Polarizabilities of CO, N_2, HF, Ne, BH, and CH^+ from *ab initio* calculations: Systematic studies of electron correlation, basis set errors, and vibrational contributions

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(Received 7 April 1998; accepted 16 June 1998)

The dipole-polarizabilities of CO, N_2, HF, Ne, BH, and CH^+ have been investigated using coupled-cluster methods. An extensive basis set study has been carried out and electron correlation effects have been studied employing a hierarchy of coupled-cluster models. Vibrational-averaged electronic polarizabilities as well as the pure vibrational polarizabilities have been calculated based on *ab initio* energy and property curves. The frequency-dependency of the vibrationally-averaged electronic polarizabilities and vibrational polarizabilities are discussed. The final results are compared with available experimental data. © *1998 American Institute of Physics.* [S0021-9606(98)30136-1]

I. INTRODUCTION

The frequency-dependent electric-dipole polarizabilities and hyperpolarizabilities are fundamental quantities for the comparison of theory and experiment.[1–5] However, the quantum chemical *ab initio* calculation of these quantities is often quite challenging. Electron correlation effects are significant and extended one-electron basis sets are required for reliable predictions. Furthermore, accurate prediction of the frequency-dependence is important, since most experiments relate to frequency-dependent rather than static polarizabilities. Another aspect is that not only the electronic degrees of freedom contribute to the polarizabilities but also the nuclear degrees of freedom. Experimental results often refer to specific (typically the lowest) vibrational state and thus a vibrational averaging of the electronic contribution is appropriate. There is also a pure vibrational contribution to the polarizabilities though this contribution often is neglected in calculations. All these issues together complicate *ab initio* calculations of polarizabilities and hyperpolarizabilities as well as the comparison of experimental and theoretical results. In this study we focus on the accurate calculation of frequency-dependent polarizabilities. An accurate description of the polarizability is naturally a necessary prequisite for accurate predictions of hyperpolarizabilities, the latter typically being even more computational challenging.

In the recently established hierarchy of iterative coupled-cluster (CC) models, CCS (coupled-cluster singles), CC2,[5] CCSD (coupled-cluster singles and doubles),[6] CC3,[7,8] and CCSDT (coupled-cluster singles, doubles and triples)[9–11] dynamical molecular properties can be calculated with increasing accuracy at the expense of increasing complexity. The accuracy of calculated excitation energies are improved at each level of the hierarchy and consequently the accuracy of both static and frequency-dependent polarizabilities is improved when going to higher levels within this hierarchy. Calculation of frequency-dependent CCSD polarizabilities based on CC linear-response theory was first presented by Kobayashi *et al.*[12] Recently, a more general form of the linear-response function[13] was implemented for CCS, CC2, and CCSD,[14] extending the integral direct CC algorithm[15] to the calculation of frequency-dependent polarizabilities. Static polarizabilities can also be calculated within the CCSD(T) model[16] using analytical methods.[17,18] However, this CC model is not suitable for calculation of frequency-dependent properties (see discussion in Ref. 13), while the better suited CC3 and CCSDT models have not yet been implemented for calculation of frequency-dependent polarizabilities. Static polarizabilities can be obtained for these methods by employing finite-field techniques.

We focus in this study on the calculation of frequency-dependent polarizabilities for the neon atom and the diatomics BH, CH^+, CO, N_2 and HF. The small size of these systems makes calculations all the way to CCSDT possible in reasonable basis sets. For BH and CH^+ full configuration interaction (FCI) results are available for comparison,[19,20] while for the other systems the CCSDT results are taken as reference. Furthermore we report calculations at the CCSD level employing basis set of correlation consistent type[21–24] up to multiple augmented correlation-consistent pentuple basis sets. The twin adoption of a hierarchy of CC models and a hierarchy of correlation-consistent basis sets is important for monitoring the accuracy of calculated electronic polarizabilities and establishing accurate benchmark results. We also discuss the effect of orbital relaxation and different treatments of the core electrons in polarizability calculations. On the basis of CC calculations of potential curves and electronic property functions, the convergence of vibrationally

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averaged polarizabilities and pure vibrational contributions with respect to the level of treatment of the potential energy surface and the property surface is investigated. The frequency-dependence of vibrationally averaged electronic polarizabilities and the pure vibrational polarizabilities are discussed.

II. THEORY

The electronic contribution to the frequency-dependent polarizability can be obtained from the negative linear-response function,[2,4]

$$\alpha_{ij}(-\omega;\omega) = -\langle\langle \mu_i, \mu_j \rangle\rangle_\omega , \tag{1}$$

where μ_i and μ_j denotes the ith and jth components of the electric dipole operator and $\langle\langle X,Y\rangle\rangle_\omega$ the linear-response function. The exact linear-response function can be written in terms of the eigenstates $\{|O\rangle,|K\rangle\}$ of the field free electronic Hamiltonian H_o as

$$\langle\langle X,Y\rangle\rangle_{\omega_y} = P^{XY} \sum_K \left[\frac{\langle O|X|K\rangle\langle K|Y|O\rangle}{\omega_y - \omega_K} \right]. \tag{2}$$

Here ω_K denotes the excitation energy, $\omega_K = E_K - E_o$, where E_o is the ground-state energy and E_K the excited state energy. X and Y may be general operators, but refer in this study exclusively to components of the dipole operator. P^{XY} generates the two permutations of the operators X and Y with related frequencies ($P^{XY} f(X,\omega_x,Y,\omega_y) = f(X,\omega_x,Y,\omega_y) + f(Y,\omega_y,X,\omega_x)$ with $\omega_x = -\omega_y$).

The derivation of response functions for approximate wave functions has a long history (see Refs.2,4,13,25,26 and references therein). We will briefly summarize a convenient approach for the derivation of response functions for CC models, with emphasis on the differences between the so-called orbital-relaxed and the unrelaxed approaches. As shown in Ref. 13, response functions can be determined as derivatives of a so-called time-averaged quasienergy

$$\langle\langle X,Y\rangle\rangle_{\omega_y} = \frac{d^2\{Q(t)\}_T}{d\epsilon_X(\omega_x) d\epsilon_Y(\omega_y)}, \tag{3}$$

where $\{\ \}_T$ denotes the time-average over a full period of the periodic Hamilton operator containing terms of the type $\epsilon_Y(\omega_y) Y \exp(-i\omega_y t)$. $\epsilon_X(\omega_X)$ and $\epsilon_Y(\omega_y)$ are the field-strengths for the perturbation operators X and Y with associated frequency ω_x and ω_y. $Q(t)$ is the time-dependent quasienergy. For variational wave functions $Q(t) = \langle \tilde{O}(t)|(H(t) - i\partial/\partial t)|\tilde{O}(t)\rangle$ where $|\tilde{O}(t)\rangle$ denotes the phase-isolated wave function.

The above formulation is especially convenient for the derivation of response functions for nonvariational methods such as the CC models used in this study. To compensate for the nonvariational nature of these methods, the time-dependent quasienergy is augmented by terms consisting of Lagrangian multipliers multiplied by the time-dependent constraints on the coupled cluster wave function parameters. This defines the so-called quasienergy Lagrangian for CC wave functions[7,13]

$$\begin{aligned} L_{\mathrm{CC}} = {} & \langle \mathrm{SCF}|H(t)\exp(T(t))|\mathrm{SCF}\rangle \\ & + \sum_{i,\mu_i} \bar{t}_{\mu_i}(t) \langle \mu_i | \exp(-T(t))(H(t) - i\partial/\partial t) \\ & \times \exp(T(t))|\mathrm{SCF}\rangle . \end{aligned} \tag{4}$$

The operator $T(t)$ is the time-dependent CC operator parametrizing the electronic ground state in terms of excitations (singles, doubles,...) out of the self-consistent-field (SCF) reference ($|\mathrm{SCF}\rangle$). The parameters $\bar{t}_{\mu_i}(t)$ are the time-dependent Lagrangian multipliers that are multiplied with the time-dependent equations for the CC parameters. The given definition of the Lagrangian is sufficient to determine the response functions by substitution of $Q(t)$ in Eq. (3) with the CC quasienergy (see Refs. 7,13 for details). Without approximations in the cluster operator T, the parametrization has the flexibility to represent the exact quasienergy Lagrangian within a given one-electron basis. Approximate CC models are obtained by truncating the cluster operator T. This defines the series of CC approximations: CCS, CCSD, CCSDT, ..., where CCS is obtained when only single excitation out of the SCF reference are considered ($T = T_1$), CCSD when only single and double excitations are included ($T = T_1 + T_2$), and so on. Other approximate CC models such as CC2 and CC3 are obtained by additional approximations in the cluster amplitude equations which in this context correspond to introducing additional approximations in the time-dependent CC equations that in Eq. (4) are multiplied by the Lagrangian multipliers $\bar{t}_{\mu_i}(t)$.

The Lagrangian given in Eq. (4) describes the case where the molecular orbitals are frozen in the presence of the perturbations. In the so-called relaxed CC approach, the orbitals are allowed to relax to the external perturbation, thus necessitating the introduction of explicit time-dependent orbitals. The orbital-relaxed time-dependent CC Lagrangian can be written as

$$\begin{aligned} L_{\mathrm{CC}} = {} & \langle \mathrm{SCF}|\exp(-\kappa(t))(H(t) - i\partial/\partial t)\exp(\kappa(t))\exp(T(t))|\mathrm{SCF}\rangle \\ & + \sum_{i,\mu_i} \bar{t}_{\mu_i}(t) \langle \mu_i | \exp(-T(t))\exp(-\kappa(t))(H(t) - i\partial/\partial t)\exp(\kappa(t))\exp(T(t))|\mathrm{SCF}\rangle \\ & + \sum_{mn} \bar{\kappa}_{mn}(t) \langle \mathrm{SCF}|[E_{mn}, \exp(-\kappa(t))(H(t) - i\partial/\partial t)\exp(\kappa(t))]|\mathrm{SCF}\rangle . \end{aligned} \tag{5}$$

TABLE I. Comparison of relaxed and unrelaxed methods. The order in Møller-Plesset perturbation theory through which unrelaxed and relaxed CC methods are correct for the static polarizability.

Model	Unrelaxed	Relaxed
CCS	0	1
CC2	1	2
CCSD	2	3
CC3	3	4
CCSDT	3	4

The operator $\exp((\kappa(t))$ generates the time-dependent rotations of the orbitals in the SCF reference state with E_{mn} as corresponding generators of orbital rotations. Note that compared to Eq. (4) we have the time-dependent SCF equations as additional constraints (third term) in Eq. (5). The corresponding Lagrangian-multipliers are denoted by $\bar{\kappa}_{mn}(t)$, and the summation over m,n denotes summation over nonredundant orbital-rotations. For a closed-shell SCF reference those are the rotations which mix occupied and virtual orbitals. The second derivative of this Lagrangian defines the so-called relaxed linear-response function.

There has been some discussion in the literature, whether the unrelaxed or relaxed approach are preferable (see Ref. 20 and references therein). Theoretically, the unrelaxed approach is preferable in calculations of frequency-dependent properties as the linear-response function in this case contains only one set of poles (from the CC parameters), while the linear-response function in the relaxed approach also contain additional poles due to the orbital-rotations. The SCF poles occur at the values of the SCF (or RPA) excitation energies, while the CC poles occur at the values of the CC response theory excitation energies. The additional SCF poles in the orbital-relaxed approach are most likely to spoil the dispersion of the frequency-dependent polarizability, as the SCF excitation energies are of significantly poorer quality than for example CCSD excitation energies. Furthermore it should be noted that the electronic states represented by the SCF poles are already represented by the CC poles.

In the frequency-independent limit both the relaxed and the unrelaxed approaches are viable options, though quite different both in theory and practice. One way of analyzing the differences is by comparing the order in Møller-Plesset perturbations theory through which the static polarizability is correct. It is here important to stress that the CC approach is an infinite order approach and thus contains higher order terms. The relaxed approach obviously gives the static polarizability correct through the same order as the ground state energy. For the unrelaxed approach, the situation is different and an explicit analysis is required. The result of such an analysis is given in Table I together with the result for the relaxed approach. It is seen that one order is ''lost'' in the unrelaxed approach relative to the relaxed approach for static polarizabilities. This should not be taken as a proof of that the relaxed approach is better than the unrelaxed for static polarizabilities. The perturbation analysis is only of limited value as divergent perturbation series are often obtained when using extended basis sets as required for reliable polarizability calculations.[27,28] However, the perturbational analysis does illustrate that the relaxed and unrelaxed approach are quite different. Therefore care is required when mixing the two approaches. For example, it is often of interest to extrapolate the effect of triples excitations from the static polarizability to the dynamic polarizability. The above analysis can be of help to avoid errors. As an example, let us consider the addition of a relaxed triples contribution (e.g. the difference of relaxed CCSD(T) and relaxed CCSD containing fourth and higher-order contributions) to an unrelaxed CCSD result. This extrapolation is most likely to give wrong results as all third-order terms are included by the relaxed CCSD result, but some third-order terms are not present within the unrelaxed CCSD result. Thus such an extrapolation exclude some third order terms while at the same time including fourth and higher-order terms. It is therefore unbalanced and not recommended.

In the preceding sections we discussed the electronic contribution to the polarizability. For later reference we shall also discuss the vibrational contributions. In the Born-Oppenheimer approximation the wave function is written as product of an electronic wave function (denoted by large letter bra-kets $|K\rangle$) and a nuclear wave-function (denoted $|k_K\rangle$ - we consider here only the effect of quantized vibration) for each electronic state K. Denoting the energy difference between the (K,k_K)-state and the (O,o_O) state by ω_{k_K} and the pure electronic energy difference as ω_K we obtain in analogy with to Eqs. (1)–(2)

$$
\begin{aligned}
&\langle\langle X,Y\rangle\rangle_{\omega_y} \\
&\quad = P^{XY}\left\{\sum_{K,k_K\neq O,o_O}\frac{\langle o_O|\langle O|X|K\rangle|k_K\rangle\langle k_K|\langle K|Y|O\rangle|o_O\rangle}{\omega_y-\omega_{k_K}}\right\} \\
&\quad \simeq P^{XY}\left\{\sum_{k_O\neq o_O}\frac{\langle o_O|\langle O|X|O\rangle|k_O\rangle\langle k_O|\langle O|Y|O\rangle|o_O\rangle}{\omega_y-\omega_{k_O}}\right. \\
&\qquad \left.+\langle o_O|\sum_{K\neq O}\frac{\langle O|X|K\rangle\langle K|Y|O\rangle}{\omega_y-\omega_K}|o_O\rangle\right\} \\
&\quad \equiv \langle\langle X,Y\rangle\rangle^{v}_{\omega_y}+\langle\langle X,Y\rangle\rangle^{e-\text{vib. ave.}}_{\omega_y}. \qquad (6)
\end{aligned}
$$

In Eq. (6) it is assumed that the vibrational energy differences are small compared to the electronic energy differences, allowing the use of closure over the vibrational states in the excited state K. The polarizability is then obtained as a sum of two terms: a pure vibrational term referring to the ground-state vibrational levels only, and a term consisting of the average of the electronic polarizability over the vibrational ground state. The first term (commonly denoted the pure vibrational contribution) is a sum-over-state expression involving vibrational transition matrix elements over the electronic expectation values of the relevant operators as a function of nuclear coordinates. The electronic expectation values are normally reasonably smooth functions of the nuclear coordinates, and the vibrational transition matrix elements are therefore normally very rapidly decreasing with increasing k. It can therefore be expected that a sum-over-

states approach is rapidly convergent for the vibrational polarizability, in contrast to the situation for the electronic polarizability.

III. COMPUTATIONAL DETAILS

A local version of the ACESII code[29] has been used for the CCSD(T) polarizability calculations employing the newly developed code for analytical calculation of second-order properties with inclusion of connected triples.[17,18] The CC3 and CCSDT results were obtained using finite field techniques on the basis of the CCSDT energy code in ACESII.[11] For the remaining calculations, a local version of the DALTON program[30] including the integral-direct CC linear-response program[14] has been used.

In our study of correlation effects and basis set effects the following fixed bond length were used for BH, CH^+, CO, N_2 and HF: $R_{BH}=2.3289$ a.u., $R_{CH}=2.13713$ a.u., $R_{CO}=2.132$ a.u., $R_{NN}=2.068$ a.u., $R_{HF}=1.7328$ a.u. The benchmark calculations against previous FCI results for CH^+ and BH were carried out using the basis sets used in Ref. 19 and Ref. 20, respectively. For CO, N_2, HF and Ne we used CCSDT as a reference in calculations using the aug-cc-pVTZ basis set. The basis sets study was carried out with the correlation-consistent basis sets developed by Dunning and co-workers:[21–23] cc-pVXZ, aug-cc-pVXZ, x-aug-cc-pVXZ, where X=D,T,Q,5 and x=d,t,q. For the first set of augmented diffuse functions the exponent of Kendall *et al.* were used,[22] while further extensions for d-aug, t-aug and q-aug were made with exponents obtained from a geometric series following the recipe given by Woon and Dunning.[23] To test the importance of core effects additional calculations were performed with selected basis set using the frozen core approach (denoted f.c. in the tables), as well as all-electron calculations with inclusion of the additional core basis functions of Ref. 24. The resulting basis sets are denoted by aug-cc-pVCXZ. The largest basis used in this study was the d-aug-cc-pV5Z set consisting of a $(16s10p6d5f4g3h)$ primitive set contracted to $(8s7p6d5f4g3h)$ for B-Ne and a $(10s6p5d4f3g)$ set contracted to $(7s6p5d4f3g)$ for hydrogen. These calculations comprised up to 326 basis functions.

In addition to the correlation consistent basis sets we test the performance of Sadlej's medium sized basis sets[31] that were especially designed for polarizability calculations.

For the calculation of potential energy surfaces and property surfaces, the aug-cc-pVQZ basis set was used in all calculations. Generally, the potential and the property curves were obtained from the same type of calculations (under the label of CCS, CC2, CCSD and CCSD(T)), with the only exception being CCSD(T)/CCSD where the potential energy curve was obtained in the CCSD(T) approximation and the properties were calculated at the CCSD level. The core electrons were kept frozen in the CCS, CC2, CCSD and CCSD(T)/CCSD calculations and the unrelaxed approach was used in the calculation of the electronic properties. All electrons were correlated in the pure CCSD(T) calculations and the relaxed approach was used.

The vibrationally-averaged polarizabilities and the vibrational contributions were calculated using a self-written program performing numerical integration of the nuclear Schrödinger equation based on the renormalized Numerov-Cooley approach as described in Ref. 32. Vibrational averages and transition matrix elements were calculated using a spline interpolation for the property curves and standard numerical integration procedures.[33] The vibrational polarizabilities were calculated by a straightforward sum-over-states approach. Test for convergence with respect to the number of included vibrational states indicate that convergence of the vibrational polarizabilities was obtained within the presented number of reported digits.

We compare with experimental results for the isotropic polarizability ($\bar{\alpha}=\frac{1}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$) and the polarizability anisotropy ($\Delta\alpha=2^{-\frac{1}{2}}[(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{yy}-\alpha_{zz})^2+(\alpha_{zz}-\alpha_{xx})^2]^{\frac{1}{2}}$).

TABLE II. Error in dipole moments (a.u.) and static electronic polarizabilities (a.u.) relative to FCI for CH^+ and BH.[a]

	CH^+			BH		
	μ_z^c	α_{xx}	α_{zz}	μ_z	α_{xx}	α_{zz}
Unrelaxed properties						
CIS	−0.1348	−3.315	−0.262	−0.1690	−9.569	−1.115
CCS	−0.1348	−1.584	0.162	−0.1690	−4.528	−0.059
CC2	−0.0781	−0.915	0.146	−0.1013	−1.906	0.427
CCSD	−0.0079	−0.064	0.058	−0.0127	−0.144	0.262
CC3	−0.0022	−0.020	0.016	−0.0042	−0.049	0.097
CCSDT	−0.0005	−0.006	0.001	−0.0009	−0.011	0.013
Relaxed properties						
SCF	−0.1348	−0.930	0.458	−0.1690	−2.473	0.723
MP2	−0.0814	−0.590	0.271	−0.1067	−1.841	0.110
CC2	−0.0801	−0.595	0.276	−0.1057	−1.847	0.104
CCSD	−0.0046	−0.031	0.027	−0.0085	−0.019	0.161
CCSD(T)	−0.0007	−0.008	0.002	−0.0019	−0.009	0.036
CC3	−0.0012	−0.011	0.006	−0.0028	−0.021	0.046
CCSDT	−0.0004	−0.004	0.000	−0.0006	−0.010	0.012
FCI[b]	0.6374	5.690	8.327	0.5171	20.289	23.306

[a]Basis set and geometry as in Ref. 19 for CH^+ and Ref. 20 for BH.
[b]FCI results from Refs. 19,20
[c]Nuclear contribution: −0.978 060 62.

IV. ELECTRON CORRELATION BENCHMARK CALCULATION

A. Full configuration benchmark calculations for BH and CH^+

Table II gives the errors in the dipole moments and polarizabilties for BH and CH^+ as obtained from our calculations compared to the previous FCI calculations.[19,20] We will first discuss CIS (configuration interaction singles), CCS and SCF results. The dipole moments are the same for all three approaches (i.e., the SCF expectation values), while the polarizabilities differ. We note that the CIS α_{xx} component for both molecules are in error by several atomic units. The CCS method gives a significant improvement compared to CIS while including only an additional single noniterative term

TABLE III. Dipole moments (a.u.) and static electronic polarizabilities (a.u.) for CO, N_2, HF, and Ne using the aug-cc-pVTZ basis set.[a]

	CO			N_2		HF			Ne
	μ_z	α_{xx}	α_{zz}	α_{xx}	α_{zz}	μ_z	α_{xx}	α_{zz}	α
Unrelaxed properties									
CIS	−0.1050	13.567	17.188	11.649	18.428	0.7575	4.683	6.519	2.384
CCS	−0.1050	12.045	15.263	10.440	15.828	0.7575	4.443	6.014	2.276
CC2	0.1697	12.101	16.088	10.215	14.343	0.6920	5.218	6.725	2.514
CCSD	0.0562	11.815	15.700	10.126	14.578	0.7072	4.901	6.352	2.433
CC3	0.0543	11.889	15.499	10.213	14.860	0.7039	4.890	6.327	2.421
CCSDT	0.0564	11.857	15.562	10.187	14.753	0.7044	4.892	6.330	2.423
Relaxed properties									
SCF	−0.1050	11.225	14.490	9.764	14.951	0.7575	4.268	5.713	2.194
MP2	0.1104	11.918	15.623	10.086	14.240	0.7099	4.943	6.321	2.435
CC2	0.1250	12.060	15.569	10.240	14.446	0.7010	5.108	6.499	2.470
CCSD	0.0285	11.702	15.411	10.060	14.615	0.7124	4.772	6.199	2.389
CCSD(T)	0.0511	11.851	15.519	10.182	14.752	0.7055	4.873	6.305	2.418
CC3	0.0536	11.879	15.484	10.196	14.821	0.7040	4.907	6.341	2.426
CCSDT	0.0489	11.843	15.497	10.177	14.780	0.7053	4.875	6.308	2.419

[a]$R_{CO}=2.132$ a.u., $R_{NN}=2.068$ a.u., $R_{HF}=1.7328$ a.u.

for the polarizability relative to CIS (see Ref. 14). The SCF approximation gives better results for the α_{xx}'s than CCS though the α_{zz} results deteriorate.

Next we consider the CCS, CC2, CCSD, CC3 and CCSDT results in the unrelaxed approximation. CC2 improves on CCS for all properties (except α_{zz} for BH). However significantly better results are obtained with CCSD. In the worst case for CC2 (BH, α_{xx}) the error is 1.9 a.u. First at the CCSD level the error in the polarizability is less than 0.3 a.u. for both components in both molecules. At the CC3 level all errors are less than 0.1 a.u. The CCSDT errors are smaller than 0.01 a.u. for all polarizability components.

Consider now the orbital relaxed results relative to the unrelaxed results. We see a tendency towards smaller errors in the relaxed approach relative to the unrelaxed results (where we note that relaxed CCS is identical to SCF). For example at the CCSD and CC3 level there is a reduction in the mean absolute error of more than 40%. In connection with our perturbational analysis in the theory section it is interesting to note that the Møller-Plesset perturbation energy series of BH (and presumably also CH^+) appears to be monotonically (slowly) convergent in moderate sized basis sets like the present ones.[27] The consistent improvements of the relaxed approach over the unrelaxed is from this perspective not surprising as the relaxed results are correct through one order higher than the unrelaxed results and should thus give an improvement in the case of monotonic and convergent perturbation series. However we note that monotonic and convergent perturbation series should be considered more unusual rather than typical.

We finally note that MP2 gives results of similar quality as CC2. BH and CH^+ are difficult systems for a perturbation treatment as the weights of the reference states in the FCI solutions are small ($\sim$ 90%). The iterative CC2 model does not improve upon MP2 for such cases as have been found previously.[34] CCSD(T) improves the relaxed CCSD results significantly (with a factor of 4-14). The CCSD(T) results are in fact somewhat better than both the relaxed and unrelaxed CC3 results.

B. Benchmark calculations against CC singles, doubles and triples for CO, N_2, HF and Ne

In the previous subsection we saw that the CCSDT model provided very accurate polarizabilities for CH^+ and BH. Consequently, we discuss our results for CO, N_2, HF and Ne taking the CCSDT results as the reference. (See Table III.) However, we note that the differences between the relaxed and unrelaxed CCSDT results are significantly larger for these molecules than for CH^+ and BH. In fact the relative performance of the relaxed and unrelaxed approaches are somewhat more complicated. When going from unrelaxed CC2 to relaxed CC2 we obtain polarizabilities correct through second order and indeed the results appear to be improved in almost all cases. Unrelaxed CCSD also is only correct through second order but gives overall significantly better results than CC2. However, going to the relaxed CCSD approach (correct through third order) does not lead to further improvement. It is in this context interesting to note that for Ne and HF oscillating and divergent Møller−Plesset perturbation series are obtained in extended basis set.[27] Unfortunately Møller-Plesset perturbation series and FCI results are only available for modest basis set for N_2, but these results also indicate an oscillatory behavior. With such oscillatory perturbation series errors of similar magnitude but opposite sign are often obtained when going to the next higher order. Now, both relaxed and unrelaxed CC methods are true infinite order models and therefore the situation is even less clear. However the complicated behavior for CO, N_2, HF and Ne relative to the simpler behavior for CH^+ and BH, can to some extent be understood in terms of the widely different characteristics of the perturbation series.

TABLE IV. CCSD unrelaxed static electronic polarizabilities (a.u.) for BH, CH^+, CO, N_2, HF, Ne using various basis sets.[a,b]

		BH		CH^+		CO		N_2		HF		Ne
Basis set	N[c]	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α
cc-pVDZ	19/28	15.923	20.479	6.022	8.337	8.164	12.954	5.797	12.756	1.607	4.206	0.483
aug-cc-pVDZ	32/46	20.527	23.171	6.970	8.432	11.617	15.823	10.003	14.610	4.339	6.282	2.003
d-aug-cc-pVDZ	45/64	20.762	23.334	6.962	8.441	11.912	15.910	10.192	14.740	5.288	6.456	2.707
t-aug-cc-pVDZ	58/82	20.778	23.347	6.958	8.439	11.917	15.913	10.203	14.745	5.306	6.443	2.715
q-aug-cc-pVDZ	71/100	20.782	23.349	6.959	8.439	11.921	15.918	10.206	14.747	5.307	6.439	2.715
cc-pVTZ	44/60	18.268	21.361	6.659	8.388	9.971	14.303	7.469	13.802	2.722	5.272	1.032
aug-cc-pVTZ	69/92	21.014	22.901	7.050	8.337	11.815	15.700	10.126	14.578	4.901	6.352	2.433
d-aug-cc-pVTZ	94/124	21.039	22.955	7.045	8.337	11.866	15.706	10.153	14.604	5.255	6.401	2.698
t-aug-cc-pVTZ	119/156	21.045	22.953	7.043	8.334	11.869	15.697	10.154	14.604	5.253	6.410	2.699
q-aug-cc-pVTZ	144/188	21.045	22.953	7.043	8.334	11.869	15.699	10.154	14.608	5.254	6.411	2.700
cc-pVQZ	85/110	19.618	21.952	6.911	8.293	10.900	15.058	8.679	14.218	3.506	5.736	1.522
aug-cc-pVQZ	126/160	21.050	22.793	7.061	8.286	11.809	15.615	10.108	14.541	5.080	6.341	2.598
d-aug-cc-pVQZ	167/210	21.052	22.814	7.060	8.289	11.815	15.609	10.109	14.548	5.197	6.355	2.680
cc-pV5Z	146/182	20.130	22.408	7.001	8.263	11.334	15.437	9.273	14.409	4.063	5.991	1.863
aug-cc-pV5Z	207/254	21.038	22.747	7.064	8.269	11.786	15.569	10.085	14.512	5.121	6.329	2.643
d-aug-cc-pV5Z	268/326	21.042	22.751	7.065	8.270	11.790	15.569	10.085	14.516	5.171	6.335	2.668
aug-cc-pCVDZ	36/54	20.504	23.184	6.964	8.463	11.592	15.830	9.978	14.604	4.335	6.276	2.003
aug-cc-pCVTZ	82/118	20.940	22.849	7.033	8.318	11.780	15.663	10.098	14.556	4.885	6.339	2.427
aug-cc-pCVQZ	155/218	20.984	22.757	7.049	8.273	11.782	15.590	10.089	14.526	5.070	6.332	2.593
aug-cc-pVDZ/f.c.	32/46	20.514	23.170	6.964	8.431	11.618	15.820	10.004	14.608	4.339	6.283	2.003
aug-cc-pVTZ/f.c.	69/92	20.964	22.952	7.030	8.351	11.826	15.712	10.138	14.588	4.908	6.360	2.435
aug-cc-pVQZ/f.c.	126/160	21.006	22.881	7.038	8.311	11.833	15.639	10.131	14.561	5.094	6.354	2.603
Sadlej	33/48	-[d]	-[d]	6.764	8.251	11.679	15.848	9.970	14.719	5.334	6.503	2.433
Sadlej/f.c.	33/48	-[d]	-[d]	6.751	8.254	11.678	15.847	9.972	14.719	5.334	6.504	2.435

[a] $R_{BH}=2.3289$ a.u., $R_{CH}=2.13713$ a.u., $R_{CO}=2.132$ a.u., $R_{NN}=2.068$ a.u., $R_{HF}=1.7328$ a.u.
[b] f.c. denotes that the core orbitals are frozen (to the canonical SCF orbitals) in the CC calculations.
[c] Number of basis sets for XH/XY systems where X and Y are second row atoms.
[d] Sadlej's basis are not available for boron.

In view of this, we do not find it possible to conclude that the unrelaxed nor the relaxed is the better method. It appears rather that the errors of the two approaches are of similar magnitude and often of opposite sign.

According to the discussion in the preceeding paragraph, the CCSDT results can only be taken as an accurate benchmark within the uncertainty given by the difference between CCSDT relaxed and unrelaxed. Increasing accuracy is obtained in the CCS, CC2, CCSD, CC3, unrelaxed sequence also for CO, N_2, HF and Ne. We note that again the difference between the CCSD(T) and CCSDT relaxed results are very small. Larger differences are obtained for CC3. The differences are, however, still only of the order of a few hundredth of an a.u. and thus only slightly larger than the differences between the relaxed and unrelaxed CCSDT values. Thus CC3 is a significant improvement over CCSD. Finally it is also interesting to note that the MP2 results have errors of similar magnitude as the relaxed CC2 results.

V. BASIS SET BENCHMARK STUDY OF THE STATIC ELECTRONIC POLARIZABILITY

We have carried out an extensive basis set study of the polarizabilities using the unrelaxed CCS, CC2 and CCSD approaches. The CC2 and CCSD models show similar basis-set convergence pattern, while the CCS model, not unexpectedly, exhibits faster basis convergence than CC2 and CCSD. For the sake of conciseness we here only present and discuss the CCSD results which can be expected to give an accurate exposition of the basis set dependency of the polarizability. We note that for Ne and partially for N_2 a similar type of systematic basis set investigation was carried out by Woon and Dunning using MP and relaxed CC methods.[23] In Table IV CCSD results for the static polarizability are reported for different basis sets. The single most important effects comes from augmenting the cc-pVXZ (X=D, T, Q, and 5) basis sets with diffuse functions. Double augmentation of the basis set has in most cases only small effects on the polarizability and the effects of further augmentation is marginal. The effects of the second augmentation decrease drastically in the X=D, T, Q, 5) series. At the double zeta level, the second augmentation leads to an increase in the polarizability components of roughly up to 0.3 a.u. for BH, CH^+, CO and N_2 and somewhat more for HF and Ne. At the triple zeta level the increase is reduced to less than 0.05 for BH, CH^+, CO and N_2 and to about 0.3 au for HF and Ne. The effect is further diminished at the quadruple and pentuple zeta levels, i.e., at the pentuple zeta level the difference between the d-aug-cc-pV5Z and the aug-cc-pV5Z results is less than

TABLE V. Equlibrium and vibrational average dipole moments (a.u.).[a]

		SCF(CCS)	CC2	CCSD	CCSD(T)/CCSD	CCSD(T)	Expt.
CO	R_e-value	−0.054	0.157	0.055	0.046	0.048	
	vib. ave.	−0.061	0.157	0.050	0.041	0.042	−0.048[c]
	diff.[d]	−0.007	−0.000	−0.005	−0.005	−0.006	
HF	R_e-value	0.741	0.696	0.708	0.710	0.708	
	vib. ave.	0.753	0.705	0.717	0.719	0.717	0.71847[d]
	diff.[b]	0.012	0.009	0.009	0.009	0.009	
BH	R_e-value	0.700	0.639	0.559	0.558	0.556	
	vib. ave.	0.672	0.612	0.531	0.530	0.528	0.4997[e]
	diff.[b]	−0.028	0.027	−0.028	−0.028	−0.028	

[a]All calculations carried out with the aug-cc-pVQZ basis set.
[b]Vibrational averaged minus equilibrium value.
[c]Reference 59.
[d]Reference 57.
[e]Reference 60.

0.005 a.u. for BH, CH^+, CO and N_2, while for HF and Ne the second augmentation leads to an increase in the polarizability components of roughly 0.03 a.u.

Diffuse basis functions are more important for the perturbed system than for the unperturbed system. Therefore the polarizability increases when diffuse functions are augmented and in the cc-pVXZ, X=D,T,Q,5 series which also slowly gets more and more diffuse. The decrease in the effect of the second augmentation in the D=D,T,Q,5 sequence is due to the increase in the diffusity of the pure correlation consistent set cc-pVXZ and thereby also the corresponding first set of diffuse functions in the X=D,T,Q,5 series. On the other hand the increase in the cardinal number X has another important effect as also the description of correlation effects is improved in the X=D,T,Q,5 series. Note for example that all polarizability components decrease in the d-aug-cc-pVXZ, X=D,T,Q,5 series (except for α_{xx} for BH and CH^+). The aug-cc-pVQZ results are within 0.05 a.u. of the results obtained using the much larger d-aug-cc-pV5Z basis set for BH, CH^+, CO and N_2 and with only slightly larger differences (0.07 a.u. and 0.09) for Ne and the α_{xx} polarizability for HF.

We now discuss the effect of different treatment of the core effects: 1. complete neglect by freezing of core-electrons, 2. inclusion of core-electrons with no additional functions, and 3. inclusion of core-electrons but with addition of additional tight functions.[24] We simply denote the additional function as core functions. First we note that the effect of freezing the 1s electrons is moderate and tend to increase the polarizability. The effect increases in the aug-cc-pVXZ, X=D,T,Q series, from being of order 0.001(D) over 0.01(T) to 0.02(Q) (slightly larger for BH). This demonstrates the increasing possibility of the basis sets in describing at least some core effects. Including core-correlating functions give effects of the same order of magnitude. Note, however, that while inclusion of core-correlating functions tends to decrease the polarizability, while freezing the core tend to increase it. Therefore freezing the core-orbitals does not for polarizabilities solve the core-orbital issue, though it for other reasons may be advantageous as it reduces the computational cost. We furthermore note that the effect of core functions cannot be considered constant in the cc-pVXZ, X=D,T,Q series. At the cc-pVDZ level the effect of including core functions is sometimes in the other direction than for the larger basis sets. The effect at the triple zeta level is numerically somewhat larger than that found at the quadruple zeta level. The effects are though overall quite small (of the order a few hundredth of an a.u.) and we also note that going from the aug-cc-pVQZ to the d-aug-cc-pV5Z zeta level gives larger effects in the same direction as including core functions at the quadruple zeta level.

Finally we consider the performance of the basis set proposed by Sadlej for calculation of polarizabilities. Due to its more diffuse nature the Sadlej basis set behaves better than the slightly smaller aug-cc-pVDZ basis set for HF and Ne, while it is marginally poorer for CH^+, N_2 and CO.

VI. VIBRATIONAL EFFECTS

Table V reports molecular dipole moments as obtained at the optimium geometry (R_e-values) and after vibrational averaging. We note that the difference between the R_e values and the vibrationally averaged results are somewhat dependent on method and molecule. The use of CCSD(T) potential energy curves with CCSD dipole moments give similar results as the pure CCSD results for the difference between the R_e-value and the vibrational average. However, the CCSD values at the CCSD(T) optimum points are somewhat different from those at the CCSD optimum points, this being the major reason for the differences between the vibrationally averaged results. It appears that the CCSD(T)/CCSD only gives modest improvements of CCSD relative to the complete CCSD(T) results.

In Table VI are given R_e-values and vibrationally averaged results for static polarizabilities. We see that the absolute vibrationally averaged polarizabilities vary significant between the different models as should be expected from the preceding correlation study. However the variation of the difference between the vibrationally average values and the R_e-values are significantly more modest in absolute num-

TABLE VI. Electronic and vibrational contributions to static polarizabilities (a.u.) for N_2, CO, HF, BH, and CH^+.[a]

		CCS		CC2		CCSD		CCSD(T)/CCSD		CCSD(T)	
		α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}
N_2	R_e-value	10.22	15.10	10.35	14.70	10.12	14.54	10.17	14.68	10.20	14.79
	vib. ave.	10.25	15.18	10.38	14.77	10.15	14.61	10.20	14.76	10.23	14.88
	diff.[b]	0.03	0.09	0.02	0.07	0.03	0.07	0.03	0.08	0.03	0.09
CO	R_e-value	11.93	14.72	12.21	16.45	11.82	15.56	11.85	15.72	11.86	15.45
	vib. ave.	11.96	14.81	12.24	16.62	11.84	15.67	11.87	15.83	11.88	15.56
	diff.	0.03	0.08	0.03	0.16	0.02	0.10	0.02	0.11	0.02	0.11
	pure vib.	0	0.68	0	0.07	0	0.36	0	0.38	0	0.37
	total	11.96	15.49	12.24	16.69	11.84	16.03	11.87	16.22	11.88	15.93
HF	R_e-value	4.56	5.84	5.47	6.78	5.09	6.33	5.10	6.36	5.07	6.31
	vib. ave.	4.59	6.04	5.53	7.03	5.13	6.55	5.14	6.59	5.11	6.53
	diff.	0.03	0.20	0.06	0.25	0.04	0.22	0.04	0.23	0.04	0.22
	pure vib.	0	0.24	0	0.17	0	0.18	0	0.18	0	0.18
	total	4.59	6.28	5.53	7.19	5.13	6.73	5.14	6.77	5.11	6.70
BH	R_e-value	25.01	22.92	23.32	22.78	21.01	22.88	21.00	22.91	20.88	22.97
	vib. ave.	24.95	23.66	23.26	23.50	20.97	23.54	20.96	23.58	20.84	23.62
	diff.	−0.06	0.74	−0.06	−0.72	−0.04	0.66	−0.04	0.67	−0.04	0.65
	pure vib.	0	2.01	0	1.98	0	2.04	0	2.07	0	2.00
	total	24.95	25.66	23.26	25.48	20.97	25.66	20.96	25.65	20.84	25.2
CH^+	R_e-value	7.04	8.28	7.77	8.13	7.04	8.28	7.04	8.30	6.99	8.31
	vib. ave.	7.06	8.62	7.79	8.48	7.06	8.62	7.06	8.64	7.02	8.65
	diff.	0.03	0.34	0.02	0.35	0.03	0.34	0.03	0.34	0.03	0.34

[a]Using aug-cc-pVQZ basis sets.
[b]Vibrational-averaged results minus equilibrium value.

bers. The simplest model (CCS) appears to give the trends correct within 10%–30% compared to CCSD(T). It appears that CCSD(T)/CCSD is not a good choice as in some cases (CO and HF) the shift of the total vibrationally averaged result relative to CCSD is in the opposite direction of the consistent CCSD(T) result. This gives an indication of that a balanced treatment of the energy surface and the property surface is required for high accuracy. The improvement of only one of these does not necessarily lead to consistent improvements in accuracy.

Not unexpectedly the importance of the vibrational averaging is rather different for the different molecules. Consistent is only that the effect of the averaging procedure is smallest for the α_{xx} component: 0.02-0.05 a.u. The variation of the effect of vibrational averaging for the α_{zz} component is somewhat larger. The vibrational averaging effect is smallest for N_2 (approx. 0.07 a.u.) and largest for BH (approx. 0.66 a.u.).

The pure vibrational contributions to the static polarizability are included in Table VI. For HF, and BH the CCS, CC2 and CCSD results agree within 10%–20%, while for the triple-bonded CO rather dramatic variations are obtained in the CCS, CC2 and CCSD sequence. The CCSD results are in all cases within 10% of the CCSD(T) results.

VII. FREQUENCY-DEPENDENT POLARIZABILITIES

We have calculated vibrationally-averaged electronic polarizabilities and pure vibrational polarizabilites for a number of different frequencies. Due to the very large number of data we restrict our presentation to the most important results. To represent the frequency-dependence of the electronic polarizability in a concise way, we fitted the vibrationally averaged polarizability to an expansion in powers of ω^2

$$\alpha_{XY}(-\omega,\omega)=\sum_{k=0} S_{XY}(-2k-2)\omega^{2k}, \tag{7}$$

where $S_{XY}(-2k-2)$ are the Cauchy moments. We have previously studied the Cauchy moments of Ne using an analytical approach for this calculation and we refer to that paper for accurate values for Ne.[35] Since no experimental data exist for polarizabilities of BH and CH^+ and since the lower excitation energies of these systems makes it difficult to obtain a reliable fit over an appreciable frequency region with a limited number of Cauchy moment, we present in the following only Cauchy moments for N_2, CO and HF obtained at the CCSD/aug-cc-pVQZ level. The corresponding values are given in Table VII. When using these Cauchy moments in Eq. (7) the components of the frequency-dependent polarizability at the CCSD/aug-cc-pVQZ level can be obtained with an accuracy of 0.01 a.u. for $\omega \leqslant 0.02$ a.u. for N_2 and HF and $\omega \leqslant 0.01$ a.u. for CO. (Note that CO has a somewhat lower dipole-allowed excitation energy.)

A closer look at the data reveals that the difference between the vibrationally averaged and the equilibrium polarizability is relatively constant as a function of frequency. This may be of practical value for other studies since it opens

TABLE VII. Cauchy moments (a.u.) for N_2, CO and HF vibrationally-averaged polarizablilities obtained in the unrelaxed CCSD/aug-cc-pVQZ approximation.

	$S_{xx}(-2)$	$S_{zz}(-2)$	$S_{xx}(-4)$	$S_{zz}(-4)$	$S_{xx}(-6)$	$S_{zz}(6)$	$S_{xx}(-8)$	$S_{zz}(8)$
CO	11.837	15.666	46.4	49.2	315	194	0.3×10^4	0.8×10^3
N_2	10.147	14.612	23.6	37.8	74	121	0.3×10^3	0.5×10^3
HF	5.132	6.553	11.4	13.5	39	37	0.7×10^3	0.1×10^3

the possibility for approximate treatments of vibrational effects on the dispersion.

In Figs. 1 and 2 the α_{zz} components of the CCSD/aug-cc-pVQZ total polarizability (vibrationally averaged electronic + vibrational polarizabilities) are given as function of frequency for CO and HF, respectively. The vibrational contribution can be written as

$$\langle\langle X,Y\rangle\rangle^{v}_{\omega_y} = \sum_{k_O \neq o_O} \left[\frac{f^{XY}_k}{(\omega_y)^2 - (\omega_{k_O})^2} \right] = \frac{f^{XY}_1}{(\omega_y)^2 - (\omega_{1_O})^2} + \frac{f^{XY}_2}{(\omega_y)^2 - (\omega_{2_O})^2} + \cdots, \tag{8}$$

where we have assumed real arithmetic and introduced the vibrational oscillator strengths

$$f^{XY}_k = 2\,\omega_{k_O} \langle o_O|\langle O|X|O\rangle|k_O\rangle\langle k_O|\langle O|Y|O\rangle|o_O\rangle. \tag{9}$$

In Eq. (8) it is indicated that only the first few terms will give an important contribution. The remaining terms are negligible for the considered systems, except from very narrow intervals around the resonances. Vibrational frequencies and oscillator strength are given in Table VIII, from which the vibrational polarizabilities can easily be calculated using Eq. (8).

The above considerations give a simple interpretation for the general structure of the frequency-dependency of the polarizability as seen in Figs. 1 and 2. The results presented there are in good agreement with what should be expected from a smooth electronic frequency-dependency [given by Eq. (7)] overlapped by a vibrational frequency-dependency with poles of increasing sharpness [given by Eq. (8)]. Note that only the lowest vibrational poles are considered explicitly in Figs. 1 and 2.

The pure vibrational contribution may be important for polarizabilities for small frequencies as well as in the static limit, though it evidently becomes less important for higher frequencies where most experiments are carried out. The above discussion may thus be important when comparing calculated and experimental static polarizabilities, since the latter are often extrapolated from optical frequency experiments. Such extrapolations do not – or only partially – include the vibrational contribution. Even though overall the same qualitative picture is obtained for quite simple models like SCF and CCS, the accurate prediction of the absolute vibrational polarizability for a given frequency in the vicinity of the first pole is difficult and requires accurate fundamental frequencies. This dependency is somewhat smeared out for larger frequencies.

VIII. COMPARISON WITH PREVIOUS CALCULATIONS AND EXPERIMENT

In Table IX we report final estimates for static electronic polarizabilities. The first estimate is obtained from the CCSD(T)/aug-cc-pVQZ results with a CCSDT-CCSD(T) (relaxed) correlation correction from the benchmark studies (see Tables II and III) and a basis set correction from the difference between the unrelaxed CCSD/d-aug-cc-pV5Z and CCSD/aug-cc-pVQZ results (Table IV). A second estimate is obtained from the unrelaxed CCSD result in the d-aug-cc-pV5Z basis set with a correlation corrected obtained for the CCSDT-CCSD (unrelaxed) difference (Tables II and III). It

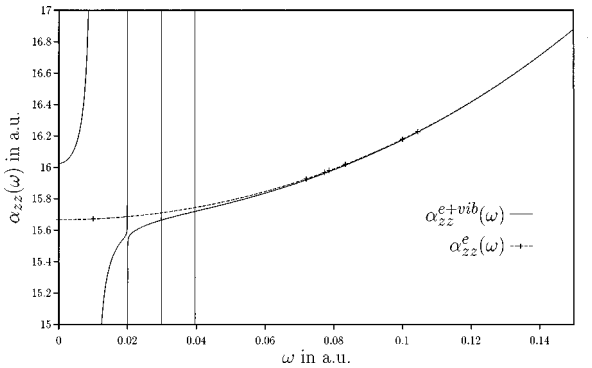


FIG. 1. Vibrationally averaged electronic and vibrational $\alpha_{zz}(-\omega,\omega)$ polarizability (a.u.) for CO obtained in the CCSD/aug-cc-pVQZ approximation as a function of frequency (a.u.). Note that only the lowest vibrational poles are indicated explicitly.

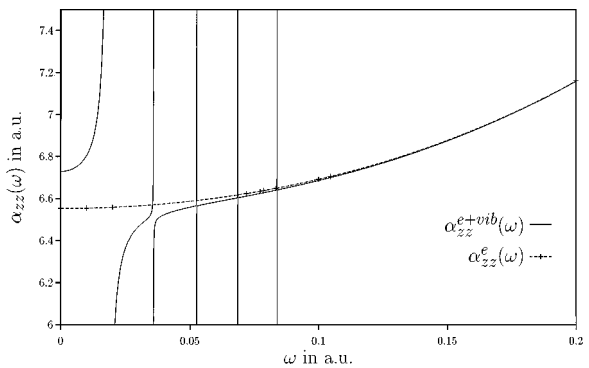


FIG. 2. Vibrationally averaged electronic and vibrational $\alpha_{zz}(-\omega,\omega)$ polarizability (a.u.) for HF obtained in the CCSD/aug-cc-pVQZ approximation as a function of frequency (a.u.). Note that only the lowest vibrational poles are indicated explicitly.

TABLE VIII. Vibrational frequencies (a.u.) and oscillator strengths obtained in the CCSD and CCSD(T) approximations using the aug-cc-pVQZ basis set.

	ω_1	f_1	ω_2	f_2	ω_3	f_3	ω_4	f_4
CCSD								
CO	0.01006	0.3623×10^{-4}	0.02000	0.218×10^{-6}	0.02984	0.12×10^{-8}	0.03957	0.5×10^{-11}
HF	0.01829	0.5851×10^{-4}	0.03582	0.162×10^{-5}	0.05260	0.47×10^{-7}	0.06866	0.22×10^{-8}
CCSD(T)								
CO	0.09785	0.3572×10^{-4}	0.01954	0.299×10^{-6}	0.02917	0.50×10^{-8}	0.03868	0.1×10^{-11}
HF	0.01808	0.5691×10^{-4}	0.03532	0.166×10^{-5}	0.05175	0.38×10^{-7}	0.06749	0.5×10^{-12}

is reassuring that the two estimates agree within a few hundredths of an a.u. The smallness of triples excitation effects beyond CCSD(T) and basis set effects beyond aug-cc-pVQZ together with the close agreement between the two different estimates suggest that the polarizability components are accurate within a few hundredth of an a.u. Estimates of the vibrationally averaged polarizabilities and the sum of the vibrationally averaged and pure vibrational polarizabilities are given using the same corrections for estimate 1. The corresponding results are also included in Table IX.

The purpose of this paper is not to review the large number of previous calculations on the chosen set of systems. We report in Table IX only selected previous calculations and values for the static electronic polarizability and refer to Refs. 2,4,36–51 for a more complete discussion. There have been some previous calculations of the pure vibrational con-

TABLE IX. Static polarizabilities (a.u.) for BH, CH^+, CO, N_2, HF, Ne from *ab initio* calculations.

	BH		CH^+		CO		N_2		HF		Ne
Method	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α
Static polarizability at fixed internuclear distances[a,b]											
CCSD(T)/aQ	20.858	23.080	6.995	8.372	11.856	15.451	10.175	14.714	5.069	6.308	2.590
CCSD(u)/da5-aQ	−0.008	−0.042	0.004	−0.016	−0.019	−0.046	−0.023	−0.025	0.091	−0.006	0.070
CCSDT(r)−CCSD(T)[b]	−0.009	0.036	−0.008	0.002	−0.008	−0.022	−0.005	0.028	0.002	0.003	0.001
Estimate 1	20.841	23.074	6.991	8.358	11.829	15.383	10.147	14.717	5.162	6.305	2.661
CCSD(u)/da5	21.042	22.751	7.065	8.270	11.790	15.569	10.085	14.516	5.171	6.335	2.668
CCSDT(u)-CCSD(u)[b]	−0.133	0.249	−0.058	0.057	0.042	−0.138	0.061	0.175	−0.009	−0.022	−0.010
Estimate 2	20.090	23.000	7.007	8.327	11.832	15.431	10.146	14.691	5.162	6.313	2.658
Final estimate	20.87	23.04	7.00	8.34	11.83	15.41	10.15	14.70	5.16	6.31	2.66
Selected previous calculations of the electronic contribution											
MCSCF[c]	20.62	23.60			11.54	15.11	10.14	14.50	5.028	6.167	2.672
SOPPA[d]	22.78	22.98			11.73	16.30	9.90	14.13	4.996	6.398	
MP2[e]				11.97	15.60	10.12	14.29				
CCSD(T)[f]				11.73	15.65	10.13	15.00	5.34	6.44		
Vibrationally averaged static polarizabilities											
CCSD(T)/aQ	20.84	23.62			11.88	15.56	10.23	14.88	5.11	6.53	
Estimate 1	20.82	23.61			11.85	15.49	10.20	14.88	5.20	6.53	
DOSD[g]					11.89	15.46	10.21	14.80			
Vibrationally averaged electronic + pure vibrational polarizabilities											
CCSD(T)/aQ	20.84	25.62			11.88	15.93	10.23	14.88	5.11	6.70	
Estimate 1	20.82	25.61			11.85	15.86	10.20	14.88	5.20	6.70	

[a](u) denotes unrelaxed results, (r) relaxed. CCSD(T) denotes always the relaxed approach.
$R_{BH}=2.3289$ a.u., $R_{CH}=2.13713$ a.u., $R_{CO}=2.132$ a.u., $R_{NN}=2.068$ a.u., $R_{HF}=1.7328$ a.u.
[b]From Tables II and III.
[c]MCSCF results from Reference 48 (BH with $R_{BH}=2.3289$ a.u. and CO with $R_{CO}=2.13221$ a.u.) Reference 41 (N_2 with $R_{NN}=2.07432$ a.u.), Ref. 40 (HF with $R_{HF}=1.7328$ a.u.), Ref. 43 (Ne).
[d]Second order polarization propagator results from Ref. 45.
[e]MP2 results from Ref. 47 with $R_{CO}=2.132$ a.u. and $R_{NN}=2.074$ a.u.
[f]CCSD(T) results from Ref. 42. ($R_{CO}=2.13221$ a.u., $R_{NN}=2.07432$ a.u., $R_{HF}=1.7328$ a.u.).
[g]Reference 50 (N_2) and Ref. 51 (CO)

TABLE X. Calculated and experimental polarizabilities (a.u.).

		CO		N_2		HF		Ne
	wavelength/nm	α	$\Delta\alpha$	α	$\Delta\alpha$	α	$\Delta\alpha$	α
Electronic[a]	∞	13.06	3.64	11.76	4.68	5.64	1.33	2.66
Electronic+Vibrational[a]	∞	13.18	4.01	11.76	4.68	5.70	1.50	
Electronic[a]	457.9	13.56	3.65	12.05	4.83	5.77	1.35	
	488.0	13.50	3.65	12.01	4.81	5.75	1.35	
	514.8	13.45	3.65	11.99	4.79	5.74	1.35	
	632.8	13.32	3.65	11.91	4.75	5.71	1.34	
Vibrational[a]	457.9	−0.001	−0.004	0	0	−0.002	−0.006	
	488.0	−0.001	−0.004	0	0	−0.002	−0.007	
	514.8	−0.002	−0.005	0	0	−0.003	−0.008	
	632.8	−0.002	−0.007	0	0	−0.004	−0.012	
Experiment	∞	13.08[b]		11.74[d]		5.60[b]		2.669[f]
	∞				4.45[d]			
	∞				4.69[g]			
	∞						1.49[f]	
	457.9			12.06[d]	4.89[d]			
	488.0			12.03[d]	4.85[d]			
	514.8			12.00[d]	4.82[d]			
	632.8			11.88[d]	4.69[d]			
	632.8	13.34[c]	3.59[c]	11.92[c]	4.70[c]			

[a]This study. See text for description.
[b]Extrapolated from refractive index in Ref. 36.
[c]Reference 58.
[d]From Ref. 55.
[f]From Ref. 57.
[g]Reference 49.
[h]Reference 56.

tribution to the polarizability of HF: $\alpha^v_{zz}(0{:}0)=0.243$ a.u. (SCF, Bishop and Lam as cited in Ref. 54), $\alpha^v_{zz}(0{:}0)=0.144$ a.u.,[52] $\alpha^v_{zz}(0{:}0)=0.168$ a.u.,[53] and most recently by Bishop and Kirtman $\alpha^v_{zz}(0{:}0)=0.170$ a.u. (Ref. 54). These values should be compared with our best estimate of 0.175 a.u. obtained from the CCSD(T) results in Table VIII. We also mention that at an optical frequency of 0.07 a.u. we obtain for $\alpha^v_{zz}(-0.07{:}0.07)$ a value of -0.013 a.u. in good agreement with the -0.012 a.u. value reported by Bishop and Kirtman.

In Table X we compare our final theoretical results for the polarizabilities with experimental results. The static vibrationally-averaged electronic polarizabilities and the total polarizabilities are obtained from estimate 1 discussed above. The frequency-dependency of the electronic polarizabilities are determined from the Cauchy expansion in Eq. (7) with the Cauchy moments in Table VII ($S(-2k-2),k\geqslant 0$). The pure vibrational polarizabilities are obtained from the CCSD(T)/aug-cc-pVQZ results given in Table VIII.

The experimental static polarizabilities have in most cases been obtained as extrapolation of optical results to zero frequency. For the isotropic part the values obtained in this way agrees within 0.05 a.u. with the given estimates for the electronic contributions, while the agreement is noticeable less satisfactory when comparing with the total polarizability (the sum of the electronic and the pure vibrational polarizability). This is easily understood in light of Figs. 1 and 2. The vibrational contribution for the typical experimental frequencies ($\omega=$ 0.05 - 0.15 a.u.) is negative and small while in the static limit it is positive and orders of magnitudes larger. The calculated total isotropic and anisotropic polarizabilities should therefore be expected to be slightly larger than the zero-frequency results extrapolated from experiment, which is indeed found.

Different values of the static polarizability anisotropy have been reported for N_2: 4.45 a.u. with an uncertainty of 3%,[55] and 4.69 a.u. (Ref. 56). In the latter case the same value was adopted for the static polarizability as for the frequency-dependent polarizability at a wavelength of 632.8 nm. We note that our computed result is in between the two above-mentioned experimental results. The calculated results show that the static and the frequency-dependent anisotropy (at a wavelength of 632.8 nm) differ by approximately 0.07 a.u. which is thus the minimum uncertainty of the latter experimental values. On the other hand, the former experimental value is 0.18 a.u. lower than our predicted value, which is somewhat larger than the expected uncertainty in the theoretical predictions.[61,62]

The calculated frequency-dependent polarizabilities for N_2 is in good agreement with the experimental polarizability. There appears to be a tendency towards that the experimental results show a slightly larger frequency-dispersion than the calculated one. We note that the predicted dispersion has been obtained at the CCSD level and since the lowest dipole-allowed transition (for the $1\,^1\Pi_u$ state) is predicted slightly too high in CCSD (Ref. 63) a slightly too small dispersion is to be expected.

The polarizability anisotropy of HF has been determined from Stark effect measurements.[57] Since this experiment relates to a static electric field there is no extrapolation to zero

frequency involved, and the resulting polarizability anisotropy include the pure vibrational contribution. In agreement with that, we find that the experimental value is very close to our theoretical estimate for the total polarizability anisotropy, which differs by 0.17 a.u. from the pure electronic value.

For CO, we find that the experimental value of polarizability anisotropy for a wavelength of 632.8 nm (Ref. 58) is within 0.06 a.u. of our theoretical predictions.

IX. SUMMARY

In this study we have compared several many-electron *ab initio* methods for the calculation of polarizabilties. Below we summarize the merits of the used approaches as found in this study.

In the CCS-CC2-CCSD-CC3-CCSDT hierarchy of coupled cluster methods, polarizabilities are predicted with increasing accuracy at the expense of increasing computational cost. In terms of the number of orbitals N the computational scaling of the different CC methods are N^4(CCS), N^5(CC2), N^6(CCSD), N^7(CC3), N^8(CCSDT). The merit of CCS is its simplicity. However, in most cases the almost equally simple SCF response approach (often denoted RPA - random phase approximation) provides better results. The most important role of CCS is therefore that it represent the first member in the CCS-CC2-CCSD-CC3-CCSDT hierarchy of coupled cluster models. The CC2 model gives improved results relative to CCS. It is noteworthy that the slightly simpler MP2 method gives static polarizabilities of similar quality as CC2, but the MP2 frequency-dependent polarizability has a spurious pole-structure (see discussion in Ref. 13). MP2 is therefore a cost-efficient method for the calculation of static polarizabilities, while (orbital unrelaxed) CC2 is preferable for the prediction of the frequency-dependent polarizabilities. The well-known CCSD method gives results of increasing accuracy compared to the CC2 model. Even more accurate results are obtained at the CC3 level and, in case of static polarizabilities, at the CCSD(T) level. A similar dilemma as between CC2 and MP2 also holds between CC3 and CCSD(T). The former iterative model allows for prediction of both static and frequency-dependent polarizabilities, while the latter at lower computational costs yields the polarizabilities with similar accuracy. CCSDT is the most accurate CC method used in this study and is in principle applicable to both static and frequency-dependent polarizabilities.

We have furthermore shown that the orbital-relaxed and unrelaxed CC approaches for calculation of polarizabilities may give quite different results. There is no clear preference for either choice in the calculation of static polarizabilities, but it has been argued that the unrelaxed approach is theoretically preferable for the calculation of frequency-dependent properties. It should be noted that the situation for polarizabilities is quite different from that of calculation of molecular gradients and Hessians, where the relaxed approach is the only suitable choice.

The basis set study indicates that for correlated calculations of dipole polarizabilities it is important to include one set of diffuse orbitals but that thereafter it is often more important to go to higher levels in the aug-pVXZ, X=D,T,Q,5 hierarchy of basis sets than to include further diffuse functions. From our correlation and basis set benchmark studies, final estimates have been given for the electronic polarizabilities. In addition, vibrationally-averaged electronic polarizabilities and pure vibrational polarizabilities have been calculated. The pure vibrational contribution has been shown to be important for obtaining accurate static polarizabilities. Our theoretical results have been compared with experimental results and the experimental and theoretical results for static and frequency-dependent polarizabilities have been discussed critically.

We hope that the results and analysis of the different contributions to the polarizabilities may be useful as inspiration and calibration of strategies for polarizability calculations of larger molecules.

ACKNOWLEDGMENTS

This work has been supported by the Alexander von Humboldt Foundation (O.C.), the European Commission through the Training and Mobility of Researchers (TMR) Programm (C.H.), the Deutsche Forschungsgemeinschaft (J.G.) and the Fonds der Chemischen Industrie (J.G.).

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