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Correlated, Static and Dynamic Polarizabilities of Small Molecules. Comparison of Four "Black Box" Methods

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Molecular static and dynamic polarizabilities for thirteen small molecules have been calculated using four "black box" ab initio methods, the random phase approximation, RPA, the second-order polarization propagator approximation, SOPPA, the second-order polarization propagator approximation with coupled cluster singles and doubles amplitudes, SOPPA(CCSD), and the coupled cluster singles and doubles linear response function method, CCSDLR. The frequency dependence of the polarizabilities is given in terms of the dipole oscillator strength sum rules or Cauchy moments $S(-4)$ and $S(-6)$. Two basis sets were employed, Sadlej's medium size polarized basis set and Dunning's correlation consistent basis set of triple-ζ quality augmented by two diffuse functions of each angular momentum (daug-cc-pVTZ). The results are compared to other theoretical results as well as to experimental values for the static polarizabilities, polarizability anisotropies, and Cauchy moments. Frequency-dependent polarizabilities and polarizability anisotropies, calculated at the CCSDLR level using the daug-cc-pVTZ basis set, are presented for five typical laser frequencies.

1. Introduction

The molecular dipole polarizability enters into the description of many physical and chemical processes, such as the scattering of light by molecules, and intermolecular interactions. Calculated polarizabilities are often used in the verification of experimental data and in the prediction of properties of new chemical species. An accuracy of a few percent in the calculated values is necessary for this purpose.

Over the years several methods for the calculation of molecular properties have emerged. Among these are correlated methods, i.e. methods trying to improve on the Hartree−Fock approximation by perturbation theory or a multiconfigurational ansatz, as well as density functional theory (DFT) methods. Most of these methods, however, are only capable of calculating static properties like the static molecular polarizability, excitation energies, and transition moments. A direct comparison of calculated and experimental polarizabilities requires the ability to calculate frequency-dependent polarizabilities since experiments are mostly performed at nonzero frequencies.

In an earlier study[1] the performance of some perturbation theory methods in the calculation of static polarizabilities was investigated. In this work, calculations of static and dynamic molecular polarizabilities are presented using four different "black box" methods, that is, methods where the only choices to be made are of the basis set and molecular geometry. These methods are in contrast to multiconfigurational methods where the selection of configurations to be included in the wave function requires considerable experience and might even become impossible for larger molecules. The black box methods, on the other hand, are relatively easy to use also by nonexperts, and their application is, apart from hardware limitations, not restricted to small molecules.

The methods employed here are the random phase approximation, RPA,[2] the second-order polarization propagator approximation, SOPPA,[3,4] the second-order polarization propagator approximation with coupled cluster singles and doubles amplitudes, SOPPA(CCSD),[5] and finally the coupled cluster singles and doubles linear response, CCSDLR[6] method. Thirteen molecules containing atoms from the first to third row of the periodic table have been investigated. Static polarizabilities of the same set of molecules were recently calculated as energy derivatives by McDowell et al.[7] using some perturbation and DFT methods. Our results for the static polarizability and polarizability anisotropy are compared with their calculations as well as with experimental values. The calculated frequency dependence of the polarizability, in terms of dipole oscillator strength sum rules or Cauchy moments, is compared with experimental sum rules obtained by Meath and co-workers[8−14] and Hohm.[15,16] Finally we give our best estimate of the value of the dipole polarizability and anisotropy for each of the thirteen molecules for a set of five commonly used experimental frequencies.

2. Theory

The methods used in this study are all response methods. This means that they describe the response of an observable to an external or internal perturbation. The use of response methods originated in various disciplines in physics. In statistical physics, they were used as time-correlation functions in various problems in the form of Greens functions.[17,18]

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Linderberg and Öhrn first showed the usefulness of the response functions in quantum chemistry.[19] Since then a number of methods have been developed on the basis of their original ideas. Four of these methods are employed here.

In the response function terminology the frequency dependent polarizability $\alpha(-\omega;\omega)$ is defined through an expansion of the ith Cartesian component of the time-dependent electronic dipole moment, $\mu_i(t)$, in the periodic electric field of strength $\mathbf{E}^{\omega}$

$$\mu_i(t) = \mu_i(0) + \int_{-\infty}^{+\infty} d\omega\, \alpha_{ij}(-\omega;\omega) E_j^{\omega}\, e^{(-i\omega+\epsilon)t} + ... \quad (1)$$

where $\mu_i(0)$ is the ith Cartesian component of a possible permanent electronic dipole moment. In exact response theory the time-dependent dipole moment is expressed as a time-dependent expectation value of the dipole operator $\hat{\mu}_i$,

$$\mu_i(t) = \langle 0(t)|\hat{\mu}_i|0(t)\rangle \quad (2)$$

An ansatz is made for the exact time-dependent wave function, $|0(t)\rangle$, in eq 2, the time-dependent coefficients of the wave function, $|0(t)\rangle$, are expanded in orders of the perturbation, and the coefficients are determined by means of a time-dependent variation principle. In analogy to eq 1 an expression for the frequency-dependent polarizability can then be obtained from the Fourier transform of the first-order term in the expansion of eq 2, i.e. the term which is linear in the perturbation

$$\alpha_{ij}(-\omega;\omega) = -\langle 0|[\hat{\mu}_i, \tilde{\mathbf{h}}]|0\rangle\langle 0|[\mathbf{h}^{\dagger},[\omega\mathbf{1} - \hat{H}, \tilde{\mathbf{h}}]]|0\rangle^{-1}\langle 0|[\mathbf{h}^{\dagger},\hat{\mu}_j]|0\rangle \quad (3)$$

where $\mathbf{h}$ is an excitation/deexcitation operator manifold containing all single, double, etc., excitations and deexcitations.

Different approximations can be applied to this exact expression by truncating the operator manifold, $\mathbf{h}$, and choosing an approximate time-independent wave function, $|0\rangle$ for example by employing the standard Møller−Plesset expansion of the wave function and partitioning of the Hamiltonian.[20] Keeping all terms through zeroth order only, the uncoupled Hartree−Fock method[21] is obtained, while retaining all first-order terms yields the RPA[2] or time-dependent Hartree−Fock, TDHF.[22] For static properties this method is equivalent to the coupled Hartree−Fock method[23] or to the finite field method[24] using an SCF wave function. Including also second-order terms in the response function the SOPPA[3,4] is obtained. The SOPPA method gives excitation energies and transition moments correct to second order, whereas the response function like the frequency-dependent polarizability is correct through second order, meaning that in addition to all second-order terms also some higher-order terms are included. The SOPPA response function, however, is not the response of a second-order wave function.[25] Replacing the second-order Møller−Plesset perturbation theory (MP2) correlation coefficients in the SOPPA equations with the singles, t_1, and doubles amplitudes, t_2, from the CCSD wave function, the SOPPA(CCSD) method[5] is obtained. The last method considered here is the CCSDLR method as described by Koch and Jørgensen.[6] In the CCSDLR method the frequency-dependent polarizability can also be identified from the time evolution of the dipole moment, which can be calculated as a transition expectation value between the coupled cluster state, $|CC\rangle$, and a dual state, $\langle\Lambda|$,

$$\mu_i(t) = \langle\Lambda(t)|\hat{\mu}_i|CC(t)\rangle \quad (4)$$

Again, the coefficients describing the time dependence of the approximate coupled cluster wave functions, $|CC(t)\rangle$ and $\langle\Lambda(t)|$, are expanded in the perturbation and are determined from the coupled cluster time-dependent Schrödinger equation. The frequency-dependent polarizability in the CCSDLR method is then obtained from the term linear in the perturbation in the expansion of eq 4. The CCSDLR method is the computationally most expensive and is expected to be the most accurate of the four methods presented here.

Although both the SOPPA(CCSD) and the CCSDLR methods build on the CCSD wave function, SOPPA(CCSD) is still only correct through second order, whereas CCSDLR is really the response of a CCSD wave function. Since the MP2 correlation coefficients are the result of the first iteration for the CCSD amplitudes, the CCSD amplitudes give a more accurate description of the electron correlation. Thus, it may be anticipated that the SOPPA(CCSD) method will have less tendency to overshoot the correlation contribution than the SOPPA method. The accuracy of the methods considered here is therefore expected to be in the order RPA < SOPPA < SOPPA(CCSD) < CCSDLR. In addition to the accuracy, the computational cost of the methods has to be considered, which increases also from RPA over SOPPA and SOPPA(CCSD) to CCSDLR.

A convenient way of describing the frequency dependence of the isotropic polarizability is by use of the negative even dipole oscillator strength sum rules or Cauchy moments, $S(-k)$, $k = 2, 4, 6, ...$.[26] In terms of these the isotropic dynamic polarizability can be written as

$$\bar{\alpha}(-\omega;\omega) = \sum_{k=0}^{\infty} S(-2k-2)\omega^{2k} \quad (5)$$

where $\bar{\alpha} = {}^1/_3\sum_{i=x,y,z}\alpha_{ii}$ and the components of the sum rules S are combined in a similar fashion. From the above expression $S(-2)$ sum rule can be identfied as the static polarizability. The polarizability anisotropy $\Delta\alpha$ of a general molecule is defined as

$$\Delta\alpha = {}^1/_2[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2} \quad (6)$$

3. Details of the Calculations

All RPA, SOPPA, and SOPPA(CCSD) calculations were performed with the DALTON program package,[27] whose SOPPA module[28] was modified to perform SOPPA(CCSD) calculations.[5] The CCSD amplitudes were obtained from the integral-direct coupled cluster program by Koch and coworkers.[29,30] For the CCSDLR calculations the implementation of this method in the ACES2[31] program was used.

Two basis sets were employed. Basis set I is Sadlej's medium size polarized basis set,[32−34] which was also used by McDowell et al.[7] These basis sets are rather small, but are nevertheless found to give quite reliable results. However, to estimate the basis limit, also the large daug-cc-pVTZ basis set was used as basis set II for all molecules. This basis set is Dunning's correlation consistent valence triple-ζ basis set[35] augmented by two diffuse polarization functions for all angular momenta in the basis sets added in an even tempered fashion.[36,37] In a recent study by Peterson and Dunning[38] on the CO molecule a large set of the cc-pVnZ basis sets was tested for the calculation of molecular properties, and it was found that the basis set employed in this study yields results close to the Hartree−Fock limit.

The molecular geometries are given in Table 1 and are, where available, experimental equilibrium geometries.

The dipole oscillator strength sum rules $S(-2)$, $S(-4)$, and $S(-6)$ were calculated directly in the RPA, SOPPA, and

TABLE 1: Molecular Geometries

molecule	geometry
HF	$R_{HF} = 0.917$ Å[a]
HCl	$R_{HCl} = 1.2746$ Å[a]
H_2O	$R_{HO} = 0.9572$ Å, $\angle_{HOH} = 104.52°$ [b]
H_2S	$R_{HS} = 1.328$ Å, $\angle_{HSH} = 92.2°$ [b]
NH_3	$R_{NH} = 1.012$ Å, $\angle_{HNH} = 106.67°$ [b]
PH_3	$R_{PH} = 1.421$ Å, $\angle_{HPH} = 93.34°$ [b,c]
CH_4	$R_{CH} = 1.094$ Å[b]
SiH_4	$R_{SiH} = 1.4811$ Å
F_2	$R_{FF} = 1.4119$ Å[a]
Cl_2	$R_{ClCl} = 1.9879$ Å[a]
C_2H_4	$R_{CH} = 1.103$ Å, $R_{CC} = 1.337$ Å, $\angle_{HCH} = 125.6°$
CO_2	$R_{CO} = 1.1621$ Å [b,c]
SO_2	$R_{SO} = 1.4308$ Å, $\angle_{OSO} = 119.3°$ [b]

[a] Reference 44. [b] Reference 45. [c] r_0,α_0 value.

SOPPA(CCSD) methods using the method described by Fowler et al.,[39] while the CCSDLR results were found by fitting the frequency-dependent polarizability calculated for 10 different optical frequencies in the range from $\hbar\omega = 0.00\ E_h$ to $\hbar\omega = 0.09\ E_h$ to a polynomial in the square of the frequency. The optimal degree of the fitting polynomial was determined from similar fits to data calculated at the RPA, SOPPA, and SOPPA(CCSD) levels, which were compared to the sum rules calculated directly. In most cases fitting polynomials of degrees 3−8 were found to provide reliable and stable values of the sum rules. However, as the numerical instabilities increase for higher-order coefficients in the fitting polynomials, we quote the $S(-2)$ sum rule or static polarizability with five digits, the $S(-4)$ with four, and the $S(-6)$ sum rule with three digits. Taking into account that the $S(-6)$ sum rule is the coefficient of the frequency to the fourth power, an error on the third digit will lead to errors which are insignificant compared to other errors in the calculation, such as the lack of vibrational averaging.

4. Discussion

4.1. Static Isotropic Polarizability. The results for the static isotropic polarizabilities, $\bar{\alpha}$, calculated with Sadlej's medium size polarized basis sets (basis set I) and the near basis set limit daug-cc-pVTZ basis sets (basis set II) are collected in Table 2. At the uncorrelated RPA level, Sadlej's basis set gives, with the exception of PH_3 and SiH_4, smaller values for the isotropic polarizabilities than basis set II. At the correlated levels, however, the situation is reversed and larger values for $\bar{\alpha}$ are obtained using basis set I with the few exceptions of Cl_2 at the SOPPA level and HCl, Cl_2, and C_2H_4 at the SOPPA(CCSD) level. The correlation contribution is thus larger in basis set I than in basis set II for all molecules except for SiH_4 and C_2H_4 in the SOPPA(CCSD) calculations and for the Cl_2 molecule at the both SOPPA and SOPPA(CCSD) levels. Assuming that basis set II is the better of the two, one can say that Sadlej's medium size polarized basis sets overestimate the correlation contributions in this set of molecules apart from the exceptions mentioned above.

Comparing the results of the different methods with the experimental values for $\bar{\alpha}$, it is most prominent that the RPA values, independent of the basis set, are lower than the experimental values for all systems except C_2H_4 and F_2, which was also observed by Spackman.[40] The root-mean-square (rms) deviation of the RPA results from the experimental values are 6.5% (with a maximum deviation of 13.0%) for basis set I and 6.3% (12.3%) for the larger basis set. The results of the three correlated methods are for all other molecules than C_2H_4 and F_2 larger than the RPA results. SOPPA, in particular, tends to overestimate the correlation correction and gives thus generally the highest values. For most of the molecules, the SOPPA values are nevertheless in better agreement with experiment and the average percentage deviation is only between 4.5% (11.9%) and 3.7% (10.2%), depending on the basis set. It is further reduced to between 2.9% (7.0%) and 2.6% (6.3%) at the SOPPA(CCSD) level. As expected the CCSDLR method is the most accurate and the mean percentage deviation is only 1.7% (with a maximum deviation of 3.3%), using the smaller basis set and 1.4% (3.6%) in basis set II. The fact that Sadlej's basis set overestimates the correlation correction can lead to accidentally better agreement with experiment for those molecules for which the calculated values are smaller than the experimental ones. This is also the reason for the smaller maximum percentage deviation of basis set I at the CCSDLR level.

Comparison of our basis set I results with the study of McDowell et al.[7] shows that the SOPPA results are always larger than results at the level of second- (MP2) and fourth-order (MP4) Møller−Plesset perturbation theory, whereas the SOPPA(CCSD) results are close to the MP4 values, though generally lower. The latter are, however, still in better agreement with experimental data than the SOPPA(CCSD) values for all molecules but F_2 and Cl_2. The Brueckner orbitals coupled cluster variant with perturbative triples corrections (BD(T)) gives always smaller isotropic polarizabilities than the CCSDLR method, which does not include any triple excitations, and is thus for basis set I closer to experiment for HF, HCl, H_2O, F_2, Cl_2, CO_2, and SO_2. The CCSDLR results obtained using the larger basis set, however, are very close to the BD(T) results of ref 7 and, in fact, for the HF molecule the values are identical. In a recent study of the electrical properties of the second-row hydrides by Russell and Spackman[41] the pure electronic contributions to the dipole polarizability and polarizability anisotropy are very close to the results obtained in this work. The above-mentioned calculations employ slightly different geometries and basis sets of triple-ζ quality. The SCF results differ by no more than 1% for the average polarizability. The MP2 numbers are closer to the SOPPA(CCSD) numbers than to the SOPPA results, again reflecting the tendency of the SOPPA method to overestimate the correlation correction.

4.2. Static Polarizability Anisotropy. Table 3 compares the results for the polarizability anisotropy $\Delta\alpha$ obtained with basis sets I and II. In general, Sadlej's basis set gives larger values for $\Delta\alpha$ than the near basis set limit basis set II with few exceptions: F_2, C_2H_4 at all levels, NH_3 at the RPA, H_2O at the SOPPA(CCSD), HCl and H_2O in CCSDLR, and Cl_2 at all three correlated levels of approximation. The correlation corrections are nevertheless again larger with basis set I with the exceptions of HF and HCl. Quite large differences in the correlation contribution between the two basis sets are found for NH_3, PH_3, and H_2S. Besides these three cases, the differences between the correlation corrections to $\Delta\alpha$, predicted using the two basis sets, are not larger than for $\bar{\alpha}$.

Comparison of the calculated and experimental values of the polarizability anisotropies is less conclusive than for the isotropic static polarizabilities. The experimental values are usually less accurate than for the mean polarizability, since they are more difficult to measure. In addition some of the experimental data in Table 3 are not static values. Nevertheless it can be concluded that the overall agreement between theory and experiment for $\Delta\alpha$ is not as good as for $\bar{\alpha}$. This is to be expected, since a much higher accuracy of the individual tensor components is required for accurate anisotropies $\Delta\alpha$ than for

TABLE 2: Static Isotropic Polarizabilities $\bar{\alpha}$ ($e^2a_0^2E_h^{-1}$)

	basis set I				basis set II				
	RPA	SOPPA	SOPPA (CCSD)	CCSDLR	RPA	SOPPA	SOPPA (CCSD)	CCSDLR	exptl
HF	4.874	6.085	5.818	5.724	4.913	5.952	5.731	5.637	5.60[a]
HCl	16.664	17.671	17.352	17.499	16.728	17.651	17.368	17.467	17.39[a]
H_2O	8.492	10.319	9.939	9.824	8.538	10.089	9.782	9.649	9.64[b]
H_2S	23.614	24.922	24.343	24.604	23.681	24.756	24.243	24.446	24.71[c]
NH_3	12.926	14.736	14.366	14.411	12.960	14.441	14.161	14.155	14.56[b]
PH_3	29.915	31.120	30.184	30.674	29.829	30.881	30.076	30.506	30.93[d]
CH_4	16.120	16.853	16.520	16.709	16.217	16.754	16.510	16.654	17.27[e]
SiH_4	29.960	31.414	30.742	31.467	29.776	31.153	30.606	31.243	31.90[d]
F_2	8.593	8.903	8.525	8.550	8.597	8.760	8.456	8.465	8.38[d]
Cl_2	29.886	31.346	30.556	30.905	29.939	31.411	30.651	30.894	30.35,[d] 30.417[f]
C_2H_4	28.303	28.329	27.482	27.534	28.493	28.145	27.537	27.531	27.70[g]
CO_2	15.841	19.444	18.726	18.013	15.920	19.238	18.611	17.831	17.51[h]
SO_2	23.653	28.659	27.407	26.444	23.698	28.235	27.116	26.055	25.61[i]

[a] Reference 13. [b] Reference 8. [c] Reference 14. [d] Reference 46. [e] Reference 9. [f] Reference 16. [g] Reference 11. [h] Reference 10. [i] Reference 12.

TABLE 3: Static Polarizability Anisotropies $\Delta\alpha$ ($e^2a_0^2E_h^{-1}$)

	basis set I				basis set II				
	RPA	SOPPA	SOPPA (CCSD)	CCSDLR	RPA	SOPPA	SOPPA (CCSD)	CCSDLR	exptl
HF	1.285	1.244	1.204	1.170	1.251	1.187	1.165	1.146	1.33[a]
HCl	1.867	1.832	1.677	1.722	1.846	1.786	1.642	1.735	1.51[a]
H_2O	1.165	0.470	0.497	0.521	1.103	0.459	0.502	0.545	0.67[a,d]
H_2S	0.393	0.848	0.974	0.912	0.383	0.564	0.670	0.546	0.67[b,e]
NH_3	0.520	2.019	1.919	1.892	0.524	1.806	1.710	1.653	1.94[b,e]
PH_3	1.001	1.726	1.767	1.605	0.969	1.475	1.539	1.356	
F_2	9.025	6.038	5.657	5.727	9.079	6.213	5.954	6.007	
Cl_2	18.320	17.704	16.595	16.962	18.285	17.918	16.804	17.199	17.53[a,e]
C_2H_4	12.072	10.781	9.819	10.398	12.079	10.833	9.928	10.420	11.4[b]
CO_2	12.099	18.368	17.020	15.427	11.757	17.676	16.383	14.732	13.83[c]
SO_2	12.571	17.976	16.382	14.799	12.007	16.936	15.501	13.937	13.0[b]

[a] Reference 46. [b] Reference 42. [c] Reference 47. [d] Dynamic value at 514.5 nm. [e] Dynamic value at 632.8 nm.

$\bar{\alpha}$ of the same accuracy.[42] Most striking is the erratic behavior of the RPA for H_2O, H_2S, and especially NH_3, leading to an rms percentage deviation of 26.9% with a maximum deviation of 73.9% for basis set I and 26.8% (73.0%) for basis set II. RPA predicts larger values for $\Delta\alpha$ than the correlated methods for HF, HCl, F_2, Cl_2, H_2O, and C_2H_4 and smaller values for NH_3, PH_3, H_2S, CO_2, and SO_2. With the exceptions of H_2O, in both basis sets, and H_2S, in basis set I, SOPPA gives again higher values than SOPPA(CCSD) and CCSDLR. For the PH_3 molecule in both basis sets and H_2S in basis set II, the SOPPA value is between the SOPPA(CCSD) and CCSDLR results. The rms percentage deviations for SOPPA is 18.4% (38.3%) in basis set I and 16.5% (31.5%) in basis set II. The SOPPA(CCSD) results are again in overall better agreement with a rms percentage deviations of 17.9% (basis set I) and 12.5% (basis set II), but the maximum deviations are 45.1% and 25.1%, respectively, and thus the largest error for basis set I is larger in SOPPA(CCSD) than in SOPPA. Finally, the rms percentage deviations of CCSDLR using basis set I is 13.8% (36.1%) and in basis set II 11.7% (18.7%), reflecting a better agreement with experiment than SOPPA(CCSD) apart from HF, HCl, H_2S, and NH_3.

Contrary to $\bar{\alpha}$, the SOPPA values for $\Delta\alpha$ are smaller than the MP2 and MP4 results of McDowell et al.[7] with the exception of H_2S, whereas the SOPPA(CCSD) results are again close to the MP4 values apart from the results for CO_2 and SO_2. The triples corrections in the BD(T) method lead also to smaller values for $\Delta\alpha$ compared with CCSDLR for all molecules but F_2, H_2, and NH_3. However, it cannot be said which of the two methods performs better in general. Using the large daug-cc-pVTZ basis set decreases the error for the CCSDLR results, and the comparison with the experimental values is generally more favorable than that for the BD(T) results using Sadlej's basis set (basis set I).

4.3. Frequency Dependence. The frequency dependence of the isotropic polarizability, expressed in terms of the dipole oscillator strength sum rules or Cauchy moments $S(-4)$ and $S(-6)$, is given in Tables 4 and 5. As for the static mean polarizability values obtained for $S(-4)$ at the RPA level using Sadlej's basis set (I) are smaller than those using the daug-cc-pVTZ basis set (II) except for the CH_4, SiH_4, C_2H_4, and SO_2 molecules. For $S(-6)$ the situation is identical, but here only CH_4 and SO_2 have larger sum rules using basis set I than using basis set II. The dispersion at the RPA level is thus for most molecules smaller with Sadlej's basis set. At the correlated levels the situation is reversed, as basis set I gives smaller values of the sum rules only for HCl and Cl_2. Thus, as was found for the static isotropic polarizability Sadlej's basis set also overestimates the correlation corrections to the dispersion of the mean polarizability.

The RPA values for $S(-4)$ and $S(-6)$ for all molecules but C_2H_4 and F_2 are smaller than the correlated results. Correlation thus increases the dispersion of the mean polarizability for all but these two molecules. This is expected since it is often seen that the lowest lying excitation is too high in RPA compared to correlated calculations, and the higher Cauchy moments are dominated by the lowest lying excitations. Comparison of the three correlated methods shows that SOPPA gives the largest values for the dispersion of the mean polarizability ($S(-4)$ and $S(-6)$), again overestimating the correlation contribution for most molecules. This is often observed in the SOPPA method as it tends to overestimate the correlation contribution to the

TABLE 4: Isotropic Dipole Oscillator Strength Sum Rules $S(-4)$ ($e^2a_0^2E_h^{-3}$)

	basis set I				basis set II				
	RPA	SOPPA	SOPPA (CCSD)	CCSDLR	RPA	SOPPA	SOPPA (CCSD)	CCSDLR	exptl
HF	8.267	15.51	14.47	12.62	8.611	15.05	14.21	12.45	14.40[a]
HCl	58.83	71.49	68.87	67.57	60.23	71.51	69.05	67.59	67.12[a]
H_2O	23.07	43.07	40.40	35.39	23.62	40.64	38.61	33.92	35.42[b]
H_2S	120.0	144.5	137.4	135.5	121.7	140.9	134.5	132.1	138.3[c]
NH_3	49.00	79.60	75.35	70.70	49.35	74.49	71.44	66.76	71.44[b]
PH_3	182.3	205.6	191.1	191.5	182.7	201.9	189.4	188.7	
CH_4	52.71	60.73	58.03	58.12	52.44	58.35	56.37	56.24	62.41,[d] 63.22[e]
SiH_4	147.7	168.2	159.1	165.9	147.1	166.5	158.9	164.6	
F_2	20.74	20.83	19.72	17.07	20.76	20.84	20.05	17.16	
Cl_2	114.9	136.6	129.7	123.1	115.9	137.6	130.9	123.2	138 ± 5[f]
C_2H_4	166.8	163.7	153.9	140.7	166.5	157.5	151.3	137.4	143.5,[g] 146.7[e]
CO_2	37.53	70.59	67.83	52.17	37.56	68.55	66.62	50.26	50.99[h]
SO_2	101.3	170.7	165.5	117.0	100.4	164.9	162.2	113.0	115.6[i]

[a] Reference 13. [b] Reference 8. [c] Reference 14. [d] Reference 9. [e] Reference 15. [f] Reference 16. [g] Reference 11. [h] Reference 10. [i] Reference 12.

TABLE 5: Isotropic Dipole Oscillator Strength Sum Rules $S(-6)$ ($e^2a_0^2E_h^{-5}$)

	basis set I				basis set II				
	RPA	SOPPA	SOPPA (CCSD)	CCSDLR	RPA	SOPPA	SOPPA (CCSD)	CCSDLR	exptl
HF	22.7	71.4	65.5	49.0	24.7	66.0	61.8	47.0	68.96[a]
HCl	276	410	386	369	300	414	391	374	389.3[a]
H_2O	106	357	328	240	112	308	290	217	240.1[b]
H_2S	874	1294	1189	1150	923	1225	1131	1094	1136[c]
NH_3	330	889	814	689	339	774	727	615	684.0[b]
PH_3	1544	1924	1698	1694	1560	1845	1653	1634	
CH_4	219	283	263	250	216	261	246	243	298.3,[d] 293.8[e]
SiH_4	823	1029	939	1007	823	1011	935	995	
F_2	80.1	111	103	65.0	80.8	104	100	63.0	
Cl_2	657	1137	1005	828	670	1143	1010	820	
C_2H_4	1632	1526	1401	1127	1641	1445	1375	1090	1202,[f] 1227[e]
CO_2	120	354	344	206	121	340	337	194	211.4[g]
SO_2	1238	2429	2542	1147	1164	2319	2502	1089	1227[h]

[a] Reference 13. [b] Reference 8. [c] Reference 14. [d] Reference 9. [e] Reference 15. [f] Reference 11. [g] Reference 10. [h] Reference 12.

TABLE 6: Frequency-Dependent Dipole Polarizabilities ($e^2a_0^2E_h^{-1}$) at the CCSDLR Level Using Basis Set II

	for given wavelengths, nm									
	632.990		594.096		543.516		514.500		325.130	
molecule	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$
HF	5.703	1.147	5.712	1.147	5.727	1.146	5.738	1.146	5.900	1.143
HCl	17.827	1.692	17.877	1.685	17.960	1.674	18.020	1.665	18.939	1.517
H_2O	9.831	0.460	9.856	0.448	9.898	0.427	9.928	0.412	10.399	0.156
H_2S	25.160	0.905	25.261	0.960	25.428	1.053	25.549	1.122	27.462	2.341
NH_3	14.517	2.006	14.569	2.059	14.655	2.148	14.716	2.212	15.703	3.326
PH_3	31.528	1.613	31.672	1.651	31.913	1.716	32.086	1.763	34.842	2.577
CH_4	16.952		16.993		17.061		17.110		17.852	
SiH_4	32.123		32.246		32.449		32.595		34.859	
F_2	8.556	6.122	8.568	6.138	8.589	6.164	8.603	6.182	8.826	6.461
Cl_2	31.554	17.764	31.647	17.842	31.800	17.971	31.911	18.064	33.630	19.466
C_2H_4	28.272	10.964	28.377	11.042	28.550	11.172	28.676	11.267	30.650	12.807
CO_2	18.097	15.104	18.133	15.156	18.194	15.241	18.237	15.303	18.893	16.238
SO_2	26.670	14.502	26.757	14.582	26.903	14.714	27.008	14.810	28.694	16.321

lowest lying excitations. Using the CCSDLR method, the smallest correlated values are obtained with the exception of $S(-4)$ for PH_3, CH_4, and SiH_4 in basis set I and SiH_4 in basis set II.

Comparison with the experimental sum rules shows that the RPA $S(-4)$ and $S(-6)$ sum rules are smaller than the experimental ones except for C_2H_4, as previously shown by Spackman,[40] whereas the SOPPA sum rules are for all molecules but CH_4, larger than and in better agreement with the experimental data. The rms deviations for the $S(-4)$ sum rules are in basis set I 22.0 (RPA), 15.4 (SOPPA), 11.9 (SOPPA(CCSD)), and 4.3% (CCSDLR) and in basis set II 21.3 (RPA), 12.4 (SOPPA), 10.6 (SOPPA(CCSD)), and 6.1% (CCSDLR). The deviations for the $S(-6)$ sum rules are about twice the ones for the $S(-4)$ sum rules showing the increased difficulty in calculating the high-order Cauchy moments. An interesting point is that both in the SOPPA and SOPPA(CCSD) methods the $S(-6)$ sum rules for the SO_2 molecule has an error of about 100%.

In Table 6 we give our best values for the isotropic polarizability for five commonly used experimental frequencies using the dipole oscillator strength sum rules calculated at the CCSDLR level with basis set II. We also give estimates of the polarizability anisotropy calculated from an interpolation of the anisotropy calculated at 10 frequencies (the same that were used in the fit to get the oscillator strength sum rules) by a polynomial of degree 5 in the square of the frequencies. It should be remembered that these values are pure electronic values not including any vibrational averaging. On the basis the rms deviations seen above for both the static polarizability and the dipole oscillator strength sum rules, we expect that the frequency-dependent values all are within 5% of the experimental values, even though the majority of the molecules may be even more accurately described. For the anisotropy an estimate of the error is difficult to give since experimental results are not known for all molecules. However, it is expected that the accuracy is not as high as for the isotropic polarizability.

The size of vibrational corrections to our results is difficult to give. Recent investigations by Russell and Spackman[41,43] show that averaging the static dipole polarizability in the vibrational ground state (zero-point vibrational averaging) changes the property by only a small amount. For the dipole polarizability the change is seen to be around 1−2%. The polarizability anisotropy is more sensitive, giving in some cases changes of close to 10%. A direct comparison of the properties obtained in this work is, however, not possible, since Russell and Spackman have employed basis sets and geometries different from those we have used. It is obvious, though, that a large fraction of the remaining discrepancy between our results and the experimental values can be removed by including the zero-point vibrational corrections. A problem associated with the calculation of vibrational averaged properties is that it requires the evaluation of the properties in question for several different geometries, a problem which makes their calculation computationally quite demanding and is therefore outside the scope of this investigation.

5. Summary

With comparison of the two basis sets it was found for the majority of the molecules studied here that Sadlej's medium size polarized basis sets give smaller values of the static polarizability and the Cauchy moments at the RPA level and larger values at the correlated levels than the daug-cc-pVTZ basis sets. The correlation corrections to these quantities is thus overestimated in Sadlej's basis sets. The polarizability anisotropies obtained with the medium size polarized basis sets are for most molecules larger than the daug-cc-pVTZ results independent of the method. Nevertheless, the contribution of electron correlation to the anisotropy is again overestimated using the medium size polarized basis sets. The agreement with experimental data is in general better for the mean static polarizability than for the dispersion and the anisotropy. Comparison of the four methods shows that for the majority of molecules in this study the accuracy of the four methods increases in the following sequence: RPA < SOPPA < SOPPA(CCSD) < CCSDLR. In particular, the RPA predicts smaller static values and dispersions of the mean polarizability than those found experimentally, whereas nothing general can be said about the polarizability anisotropy. SOPPA, on the other hand, gives larger values and thus tends to overestimate the correlation corrections to the mean polarizability and Cauchy moments. The agreement with the experimental values is nevertheless in general better at the SOPPA level. The usage of the coupled cluster amplitudes in SOPPA(CCSD) reduces the tendency to overestimate the correlation correction and SOPPA(CCSD) results are thus closer to the CCSDLR results and the experimental data than the SOPPA values. For the static isotropic and anisotropic polarizability the SOPPA(CCSD) results were found to be close to MP4 results. Finally, the CCSDLR results agree best with the experimental data, as is to be expected. We expect that inclusion of vibrational corrections such as zero-point vibrational averaging will remove most of the remaining discrepancy between experimental values and our results. The calculation of these remains, however, a subject for further investigations.

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