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Correlated dipole polarizabilities and dipole moments of the halides HX and CH_3X (X = F, Cl and Br)

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Summary. We report values of the correlated dynamic dipole polarizability for the halides HX and CH_3X (X = F, Cl and Br). The polarizabilities are calculated within the second-order polarization propagator approximation (SOPPA). The correlated results are in much better agreement with the available experimental results, compared to RPA. We also report the second-order dipole moments using both the "relaxed" and "unrelaxed" MP2 density matrices. The relaxed results are in better agreement with experiment.

Key words: Polarization propagator – SOPPA – Dynamic polarizability – Depolarization ratio – Dipole moment

1 Introduction

The use of propagator techniques in molecular physics was pioneered by Linderberg and Öhrn [1], based on the development and formulation of Zubarev [2]. Linderberg and Öhrn pointed out the usefulness of the propagator concept for determining transition moments and energy differences, as residues and poles of the propagator, respectively. They also made us aware of the fact that propagators can be identified with second-order response properties. When calculating frequency-dependent polarizabilities, the correct position of the energy asymptotes (that is the poles of the propagator) is of increasing importance as the applied frequency increases. In retaining the structure of the exact response function, by using the polarization propagator, we can ensure that the poles are evaluated consistently. This is the main reason why we have chosen to demonstrate the potential of propagator methods by calculating frequency-dependent polarizabilities.

Even though propagator methods, in many disguises, were an integral part of Linderberg and Öhrn's research papers for several years, it was not until the appearance of their "yellow book" [3] that the power of the methods was displayed in unified form. In this book, the versatility of propagators for calculating a range of molecular properties was demonstrated and since then, many such calculations

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have appeared, often authored by scientists who have their roots in the Aarhus group [4].

Use of the polarization propagator is centred around the computation of second-order properties, as the linear response of a perturbed system. The dipole polarizability, for example, is determined from an expansion of the induced dipole moment, rather than of the electronic energy. This difference is immaterial for methods that fulfill the Hellmann–Feynman theorem [5] (e.g. SCF, MCSCF), for which the two approaches will yield identical results. This will not be the case for perturbative methods, however, such as the one we apply here. We therefore examine the difference between the induced dipole and energy derivative results, at MP2 level. Another way of explaining the difference between these two approaches is to observe that the energy derivative method uses relaxed orbitals [6], while the perturbative linear response employs the unrelaxed orbitals, in accounting for the correlation effects. We found it of interest also to examine how much the correlated dipole moment was affected by the use of relaxed as opposed to unrelaxed orbitals, the latter being more akin to the definition of the polarizability from the induced dipole moment.

We have chosen to investigate the above points for a series of molecules, the halides and the methyl halides, for which we know that we need to go beyond RPA in order accurately to describe the dispersion of the polarizability and for which there is ample experimental data available. We also had in mind that these molecules are singly bonded and should therefore be amenable to a description based on Møller–Plesset perturbation theory.

2 Theory

The equation of motion for the propagator, in the energy representation, is

$$\omega\langle\langle A;B\rangle\rangle_\omega = \langle 0|[A,B]|0\rangle + \langle\langle [A,H];B\rangle\rangle_\omega. \tag{1}$$

$\langle\langle A;B\rangle\rangle_\omega$ is therefore defined in terms of a ground state expectation value and another propagator, which involves a commutator of A with the Hamiltonian. It is possible to develop approximations to the propagator by iterating upon Eq. (1) and employing the superoperator formalism [7]. In the case of the frequency-dependent dipole polarizability, $\alpha(-\omega;\omega)$, we obtain [8]

$$\begin{aligned} -\alpha(-\omega;\omega) &= \langle\langle r;r\rangle\rangle_\omega \\ &= (r|h)(h|\omega\hat{1} - \hat{H}|h)^{-1}(h|r) \\ &= t(r)P_\omega^{-1}t(r). \end{aligned} \tag{2}$$

Various levels of approximation can be used to calculate $\alpha(-\omega;\omega)$ from Eq. (2). Utilizing the standard Møller–Plesset partitioning of the SCF Hamiltonian [9], we obtain uncoupled Hartree–Fock [10] if we retain only zeroth-order terms within the transition moments, t, and the propagator matrix, P. The random phase approximation (RPA) follows from keeping all terms to first order; this approximation is equivalent to time-dependent Hartree–Fock [11] as well as to the finite field approach for static properties [12]. The second-order polarization propagator approximation (SOPPA) retains all terms in t and P which are up to second order in the fluctuation potential [13, 14], yielding a polarizability which is also of at least second order. The use of the propagator ensures that in both RPA and

SOPPA, there are contributions summed to infinite order in the fluctuation potential [13]. An important aspect of the SOPPA method is that both the poles of the propagator and the transition moments are corrected to second order. This means that the dispersion of the polarizability should be described more consistently than in RPA, or in any other method in which the RPA or lower-order poles are used [15]. A coupled cluster variant of SOPPA has also been defined [17], in which cluster amplitudes replace the Møller–Plesset correlation coefficients. Although it includes more correlation than SOPPA, the coupled cluster propagator is still only consistent through second order. This method has been found to be more successful than SOPPA in treating properties of molecules with near degeneracies in their ground state electronic configurations [17], but for the property and systems which we are studying, there is little diffenence between the two approaches [18, 19]. Explicit expressions for the transition moments and propagator matrix have been given by Oddershede et al. [8].

Although there are many methods available for calculating static correlated polarizabilities [20], there are fewer which can also treat the dynamic polarizability to the same level of approximation. There is, for example, the multi-configurational RPA approach [21], the use of pseudo-energy derivatives within the MP2 approximation [22], the coupled cluster linear response [23] and effective Hamiltonian [24] methods. The MP2 pseudo-energy approach is closest to SOPPA, in terms of the level of approximation, the main differences being that SOPPA determines the property from the induced dipole moment, as opposed to an energy derivative and that the energy asymptotes in SOPPA are correct to second order, but not necessarily so for MP2 [15]. Both methods will recover the dynamical correlation contribution and should be applied only to those systems which can be represented well by a single reference ground state. It should also be noted that the static MP2 polarizability, evaluated as an analytic energy derivative, is equivalent to the finite field result [16]. SOPPA, on the other hand, cannot be defined in such a way. Previous calculations of the dynamic polarizability in SOPPA can be found in Refs. [19, 25].

If we wish to calculate the dipole moment to second order in the Møller–Plesset expansion, we can adopt two approaches. The "unrelaxed" dipole moment is obtained from the expectation value

$$\begin{aligned}\mu_z &= -\langle 0|z|0\rangle \\ &= -tr z\rho, \end{aligned} \tag{3}$$

where ρ is the one-density matrix

$$\rho_{pq} = \langle 0|a_q^\dagger a_p|0\rangle . \tag{4}$$

This one-density can then be determined through second order

$$\begin{aligned}\rho_{pq}^{(2)} &= \langle 0^{(0)}|a_q^\dagger a_p|0^{(0)}\rangle + \langle 0^{(1)}|a_q^\dagger a_p|0^{(1)}\rangle \\ &\quad + \langle 0^{(2)}|a_q^\dagger a_p|0^{(0)}\rangle + \langle 0^{(0)}|a_q^\dagger a_p|0^{(2)}\rangle ,\end{aligned} \tag{5}$$

where $0^{(n)}$ represents the nth-order MP wave function. Explicit expressions for $\rho^{(2)}$ have been given by Jensen et al. [26]. This approach to calculating the correlated dipole moment has been used previously by Amos [27].

The alternative approach is to evaluate the dipole as the first derivative of the energy, with respect to the electric field [6, 28]. This is termed the relaxed dipole moment, since it allows for orbital relaxation within the correlated density. This is not the case for Eq. (5), where only the unperturbed molecular orbitals are used. The results for these two methods will therefore differ in a second-order theory, although they will yield the same result in the exact limit. The difference arises from the non-fulfillment of the Hellmann–Feynman theorem, when the Møller–Plesset expansion is truncated to second order. It is generally assumed that the relaxed dipole is the more consistent definition and should give better agreement with experiment. The unrelaxed expression seems to be more consistent with the SOPPA method, however, since SOPPA also uses unperturbed orbitals in the correlation coefficients, which enter the propagator and transition moment matrices of Eq. (2).

3 Computational details and basis sets

All response calculations were performed using the Odense version of the RPAC program [29]. The necessary SCF information came from Gaussian92 [30]. The second-order dipole moments calculated from the expectation value Eq. (3) were obtained from the SIRIUS/RESPONS programs [31]. We have studied the halides HX and CH_3X, where X = F, Cl and Br. The polarized basis sets of Sadlej [32, 33] were used for the hydrogen, fluorine and carbon atoms, with all orbital contractions removed. These basis sets are then (6*s*4*p*) on H, and (10*s*6*p*4*d*) on C and F. We also used basis sets designed by Sadlej [33, 34] for chlorine and bromine. In the Cl basis we removed all contractions except on the tightest *s* and *p* functions, giving (14*s*10*p*4*d*/9*s*7*p*4*d*). In the Br basis, for HBr, we uncontracted the lowest two *p* exponents and the lowest six *d* exponents to obtain a basis of (15*s*12*p*9*d*/9*s*9*p*4*d*); for CH_3Br the bromine basis was as given in [34], consisting of (15*s*12*p*9*d*/9*s*7*p*4*d*). The molecular geometries were all taken at their ground state equilibrium values, which for HX were taken from [35] and for CH_3X from [36]; they are listed in the footnote to Table 1.

The Thomas–Reiche–Kuhn (TRK) sum rule in the length, mixed and velocity representation, at RPA level, is given in Table 1. This sum rule is equal to the number of electrons, N_e, in a complete basis, so that its fulfillment gives an indication of the quality of the basis set. The basis sets for CH_3F and HF are clearly

Table 1. Values of the Thomas–Reiche–Kuhn sum rule, $S(0)$, in the length, velocity and mixed representations, at RPA level. ∥ refers to the component parallel to the X–H bond axis in HX molecules or the X–C bond in CH_3X molecules; ⊥ refers to the perpendicular component

Molecule[a]	$S^L_\perp(0)$	$S^M_\perp(0)$	$S^V_\perp(0)$	$S^L_\parallel(0)$	$S^M_\parallel(0)$	$S^V_\parallel(0)$	N_e
CH_3F	18.04	17.88	17.74	17.93	17.89	17.88	18
CH_3Cl	19.98	19.69	19.54	19.90	19.73	19.72	26
CH_3Br	23.03	22.88	22.82	22.64	22.70	22.91	44
HF	10.03	9.92	9.83	9.93	9.93	9.95	10
HCl	12.53	12.21	12.01	12.45	12.26	12.21	18
HBr	19.78	19.35	19.04	19.71	19.42	19.26	36

[a] Total SCF energies and geometries were as follows:
CH_3F, E = − 139.091819 a.u.; R(CF) = 1.383 Å, R(CH) = 1.086 Å, $\angle FCH = 108.8°$; CH_3Cl, E = − 499.118058 a.u.; R(CCl) = 1.7854 Å, R(CH) = 1.090 Å, $\angle HCH = 110.75°$; CH_3Br, E = − 2611.998309 a.u.; R(CBr) = 1.933 Å, R(CH) = 1.086 Å, $\angle HCH = 111.17°$; HF, E = − 100.057666 a.u.; R(HF) = 0.9168 Å; HCl, E = − 460.078405 a.u.; R(HCl) = 1.27455 Å; HBr, E = − 2572.969191 a.u.; R(HBr) = 1.41443 Å

very good, the sum rule being satisfied to within 2% in all three representations. The sum rule is fulfilled only to within 60–70% for CH_3Cl and HCl, while for CH_3Br and HBr it is fulfilled to around 50%. Given the results for the fluorides, it is clear that the problem is caused by deficiencies in the Br and Cl basis sets. This is to be expected, since both atoms have occupied *d*-orbitals, so that *f* and *g* polarization functions should really be included, to satisfy the TRK sum rule. The basis sets were designed for the calculation of dipole moments and polarizabilities, however, and extra polarization functions would not be expected to have too great an effect on these properties [33].

4 Results and discussion

We have chosen to study the hydrogen and methyl halides since they are described well by a single reference wave function and are therefore suited to the SOPPA approach. Previous calculations of the electric properties of these systems can be found in the following references: HF [11, 37], HCl [38], HBr [39], CH_3F [11, 40]. There do not seem to be any previous calculations of the dynamic polarizability of CH_3Cl or CH_3Br.

Experimental results for CH_3X come from the work of Bogaard et al. [41], Alms et al. [42] and Burnham et al. [43]. These authors report the depolarization ratio, ρ_0, which is related to the isotropic and anisotropic polarizabilities, as detailed in [41]. The RPA results for the methyl halides, given in Table 2, are quite reasonable at all frequencies, being within 10% of the experimental values [41]. The SOPPA results, however, are consistently better than RPA, being within 1% of experiment at 6328 Å. The uncertainty in the experimental isotropic polarizabilities is given as ± 2% [42], meaning that our SOPPA results are within the error bars. The performance of SOPPA, for all three halides, clearly demonstrates its suitability for studying these systems. The depolarization ratios are listed in Table 3. There is a dramatic improvement in ρ_0 for CH_3F on correlating. However, the calculated dispersion is opposite to that predicted from a comparison of two experiments [41, 43] at two different frequencies, with ρ_0 decreasing as the applied frequency increases. Since none of the experiments are performed at more than one frequency it is difficult to draw any firm conclusion about agreement/disagreement between theory and experiment for CH_3F. The dispersion of ρ_0 is correctly described for CH_3Cl and CH_3Br. The SOPPA results for these two molecules are again better than RPA. The estimated experimental error in ρ_0 is given as ± 3% [41], which means that we are not within the error bars for this property at SOPPA level, although for CH_3Cl and CH_3Br we are within 5% of experiment, which is quite reasonable.

There are two sources of experimental data for the isotropic polarizabilities of the HX molecules. One is from direct measurements of the polarizability, which are available from Ref. [44] for HCl and HBr and from Penning et al. [45] for HF. These results are listed in column A of Table 2. The alternative is to use the dipole oscillator sum rules, $S(k)$, obtained by Kumar and Meath [46]. These sum rules are determined from experimental photoabsorption cross-sections, with constraints provided by the TRK sum rule and refractivity data. The even negative sum rules can be used to obtain the dynamic polarizability at any frequency by using the Cauchy expansion [19]

$$\alpha(-\omega;\omega) = \sum_{k=0}^{\infty} S(-2k-2)\omega^{2k}. \tag{6}$$

Table 2. Frequency dependence of the isotropic polarizability, $\bar{\alpha}(-\omega;\omega)$. Polarizability is given in atomic units: 1 a.u. of $\alpha = e^2 a_0^2 E_h^{-1} \approx 1.648778 \times 10^{-41}\,\mathrm{C^2\,m^2\,J^{-1}}$

				Expt.	
	Wavelength(Å)[a]	RPA[b]	SOPPA[b]	A	B
CH_3F[c]	∞	15.78	17.20	–	–
	6328	15.99	17.47	17.61	–
	5145	16.10	17.61	17.76	–
	4880	16.14	17.66	17.81	–
CH_3Cl[c]	∞	28.61	30.00	–	–
	6328	29.14	30.63	30.57	–
	5145	29.43	30.97	30.93	–
	4880	29.52	31.09	31.05	–
CH_3Br[c]	∞	35.38	37.15	–	–
	6328	36.17	38.11	37.72	–
	5145	36.61	38.63	38.21	–
	4880	36.75	38.81	38.39	–
HF[d]	∞	4.90	5.90	–	5.60
	5790	4.95	6.00	5.32	5.69
	5460	4.96	6.01	5.36	5.70
	4360	4.99	6.07	5.52	5.77
HCl[e]	∞	16.72	17.47	–	17.39
	6328	17.04	17.85	17.55[f]	17.74
	5677	17.12	17.95	17.87	17.82
	4109	17.51	18.42	18.31	18.23
	3802	17.65	18.59	18.48	18.37
	2675	18.77	20.01	19.80	19.47
HBr[e]	∞	23.23	24.19	–	23.74
	5677	23.93	25.01	24.57	24.53
	4109	24.63	25.84	25.36	25.32
	3802	24.88	26.15	25.66	25.62
	2675	26.98	28.79	28.13	28.08

[a] Wavelength $\lambda = 2\pi c/\nu$ where ν is the perturbing frequency. Conversion to frequency in a.u. is $\nu = 455.6335/\lambda$

[b] Isotropic polarizability is given as $\bar{\alpha} = \frac{1}{3}\{2\alpha_\perp + \alpha_\parallel\}$

[c] Experimental results for CH_3X molecules in column A taken from [41]

[d] Experimental results in column A are from [45]. Experimental results in column B are from [46]; the dynamic polarizability in B is obtained by fitting to the Cauchy expansion up to $S(-10)$ – see text

[e] For HCl and HBr, experimental results in column A were obtained from [44] whilst those in column B were obtained from the dipole oscillator sum rules given in [46], using the fit to the Cauchy expansion

[f] This value is taken from [49]

The summation is formally over all $k = 0, \ldots, \infty$, although for the frequencies in which we are interested, the series should converge rapidly. The experimental results listed in column B of Table 2 were obtained by expanding Eq. (6) up to and including S(− 10). We note that for HCl and HBr there is little difference between the two sets of experimental data. There is a significant discrepancy for HF, however, which may be related to difficulties in measuring the polarizability of this

Table 3. Frequency dependence of the depolarization ratio, 100 ρ_0

	Wavelength(Å)[b]	RPA[c]	SOPPA[c]	Expt.[a] A	Expt.[a] B
CH_3F	∞	0.034	0.086	–	–
	6328	0.032	0.084	0.094	–
	4880	0.031	0.082	–	0.10
CH_3Cl	∞	0.796	0.778	–	–
	6328	0.816	0.796	0.755	–
	5145	0.825	0.805	0.779	0.78
	4880	0.829	0.808	0.787	0.78
CH_3Br	∞	0.906	0.819	–	–
	6328	0.931	0.836	0.86	–
	5145	0.943	0.844	0.885	–
	4880	0.948	0.847	0.890	0.85
HF	∞	0.425	0.279	–	–
HCl	∞	0.074	0.071	–	–
	6328	0.069	0.065	0.079[d]	–
HBr	∞	0.056	0.054	–	–

[a] Results in column A are from Ref. [41]; results in column B are from Ref. [42] for CH_3Cl and from Ref. [43] for CH_3F and CH_3Br

[b] Wavelength $\lambda = 2\pi c/\nu$ where ν is the perturbing frequency. Conversion from Å to frequency in a.u. is $\nu = 455.6335/\lambda$

[c] Depolarization ratio is given as [41]: $\rho_0 = 3\kappa^2/(5 + 4\kappa^2)$; $\kappa = (\alpha_\parallel - \alpha_\perp)/3\bar{\alpha}$

[d] Ref. [49]

molecule [45]. Neither the RPA nor the correlated results for HF are sufficiently close to experiment, compared with the methyl halides. The estimated error in the data from Ref. [45] is ± 2.5% while for Ref. [46] it is ± 1%. Our correlated results do not lie within these error bars. Previous calculations have predicted a lower value for the correlated polarizability of HF [37]. The RPA results for HCl and HBr lie within 6–7% of experiment at all frequencies. SOPPA tends to overestimate the polarizability for these two molecules, although it is generally better than RPA. We find good agreement with other correlated calculations. Maroulis [38] obtained $\bar{\alpha}(0;0) = 17.68$ a.u. for HCl at SDQ-MP4 level, while Sadlej [34] computed a value of $\bar{\alpha}(0;0) = 23.82$ a.u. for HBr at SDQ-MBPT(4) level, the latter being in close agreement with the static experimental value used by Kumar and Meath [46].

In order to compare the SOPPA results directly with the MP2 polarizabilities, we have also calculated the latter quantities. The present calculations are restricted to the static polarizability, although a dynamic generalization has been given [22], as already mentioned. It can be seen from Table 4 that the SOPPA and MP2 results are rather close, with SOPPA giving polarizabilities which are consistently higher than MP2. This can be explained by the fact that SOPPA includes pole energies corrected to second order, whilst MP2 uses the RPA poles. It has been found that the singlet second-order pole energies are often lower than at RPA [14], and hence the SOPPA polarizabilities should exceed the MP2 values. The MP2 results are generally closer to experiment, although both methods lie within the

Table 4. Static dipole polarizability at RPA, SOPPA and relaxed MP2 levels. Units are a.u. (see Table 2)

Molecule	Static polarizability			
	RPA	SOPPA	Relaxed MP2	Expt.[a]
CH_3F	15.78	17.20	16.79	16.94
CH_3Cl	28.61	30.00	29.60	29.96
CH_3Br	35.38	37.15	36.34	36.03
HF	4.90	5.90	5.64	5.60
HCl	16.72	17.47	17.35	17.39
HBr	23.23	24.19	23.82	23.74

[a] Experimental results for HX are taken from Table 2. Experimental results for CH_3F and CH_3Br were obtained by the authors from a linear extrapolation to zero frequency; experimental result for CH_3Cl is taken from [42]

Table 5. Dipole moments calculated at SCF, relaxed and unrelaxed MP2 level. Atomic units are used: 1 a.u. of $\mu = ea_0 \approx 8.478358 \times 10^{-30}$ C m

Molecule	Dipole moment			
	SCF	Unrelaxed MP2	Relaxed MP2	Expt.[a]
CH_3F	0.8443	0.7521	0.7380	0.7312
CH_3Cl	0.8095	0.7271	0.7589	0.7461
CH_3Br	0.8456	0.7524	0.7462	0.7162
HF	0.7570	0.6994	0.7100	0.7094
HCl	0.4725	0.4455	0.4419	0.4305
HBr	0.3777	0.3375	0.3417	0.3219

[a] Experimental results for HX molecules are the equilibrium dipole moments from Ref. [47]. Experimental results for CH_3X molecules from Ref. [36]

error bars of the experimental values for the methyl halides. The static experimental values for CH_3F and CH_3Br were obtained by us from extrapolation to zero frequency, and should therefore be treated with some caution.

Table 5 reports the dipole moments obtained from the relaxed and unrelaxed MP2 densities. The unrelaxed values were obtained using the expectation value from Eq. (3). The relaxed values were computed using the analytic derivative code from Gaussian 92 [30]. The experimental results for the HX molecules are taken from Ogilvie et al. [47]. These are the equilibrium dipole moments, for the equilibrium bond lengths at which our calculations were performed. The experimental results for CH_3X are taken from Ref. [36]. Both the relaxed and unrelaxed MP2 dipole moments are significantly better than the SCF values, as we would expect. The SCF dipoles range from being within 7% of experiment for HF to within only 18% of experiment for CH_3Br. The correlated results are within 5% of experiment for all six molecules. It is also clear that the relaxed dipole moments are slightly better than the unrelaxed, except for HBr. We might expect this behaviour, since the unrelaxed density is not accounting for the effect of the electric field on the correlation coefficients. The difference between the relaxed and unrelaxed results is quite small however, especially given the extra computational cost involved in obtaining the relaxed value, compared with the unrelaxed.

There are three effects which we have neglected in our calculations, which may have some bearing on the results. There is a vibrational (or infra-red) contribution to the polarizability [42, 48], which arises from infra-red active transitions. This effect can be quite appreciable for measurements of the static polarizability, but can usually be neglected for dynamic values, since the vibrational transitions occur at low frequencies [48]. Since we have compared with polarizabilities measured at optical frequencies, we should not need to correct the results for this effect. There may also be a relativistic correction to the properties of HBr and CH_3Br. Kellö and Sadlej [39] estimated this correction to the dipole moments and polarizabilities of HCl and HBr. They found that both properties could be calculated reliably for HCl using non-relativistic approaches. The dipole moment of HBr altered by -0.0179 a.u. on including the relativistic correction while the polarizability was unaffected. This observation can be rationalized by the fact that three most diffuse occupied orbitals in HBr, in our calculation, contribute 99.4% of the static isotropic polarizability. The relativistic correction for these orbitals will be insignificant and it will consequently have no effect on the response property. The same will hold true for CH_3Br, in which the five most diffuse orbitals contribute 98.1% of the static polarizability. We believe therefore that neglect of such effects is justified.

The third effect that was neglected in the results reported so far is the direct vibrational effect, that is, the averaging of the electronic quantities in the rovibrational ground state. The averaging will not affect the conclusions concerning the relationships between the different levels of theory. However, when comparing to experiment it is important to include vibrational effects unless the direct experimental data have been used to derive an equilibrium quantity as e.g. in the case for the dipole moments listed in Table 5 [47]. Since it is straightforward to perform a vibrational averaging for the three linear molecules we did so in order to determine the magnitude of this effect and the results are reported in Table 6. Comparing with Tables 4 and 5 we see that vibrational averaging increases both α and μ relative to their equilibrium values by between 1.0% and 2.1%, illustrating that α and μ are increasing as a function of internuclear separation. Since SOPPA (and relaxed MP2) tend to overestimate the calculated static polarizabilities relative to their experimental values (see Table 4) inclusion of vibrational corrections will cause a slight increase in the disagreement between theory and experiment at the two levels of theory.

Table 6. Vibrationally averaged static dipole polarizabilities and dipole moments. Atomic units are used (see Tables 4 and 5)

Molecule[a]	α_{xx}	α_{zz}	$\bar{\alpha}$	μ
HF	5.56	6.96	6.02	0.709
HCl	16.95	19.18	17.69	0.454
HBr	23.54	26.21	24.43	0.342

[a] The polarizabilities are computed in SOPPA whilst μ is obtained at the unrelaxed MP2 level

5 Conclusions

We have seen that calculating the dipole moment using the unrelaxed and relaxed MP2 density yields similar results, although the relaxed density generally gives better agreement with experiment. It can be argued that using the relaxed dipole moment is more consistent with experiment [6], since the orbitals are optimized within the perturbing field. The unrelaxed formalism is closer to the philosophy of the SOPPA response, however. This follows from the fact that the polarization propagator is obtained from an expansion of the induced dipole moment, defined as an expectation value [8]. The correlation coefficients which enter the propagator matrix will therefore correspond to the unrelaxed orbitals.

We have shown that SOPPA is a valid and accurate method for calculating the dynamic polarizability of the hydrogen and methyl halides. The success of SOPPA is no doubt due to the fact that the systems studied are suited to a Møller–Plesset-type approach. The dispersion of the polarizability is consistently well described by SOPPA out to wavelengths of 2568 Å. This can be attributed to the second-order pole structure of the propagator matrix, which gives a better excitation energy spectrum than RPA. The depolarization ratios of the methyl halides are also predicted accurately by SOPPA, being within 5% of the experimental values. It has been seen that the MP2 static polarizabilities, evaluated as the second derivative of the MP2 energy, are in somewhat better agreement with experiment than SOPPA. Both methods, however, are within the experimental error bars, where these are available. The exception is HF, for which SOPPA appreciably overestimates the polarizability. Despite this, the propagator approach is ideally suited to the determination of dynamic properties, which is where its main strengths lie.

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