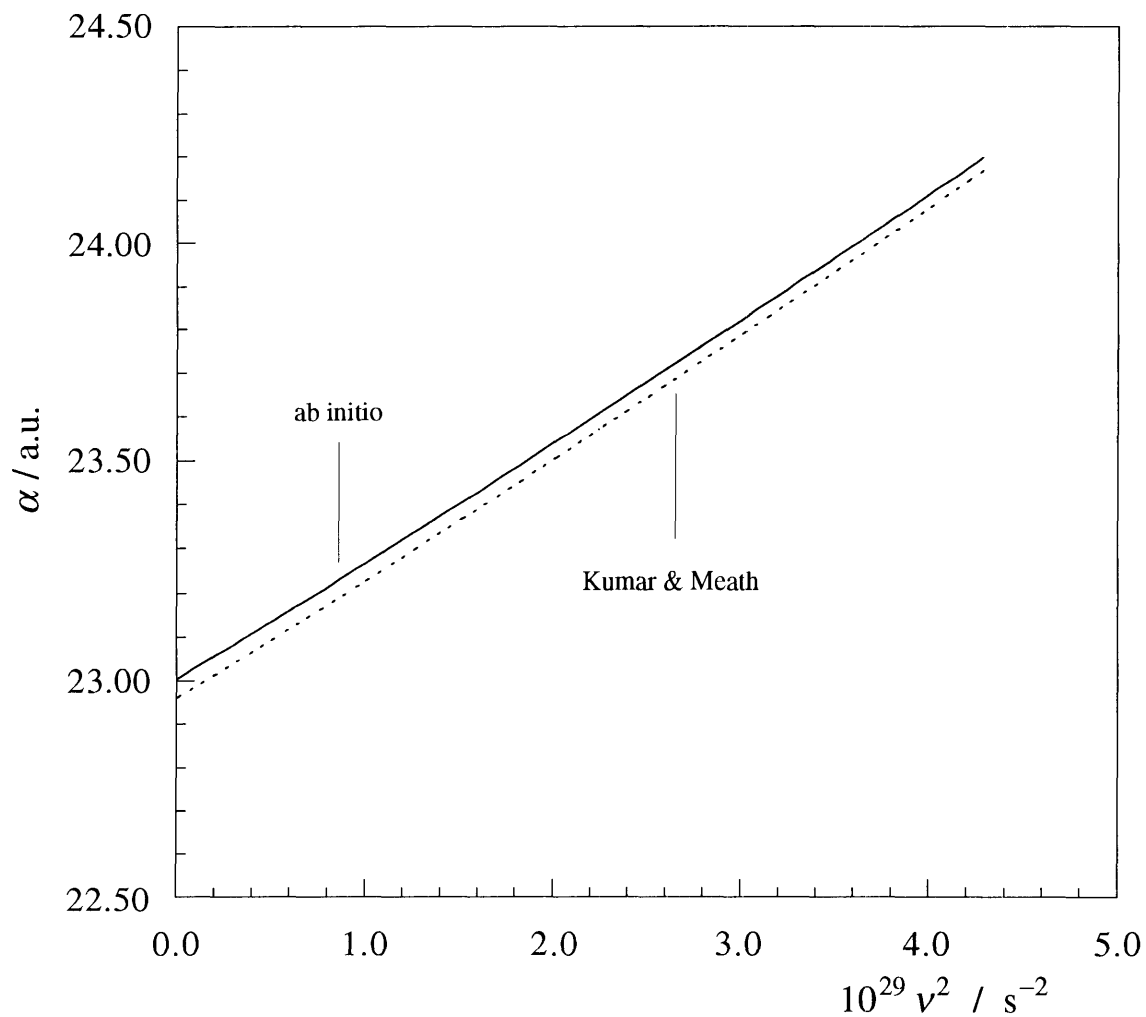
Figure 5.3. Dispersion of the mean polarizability for acetylene. The solid line is based on TDHF/TZP2(f,d) polarizabilities computed at six laser frequencies and scaled to match the static BD(T) value, with added ZPVC from MP2/TZP2(f) calculations. The dashed line is the experimental DOSD curve from Kumar and Meath [28].

Experimental determination of $\Delta\alpha$ is notoriously difficult and a variety of estimates have been obtained for this property. These are presented graphically in Figure 5.4 and give an indication of the problems encountered when comparing with theoretical predictions of this property. Most theoretical estimates of $\Delta\alpha$ pertain to the *static* zero-frequency case and are usually compared to experimental static numbers calculated from Rayleigh light scattering depolarization ratios measured at a number of different wavelengths and then extrapolated to zero frequency (infinite wavelength) as previously discussed for the polarizability. While this may be a satisfactory procedure for the majority of cases, it does not appear to be reliable for acetylene since all of the extrapolated estimates* significantly underestimate the present most accurate theoretical estimate of 12.313 au. A very recent experimental determination of $\Delta\alpha$ by Barnes *et al.* [25] via Stark field induced perturbations of the $v_1 + 3v_3$ vibrational overtone band yielded a static value of 12.09 au which appears to be a reliable measurement and, of all the available static estimates, this value is in closest agreement with the current results. A value of 12.88(197) au has been obtained from Kerr effect measurements [24] but sheds little light on the discrepancy.

It is readily observed from Figure 5.4 that the present TDHF/TZP2(f,d) estimate of the dispersion in $\Delta\alpha$ is considerably smaller than experiment. Although there may be problems with the theoretical dispersion, notably the lack of rigorous treatment of electron correlation for the dynamic values, it is suspected that the inclusion of vibrational Raman lines in the Rayleigh light scattering measurements may lead to an overestimate of the dispersion. Keir [9] has recently performed extensive Rayleigh light scattering measurements on acetylene and has reported $\Delta\alpha$ values at 632.8 nm of 12.43±0.07 au and 12.17±0.02 au with inclusion and exclusion of vibrational Raman lines respectively. Obviously, further work is required to determine the source of this discrepancy, but it appears to display similar features to earlier work on cyclohexane [40] and other molecules [41, 42].

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* 11.99(4) [35], 11.87(17) au [37] and 11.5(6) au [38], all obtained in this work via a weighted least squares fit, the figures in parentheses are estimated errors in the intercepts in each case.
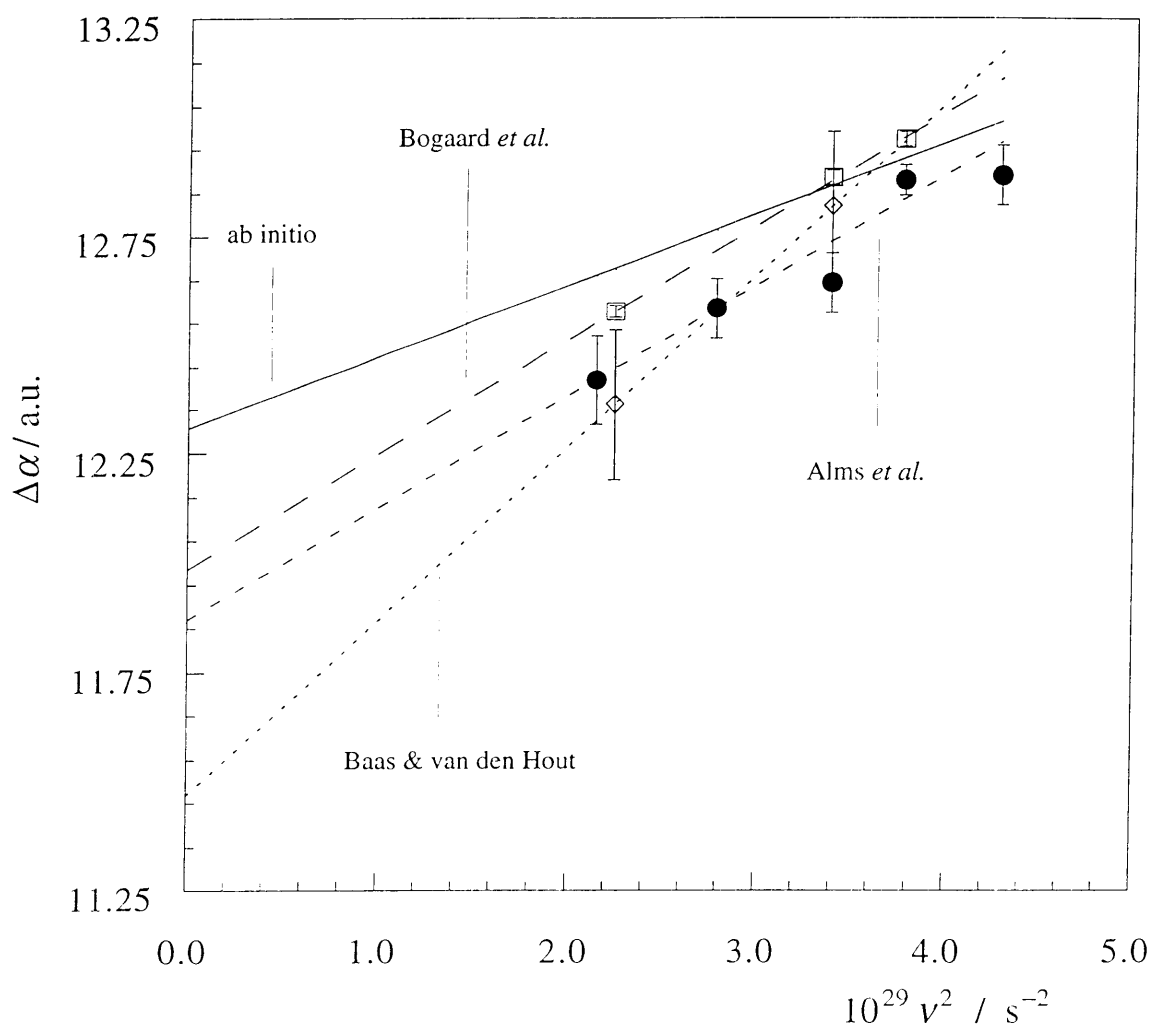
Figure 5.4. Dispersion of the polarizability anisotropy for acetylene. The solid line is based
on TDHF/TZP2(f,d) polarizabilities computed at six laser frequencies and scaled to match
the static BD(T) value, with added ZPVC from MP2/TZP2(f) calculations. The various
dashed lines are weighted least squares fits based on experimental Rayleigh
depolarization ratios from labelled sources [35, 37, 38] combined with $\alpha(\omega_\sigma)$ from Kumar
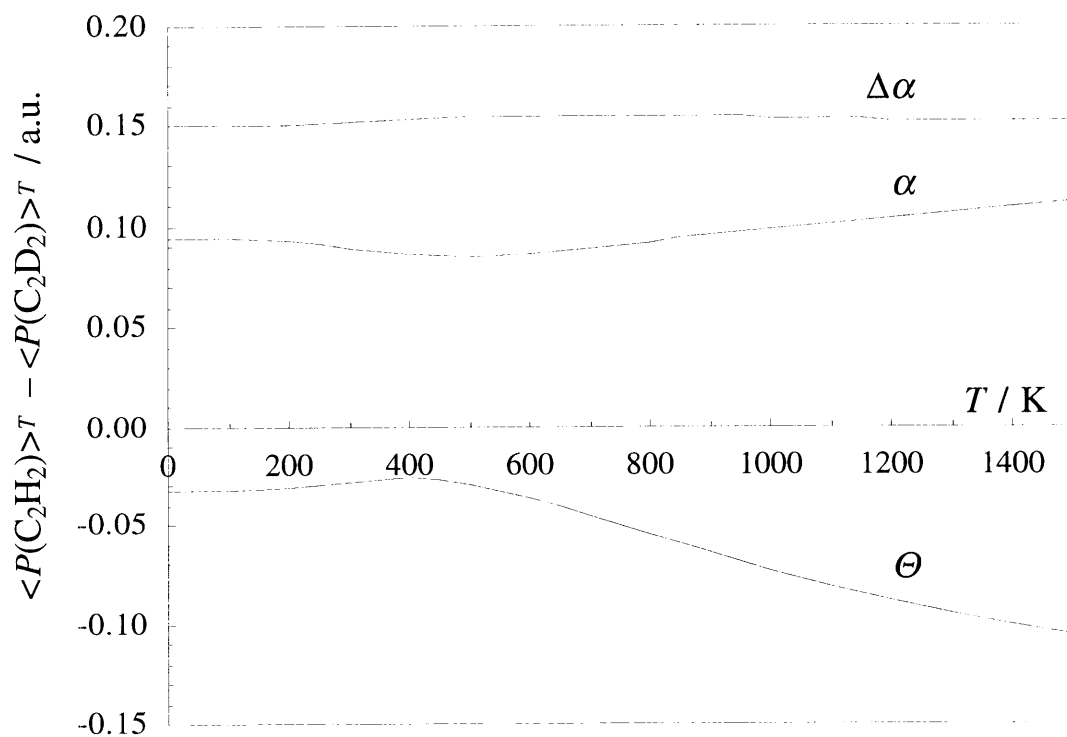and Meath [28] (see Table 5.6).

Figure 5.5. Temperature dependence of the isotope effect $\langle P(\mathrm{C_2H_2})\rangle^T - \langle P(\mathrm{C_2D_2})\rangle^T$ for acetylene based upon MP2/TZP2(f) calculations (see Table 5.7).

5.4 Conclusion

Through the present study of the vibrational and rotational contributions to the electrical properties of acetylene, it has been successfully demonstrated that *ab initio* calculations are capable of highly accurate predictions that may, in many instances, rival experimental results. However, to attain such accuracy, it is important that the vibrationless calculations of the properties are reliable, and that all effects contributing to the measured property are included in the theoretical predictions. In particular, the effects of zero-point vibrational motion are important and should not be overlooked in any theoretical study interested in "definitive" results. Generally, the ZPVC was found to be sufficient to improve agreement with experiment for the properties considered, with the A terms of the vibrational average offering the largest contribution. Calculation of the B terms should generally require very little extra computational effort for small molecules, but for larger cases the extra work would be substantial and perhaps not warranted. Thermal averaging and the contribution from excited vibrational and rotational states is likely to be less important in most instances and may only be required for resolving small discrepancies between theory and experiment. The most convincing demonstration of the success of *ab initio* methods is the prediction of the mean polarizability where sufficiently reliable experimental values have also been reported. Nevertheless, it should be noted that many problems exist with theoretical estimations of $\Delta\alpha$, especially with regard to the frequency dependence of this difficult property. Further theoretical and experimental work is therefore required to firmly establish the role of dispersion. Experimental determinations of Θ are quite rare and therefore further investigations would help to resolve many problems with the accuracy and precision of these measurements. In many respects, it is hoped that the present study will stimulate further experimental and theoretical research in this area and help to establish closer ties between theory and experiment.

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The Fluoromethanes :
CH_3F, CH_2F_2, CHF_3 and CF_4

6.1 Introduction

Electrical properties of the fluoromethanes CF_4, CHF_3, CH_2F_2 and CH_3F have been well-studied experimentally. A considerable number of accurate measurements of the electric dipole moments have been carried out via molecular beam experiments [1-3] with the polarizability and polarizability anisotropy receiving much attention [4-6]. Electric quadrupole moments for CHF_3, CH_2F_2 and CH_3F via the molecular Zeeman effect [7, 8] and molecular beam experiments [1] exist, although some gaps in experimental knowledge remain. In particular, the mean polarizability of CH_2F_2 appears not to have been measured via refractivity methods but only estimated from the average of the refractivities of CF_4 and CH_4 [5, 9]. A greater number of investigations exist concerning the first and second-hyperpolarizabilities [4, 10-13] than studies of the dipole-polarizabilities for this series of molecules. While a sizeable body of experimental information has been accumulated, comparatively fewer accurate theoretical studies on the complete set of molecules [14] are available. Theoretical investigations have been carried out on CH_3F [15], CHF_3 [16] and CF_4 [17] but only one study forwarding correlated estimates of the electrical properties for CH_2F_2 has ever been published [14]. Two studies [18, 19] exploring the vibrational state dependence of the dipole moment of CH_3F have been presented but the vibrational corrections to other electrical properties have not been considered.

With these considerations as background, an investigation of the vibrational corrections to the dipole and quadrupole moments, polarizabilities and polarizability anisotropies for this series of molecules is presented in this Chapter with an emphasis on reliable predictions of the dipole and quadrupole moments, polarizability and polarizability anisotropies. As with previous investigations on the second-row hydrides (Chapter 4) and

acetylene (Chapter 5), high-level *ab initio* estimates, at an r_e or similar geometry, are combined with zero-point vibrational corrections (ZPVCs) calculated at optimized theoretical geometries (described in Chapter 3). The Brueckner doubles method of electron correlation [20-22] is used for the most accurate predictions of electrical properties, with vibrational corrections computed at the SCF and MP2 levels of theory. The pure vibrational polarizability is also calculated and compared with experimental estimates derived from infrared intensity measurements. Extensive comparison is made between the theoretical predictions and available experimental data to assess accuracy of both theory and experiment. In situations where theory and experiment do not concur, considerable effort has been made to resolve the discrepancies.

6.2 Computational methods

The least-squares property derivatives method, as described in Chapter 3, was used to generate energy, dipole moment, quadrupole moment and polarizability derivatives. Standard quartic grids were used in the present investigation with all normal modes used in the grid generation. Exponents and contraction coefficients for the DZP–ANO2 and DZP–ANO1 basis sets, used in the present and later Chapters, are supplied in Appendix IV. The DZP–ANO2 basis set may be represented as $[5s3p2d/3s2p]$ for heavy atoms / hydrogen and utilises the double-zeta (DZ) substrate from Thakkar *et al.* [23] in combination with the MP2–ANO polarization functions. The DZP–ANO1 molecular basis set was constructed by removing a d-type polarization function from heavy atoms, thus leading to a $[5s3p1d/3s2p]$ basis. For CF_4, the smaller DZP–ANO1 basis was utilised for vibrational calculations due to the high computational cost associated with using the DZP–ANO2 basis for MP2 analytic second-derivative calculations.

There appears to be no consistent set of experimental r_e geometries available for the fluoromethanes, although a number of r_0 and r_g estimates exist for the molecular structures [24]. In order to provide complete *ab initio* predictions and a consistent set of nuclear geometries for the molecules, DFT–B3LYP [25] geometry optimizations with the Dunning cc-pVTZ basis set [26] were carried out. The DFT–B3LYP method has been shown to give good quality geometries comparable to CCSD(T) in accuracy [27] and therefore the density-functional method was used as a low computational cost alternative to the MP2 level of theory (the computational cost becomes quite significant for CF_4 with 175 basis functions). Optimized geometries from the B3LYP/cc-pVTZ calculations are reported in Appendix III and were used for the SCF, MP2, BD and BD(T) finite-field and finite-field-gradient

vibrationless property calculations. Field strengths of 0.002 au and field-gradients of 0.0005 au were utilised with numerical errors in the mean polarizability and polarizability anisotropy estimated to be less than 0.0003 au. Corresponding numerical errors in the quadrupole moment are expected to be smaller than 0.0001 au.

6.3 Results and discussion

6.3.1 *Zero-point vibrational corrections*

Zero-point vibrational corrections to the electrical properties are presented in Table 6.1. It is apparent from the results that the corrections to the dipole moment are relatively small and typically less than 0.5% of the vibrationless equilibrium property. The corrections tend to decrease $|\mu_z|$ for CH_3F and CH_2F_2 but increase the magnitude of the dipole moment for CHF_3. Kondo [18] has calculated SCF/4-31G* dipole moment derivatives at the MP2/6-311G** optimized geometry and combined these with an MP2/6-311G** forcefield to calculate a ZPVC to the dipole moment of CH_3F; the resulting value of 0.00445 au is in excellent agreement with the present MP2 results for this molecule. For quadrupole moments, the largest correction is observed for CH_3F where, at the MP2 level, Θ_{zz} is decreased by 8.1%. Corrections to the quadrupole moment of trifluoromethane are approximately 0.5% as are the corrections to the zz component of CH_2F_2. The yy component for CH_2F_2 is more strongly affected by vibrational motion than either the xx or zz components, most likely due to the stronger influence of the $>CH_2$ group vibrations as opposed to the $>CF_2$ group which lies along the z axis in the xz plane. For the mean polarizability there is a regular increase in relative corrections moving from CF_4 through to CH_3F roughly corresponding to a relative percentage increase of 1% with substitution of a C–F bond with a C–H. This may be partially explained by recognising that a C–F bond is much stiffer than a C–H bond in CH_2F_2. It is likely that the vibration of C–H bonds will more strongly affect the average molecular size and hence the mean polarizability. Corrections to the polarizability anisotropy demonstrate the importance of including the effects of vibrational motion into theoretical predictions of electrical properties. Due to the small magnitude of $\Delta\alpha$, corrections to the anisotropy are especially large and in the range 11–13% and 6–7% for SCF and MP2 levels respectively. The large difference between SCF and MP2 percentage corrections for this property can be ascribed to the underestimation of $\Delta\alpha$ by SCF methods. Generally, the dipole-polarizability tensor becomes more isotropic with inclusion of vibrational motion and this is supported by the decrease in $|\Delta\alpha|$ found for the dipolar molecules.

Table 6.1.

SCF and MP2 DZP–ANO2 vibrationless properties and zero-point vibrational corrections (ZPVCs) (in au) to the electrical properties of the fluoromethanes.[a]

		SCF		MP2	
	Property	P_e	ZPVC	P_e	ZPVC
CF_4	α	16.086	0.1727	18.883	0.2274
CHF_3	μ_z	0.6948	0.00419	0.6547	0.00301
	Θ_{zz}	2.973	0.0171	2.790	0.0131
	α	16.169	0.3322	18.699	0.3923
	$\Delta\alpha$	−0.890	0.1166	−1.488	0.1000
CH_2F_2	μ_z	−0.8417	−0.00034	−0.7996	0.00116
	Θ_{xx}	−3.144	0.0033	−2.993	0.0097
	Θ_{yy}	1.503	−0.0117	1.392	−0.0175
	Θ_{zz}	1.641	0.0083	1.601	0.0077
	α_{xx}	16.481	0.4203	19.002	0.4883
	α_{yy}	15.131	0.5981	16.649	0.6194
	α_{zz}	15.734	0.5156	17.687	0.5706
	α	15.782	0.5113	17.779	0.5594
	$\Delta\alpha$	1.171	−0.1541	2.043	−0.1144
CH_3F	μ_z	−0.7890	0.00261	−0.7626	0.00433
	Θ_{zz}	−0.380	0.0184	−0.283	0.0228
	α	15.649	0.7033	17.010	0.7312
	$\Delta\alpha$	1.060	−0.1194	1.795	−0.0652

[a] In each case the principal rotation axis was chosen to be the z axis. The CF_2 group of CH_2F_2 lies along the $+z$ axis in the xz plane, with the H atom of CHF_3 and the F atom of CH_3F set to lie along the $+z$ axis. Quadrupole moment corrections refer to centre of mass coordinates. Optimized geometries are supplied in Appendix III. The results for CF_4 were calculated using the DZP–ANO1 basis set.

6.3.2 *Pure vibrational polarizabilities*

Compared to the electronic component of the mean polarizabilities, the fluoromethanes exhibit relatively large pure vibrational polarizabilities. Examining the MP2 results in Tables 6.1 and 6.2, the mean vibrational polarizability contribution relative to the mean electronic polarizability is found to be 36, 29, 17 and 5.7% for CF_4, CHF_3, CH_2F_2 and CH_3F respectively. The SCF and MP2 pure vibrational mean polarizabilities are in close agreement, but for $\Delta\alpha^v$, MP2 theory provides distinctly better estimates. For CF_4, both SCF and MP2 effectively bracket the result from Lu and Shelton [6] with MP2 lying within 2.7% of experiment. In the case of CHF_3, the relative intensities of the v_2 and v_5 bands appear to be important in obtaining reliable pure vibrational polarizability anisotropies. Utilising an A_5/A_2 intensity band ratio of 6.3697 from an MP2/DZP–ANO2 anharmonic intensity calculation and the measured intensity of the combined v_2 and v_5 bands [28], exceptional agreement is obtained between theory and experiment for $\Delta\alpha^v$ in Table 6.2. (The mean vibrational polarizability is, of course, unaffected by the use of the theoretical band intensity ratio since it depends only on the sum of the experimental intensities).

The precision of the experimental intensities for CH_2F_2 makes it difficult to ascertain the accuracy of the present theoretical estimates since both SCF and MP2 results for the mean vibrational polarizability are quite close but those for the anisotropy differ by about 0.6 au. Several recent intensity measurements have been published for CH_3F [29-31] and these have been utilised in calculating the experimental pure vibrational polarizability and polarizability anisotropy. It is somewhat puzzling that a newer measurement of the v_3 band intensity [29] should provide a poorer description of the vibrational polarizability tensor. When the v_3 band intensity is replaced with an older value of 108.4 km mol^{-1} from Barrow and McKean [32], the present MP2 estimates are found to lie within 1.4 and 0.9% of experiment for α^v and $\Delta\alpha^v$ respectively. Apparently further work is required to establish the accuracy of the v_3 band intensity for this molecule.

Table 6.2.

SCF and MP2 pure vibrational polarizabilities and polarizability anisotropies (in au) for the fluoromethanes.^{a}

		Level of Theory		
		SCF	MP2	Experiment
CF_4	α^{v}	6.3591	7.0335	$6.79(17)^b$, $6.85(17)^c$
CHF_3	α^{v}	5.1411	5.4718	$5.62(28)^d$, $5.3(5)^e$
	$\Delta\alpha^{v}$	−2.9193	−4.0888	$-4.15(21)^d$, $-2.7(3)^e$
CH_2F_2	α^{v}_{xx}	5.3633	5.9264	
	α^{v}_{yy}	0.4921	0.3769	
	α^{v}_{zz}	3.1354	2.7692	
	α^{v}	2.9969	3.0242	$2.6(3)^f$, $2.8(3)^g$
	$\Delta\alpha^{v}$	4.2237	4.8213	$4.8(4)^f$, $4.3(4)^g$
CH_3F	α^{v}	1.1826	1.0058	$0.92(9)^f$, $1.02(5)^h$, $0.90(5)^i$
	$\Delta\alpha^{v}$	2.9038	2.5678	$2.26(23)^f$, $2.59(13)^h$, $2.23(11)^i$

^{a} See footnote(a) of Table 6.1 for coordinate systems and orientation.

^{b} Derived from experimental (IR) intensities [6]. A 2.5% error has been estimated.

^{c} Derived from a dielectric constant measurement of the mean polarizability [33] and a static estimate from an extrapolation of refractivity data [34].

^{d} Calculated from experimental IR intensities [28]. Intensities for the v_2 and v_5 bands have been estimated by assuming an A_5/A_2 ratio of 6.3697 derived from an MP2/DZP–ANO2 anharmonic intensity calculation. A 5% error has been applied.

^{e} Calculated from experimental IR intensities [35]. A 10% error has been estimated.

^{f} Derived from experimental IR intensities [36].

^{g} Calculated from experimental IR intensities [37].

^{h} Calculated from experimental IR intensities from various sources : v_1 and v_4 bands [36, 38], v_2 and v_5 bands [31], v_6 band [30] and v_3 band [32].

^{i} Calculated using the IR intensities from above (h) but replacing the v_3 IR band intensity by a more recent measurement [29].

6.3.3 Dipole and quadrupole moments

Vibrationally averaged dipole and quadrupole moments for this series of molecules (Table 6.3) are in remarkable agreement with experiment. Surprisingly, MP2 predictions for the dipole moment are closer to experiment than their more complete BD(T) counterparts. It is expected that the B3LYP/cc-pVTZ geometry used for the vibrationless electrical property calculations is responsible for the discrepancies since the ZPVCs are relatively small and do not significantly alter the electronic property. In order to test the effect of reference geometry on the properties, BD(T) electrical property calculations were performed at the BD(T)/TZ2P optimized geometry for CH_3F. The BD(T) geometry optimization was carried out using analytical BD(T) gradients with a $[5s4p2d/3s2p]$ TZ2P basis set previously used in vibrational frequency investigations [39, 40]. A vibrationally averaged dipole moment of -0.73077 au results, which is extremely close to the experimental measurement of $-0.731150(8)$ au. The vibrationally averaged quadrupole moment was found to be -0.2575 au which is in agreement with the reanalysed quadrupole moment estimate of $-0.259(18)$ au. The accuracy of the underlying theoretical or experimental reference geometry is clearly important in the prediction of electrical properties, especially if the ZPVCs for the properties are relatively small. Despite use of theoretical B3LYP/cc-pVTZ geometries, the BD(T) dipole moment estimates are all within 1% of experiment.

Electron-correlation is necessary to obtain reliable estimates of the quadrupole moment and although on first examination the present MP2 and BD estimates appear to be better than those at the BD(T) level, all of the correlated estimates fall within the experimental uncertainties. Observing the magnitudes of the calculated quadrupole moments with level of theory, the progression $SCF > BD > MP2 > BD(T)$ is found. Quadruple and higher substitutions in the BD electron-correlation method tend to increase the magnitude of the quadrupole moment with the connected triple excitations decreasing $|\Theta|$ thereby bringing the BD result closer to MP2. The basis sets used for these calculations are slightly deficient for quadrupole moment calculations since f-type functions are probably required on heavy atoms. In the present calculations, f-type functions were neglected for reasons of high computational cost.

On the basis of the above results for CH_3F, (using a higher quality reference geometry) it appears that a large proportion of the discrepancies from experiment for quadrupole moments may be ascribed to the present choice of reference geometry. Nevertheless, these results should be accurate enough to distinguish between contradictory experiments, specifically for the quadrupole moment of CHF_3. It is expected that even with

Table 6.3.

Vibrationally averaged DZP–ANO2 dipole and quadrupole moments (in au) for the fluoromethanes.[a]

		Level of Theory				
		SCF	MP2	BD	BD(T)	Experiment
CHF_3	μ_z	0.73508	0.64954	0.65879	0.64538	0.64975(4)[b]
	Θ_{zz}	3.1779	2.7713	2.8080	2.7462	2.79(4)[b], 2.875(18)[c]
CH_2F_2	μ_z	−0.87596	−0.78068	−0.78674	−0.77256	−0.7784(8)[d]
	Θ_{xx}	−3.3096	−2.9164	−2.9394	−2.8834	−2.94(14)[e]
	Θ_{yy}	1.5511	1.3407	1.3562	1.3277	1.41(18)
	Θ_{zz}	1.7585	1.5757	1.5832	1.5557	1.52(16)
CH_3F	μ_z	−0.81635	−0.73424	−0.73654	−0.72632	−0.731150(8)[f]
	Θ_{zz}	−0.3073	−0.2513	−0.2531	−0.2481	−0.3(7)[g],−0.259(18)[h]

[a] DZP–ANO2 vibrational corrections have been applied to property calculations at the respective theoretical B3LYP/cc-pVTZ optimized geometries using the DZP–ANO2 basis set (See text). Molecular orientation has been defined in footnote(a) of Table 6.1. Quadrupole moments refer to centre of mass coordinates.

[b] Ground vibrational state dipole and quadrupole moments from avoided-crossing molecular beam experiments [1].

[c] Molecular Zeeman effect measurement [8].

[d] Ground vibrational state dipole moment from laser Stark spectroscopy [3].

[e] Molecular Zeeman effect measurement [41].

[f] Ground vibrational state ($v = 0$, $J_K = 1_{\pm1}$) dipole moment from molecular beam electric resonance (MBER) [2].

[g] Molecular Zeeman effect measurement [7].

[h] Re-analysis of the molecular Zeeman effect measurement [7] assuming a 7% error in the measurement. The relative error of $\Delta\chi$ is assumed to be the same as the error in the quadrupole moment.

an improved theoretical reference geometry, theory would still favour the avoided-crossing molecular beam result of Meerts and Ozier [1] over the molecular Zeeman effect result [8].

Other quadrupole moment measurements have been carried out including an electric field-gradient-induced birefringence study on CH_3F [42]. Unfortunately, the measured quadrupole moment for dipolar molecules is defined with respect to the effective quadrupole centre [42] and not the centre of mass of the molecule. Consequently, due to the very small magnitude of the centre of mass quadrupole moment for CH_3F and the large contribution to the observed field-gradient-induced birefringence from the term involving $\mathbf{A}$, $\mathbf{G'}$ and μ_z, it has not been possible to extract a physically reasonable quadrupole moment from those results.

6.3.4 *Polarizabilities and polarizability anisotropies*

Vibrationally averaged polarizabilities and polarizability anisotropies are reported in Table 6.4. For all molecules in this series, the differences between MP2 and BD(T) mean polarizabilities are extremely small (0.014, 0.008, 0.023 and 0.073 au for CF_4, CHF_3, CH_2F_2 and CH_3F respectively). It is remarkable that the MP2 method performs so well for this set of molecules, especially considering the approximate computational cost of MP2 (n^5 for n basis functions) as compared to BD(T) (iterative n^6 + single n^7 step). It would be most interesting to see if this trend is reproduced for the mean polarizabilities of the corresponding chloromethanes and other molecular systems. Present BD(T) estimates are all within 2% of accurate experimental values and this agreement is quite acceptable for the size of basis set used in the calculations. For CF_4, the present results favour the older value of the mean polarizability [34, 43] but it would be illuminating to see the effect of an improvement in basis set on this value. As mentioned in the introduction, there are no refractivity estimates of the mean polarizability of CH_2F_2, however, the approximate CH_4/CF_4 average value [5] is in fine agreement with the theoretical results and would seem to validate the approximation used. A dielectric constant measurement has been published for CH_2F_2 [44] but the associated uncertainty in α is quite large.

Table 6.4.

Vibrationally averaged DZP–ANO2 polarizabilities and polarizability anisotropies (in au) for the fluoromethanes.[a]

		Level of Theory				
		SCF	MP2	BD	BD(T)	Experiment
CF_4	α	17.342	19.656	19.264	19.670	$19.488(5)^b$, $19.11(17)^c$
CHF_3	α	16.951	19.037	18.649	19.045	$18.680(2)^b$, $18.5(2)^d$
	$\Delta\alpha$	−1.054	−1.331	−1.325	−1.390	$-1.13(20)^e$, $-1.11(16)^f$ $-1.15(3)^i$
CH_2F_2	α_{xx}	17.414	19.311	18.953	19.339	
	α_{yy}	15.939	17.228	16.937	17.192	
	α_{zz}	16.538	18.185	17.802	18.124	
	α	16.631	18.242	17.897	18.219	$18.18(4)^g$, $18.1(13)^h$
	$\Delta\alpha$	1.285	1.806	1.751	1.865	$1.78(11)^e$, $1.72(5)^i$
CH_3F	α	16.598	17.636	17.347	17.563	17.335^b
	$\Delta\alpha$	1.118	1.570	1.480	1.560	$1.57(3)^i$, $2.092(22)^j$

[a] Molecular orientation has been defined in footnote(a) of Table 6.1.

[b] Static estimate from a linear extrapolation of refractivity data (five wavelengths between 644 and 436 nm) [34, 43].

[c] Static estimate deduced from a dielectric constant measurement and corrected with a pure vibrational polarizability of 6.79(17) au derived from infrared intensities [6].

[d] Dielectric constant measurement [45] combined with a semi-empirical estimate of the pure vibrational polarizability contribution of 5.62 au [35].

[e] Static estimate from a linear extrapolation of dynamic polarizability anisotropies from Rayleigh light scattering measurements [5].

[f] MBER static estimate [46].

[g] Static estimate from a linear extrapolation of empirical refractivity data. The dynamic refractivities were assumed to be the average of the refractivities of CH_4 and CF_4 [5].

[h] Dielectric constant measurement [44] corrected with a pure vibrational polarizability of 2.76 au derived from infrared intensity measurements [37].

[i] Dynamic estimates (514.5 nm) from Rayleigh light scattering and rotational Raman spectroscopy. The vibrational Raman contributions to the measured depolarization ratios were excluded [4].

[j] Dynamic estimate (632.8 nm) from Rayleigh light scattering measurements. The vibrational Raman contribution to the observed depolarization ratio was included in the measurement [47].

Turning to the polarizability anisotropy, agreement with extrapolated static estimates appears to be reasonable. However, the agreement with measurements at 514.5 nm that exclude the vibrational Raman lines from the depolarization ratios [4], is exceptional. As stated in the work on the second-row hydrides in Chapter 4, great care must be exercised in comparison of Rayleigh light scattering measurements with theory because of the vibrational Raman contribution to the observed Rayleigh depolarization ratio (ρ_0). The vibrational Raman contribution is particularly noticeable where the depolarization ratio is small, and its inclusion leads to polarizability anisotropies that are larger than expected.

In order to better illustrate this problem, theoretical pseudo-BD(T) (the pseudo-BD(T) procedure is described in Chapter 3) depolarization ratios have been calculated at six laser wavelengths and plotted with experimental Rayleigh depolarization ratios in Figure 6.1. Theoretical pseudo-BD(T) depolarization ratios are also reported in Table 6.5 for three of the six wavelengths for which experimental data is available. Experimental depolarization ratios for the fluoromethanes are supplied in Table 6.5. The measurements of Bogaard, Buckingham, Pierens and White (BBPW) [5], Baas and van den Hout [48], Bridge and Buckingham (BB) [47] and Burnham *et al.* [49] all include the vibrational Raman contribution. Only the measurements of Bogaard *et al.* at 514.5 nm (cited in Miller, Orr and Ward [4]) and Monan *et al.* at 488.0 nm [50] explicitly exclude the vibrational Raman contribution. Clearly the vibrational Raman contribution has a marked effect on not only the magnitude of the depolarization ratio but also on its frequency dependence. In all cases, the slope of the theoretical frequency dependence (in Figure 6.1) is opposite in sign to the experimental frequency dependence for experiments that include the vibrational Raman contribution.
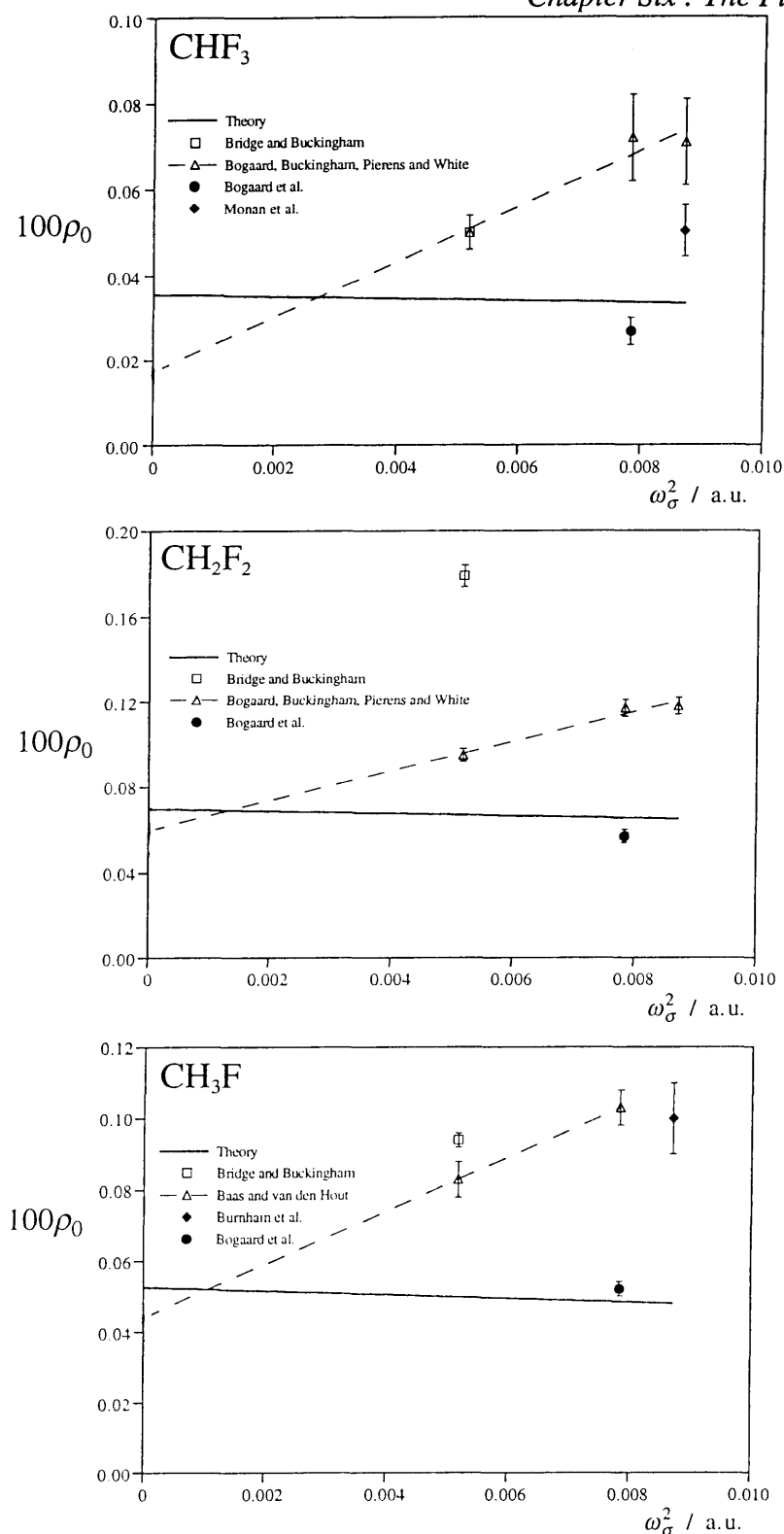
Figure 6.1. Theoretical and experimental Rayleigh depolarization ratios for the fluoromethanes. Solid line is based on pseudo-BD(T) theory with experimental depolarization ratios from various sources. (Bridge and Buckingham [47], Bogaard, Buckingham, Pierens and White [5], Monan, Bribes and Gaufres [50], Bogaard, Orr, Murphy, Srinivasan and Buckingham (unpublished) [4], Baas and van den Hout [48] and Burnham, Buxton and Flygare [49]).

Table 6.5.

Comparison of theoretical pseudo-BD(T) Rayleigh depolarization ratios with experiment for the fluoromethanes at some common optical wavelengths, λ.[a]

	λ / nm	$100\rho_0$ Theory	Experiment Vib. Raman excluded	Vib. Raman included
CHF_3	∞	0.035510		
	632.8	0.034266		$0.050(5)^b, 0.050(4)^c, 0.054(5)^d$
	514.5	0.033609	$0.0245(12)^e, 0.0267(32)^f$	$0.072(10)^c, 0.058(5)^d$
	488.0	0.033391	$0.0504(60)^g$	$0.071(10)^c$
CH_2F_2	∞	0.069769		
	632.8	0.066983		$0.095(3)^c, 0.179(5)^b$
	514.5	0.065502	$0.057(3)^e$	$0.117(4)^c$
	488.0	0.065007		$0.118(4)^c$
CH_3F	∞	0.052559		
	632.8	0.049824		$0.094(2)^c, 0.083(5)^d$
	514.5	0.048376	$0.052(2)^e$	$0.103(5)^d$
	488.0	0.047893		$0.100(10)^g$

[a] Optical frequencies corresponding to the laser wavelengths in the table are :
632.8 nm (0.072003 au), 514.5 nm (0.088559 au) and 488.0 nm (0.093368 au).
Experimental measurements in the "Vib. Raman excluded" column rigorously exclude the vibrational Raman contribution to the Rayleigh depolarization ratios. All other experimental measurements in this table include the contribution.

[b] [47]. [c] [5]. [d] [48].

[e] Bogaard, Orr, Murphy, Srinivasan and Buckingham (unpublished results). Cited in [4].

[f] [51]. [g] [50]. [h] [49].

6.4 Conclusion

In situations where the ZPVC is relatively small, the accuracy of the reference equilibrium geometry becomes increasingly important and this is particularly apparent for the dipole moments of the fluoromethanes, where the vibrational correction is smaller than 0.5% of the vibrationless property. In such instances, BD(T) property calculations carried out at CCSD(T) or BD(T) optimized theoretical geometries with good quality basis sets, may be required to obtain the vibrationless properties. Once the vibrationless properties have been well established, then vibrational corrections may be applied to hopefully attain quantitative agreement with experiment. Properties possessing relatively larger vibrational corrections should be insensitive to this problem, as any errors in the reference vibrationless property are likely to be dominated by the ZPVC. It is hoped that further experimental work, similar to the CHF_3 study of Meerts and Ozier [1] utilising the avoided-crossing molecular beam method, will be carried out on these molecules to confirm the accuracy of the present dipole and quadrupole moment predictions for CH_2F_2 and CH_3F. Experimental polarizabilities from refractivity measurements are required for the mean polarizability of CH_2F_2, and a greater number of experimental measurements of $\Delta\alpha$ from other methods such as molecular beam measurements would also be of great assistance. Further theoretical study is also desirable to investigate a method for including pure vibrational Raman contributions into theoretical Rayleigh depolarization ratios to enable a better comparison of theory with experimental Rayleigh light scattering measurements.

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