TDMP2 calculation of dynamic multipole polarizabilities and dispersion coefficients of the triplebonded molecules CO, N_2, CN^-, and NO^+

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In order to test the performance of the recently developed time-dependent second-order Møller–Plesset perturbation theory (TDMP2) for anisotropic frequency-dependent multipole polarizabilities, we have studied the isoelectronic series CO, N_2, CN^-, and NO^+. The polarizabilities of these triple-bonded diatomics are an interesting test for the TDMP2 method, because it is known that Møller–Plesset perturbation theory has its difficulties describing multiple bonds. We selected these molecules as test systems because, especially for N_2 and CO, accurate experimental and other *ab initio* data are available to compare with and their dynamical polarizabilities are needed for dispersion coefficients of van der Waals complexes, which are presently under intensive investigation. To get reliable results near the TDMP2 basis set limit we used large one-particle basis sets, optimized for polarizability calculations at the coupled Hartree–Fock level. The results show that the TDMP2 method is capable to improve for the isotropic as well as for the anisotropic polarizabilities considerably on the TDHF approximation, with the exception of the dipole polarizabilities of N_2 and NO^+, for which the static correlation effects are too strong to be treated by second-order Møller–Plesset perturbation theory. However, we find, that the TDMP2 method, due to the use of coupled (TDHF) first-order orbital rotation parameters, is somewhat more stable with respect to static correlation effects than the singles-doubles-triples many-body perturbation theory to second order [SDT-MBPT(2)] double perturbation theory. Where reference data are available, the TDMP2 results for static polarizabilities and for the first Cauchy moments are in good agreement with the best theoretical and experimental data. We also calculated dispersion coefficients for the $(N_2)_2$ and the $(CO)_2$ dimer and, utilizing the results of previous TDMP2 studies for the atoms He through Xe, also for the respective rare gas complexes of N_2, CO, CN^-, and NO^+. We estimate the results to be the most accurate *ab initio* data available for these van der Waals coefficients. © *1996 American Institute of Physics.* [S0021-9606(96)00145-6]

I. INTRODUCTION

In a recent article[1] we studied the accuracy of the time-dependent second-order Møller–Plesset perturbation theory (TDMP2)[2] for the frequency-dependent polarizabilities of the rare gas atoms argon through radon. To obtain results that are approximately unaffected by basis set deficiencies, we used large one-particle basis sets with numerous d, f, and g functions, optimized for polarizability calculations on the coupled Hartree–Fock (CHF) level of theory. For the heavier atoms Kr–Rn we also accounted for relativistic effects by combining the TDMP2 method with the spin-free no-pair Hamiltonian H_+^{sf1}.[3–5] The final results showed a reliable performance of the TDMP2 method for frequency-dependent polarizabilities of these systems, where static correlation effects are of no importance and the polarizability anisotropy vanishes. For most of the dipole properties the TDMP2 values are in agreement with the recommended constrained dipole oscillator strength distribution (DOSD) data of Kumar and Meath[6] within an error range of one percent. For all rare gas atoms, with the exception of helium, the TDMP2 method overestimates the correlation contribution to the dipole polarizabilities at imaginary frequencies and for real frequencies well below the first dipole-allowed transition, recovering about 100%–125% of the exact correlation contribution.

However, this result was not quite unexpected, because the noble gas atoms are well-suited for a perturbational treatment of correlation effects: the electron correlation is mainly dynamical in these atoms; no near degeneracies leading to static correlation effects need to be considered. This situation changes if one studies molecules. Here one must be aware of static correlation effects, which are brought about by excitations from occupied bonding orbitals to corresponding antibonding virtual orbitals. Especially for molecules with unusual long bonds or with multiple bonds, where the differences in the HF orbital energies become small for such corresponding pairs, these excitations can spoil the convergence of perturbation expansions, e.g., Møller–Plesset perturbation theory. Such excitations from bonding orbitals to corresponding antibonding orbitals can also be induced by interaction with specific multipole components of the electric field, as for example a dipole-type component parallel to the bond axes. For other components the interaction may be small or even vanish completely due to selection rules. As a consequence the individual tensor components of multipole–

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multipole polarizabilities are affected very differently by static correlation.

The intention of the present publication is to investigate the accuracy of the TDMP2 method for the calculation of frequency-dependent anisotropic polarizabilities and to test the applicability of this method for systems, where static correlation effects play an important role. As examples we choose the isoelectronic series of 14-electron systems N_2, CO, CN^-, and NO^+, because for N_2 and CO accurate constrained pseudo dipole oscillator strength distributions (DOSD), fitted to a lot of experimental data, are available.

The DOSD polarizabilities correspond to the pure electronic contributions to the total polarizabilities and only zero-point vibrational averaging must be accounted for to obtain a valid comparison of *ab initio* fixed-nuclei calculations with the DOSD data. For the triple-bonded diatomics, the effect of vibrational averaging is expected to be small. For N_2, e.g., Maroulis and Thakkar have estimated the vibrational corrections to the static isotropic and anisotropic dipole polarizabilities as 0.043 a.u. and 0.050 a.u., respectively.[7] This is well below the errors in the MP2 correlation contributions. We therefore neglect vibrational averaging in the present study and give only results of fixed-nuclei calculations. However, the most important application of our results will be their use in model potentials for van der Waals complexes. The neglect of the dependence on intramolecular vibrational coordinates is an approximation often used for van der Waals potentials, especially in supermolecular calculations.

The rare-gas complexes of the four molecules, in particular their argon complexes, and the dimers $(N_2)_2$ and $(CO)_2$ are van der Waals complexes presently under intensive investigation,[8–17] and accurate dispersion coefficients for these molecules are of great interest for people working on intermolecular forces.

A central topic of the present study is the effect of static correlation on polarizabilities. Although this effect is apparent and important to judge the reliability of *ab initio* calculations of polarizabilities, it goes practically unnoticed in the literature.

The most obvious feature is that for molecules, for which static correlation effects become important, the dipole polarizability parallel to the bond axes is largely overestimated by the uncoupled Hartree–Fock (UCHF) or SCF sum-over-states level of approximation. On the coupled Hartree–Fock (CHF) or SCF finite-field level the error is partially corrected, but often still a considerably too large polarizability is obtained, while normally UCHF and CHF both underestimate the polarizability and the CHF result is larger than the UCHF value. An overestimation by the UCHF and CHF approximations is, for example, observed for the longitudinal dipole polarizabilities of N_2 and NO^+, but not for the perpendicular components and not for the dipole polarizabilities of CO and CN^- (see Table I). Of course, it is exactly for these molecules and polarizability components that one obtains an abnormal negative correlation contribution. At the TDHF level of approximation a strong interaction between a bonding orbital and its virtual antibonding counterpart shows up by a low lying dipole-allowed excitation with an unusually large oscillator strength.

TABLE I. Comparison of UCHF and TDHF polarizabilities. $\alpha_\parallel$ and $\alpha_\perp$ are the longitudinal and perpendicular components of the dipole polarizabilities; ϵ_{Σ^+}, f_{Σ^+}, ϵ_Π and f_Π are the excitation energies and oscillator strengths of the first dipole-allowed transitions with Σ^+ and Π symmetry, respectively. All numbers are given in a.u.

	CO		N_2	
	UCHF	TDHF	UCHF	TDHF
$\alpha_\parallel$	13.78	14.47	16.06	15.03
$\alpha_\perp$	10.06	11.27	9.19	9.82
ϵ_{Σ^+}	0.56	0.44	0.63	0.51
f_{Σ^+}		0.17		2.22
ϵ_Π	0.56	0.32	0.62	0.48
f_Π		0.25		0.26
	CN^-		NO^+	
	UCHF	TDHF	UCHF	TDHF
$\alpha_\parallel$	27.10	32.51	11.10	9.22
$\alpha_\perp$	20.28	24.52	5.48	5.72
ϵ_{Σ^+}	0.24	0.20	0.87	0.62
f_{Σ^+}		0.01		1.78
ϵ_Π	0.24	0.20	0.86	0.37
f_Π		0.01		0.04

As we shall show in Sec. IV, in the case of static correlation the treatment of the relaxation of the orbitals and the density in the external electric field becomes crucial for polarizability calculations. As a consequence, the TDMP2 method[2] and the diagrammatic SDT-MBPT(2) method of Rijks and Wormer[18–20] perform differently for molecules for which static correlation effects are important, although both methods account for the electron correlation by second-order many-body perturbation theory. While the TDMP2 method incorporates the full TDHF orbital relaxation (first order in the electric field), the latter accounts for the orbital relaxation in the correlation contributions only by its (in a MBPT sense) zeroth-order approximation.

II. THEORY

A subject of central interest in the present study is the MBPT expansion of the orbital relaxation due to an external electric field. We therefore briefly sketch the closed-shell TDHF method and the expansion of the TDHF orbital rotation parameters and polarizabilities as power series in the two-electron integrals. For a detailed derivation and discussion see, for example, Refs. 21 and 22.

As in normal Hartree–Fock theory, in the TDHF method the wave function is approximated by a (now time-dependent) single determinant, which can be parametrized as

$$|\overline{0}(\omega,t)\rangle = \exp\left(-i \int_{t_0}^{t} \mathscr{W}_0^{\mathrm{HF}}(\omega,t')dt' \right) |\widetilde{0}(\omega,t)\rangle, \qquad (1)$$

$$|\widetilde{0}(\omega,t)\rangle = \exp(-\hat{\kappa}(\omega,t))|0\rangle, \qquad (2)$$

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where $|0\rangle$ denotes the unperturbed SCF wave function and $|\tilde{0}\rangle(\omega,t)$ is the phase-isolated form of the TDHF wave function.[23] The antihermitian orbital rotation operator is given by

$$\hat{\kappa}(\omega,t)=\sum_{ai}\ (\kappa_{ai}(\omega,t)\hat{E}_{ai}-\kappa_{ai}^{*}(\omega,t)\hat{E}_{ai}^{\dagger}), \tag{3}$$

and $\hat{E}_{ai}$ are the usual generators of the unitary group. Here and in the following we adopt the convention that the indices $ijkl$ denote occupied orbitals, $abcd$ virtual, and $pqrs$ general orbitals.

We define the TDHF quasi-energy $\mathscr{W}_0^{\mathrm{HF}}$, which can be calculated as

$$\mathscr{W}_0^{\mathrm{HF}}=\left\langle \tilde{0}(\omega,t)\left|\hat{H}-i\,\frac{\partial}{\partial t}\right|\tilde{0}(\omega,t)\right\rangle. \tag{4}$$

The orbital rotation parameters κ_{ai} are determined by requiring that the TDHF wave function fulfills the Frenkel principle:[24]

$$\left\langle \tilde{0}(\omega,t)\left|\left[\tilde{E}_{\mu}(\omega,t),\left(\hat{H}-i\,\frac{\partial}{\partial t}\right)\right]\right|\tilde{0}(\omega,t)\right\rangle=0,$$

$$\mu\in\{(ai),(ia)\} \tag{5}$$

as a time-dependent variation condition, with the generators of the unitary group in the time-dependent basis $\tilde{E}_{pq}(\omega,t)$ defined as

$$\tilde{E}_{pq}(\omega,t)=\exp(-\hat{\kappa}(\omega,t))\hat{E}_{pq}\ \exp(+\hat{\kappa}(\omega,t)). \tag{6}$$

In the presence of oscillating external fields we write the Hamiltonian as

$$\hat{H}=\hat{H}^{(0)}+\hat{h}_Q^{(1)}(\omega_Q,t)+\hat{h}_W^{(1)}(\omega_W,t)+\cdots\ , \tag{7}$$

$$\hat{h}_Q^{(1)}(\omega,t)=(f_Q(+\omega)e^{+i\omega t}+f_Q(-\omega)e^{-i\omega t})\hat{Q}, \tag{8}$$

where $\hat{Q}$ is the one-electron operator describing the external potential and f_Q the corresponding field strength.

Expanding Eq. (5) in a power series in the field strengths up to first order, one obtains the response equation

$$\langle 0|[\hat{E}_{\mu},[\hat{H}^{(0)},\hat{\kappa}^{(1)}]]|0\rangle-i\,\frac{\partial}{\partial t}\langle 0|[\hat{E}_{\mu},\hat{\kappa}^{(1)}]|0\rangle$$

$$=\langle 0|[\hat{E}_{\mu},\hat{h}^{(1)}]|0\rangle. \tag{9}$$

Equation (9) is usually rewritten with the Ansatz

$$\kappa_{\mu}^{(1)}(\omega,t)=f(+\omega)e^{+i\omega t}\kappa_{\mu}^{(1)}(+\omega)+f(-\omega)e^{-i\omega t}\kappa_{\mu}^{(1)}(-\omega), \tag{10}$$

and the matrices

$$A_{\mu\nu}=\langle 0|[\hat{E}_{\mu},[\hat{H}^{(0)},\hat{E}_{\nu}^{\dagger}]]|0\rangle$$

and

$$B_{\mu\nu}=\langle 0|[\hat{E}_{\mu},[\hat{E}_{\nu},\hat{H}^{(0)}]]|0\rangle, \tag{11}$$

leading to the well-known form of the first-order TDHF response equation:[23,25–28]

$$\left[\begin{pmatrix}\mathbf{A}&\mathbf{B}\\ \mathbf{B}&\mathbf{A}\end{pmatrix}-2\omega\begin{pmatrix}1&0\\0&-1\end{pmatrix}\right]\begin{pmatrix}\kappa^{(1)}(+\omega)\\ \kappa^{(1)}(-\omega)\end{pmatrix}=-2\begin{pmatrix}h^{(1)}\\ h^{(1)}\end{pmatrix}. \tag{12}$$

Alternatively, Eq. (9) can be evaluated using the technique of one-index transformations,[29] writing the first term as a Fock matrix element calculated from a Hamiltonian with one-index-transformed integrals,

$$\langle 0|[\hat{E}_{\mu},[\hat{\kappa}^{(1)}(\omega),\hat{H}^{(0)}]]|0\rangle=F_{\mu}\{[\kappa^{(1)}(\omega),H^{(0)}]\}, \tag{13}$$

$$F_{pq}\{[\kappa^{(1)}(\omega),H^{(0)}]\}$$

$$=[\kappa^{(1)}(\omega),h^{(0)}]_{pq}+\sum_{rs}\ D_{rs}([\kappa^{(1)}(\omega),g]_{rspq}-\tfrac{1}{2}[\kappa^{(1)}(\omega),g]_{rqps}) \tag{14}$$

$$=\kappa_{pq}^{(1)}(\omega)(\epsilon_p-\epsilon_q)+\sum_{rs}\ \kappa_{sr}^{(1)}(\omega)(n_s-n_r)\times(g_{rspq}-\tfrac{1}{2}g_{rqps}), \tag{15}$$

where g_{pqrs} are the usual two-electron integrals in Mulliken notation and ϵ_p and n_p unperturbed SCF orbital energies and occupation numbers, respectively. Inserting this into Eq. (9) and evaluating the remaining commutators, one obtains

$$\kappa_{ia}^{(1)}(\omega)=\frac{1}{\epsilon_i-\epsilon_a+\omega}\left(h_{ia}^{(1)}+\sum_{rs}\ \kappa_{sr}^{(1)}(\omega)(n_s-n_r)\times\left(g_{rsia}-\frac{1}{2}\,g_{rais}\right)\right). \tag{16}$$

This equation can be expanded in a power series in the two-electron integrals,

$$\kappa_{ia}^{(1,n)}(\omega)=\frac{1}{\epsilon_i-\epsilon_a+\omega}\left(h_{ia}^{(1)}+\sum_{rs}\ \kappa_{sr}^{(1,n-1)}(\omega)(n_s-n_r)\times\left(g_{rsia}-\frac{1}{2}\,g_{rais}\right)\right), \tag{17}$$

starting from the uncoupled zeroth-order solution

$$\kappa_{ia}^{(1,0)}(\omega)=\frac{h^{(1)}}{\epsilon_i-\epsilon_a+\omega}. \tag{18}$$

The respective expansion of the TDHF polarizability is defined by

$$\alpha^{(n)}(-\omega;\omega)=-2\sum_{ia}\ (\kappa_{ia}^{(1,n)}(\omega)h_{ai}^{(1)}-\kappa_{ai}^{(1,n)}(\omega)h_{ia}^{(1)}). \tag{19}$$

The power series (17)–(19) are equivalent to the MBPT expansion of the TDHF orbital rotation parameters and polarizabilities.[21] For the first- and higher-order contributions of these series, Sadlej introduced the term *apparent correlation* to distinguish them from the so-called *true correlation* contributions.[22] These many-body contributions are actually self-consistency effects, which describe the relaxation of the Hartree–Fock mean field in the external field. As

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mentioned in Ref. 2, the TDMP2 method and the SDT-MBPT(2) method differ only in the treatment of these relaxation effects.

In TDMP2, the full orbital relaxation is accounted for by calculating the correlation contributions to the polarizabilities as second derivatives of the time-dependent second-order Møller–Plesset quasi-energy:

$$\alpha_{QW}^{\mathrm{TDMP2}}(-\omega;\omega)=\alpha_{QW}^{\mathrm{TDHF}}(-\omega;\omega)+\Delta\alpha_{QW}^{\mathrm{TDMP2}}(-\omega;\omega), \tag{20}$$

$$\Delta\alpha_{QW}^{\mathrm{TDMP2}}(-\omega;\omega)=-\frac{\partial^2(\Delta\mathscr{W}_0^{\mathrm{MP2}}(\omega,t))}{\partial f_Q(-\omega)\partial f_W(+\omega)}, \tag{21}$$

with respect to the strengths of two oscillating electric fields, where $\Delta\mathscr{W}_0^{\mathrm{MP2}}$ is defined as

$$\Delta\mathscr{W}_0^{\mathrm{MP2}}(\omega,t)=\tfrac{1}{2}(\langle\widetilde{\Psi}_0^{(1)}(\omega,t)|\hat{V}|\widetilde{0}(\omega,t)\rangle + \langle\widetilde{0}(\omega,t)|\hat{V}|\widetilde{\Psi}_0^{(1)}(\omega,t)\rangle). \tag{22}$$

In the last equation $\hat{V}$ is the electron fluctuation potential and $|\widetilde{\Psi}_0^{(1)}(\omega,t)\rangle$ is the first-order Møller–Plesset correction for the wave function in the phase-isolated form.[2] These equations have been implemented recently also by Aiga and Itoh,[30] who call this method quasi-energy derivative MP2.

In the correlation contribution of SDT-MBPT(2) the orbital relaxation is approximated in zeroth order of the two-electron integrals, i.e., only the second-order true correlation diagrams are included, which are also only second order in the two-electron integrals.[20] The higher-order terms of the expansion (17) for the orbital rotation parameters would be included successively in the higher orders of the double perturbation theory of Refs. 18–20.

III. TECHNICAL DETAILS

Polarizability calculations are very sensitive to the construction of the one-particle basis sets. Especially if higher-rank polarizabilities are to be computed, standard basis sets, taken from the literature, must be augmented carefully by polarization functions with appropriate exponents and angular momenta.

For atoms it is clear from group theoretical arguments that to get the contributions from electrons in orbitals with an angular momentum l to the linear response to a multipolar electric field $Q_{l'}$, one has to include functions with angular momenta in the range $l\otimes l'=|l-l'|,\ldots,|l+l'|$. Hence, for electrons in p orbitals one needs at least d functions for the dipole polarizability, f functions for the quadrupole polarizability, etc.

A generalization of this rule to molecules is not straightforward. For linear molecules it follows from group theoretical arguments that to describe the contribution from electrons in orbitals with the quantum number l_z^{orb} to the polarizability component $\alpha_{lm,l'm}$ polarization functions with $l_z^{\mathrm{pol}}=l_z^{\mathrm{orb}}\pm m$ must be included. Together with the selection rules for the polarizability tensors

$$C_{\infty v}:\quad \alpha_{lm,l'm'}\begin{cases}\neq 0 & m=m'\\ =0 & m\neq m'\end{cases} \tag{23}$$

$$D_{\infty h}:\quad \alpha_{lm,l'm'}\begin{cases}\neq 0 & m=m' \text{ and } l+l' \text{ even}\\ =0 & m\neq m' \text{ or } l+l' \text{ odd};\end{cases} \tag{24}$$

this suggests the rule of thumb that for an appropriate treatment of all components of the polarizability tensor $\alpha_{l,l'}$ with $l>l'$ the polarization functions should have angular momenta up to $l^{\mathrm{pol}}=l_z^{\mathrm{orb}}+l'$. However, a rigorous rule similar to the one for atoms cannot be devised for molecules.

In our calculations we kept the bond distances for CO, N_2, and NO^+ fixed at the following experimental distances: $R_{C-O}=2.132$ a.u., $R_{N-N}=2.074$ a.u., and $R_{N-O}=2.008\,78$ a.u. For the CN^- anion we used the same bond length $R_{C-N}=2.210\,98$ a.u. as in Ref. 31.

In the calculations for CO and CN^- we put the carbon atom on the positive z axis; for NO^+ the oxygen atom was positioned on the positive z axis.

For all three atoms C, N, and O we started with the construction of the basis sets with the correlation-consistent aug-cc-pV5Z basis of Woon and Dunning.[32] From these basis sets we took the $(15s9p)/[7s6p]$ subsets, which we augmented by two diffuse s and p functions with exponents determined by extrapolating the most diffuse exponents as even tempered series ($\zeta_s=0.0152$, 0.0059 for C; 0.0192, 0.0071 for N and 0.0235, 0.0084 for O and $\zeta_p=0.0970$, 0.0035 for C; 0.0128, 0.0044 for N and 0.0155, 0.0054 for O).

To these sets we kept on adding a diffuse and a steep d function at a time, until with eight functions ($\zeta_{d1-d8}=\zeta_{p4-p11}$) the TDHF dipole polarizabilities for all four molecules were converged within 0.1%. Subsequently, we contracted the innermost four d functions according to pattern (22), where the contraction coefficients were determined by a scheme devised by Sadlej.[33] In this scheme the contraction coefficients of polarization functions, having common exponents with the highest occupied atomic orbital, are obtained by scaling the coefficients of this orbital with $\alpha_i^{\Delta l/2}$, where α_i is the exponent of the primitive Gaussian function and Δl the difference in the angular momenta of the highest occupied orbital and the polarization function. The TDHF dipole polarizabilities of all four molecules are affected by this contraction by less than 0.3%.

In a similar fashion we added five f functions ($\zeta_{f1-f5}=\zeta_{p5-p9}$), which were collated in (2111) contractions, and three g functions ($\zeta_{f1-f5}=\zeta_{p6-p8}$), which were left uncontracted.

In Figs. 1–3 we give information about the convergence behavior of the multipole–multipole polarizabilities in the CHF approximation during the optimization of the one-particle basis sets, starting with the $[9s8p]$ subset augmented by two primitive d functions, i.e., the smallest basis set that gave reliable dipole polarizabilities. As can be seen from these plots, it is indeed the case that for linear molecules the convergence of the higher-rank polarizability tensors $\alpha_{lm,l'm}$ is determined by the degree of freedom described by the index m. The quadrupole polarizability component $\alpha_{22,22}$, for example, increases during augmentation of the basis with f functions between 30% and 60%, while the components $\alpha_{20,20}$ and $\alpha_{21,21}$ are almost unaffected by the f functions.

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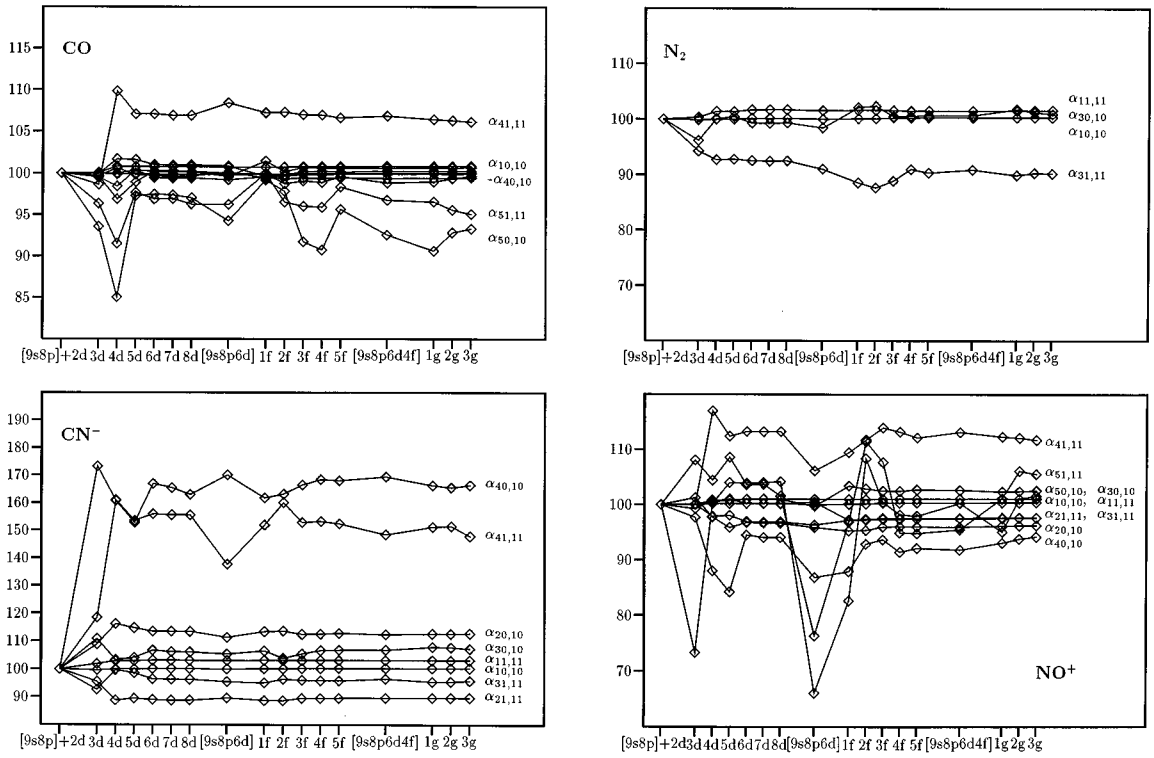


FIG. 1. Convergence of the CHF results with the basis set parameters for the components of the polarizability tensors $\alpha_{1,l}$ with $l=1,2,3,4,5$. The polarizabilities are given in arbitrary units, with the values for the $[9s8p]+2d$ basis normalized to 100. The static dipole, dipole–quadrupole and dipole–octupole polarizabilities for the final $[9s8p6d4f3g]$ basis are listed in the Tables II–V, the results for the higher-rank polarizabilities (in a.u.) with this basis are as follows: $\alpha_{40,10}$: 108.7 (CO), 257.2 (CN^-), −14.7 NO^+; $\alpha_{41,11}$: 112.5 (CO), 220.0 (CN^-), −17.4 NO^+; $\alpha_{50,10}$: 231.0 (CO), 86.0 (N_2), 650.3 (CN^-), 37.4 (NO^+); $\alpha_{51,11}$: 229.4 (CO), 95.9 (N_2), 579.3 (CN^-), 46.5 (NO^+).

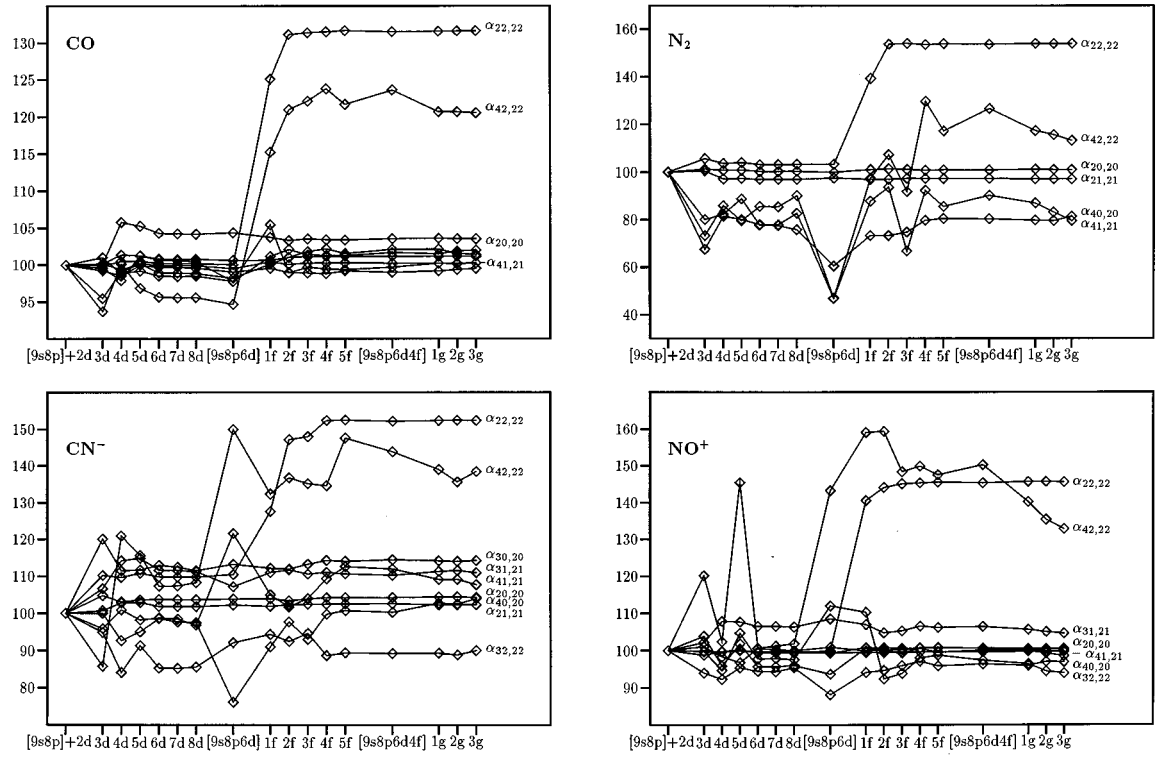


FIG. 2. Convergence of the CHF results with the basis set parameters for the components of the polarizability tensors $\alpha_{2,2}$, $\alpha_{2,3}$ and $\alpha_{2,4}$. The polarizabilities are given in arbitrary units, with the values for the $[9s8p]+2d$ basis normalized to 100. The static quadrupole polarizabilities for the final $[9s8p6d4f3g]$ basis are listed in the Tables II–V, the results for the higher-rank polarizabilities (in a.u.) with this basis are as follows: $\alpha_{30,20}$: 269.2 (CO), 729.9 (CN^-), −31.9 NO^+; $\alpha_{31,21}$: 278.8 (CO), 668.3 (CN^-), −37.3 NO^+; $\alpha_{32,22}$: 90.4 (CO), 284.1 (CN^-), −10.6 NO^+; $\alpha_{40,20}$: 969.6 (CO), 479.0 (N_2), 3532.6 (CN^-), 183.3 NO^+; $\alpha_{41,21}$: 940.8 (CO), 472.5 (N_2), 3250.0 (CN^-), 192.5 NO^+; $\alpha_{42,22}$: 372.3 (CO), 191.5 (N_2), 1522.4 (CN^-), 66.9 NO^+.

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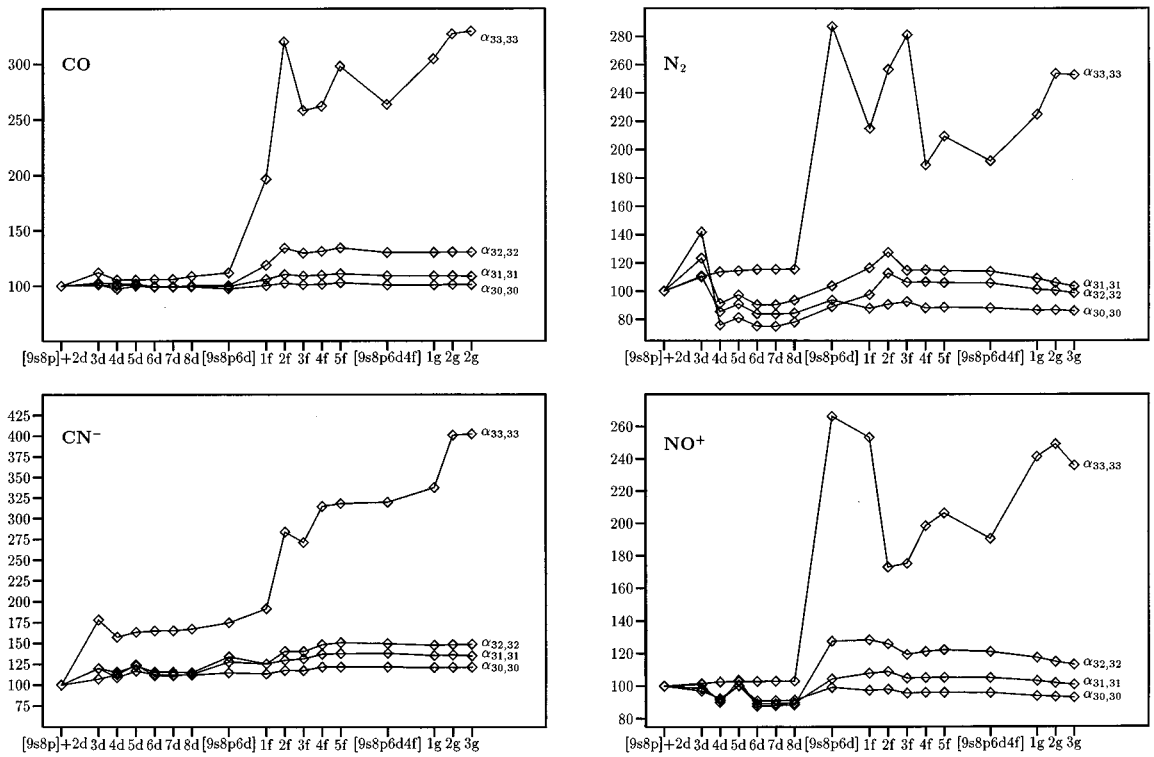


FIG. 3. Convergence of the CHF results with the basis set parameters for the components of the octupole polarizability. The polarizabilities are given in arbitrary units, with the values for the $[9s8p]+2d$ basis normalized to 100. The static octupole polarizabilities (in a.u.) for the final $[9s8p6d4f3g]$ basis are as follows: $\alpha_{30,30}$: 1772.6 (CO), 1075.0 (N_2), 9030.3 (CN^-), 351.5 NO^+; $\alpha_{31,31}$: 1636.5 (CO), 9773.5 (N_2), 8343.0 (CN^-), 322.4 NO^+; $\alpha_{32,32}$: 980.2 (CO), 760.9 (N_2), 6403.7 (CN^-), 223.3 NO^+; $\alpha_{33,33}$: 442.2 (CO), 403.3 (N_2), 4016.7 (CN^-), 94.6 NO^+.

The rule of thumb mentioned above holds in a good approximation if the differences $l-l'$ are small. The off-diagonal polarizability tensors $\alpha_{1,4}$, $\alpha_{1,5}$, and $\alpha_{2,4}$ are affected perceptibly by basis functions with higher angular momenta. But at least for the four diatomics studied in the present investigation, the off-diagonal polarizability tensors with larger differences $l-l'$ are much smaller than polarizability tensors of the type $\alpha_{l,l}$ and $\alpha_{l,l+1}$, which contribute to interaction energies in a $1/R$ expansion in the same order, i.e., to the same induction and dispersion coefficients. Therefore, we expect that these instabilities do not cause larger errors in the dispersion coefficients than the remaining basis set deficiences in the higher-rank tensors $\alpha_{2,2}$, $\alpha_{2,3}$, and $\alpha_{3,3}$.

The final $(17s11p8d5f3g)/[9s8p6d4f3g]$ basis is expected to give values converged within 0.3% for the components of the polarizability tensors $\alpha_{1,1}$, $\alpha_{2,1}$, $\alpha_{3,1}$, $\alpha_{2,2}$, and within 1% for $\alpha_{4,1}$ (CO, N_2,NO^+) and $\alpha_{3,2}$. For the components of the polarizabilities $\alpha_{4,1}$ (CN^-), $\alpha_{5,1}$, $\alpha_{4,2}$, $\alpha_{3,3}$ we estimate, that the remaining basis set deficiency errors are between 1% and 5%, depending on the difference $l-l'$ and on the index m.

For the atom–diatom complexes we give the dispersion coefficients in the usual LLM convention,[34,35] which is defined by an expansion of the dispersion energy in Legendre polynomials:[36]

$$E^{(\mathrm{disp})} = -\sum_{n=0}^{\infty} R^{-n} \sum_{L=0}^{n-4} C_n^{(L)} P_L(\cos\,\theta). \tag{25}$$

For the dispersion coefficients of the dimers $(CO)_2$ and $(N_2)_2$ we adopt the definitions of the so-called LLL convention derived by Wormer,[26,37] so that we can compare our results directly with the SDT-MBPT (2) results of the Refs. 19 and 38. From the dispersion coefficients in the LLL convention, the dispersion interaction for diatom–diatom complexes can be calculated as follows:[39]

$$\begin{aligned} E^{(\mathrm{disp})} = -\sum_{n=0}^{\infty} R^{-n} \sum_{L_A L_B L} C_n^{(L_A L_B L)} \\ \times \sum_{M_A M_B M} \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} C_{M_A}^{L_A}(\theta_A, \phi_A) \\ \times C_{M_B}^{L_B}(\theta_B, \phi_B) C_M^{L}(\theta, \phi), \end{aligned} \tag{26}$$

where θ_A, ϕ_A, θ_B, ϕ_B, θ, and ϕ are the Euler angles specifying the orientation of the two molecules and the intermolecular distance vector in a space-fixed frame.

Formulas for the transformation between the LLL and the LLM convention have been given for example by Visser *et al.*[26]

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TABLE II. Multipole moments, static polarizabilities and Cauchy moments for CO (in a.u.).

	SCF/TDHF	MP2/TDMP2	Literature	DOSD/Exp.
Q_{10}	0.104	−0.109	−.186,[b] −.1024[i]	−0.048[k]
Q_{20}	−1.530	−1.491	−1.524,[b] −1.5195[i]	−1.44[l]
Q_{30}	−4.424	−3.459	−3.879,[b] −3.908[j]	
Q_{40}	−10.687	−8.997	−9.848[j]	
$\alpha_{10,10}$	14.465	15.60	17.14,[a] 16.22,[b] 15.74[c] 15.59,[d] 16.30[e]	15.46[f]
$\alpha_{11,11}$	11.271	11.97	11.88,[a] 11.79,[b] 11.83[c] 12.02,[d] 11.73[e]	11.89[f]
$\alpha_{20,10}$	11.378	13.93	13.00,[a] 13.82[g]	
$\alpha_{21,11}$	15.899	17.49	16.39,[a] 16.70[g]	
$\alpha_{30,10}$	53.424	58.16		
$\alpha_{31,11}$	59.218	62.13		
$\alpha_{20,20}$	127.36	141.2	133.5[b], 144.1[d]	
$\alpha_{21,21}$	141.21	152.5	145.5[b]	
$\alpha_{22,22}$	52.71	57.7	55.5[b]	
$S_{10,10}(0)$	13.42	13.37		14.00[h]
$S_{10,10}(-1)$	10.57	10.87		11.13[f]
$S_{10,10}(-3)$	23.45	26.66		26.28[f]
$S_{10,10}(-4)$	41.36	49.56		51.56[f]
$S_{11,11}(0)$	13.38	13.32		14.00[h]
$S_{11,11}(-1)$	8.81	8.98		9.03[f]
$S_{11,11}(-3)$	19.63	21.70		21.46[f]
$S_{11,11}(-4)$	42.03	47.76		46.61[f]

[a]SDT-MBPT(2)+TDHF EPV terms at $R_{C\text{-}O}=2.132$ a.u., Ref. 38.
[b]SDT-MBPT(2) at $R_{C\text{-}O}=2.14$ a.u., Ref. 35.
[c]CEPA, Ref. 42.
[d]MBPT4 at $R_{C\text{-}O}=2.132$ a.u., Ref. 43.
[e]SOPPA, Ref. 44.
[f]Constrained pseudo-DOSD, Ref. 48.
[g]CI, Ref. 49.
[h]TRK sum rule.
[i]MBPT4 at $R_{C\text{-}O}=2.132$ a.u., Ref. 50.
[j]SDCI at $R_{C\text{-}O}=2.132$ a.u., Ref. 50.
[k]Exp., Ref. 51.
[l]Exp., Ref. 52.

As in our previous work,[1] we calculated the dispersion coefficients from the frequency-dependent polarizabilities by a numerical N-point Gauss–Chebyshev integration, as described in Ref. 19:

$$\frac{1}{2\pi}\int_0^\infty \alpha^A(i\omega)\alpha^B(i\omega)d\omega = \frac{1}{4N}\sum_{j=1}^{N}\frac{\alpha^A(i\cot(\phi_j))\alpha^B(i\cot(\phi_j))}{\sin^2(\phi_j)}, \tag{27}$$

with the grid points $\phi_j=\pi(2j-1)/4N$.

For all molecules studied, we calculated all considered multipole polarizabilities at the grid points for $N=10$, 15, and 20. Comparison of the dispersion coefficients obtained with 15 and 20 grid points showed, that the numerical integration for $N=15$ is converged within the number of digits given in the tables. Effective spectra were fitted to the TDMP2 results for the static polarizabilities and the dynamic polarizabilities at these totally 45 grid points

$$\alpha_{lm,l'm}(-\omega;\omega)=\sum_j \frac{f^{(j)}_{lm,l'm}}{(\varepsilon^{(j)}_{lm,l'm})^2-\omega^2}, \tag{28}$$

using a Levenberg–Marquard fit.[40] These effective spectra can be used to combine the TDMP2 polarizabilities for the molecules CO, N_2, CN^-, and NO^+ with other dynamic polarizabilities given in the literature to obtain van der Waals coefficients for complexes not considered in the present study.

We also used these effective spectra to calculate correlated (TDMP2) Cauchy moments

$$S_{lm,l'm}(k)=\sum_j (\epsilon^{(j)}_{lm,l'm})^k f^{(j)}_{lm,l'm} \tag{29}$$

for $k=0$, -1, -3, -4, while the TDHF values for the Cauchy moments were calculated directly from the complete TDHF or RPA spectra.

IV. RESULTS AND DISCUSSION

In Tables II–V we have compiled the first multipole moments, the dipole, dipole–quadrupole, dipole–octupole, and quadrupole polarizabilities, as well as some Cauchy moments for the dipole polarizabilities of the four molecules studied. Similar to the polarizabilities, the MP2 multipole

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TABLE III. Multipole moments, static polarizabilities and Cauchy moments for N_2 (in a.u.).

	SCF/TDHF	MP2/TDMP2	Literature	DOSD/Exp.
Q_{20}	−0.930	−1.193	−1.138,[e] −1.1131,[a] −1.149[i]	−1.09[j]
Q_{40}	−7.408	−6.537	−6.801,[e] −6.67[a]	−8.0[k]
$\alpha_{10,10}$	15.026	14.29	14.77,[a] 14.68,[b] 15.46[d] 13.41,[e] 14.13,[f] 14.59[i]	14.80[c]
$\alpha_{11,11}$	9.823	10.12	10.13,[a] 10.04,[b] 9.98[d] 9.87,[e] 9.90,[f] 9.34[i]	10.21[c]
$\alpha_{30,10}$	28.611	38.91	38.28[a]	
$\alpha_{31,11}$	30.116	38.13		
$\alpha_{20,20}$	94.33	104.3	103.83,[a] 96.76,[d] 98.0[e]	
$\alpha_{21,21}$	97.30	109.2	107.40,[a] 99.27,[d] 100.6[e]	
$\alpha_{22,22}$	46.00	46.9	42.53,[a] 44.48,[d] 45.3[e]	
$S_{10,10}(0)$	13.46	13.44	13.89[h]	14.00[g]
$S_{10,10}(-1)$	10.96	10.72	10.91[h]	10.84[c]
$S_{10,10}(-3)$	24.11	22.18	23.82[h]	23.65[c]
$S_{10,10}(-4)$	41.83	37.18	41.13[h]	40.84[c]
$S_{11,11}(0)$	13.41	13.43	14.03[h]	14.00[g]
$S_{11,11}(-1)$	8.69	8.71	8.65[h]	8.81[c]
$S_{11,11}(-3)$	13.47	14.48	13.11[h]	14.80[c]
$S_{11,11}(-4)$	20.51	23.07	19.89[h]	24.23[c]

[a]SDQ-MBPT(4) at $R_{N\text{-}N}$=2.074 32 bohr, Ref. 7.
[b]MCSCF, Ref. 53.
[c]Constrained pseudo-DOSD, Ref. 54.
[d]SDT-MBPT(2)+EPV correction at $R_{N\text{-}N}$=2.068 bohr, Ref. 19.
[e]SDT-MBPT(2) at $R_{N\text{-}N}$=2.068 bohr, Ref. 35.
[f]SOPPA, Ref. 44.
[g]TRK sum rule.
[h]SOPPA, Ref. 45.
[i]MBPT(4) at $R_{N\text{-}N}$=2.068 bohr, Ref. 55.
[j]Exp., Ref. 56.
[k]Exp., Ref. 57.

TABLE IV. Multipole moments, static polarizabilities and Cauchy moments for CN^- (in a.u.).

	SCF/TDHF	MP2/TDMP2	Literature
Q_{10}	−0.162	−0.294	−0.291,[a] −0.265[b]
Q_{20}	−3.327	−3.722	
Q_{30}	−4.324	−3.378	
Q_{40}	−16.937	−15.503	
$\alpha_{10,10}$	32.511	36.37	36.69,[a] 37.77[b] 37.32,[c] 32.38[d]
$\alpha_{11,11}$	24.523	27.80	27.92,[a] 28.34[b] 28.02,[c] 24.08[d]
$\alpha_{20,10}$	22.553	31.88	
$\alpha_{21,11}$	20.906	30.40	
$\alpha_{30,10}$	120.92	190.0	
$\alpha_{31,11}$	111.19	163.8	
$\alpha_{20,20}$	426.08	560.5	
$\alpha_{21,21}$	422.24	554.2	
$\alpha_{22,22}$	240.81	289.8	
$S_{10,10}(0)$	13.42	13.32	(14.00[e])
$S_{10,10}(-1)$	15.27	15.72	
$S_{10,10}(-3)$	87.00	110.31	
$S_{10,10}(-4)$	266.91	393.53	
$S_{11,11}(0)$	13.39	13.30	(14.00[e])
$S_{11,11}(-1)$	12.72	13.18	
$S_{11,11}(-3)$	64.03	81.36	
$S_{11,11}(-4)$	201.54	287.34	

[a]MBPT(2), Ref. 31.
[b]MBPT(4), Ref. 31.
[c]CCSD, Ref. 31.
[d]SOPPA, Ref. 44.
[e]TRK sum rule.

TABLE V. Multipole moments, static polarizabilities and Cauchy moments for NO^+ (in a.u.).

	SCF/TDHF	MP2/TDMP2	Literature
Q_{10}	−0.254	−0.074	
Q_{20}	0.519	0.398	
Q_{30}	1.155	0.779	
Q_{40}	−3.829	−3.089	
$\alpha_{10,10}$	9.222	8.82	9.18,[a] 8.75[b]
$\alpha_{11,11}$	5.721	5.86	5.70,[a] 5.73[b]
$\alpha_{20,10}$	−1.716	−2.67	
$\alpha_{21,11}$	−3.098	−3.55	
$\alpha_{30,10}$	15.390	18.34	
$\alpha_{31,11}$	17.852	19.75	
$\alpha_{20,20}$	40.609	43.38	
$\alpha_{21,21}$	45.221	48.13	
$\alpha_{22,22}$	16.722	16.65	
$S_{10,10}(0)$	13.43	13.29	(14.00[c])
$S_{10,10}(-1)$	8.62	8.47	
$S_{10,10}(-3)$	11.58	10.63	
$S_{10,10}(-4)$	15.89	13.79	
$S_{11,11}(0)$	13.41	13.34	(14.00[c])
$S_{11,11}(-1)$	6.64	6.64	
$S_{11,11}(-3)$	6.30	6.72	
$S_{11,11}(-4)$	8.44	9.38	

[a]TDCHF, Ref. 46.
[b]MP2, Ref. 47.
[c]TRK sum rule.

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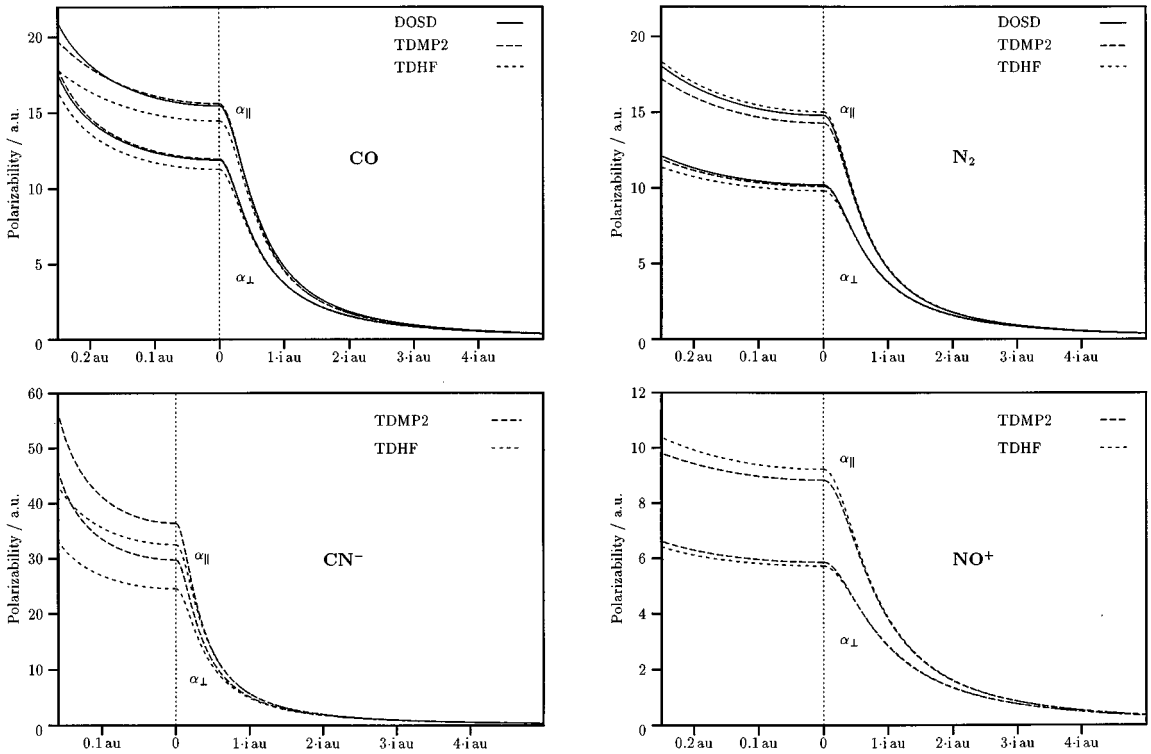


FIG. 4. The dynamic dipole polarizabilities for CO, N_2, CN^-, and NO^+. The DOSD curves for CO and N_2 have been calculated from the effective spectra given Refs. 54 and 48, respectively.

moments were calculated as energy derivatives. In Fig. 4 the frequency-dependent dipole polarizabilities are plotted.

In Tables VI–XI we give the dispersion coefficients for CO, $(CO)_2$, N_2, CN^-, NO^+, and $(N_2)_2$, which were calculated from the frequency-dependent polaritabilities, and in Tables XII–XV, effective spectra for the monomers are compiled. We compare our values with data taken from the literature.[41–59] For CO and N_2 we can compare our results with the recommended constrained dipole oscillator strength distribution (DOSD) data of Kumar and Meath, which are estimated by the authors to have an error range of less than 1%, the *ab initio* SDT-MBPT(2) data of Wormer and coworkers and the results of a recent DFT study of van Gisbergen *et al.*[41]

A. Carbon Monoxide

For the CO molecule, the TDMP2 results compare very well with the reference data. Our static polarizabilities are in good agreement with the CEPA results of Werner and Meyer[42] and the finite-field MBPT(4) results of Diercksen and Sadlej.[43] The slightly larger differences to the SOPPA results of Sauer and Oddershede[44] are probably due to deficiencies in the basis sets used for the SOPPA calculation, which were optimized for magnetizabilities, but not for polarizabilities. The differences between the TDMP2 values and the SDT-MBPT(2) results of Rijks and Wormer[38] and Hettema *et al.*[35] are also small for the perpendicular component $\alpha_{11,11}$, but pronounced for the longitudinal dipole polarizability $\alpha_{10,10}$. We give a more detailed discussion of this point later in this section.

Our final results for the static dipole polarizabilities differ by less than 1% from the DOSD values, and the Cauchy moments are also improved considerably by the TDMP2 correlation contributions to the TDHF numbers, with an error range of about 0.5%–4% for the TDMP2 results. This reflects the accuracy of the dynamic polarizabilities plotted in Fig. 4. On the imaginary axis, the TDMP2 results differ only in the region around $i\omega=1$ a.u. by more than 1% from the DOSD curve. Of course, on the real axis the errors in the TDMP2 polarizabilities increase significantly as ω approaches the first allowed transition frequency, because the TDMP2 method is not able to correlate excitation energies. The single-excitation poles are the same as on the TDHF level and the double-excitation poles occurring in the second-order correlation contributions are at the positions of SCF orbital energy differences.[2] The lack of correlation of the transition energies or poles is a structural problem, inherent in any finite-order MBPT-based response theory and could not be resolved by using third- or fourth-order time-dependent MBPT instead of a second-order approach. However, for frequencies well below the first allowed transition this is only of minor importance, as can seen be from Fig. 4.

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TABLE VI. Dispersion coefficients for the rare gas complexes of CO (LLM convention).

n	L	TDHF	TDMP2	Literature	DOSD[b]
He·CO					
6	0	9.95	10.56	10.866[a]	10.69
6	2	0.83	0.93	1.126[a]	0.99
7	1	−25.4	−29.5	−28.683[a]	
7	3	1.6	1.3	0.5896[a]	
8	0	245	265	263.39[a]	
8	2	260	277	274.91[a]	
8	4	−11	−11	−9.897[a]	
9	1	−1203	−1334		
9	3	−634	−604		
9	5	34	29		
10	0	6404	7126		
10	2	9621	10 426		
10	4	2031	1994		
10	6	−111	−91		
Ne·CO					
6	0	19.34	22.11	23.8,[c] 23.075,[d] 22.407[e]	21.87
6	2	1.58	1.90	1.96,[c] 2.736,[d] 2.270[e]	2.00
7	1	−47.4	−60.2	−57.554,[d] −57.237[e]	
7	3	2.8	2.5	1.792,[d] 1.031[e]	
8	0	513	604	592.1,[d] 590.61[e]	
8	2	504	581	571.503,[d] 567.769[e]	
8	4	−20	−21	−20.66,[d] −18.83[e]	
9	1	−2416	−2942	−2719.8[d]	
9	3	−1197	−1237	−1250.9[d]	
9	5	62	58	49.90[d]	
10	0	14 373	17 646	16 065[d]	
10	2	20 257	23 979	23 036[d]	
10	4	3848	4076	4037.3[d]	
10	6	−201	−182	−204[d]	
Ar·CO					
6	0	68.02	72.51	76.5,[c] 75.806,[d] 73.597[e]	72.26
6	2	5.84	6.53	6.52,[c] 9.4192,[d] 7.8522[e]	6.81
7	1	−185.1	−215.1	−205.96,[d] −204.86[e]	
7	3	12.6	10.4	8.141,[d] 5.492[e]	
8	0	2211	2402	2378.3,[d] 2362.1[e]	
8	2	1836	1970	1946.8,[d] 1928.1[e]	
8	4	−89	−85	−84.77,[d] −78.40[e]	
9	1	−10 415	−11 710	−10 897[d]	
9	3	−4384	−4216	−4283.1[d]	
9	5	271	231	211[d]	
10	0	76 911	85 243	79 784[d]	
10	2	90 318	98 338	948 59.8[d]	
10	4	13 284	13 123	13 007[d]	
10	6	−875	−722	−830.7[d]	
Kr·CO					
6	0	97.03	102.75	106,[c]109.63,[d] 106.43[e]	102.5
6	2	8.38	9.30	9.06,[c] 13.74,[d] 11.46[e]	9.67
7	1	−269.3	−309.9	−303.87,[d] −302.24[e]	
7	3	18.9	15.5	12.81,[d] 8.924[e]	
8	0	3424	3681	3769.5,[d] 3737.1[e]	
8	2	2648	2822	2858.9,[d] 2826.7[e]	
8	4	−133	−126	−129.8,[d] −120.5[e]	
9	1	−16 039	−17 887	−17 165[d]	
9	3	−6261	−5989	−6227.0[d]	
9	5	407	343	326.2[d]	
10	0	131 260	142 730	139 930[d]	
10	2	141 650	152 560	152 097[d]	
10	4	18 540	18 225	18 397[d]	
10	6	−1310	−1071	−1271.2[d]	
Xe·CO					
6	0	144.63	152.47	162.8,[d] 158.06[e]	151.6
6	2	12.55	13.87	20.6,[d] 17.23[e]	14.31
7	1	−410.1	−468.6	−463.09,[d] −460.64[e]	
7	3	30.0	24.6	21.15,[d] 15.29[e]	
8	0	5792	6154	6549.9,[d] 6475.4[e]	

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TABLE VI. (*Continued*.)

n	L	TDHF	TDMP2	Literature	DOSD[b]
Xe-CO					
8	2	4014	4256	4363.1,[d]4300.0[e]	
8	4	−210	−197	−207.6,[d]−193.6[e]	
9	1	−26 888	−29 743	−29 500[d]	
9	3	−9279	−8863	−9258.2[d]	
9	5	642	539	527.6[d]	
10	0			282 700[d]	
10	2			269 299[d]	
10	4			25 924[d]	
10	6			−2030.8[d]	

[a]He polarizabilities from explicitly correlated calculations of Ref. 58 combined with SDT-MBPT(2) polarizabilities for CO at $R_{C\text{-}O}=2.14$ a.u., Ref. 35.
[b]Constrained pseudo-DOSD, Ref. 48.
[c]Adiabatic local density approximation (ALDA), Ref. 41.
[d]SDT-MBPT(2)+TDHF EPV terms polarizabilities for CO at $R_{C\text{-}O}=2.132$ a.u. of Ref. 38 combined with SDT-MBPT(2) polarizabilities for Ne, Ar, Kr, and Xe, Ref. 34.
[e]SDT-MBPT(2) polarizabilities for Ne, Ar, Kr, and Xe of Ref. 34 combined with SDT-MBPT(2) polarizabilities for CO at $R_{C\text{-}O}=2.14$ a.u., Ref. 35.

The dispersion coefficients for the rare gas complexes of CO and for the $(CO)_2$ dimer are given in Tables XIII and IX, respectively. For the isotropic C_6^0 coefficients the TDMP2 results are in very good agreement with the DOSD reference values with errors less than 1.5%. The largest deviations are obtained for the He·CO (1.2%) and Ne·CO (1.1%) complexes, for which we have used the TDMP2 polarizabilities of Ref. 2. For the anisotropic C_6^2 or C_6^{022} coefficients, which are obtained as integrals of an isotropic polarizability and the anisotropic dipole polarizability $\Delta\alpha=\alpha_{10,10}-\alpha_{11,11}$ of CO, the relative deviations between the TDMP2 results and the DOSD values are about 3%–5%, only for the C_6^2 coefficient for He·CO we obtain a slightly larger error of ≈7%. The coefficients C_6^{220}, C_6^{222}, and C_6^{224} for the $(CO)_2$ dimer are obtained as integrals of two anisotropic polarizabilities. For these coefficients the error of the TDMP2 numbers is within ≈7% about twice the error for the C_6^{022} coefficient.

In comparison with the TDHF numbers, which deviate from the DOSD reference by 13%–20% for the C_6^2 or C_6^{022} coefficients and ≈22% for the C_6^{220}, C_6^{222}, C_6^{224} coefficients, the TDMP2 results provide a significant improvement, lowering the errors by a factor of 3–4.

As pointed out in Ref. 35, the SDT-MBPT(2) method cannot cope with the strong correlation effects in the CO molecule. The C_6^2 coefficients of Hettema *et al.*[35] are too large by about the same amount as the TDHF numbers were to small. The errors in the previous SDT-MBPT(2) results of Refs. 34 and 38 are even two times larger, because in these calculations TDHF exclusion principle violating (EPV) terms have been included in the polarizabilities for CO, for which it was found later that they should be omitted.[20] Therefore, the SDT-MBPT(2) results for the anisotropic C_6 coefficients of the $(CO)_2$ dimer show larger discrepancies with the DOSD values than the TDHF results.

The DFT results in the adiabatic local density approximation (ALDA) given by van Gisbergen *et al.*[41] have for the isotropic coefficients about the same accuracy as the TDHF values, but for the anisotropic coefficients the performance of the DFT method of Ref. 41 is considerable better than for

TABLE VII. Dispersions coefficients for the $(CO)_2$ dimer with $R_{C\text{-}O}=2.132$ bohr (LLL convention).

n	L_A	L_B	L	TDHF	TDMP2	Literature	DOSD
6	0	0	0	74.69	81.25	89.14,[a]83.8[b]	81.31[c]
6	0	2	2	14.33	16.37	24.78,[a]15.9[b]	17.08[c]
6	2	2	0	0.25	0.30		0.33[c]
6	2	2	2	0.68	0.81		0.87[c]
6	2	2	4	7.30	8.76	18.27[a]	9.41[c]
7	0	1	1	354.0	421.1	422.9[a]	
7	0	3	3	−37.4	−31.9	−26.6[a]	
7	1	2	1	10.0	12.5		
7	1	2	3	−50.0	−62.4	−86.3[a]	
7	2	3	1	−0.6	−0.5		
7	2	3	3	−1.3	−1.2		
7	2	3	5	−22.2	−20.0	−23.7[a]	
8	0	0	0	2989	3328	3357[a]	
8	0	2	2	4601	5050	5254[a]	
8	0	4	4	−299	−294		
8	1	1	0	301	385		
8	1	1	2	−1524	−1948	−2659[a]	
8	1	3	2	−37	−34		
8	1	3	4	189	176		
8	2	2	0	49	57		
8	2	2	2	−195	−221		
8	2	2	4	1220	1404	1974[a]	
8	2	4	2	−4	−4		
8	2	4	4	−10	−10		
8	2	4	6	−205	−212		
8	3	3	0	0.6	0.4		
8	3	3	2	−0.9	−0.7		
8	3	3	4	−4	−3		
8	3	3	6	−133	−99		

[a]SDT-MBPT(2)+TDHF EPV terms, calculated at $R_{C\text{-}O}=2.132$ bohr; Ref. 19.
[b]Adiabatic local density approximation (ALDA), Ref. 41.
[c]Calculated from the constrained pseudo-DOSD of Ref. 48.

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TABLE VIII. Dispersion coefficients for the rare gas complexes of N_2 (LLM convention).

n	L	TDHF	TDMP2	Literature	DOSD[b]
$He \cdot N_2$					
6	0	9.87	10.01	9.7617[a]	10.23
6	2	1.12	0.99	0.804 63[a]	1.05
8	0	212	226	219.17[a]	
8	2	179	211	201.85[a]	
8	4	−6	−6	−4.823[a]	
10	0	5013	5418	5184.1[a]	
10	2	5820	6965	6555.97[a]	
10	4	1068	1223	1140.3[a]	
10	6	−64	−65	−52.53[a]	
$Ne \cdot N_2$					
6	0	19.24	21.02	23.1,[c] 21.525,[d] 20.232[e]	20.97
6	2	2.10	2.03	2.38,[c] 2.639,[d] 1.625[e]	2.09
8	0	452	522	504.7,[d] 497.58[e]	
8	2	354	447	424.32,[d] 421.52[e]	
8	4	−10	−13	−9.693,[d] −9.070[e]	
10	0	11 500	13 750	12 431,[d] 12 842[e]	
10	2	12 542	16 332	15 135,[d] 15 102[e]	
10	4	2065	2521	2170,[d] 2337[e]	
10	6	−117	−130	−70.2,[d] −100[e]	
$Ar \cdot N_2$					
6	0	67.13	68.10	73.5,[c] 69.843,[d] 65.515[e]	68.69
6	2	7.97	6.98	8.02,[c] 9.0758,[d] 5.6192[e]	7.34
8	0	1961	2077	2028.8,[d] 1982.3[e]	
8	2	1257	1486	1406.5,[d] 1385.4[e]	
8	4	−45	−51	−40.70,[d] −38.60[e]	
10	0	63 380	68 200	63 406,[d] 64 192[e]	
10	2	55 864	67 245	62 278.5,[d] 62 025.4[e]	
10	4	6752	7892	6642.3,[d] 7262.3[e]	
10	6	−490	−508	−294.3,[d] −409.1[e]	
$Kr \cdot N_2$					
6	0	95.57	96.22	102,[c] 100.67,[d] 94.4[e]	97.28
6	2	11.51	9.97	11.2,[c] 13.25,[d] 8.2189[e]	10.57
8	0	3053	3192	3224.5,[d] 3138.8[e]	
8	2	1810	2122	2055.3,[d] 2013.8[e]	
8	4	−67	−75	−62.50,[d] −59.43[e]	
10	0	109 610	115 490	112 510,[d] 112 990[e]	
10	2	88 005	104 750	100 203,[d] 99 567.6[e]	
10	4	9300	10 888	9260.0,[d] 10 190[e]	
10	6	−724	−749	−451.36,[d] −623.65[e]	
$Xe \cdot N_2$					
6	0	142.08	142.26	148.84,[d] 139.5[e]	143.4
6	2	17.39	14.90	19.92,[d] 12.39[e]	15.83
8	0	5205	5359	5632.3,[d] 5451.6[e]	
8	2	2752	3196	3124.5,[d] 3029.7[e]	
8	4	−106	−117	−100.1,[d] −95.43[e]	
10	0			230 700,[d] 229 260[e]	
10	2			178 568,[d] 176 685[e]	
10	4			12 784,[d] 14 243[e]	
10	6			−721.75,[d] −990.20[e]	

[a]He polarizabilities from explicitly correlated calculations of Ref. 58 combined with SDT-MBPT(2) polarizabilities for N_2 at $R_{N\text{-}N}=2.068$ a.u., Ref. 35.
[b]Constrained pseudo-DOSD, Ref. 48.
[c]Adiabatic local density approximation (ALDA), Ref. 41.
[d]SDT-MBPT(2)+TDHF EPV terms polarizabilities for N_2 at $R_{N\text{-}N}=2.068$ a.u. of Ref. 38 combined with SDT-MBPT(2) polarizabilities for Ne, Ar, Kr, and Xe, Ref. 34.
[e]SDT-MBPT(2) polarizabilities for Ne, Ar, Kr, and Xe of Ref. 34 combined with SDT-MBPT(2) polarizabilities for N_2 at $R_{N\text{-}N}=2.068$ a.u., Ref. 35.

TDHF. The anisotropic coefficients obtained by the ALDA method for van der Waals complexes of CO have a similar accuracy as the TDMP2 coefficients. This probably reflects that the density functional theory has less difficulties with near degeneracies and static correlation effects than Hartree–Fock theory.

From Sec. II it is clear that the difference between the time-dependent Møller–Plesset perturbation theory and the

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TABLE IX. Dispersion coefficients for the rare gas complexes of CN^- (LLM convention).

		$He\cdot CN^-$		$Ne\cdot CN^-$		$Ar\cdot CN^-$		$Kr\cdot CN^-$		$Xe\cdot CN^-$	
n	L	TDHF	TDMP2	TDHF	TDMP2	TDHF	TDMP2	TDHF	TDMP2	TDHF	TDMP2
6	0	16.72	18.02	31.89	37.24	117.97	128.08	170.14	183.56	256.88	276.05
6	2	1.35	1.39	2.51	2.82	9.87	10.19	14.39	14.75	22.00	22.42
7	1	−29.5	−38.9	−54.5	−78.8	−220.0	−293.1	−323.2	−427.7	−498.3	−657.1
7	3	0.2	0.5	0.4	0.9	1.9	4.0	2.9	6.0	4.8	9.7
8	0	571	672	1150	1471	4977	5840	7661	8885	12 818	14 661
8	2	443	573	848	1184	3199	4194	4651	6070	7116	9261
8	4	−10	−12	−18	−23	−81	−93	−122	−139	−193	−219
9	1	−2090	−2736	−4052	−5825	−17 565	−23 319	−26 872	−35 415	−44 431	−58 168
9	3	−960	−1009	−1789	−2047	−7039	−7494	−10 280	−10 892	−15 742	−16 647
9	5	27	28	48	57	212	226	319	338	506	534
10	0	22 351	28 973	46 850	66 303	233 180	296 330	383 870	477 330		
10	2	23 464	32 855	47 353	72 098	208 900	293 180	324 070	450 090		
10	4	4153	5172	7799	10 500	28 997	37 010	41 568	53 071		
10	6	−167	−150	−303	−297	−1306	−1222	−1953	−1829		

diagrammatic double perturbation theory will strongly depend on the convergence of the expansion of $\kappa^{(1)}$ in powers of the two-electron integrals and on the difference between the uncoupled and the converged, coupled solution.

As indicated in Sec. I, the importance of orbital relaxation is itself strongly dependent on static correlation effects. To visualize this phenomenon, we plotted in Fig. 5 the CHF dipole polarizabilities of the molecules studied as a function of the order of the orbital rotation parameters in the two-electron integrals [see Eq. (19)]. These plots clearly show that the MBPT expansion of the CHF polarizabilities and orbital rotation parameters is extremely sensitive to static correlation effects. While the convergence for the component vertical to the bond axis $\alpha_\perp$ is reasonable for all molecules studied, the convergence of the longitudinal component $\alpha_\parallel$ is impeded by a strong interaction between the bonding orbitals and their antibonding counterparts, which is induced by the electric field oriented parallel to the bond axis.

This behavior explains why the TDMP2 and the SDT-MBPT(2) results for the rare gas atoms are very similar, but differ significantly for the triple-bonded molecules N_2 and CO, in particular for the anisotropic dispersion coefficients, where the errors in the TDMP2 results are smaller by a factor between 2 and 7.

As can be seen from Fig. 5, the convergence of the MBPT expansion of $\alpha_\parallel$ is much slower for N_2 than for CO and CN^-. For the NO^+ cation, the MBPT expansion of the

TABLE X. Dispersion coefficients for the rare gas complexes NO^+ (LLM convention).

		$He\cdot NO^+$		$Ne\cdot NO^+$		$Ar\cdot NO^+$		$Kr\cdot NO^+$		$Xe\cdot NO^+$	
n	L	TDHF	TDMP2	TDHF	TDMP2	TDHF	TDMP2	TDHF	TDMP2	TDHF	TDMP2
6	0	6.75	6.83	13.34	14.51	44.93	45.51	63.54	63.90	93.81	93.86
6	2	0.91	0.84	1.73	1.74	6.32	5.81	9.06	8.23	13.54	12.19
7	1	5.5	7.3	10.4	15.0	39.4	51.8	56.8	74.0	85.7	110.6
7	3	−0.5	−0.3	−0.9	−0.6	−4.1	−2.6	−6.1	−3.9	−9.6	−6.1
8	0	115	120	254	288	1116	1163	1751	1801	3020	3062
8	2	111	122	223	263	775	852	1115	1214	1697	1829
8	4	−5	−4	−8	−9	−36	−35	−53	−52	−83	−81
9	1	198	230	411	527	1770	2123	2746	3278	4664	5548
9	3	116	112	224	232	760	748	1063	1046	1526	1517
9	5	−9	−8	−16	−15	−67	−59	−100	−87	−156	−136
10	0	2154	2280	5223	6151	31 044	32 707	55 250	56 914		
10	2	2871	3150	6421	7685	29 241	32 334	46 643	50 965		
10	4	549	589	1074	1225	3266	3570	4384	4809		
10	6	−41	−35	−74	−70	−310	−276	−459	−407		

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TABLE XI. Dispersion coefficients for the $(N_2)_2$ dimer at $R_{N\text{-}N}=2.074$ bohr (LLL convention).

n	L_A	L_B	L	TDHF	TDMP2	Literature	DOSD
6	0	0	0	72.71	71.62	71.99,[a]75.63,[b]77.2[c]	73.41[d]
6	0	2	2	19.21	16.33	21.87,[b]18.7[c]	17.52[d]
6	2	2	0	0.49	0.35	0.59[b]	0.40[d]
6	2	2	2	1.30	0.93	1.57[b]	1.06[d]
6	2	2	4	14.04	10.06	16.99[b]	11.49[d]
8	0	0	0	2426	2549	2489[b]	
8	0	2	2	3111	3562	3476[b]	
8	0	4	4	−144.6	−157.1	−129.9[b]	
8	2	2	0	46.4	45.6	55.5[b]	
8	2	2	2	−156.9	−168.4	−200.4[b]	
8	2	2	4	1087	1104	1332[b]	
8	2	4	2	−2.9	−2.6	−2.7[b]	
8	2	4	4	−7.4	−7.1	−7.5[b]	
8	2	4	6	−154.4	−140.2	−149.6[b]	

[a]MCSCF-LR, Ref. 53.
[b]SDT-MBPT(2)+TDHF EPV terms, calculated at $R_{N\text{-}N}=2.068$ bohr, Ref. 19.
[c]Adiabatic local density approximation (ALDA), Ref. 41.
[d]Calculated from the constrained pseudo-DOSD of Ref. 59.

TABLE XII. Effective spectra for multipole polarizabilities of CO. The spectra reproduce the TDMP2 results at the 46 grid points used for the least square fit with maximum deviations less than 1×10^{-5} a.u. for $\alpha_{10,10}$ and $\alpha_{11,11}$, less than 3×10^{-3} a.u. for $\alpha_{22,22}$ and less than 1×10^{-4} a.u. for the other polarizabilities.

	$\alpha_{10,10}$	$\alpha_{11,11}$	$\alpha_{20,20}$	$\alpha_{21,21}$	$\alpha_{22,22}$
f_1	7.255 634(−1)	2.736 405(−1)	1.065 663(+1)	7.411 152	1.070 934(+1)
ϵ_1	4.370 844(−1)	3.187 255(−1)	4.492 381(−1)	3.180 358(−1)	5.350 333(−1)
f_2	2.092 052	1.089 993	1.373 003(+1)	8.633 890	1.675 075(+1)
ϵ_2	5.403 089(−1)	5.190 361(−1)	5.832 373(−1)	5.300 248(−1)	1.006 679
f_3	2.075 205	1.898 996	2.327 332(+1)	2.096 066(+1)	1.491 224(+1)
ϵ_3	8.296 428(−1)	7.766 301(−1)	8.525 050(−1)	8.172 355(−1)	2.033 552
f_4	2.211 696	2.528 906	2.309 939(+1)	2.419 556(+1)	3.453 516
ϵ_4	1.339 894	1.290 271	1.351 953	1.305 675	5.344 556
f_5	1.766 494	2.4701 172	1.610 592(+1)	1.397 944(+1)	
ϵ_5	2.306 922	2.284 292	2.339 568	2.326 780	
f_6	9.369 902(−1)	1.259 362	7.405 002	6.190 898	
ϵ_6	4.563 039	4.245 757	4.484 727	4.410 465	
f_7	1.455 805	1.567 443	8.080 741	6.799 043	
ϵ_7	1.142 369(+1)	1.057 434(+1)	1.144 878(+1)	1.111 777(+1)	
f_8	2.101 390	2.232 819	9.413 168	6.973 188	
ϵ_8	2.467 644(+1)	2.360 648(+1)	2.371 462(+1)	2.341 297(+1)	

	$\alpha_{20,10}$	$\alpha_{21,11}$	$\alpha_{30,10}$	$\alpha_{31,11}$
f_1	1.665 534	1.397 072	3.746 646	2.698 032
ϵ_1	4.415 238(−1)	3.178 302(−1)	4.352 946(−1)	3.179 547(−1)
f_2	2.841 699	7.758 740(−1)	1.687 950(+1)	4.722 634
ϵ_2	6.338 071(−1)	4.948 102(−1)	7.272 460(−1)	5.040 215(−1)
f_3	−2.877 466	7.497 262(−1)	6.004 909(+1)	7.171 054
ϵ_3	1.376 817	7.838 616(−1)	1.322 680	8.024 277(−1)
f_4	−1.533 586	−1.401 744	−5.943 019(+1)	8.038 165
ϵ_4	3.021 545	1.634 795	1.377 920	1.291 847
f_5	−8.290 433	−1.726 839	1.015 748(+1)	4.465 877
ϵ_5	8.406 227	2.925 176	1.831 146	2.463 851
f_6	9.421 844	−1.381 942(+2)	4.913 812	2.535 699
ϵ_6	9.154 424	9.127 073	3.703 293	4.817 220
f_7	−2.475 606	1.395 331(+2)	4.966 057	5.090 598
ϵ_7	6.860 187(+1)	9.164 070	1.020 402(+1)	1.147 343(+1)
f_8		−1.750 766	7.806 881	5.365 704
ϵ_8		5.451 418(+1)	2.187 515(+1)	2.345 558(+1)

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TABLE XIII. Effective spectra for multipole polarizabilities of N_2. The spectra reproduce the TDMP2 results at the 46 grid points used for the least square fit with maximum deviations less than 1×10^{-5} a.u. for $\alpha_{10,10}$ and $\alpha_{11,11}$ and less than 1×10^{-4} a.u. for the other polarizabilities.

	$\alpha_{10,10}$	$\alpha_{11,11}$	$\alpha_{20,20}$	$\alpha_{21,21}$
f_1	1.287 681	1.107 825	6.302 198	4.922 203
ϵ_1	5.090 718(−1)	5.244 440(−1)	5.346 879(−1)	3.534 763(−1)
f_2	1.560 249	1.111 165	1.098 188(+1)	9.402 686
ϵ_2	5.893 101(−1)	6.660 928(−1)	5.993 062(−1)	5.946 286(−1)
f_3	2.222 139	1.916 125	2.578 617(+1)	2.222 116(+1)
ϵ_3	8.547 186(−1)	9.617 501(−1)	8.692 327(−1)	8.915 481(−1)
f_4	2.372 058	2.748 352	2.768 854(+1)	2.582 841(+1)
ϵ_4	1.299 087	1.536 042	1.378 573	1.416 098
f_5	1.616 156	1.788 062	1.377 988(+1)	1.106 973(+1)
ϵ_5	2.218 741	2.481 044	2.359 313	2.361 705
f_6	8.403 771(−1)	1.134 896	7.192 231	6.106 448
ϵ_6	4.401 183	4.963 204	4.226 155	4.194 147
f_7	1.026 127	1.422 378	4.770 407	4.119 833
ϵ_7	1.201 259(+1)	1.366 597(+1)	1.097 367(+1)	1.136 317(+1)
f_8	2.515 854	2.196 660	1.198 964(+1)	8.943 147
ϵ_8	2.310 763(+1)	2.392 367(+1)	2.293 159(+1)	2.265 006(+1)
	$\alpha_{22,22}$	$\alpha_{30,10}$	$\alpha_{31,11}$	
f_1	2.050 036	2.057 322	7.145 201	
ϵ_1	5.253 722(−1)	4.853 708(−1)	5.285 236(−1)	
f_2	5.441 340	−2.576 201	8.908 671	
ϵ_2	5.909 918(−1)	5.384 812(−1)	9.896 626(−1)	
f_3	1.102 775(+1)	1.795 322(+1)	9.009 223	
ϵ_3	8.622 865(−1)	7.670 181(−1)	1.666 330	
f_4	1.430 054(+1)	8.861 368	3.350 687	
ϵ_4	1.428 710	1.103 503	4.339 137	
f_5	7.600 485	4.076 146	4.146 401	
ϵ_5	2.107 480	2.125 330	1.292 689(+1)	
f_6	4.197 378	4.705 448	5.924 324	
ϵ_6	3.607 878	3.815 346	2.499 476(+1)	
f_7	7.140 406(−1)	2.910 267		
ϵ_7	8.560 848	1.033 134(+1)		
f_8	3.212 235(−1)	8.954 778		
ϵ_8	2.487 028(+1)	2.221 979(+1)		

first-order TDHF response to the longitudinal field component does even diverge.

For higher-rank components we found a similar behavior: if the symmetry of the component of the electric field is Σ^+ (for N_2 Σ_u^+), the convergence is spoiled by the interaction between the bonding orbitals and their antibonding counterparts, while for tensor components with a different symmetry the convergence of the MBPT expansion (19) is reasonably good.

B. Nitrogen

The much stronger static correlation effects for the N_2 molecule as compared to CO affect also the TDMP2 results for the static dipole polarizability (Table III). At variance with the CO molecule, the TDMP2 method is not capable of improving $\alpha_{10,10}$ for N_2, although the TDMP2 result of 14.29 a.u. seems to be better than the SDT-MBPT(2) values of 15.46 a.u.[19] and 13.41 a.u.[35]

However, all other static polarizabilities, including the dipole–octupole component $\alpha_{30,10}$, which is also a response to a field component with Σ_u^+ symmetry, are in good agreement with the SDQ-MBPT(4) results of Maroulis and Thakkar.[7] The somewhat larger difference for the quadrupole polarizability component $\alpha_{22,22}$ is a basis set effect, caused by the small f space used in Ref. 7, that consists of only one primitive function.

Similar to the polarizabilities, the Cauchy moments $S_{10,10}(k)$ are also not improved by the TDMP2 correlation contributions, while the moments $S_{11,11}(k)$ on the TDMP2 level are in significantly better agreement with the DOSD reference values than the TDHF results. Surprisingly, the errors in the second-order polarization propagator approach (SOPPA) results of Ref. 45 show exactly the opposite trend: for $S_{11,11}(k)$ with $k=-1, -3, -4$, their errors are larger than the errors in our TDHF values, while with the same basis set very accurate results for $S_{10,10}(k)$ were obtained.

Despite the fact that the deviations in the static MP2 dipole polarizabilities and Cauchy moments for N_2 are somewhat larger than for CO, the average accuracy of the dynamic dipole polarizabilities for imaginary frequencies is comparable for the two molecules, because for N_2 the error in the first dipole-allowed transition energies is smaller. Hence, the accuracy of the TDMP2 results for the dispersion coefficients for the rare gas complexes of N_2 and for the

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TABLE XIV. Effective spectra for multipole polarizabilities of CN^-. The spectra reproduce the TDMP2 results at the 46 grid points used for the least square fit with maximum deviations less than 3×10^{-5} a.u. for $\alpha_{10,10}$ and $\alpha_{11,11}$ and less than 4×10^{-4} a.u. for the other polarizabilities.

	$\alpha_{10,10}$	$\alpha_{11,11}$	$\alpha_{20,20}$	$\alpha_{21,21}$	$\alpha_{22,22}$
f_1	2.997 327(−1)	2.563 368(−1)	3.724 493	3.298 341	1.754 121
ϵ_1	2.020 343(−1)	2.050 151(−1)	2.026 815(−1)	2.031 277(−1)	2.080 885(−1)
f_2	8.032 585(−1)	5.334 102(−1)	1.404 351(+1)	1.736 343(+1)	7.851 509
ϵ_2	2.755 852(−1)	2.792 232(−1)	2.567 474(−1)	2.458 098(−1)	2.616 810(−1)
f_3	2.193 771	1.841 144	2.232 164(+1)	1.263 404(+1)	1.093 987(+1)
ϵ_3	4.307 778(−1)	4.447 215(−1)	3.819 422(−1)	3.744 259(−1)	3.781 155(−1)
f_4	2.382 587	2.242 205	3.238 255(+1)	2.651 538(+1)	1.402 118(+1)
ϵ_4	7.053 028(−1)	7.619 624(−1)	6.541 069(−1)	6.296 289(−1)	6.042 650(−1)
f_5	2.497 075	2.658 458	2.945 546(+1)	2.856 702(+1)	1.661 892(+1)
ϵ_5	1.259 187	1.382 703	1.114 707	1.063 953	1.033 314
f_6	1.404 505	1.732 161	1.698 790(+1)	1.585 471(+1)	1.202 003(+1)
ϵ_6	2.426 710	2.563 142	2.067 672	1.937 223	1.778 428
f_7	8.053 841(−1)	1.014 201	7.538 529	6.789 704	3.993 205
ϵ_7	6.412 209	6.334 051	4.608 546	4.328 748	3.660 145
f_8	2.934 163	3.024 472	1.619 501(+1)	1.269 254(+1)	5.951 662(−1)
ϵ_8	1.753 729(+1)	1.728 338(+1)	1.624 770(+1)	1.557 411(+1)	1.384 815(+1)
	$\alpha_{20,10}$	$\alpha_{21,11}$	$\alpha_{30,10}$	$\alpha_{31,11}$	
f_1	4.884 655(−1)	2.727 162(−1)	1.702 361	8.823 311(−1)	
ϵ_1	1.953 795(−1)	1.956 843(−1)	1.950 189(−1)	1.942 415(−1)	
f_2	6.719 599(−1)	1.122 160	3.213 629	3.045 025	
ϵ_2	2.350 312(−1)	2.309 200(−1)	2.333 561(−1)	2.257 685(−1)	
f_3	1.149 468	3.721 703(−1)	9.795 166	1.023 353(+1)	
ϵ_3	4.030 289(−1)	3.930 226(−1)	4.500 162(−1)	4.115 764(−1)	
f_4	6.219 295(−1)	1.696 830	1.742 916(+1)	9.561 056	
ϵ_4	7.075 688(−1)	8.922 873(−1)	7.113 617(−1)	7.684 687(−1)	
f_5	−1.327 611	−1.869 190	4.926 669	7.168 786	
ϵ_5	1.090 619	9.658 642(−1)	1.363 979	1.408 618	
f_6	−8.336 774(−1)	−1.091 423	5.613 076	3.351 933	
ϵ_6	1.807 132	1.946 823	2.891 210	2.987 080	
f_7	−1.480 697(+1)	−1.299 403(+1)	3.214 273	2.896 180	
ϵ_7	5.924 501	5.833 847	7.569 169	7.338 640	
f_8	1.501 070(+1)	1.333 333(+1)	1.050 383(+1)	8.761 048	
ϵ_8	6.153 993	6.048 573	1.796 891(+1)	1.747 485(+1)	

$(N_2)_2$ dimer is similar to the accuracy of the coefficients for the analogous complexes of CO. For the isotropic C_6^0 coefficients the TDMP2 values deviate between 0.2% ($Ne\cdot N_2$) and 2.2% ($He\cdot N_2$) from the DOSD reference values, for the anisotropic C_6^2 and C_6^{022} coefficients the errors are about 3%–6% and for the C_6^{220}, C_6^{222}, C_6^{224} coefficients of $(N_2)_2$ the difference between the TDMP2 and the DOSD values are ≈13%. The SDT-MBPT(2) numbers for the C_6^2 coefficients of the rare gas complexes of N_2 deviate by more than 20% from the DOSD results.

Also, the dispersion coefficients obtained by DFT have, for these complexes, larger errors than the TDHF results, because the ALDA method overestimates the static dipole polarizabilities of N_2 by ≈5%, and the static polarizabilities of the rare gases are also overestimated. This leads to a considerable overestimation of the related dispersion coefficients, although the relative anisotropies $\gamma_6^2=C_6^2/C_6^0$ are even somewhat better than for the TDMP2 results.

C. The ions CN^- and NO^+

For the polarizabilities of the ions CN^- and NO^+ there is little reference data available in the literature. Fowler and Diercksen calculated the dipole polarizabilities of CN^- by CHF, MBPT(n) with $n=2,3,4$, and CCSD. Their study is in good agreement with our results for the static polarizabilities (Table IV) and indicates a good convergence for the true correlation contributions of the MBPT expansion for CN^-.

For the static dipole polarizabilities of the NO^+ cation our TDHF results are in good agreement with the values given by Visser and Wormer.[46] On the correlated (TDMP2) level, our result for $\alpha_{10,10}$ is similar to the MP2 value given by Fehér and Martin, while our result for $\alpha_{11,11}$ is about 2% larger than the value given in Ref. 47, due to deficiencies in the d space of the basis used by Fehér and Martin.

In Tables IX and X we give the TDHF and TDMP2 results for the dispersion coefficients of the rare gas complexes of CN^- and NO^+. From the importance of the static correlation effects, which can be estimated by the convergence of the MBPT expansion of the TDHF response (Fig. 5), we expect that our results for the static polarizabilities and the dispersion coefficients for the CN^- anion have a similar accuracy as the results for CO, while for the polarizabilities and the dispersion coefficients of the NO^+ cation we expect similar errors as for the N_2 molecule.

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TABLE XV. Effective spectra for multipole polarizabilities of NO^+. The spectra reproduce the TDMP2 results at the 46 grid points used for the least square fit with maximum deviations less than 1×10^{-5} a.u. for $\alpha_{10,10}$ and $\alpha_{11,11}$, less than 3×10^{-2} a.u. for $\alpha_{22,22}$, and less than 1×10^{-4} a.u. for the other polarizabilities.

	$\alpha_{10,10}$	$\alpha_{11,11}$	$\alpha_{20,20}$	$\alpha_{21,21}$	$\alpha_{22,22}$
f_1	2.385 956	4.585 825(−2)	1.288 344(+1)	2.578 755	1.302 750(+1)
ϵ_1	6.812 109(−1)	3.784 024(−1)	8.365 955(−1)	3.772 822(−1)	1.007 733
f_2	3.343 015	6.454 720(−1)	7.059 202(−1)	9.053 744	1.946 878(+1)
ϵ_2	1.072 993	6.281 384(−1)	1.141 341	9.001 948(−1)	2.256 429
f_3	2.343 642	1.806 452	2.022 400(+1)	2.111 030(+1)	3.511 911
ϵ_3	1.890 063	9.427 880(−1)	1.150 954	1.282 538	1.317 539(+1)
f_4	1.366 012	2.832 741	2.116 513(+1)	1.908 120(+1)	
ϵ_4	3.606 344	1.456 280	1.724 080	1.948 345	
f_5	9.072 488(−1)	2.806 497	1.395 205(+1)	1.564 234	
ϵ_5	8.614 521	2.473 276	2.828 595	2.796 338	
f_6	2.943 268	1.354 125	6.690 284	9.644 145	
ϵ_6	2.333 653(+1)	4.744 854	5.111 957	3.693 877	
f_7		1.048 235	4.894 459	3.908 122	
ϵ_7		1.101 980(+1)	1.273 400(+1)	8.491 758	
f_8		2.800 006	1.068 637(+1)	9.680 415	
ϵ_8		2.452 524(+1)	2.591 300(+1)	2.265 066(+1)	
	$\alpha_{20,10}$	$\alpha_{21,11}$	$\alpha_{30,10}$	$\alpha_{31,11}$	
f_1	2.698 712(−1)	−3.409 927(−1)	1.076 932	3.244 305(−1)	
ϵ_1	6.177 814(−1)	3.774 119(−1)	5.526 004(−1)	3.791 216(−1)	
f_2	−1.868 006(−1)	−2.547 554(−1)	−2.894 406	3.312 972	
ϵ_2	5.982 370(−1)	6.161 223(−1)	5.80 363 (−1)	6.163 735(−1)	
f_3	−2.340 428	−6.296 436(−1)	1.776 605(+1)	7.200 077	
ϵ_3	8.159 786(−1)	9.567 971(−1)	9.539 565(−1)	1.151 832	
f_4	−1.290 537	1.252 752	6.174 270	8.218 467	
ϵ_4	1.201 774	2.529 447	1.457 087	1.697 360	
f_5	2.688 099	6.636 868(−1)	6.802 343	4.357 206	
ϵ_5	1.366 514	5.990 070	3.085 266	3.188 446	
f_6	8.321 612(−1)	−8.354 503(−1)	3.299 442	2.817 587	
ϵ_6	2.837 388	1.110 766(+1)	6.576 293	7.539 931	
f_7	1.312 984(+1)		9.513 319	7.838 216	
ϵ_7	8.403 593		2.164 118(+1)	2.185 901(+1)	
f_8	−1.325 100(+1)				
ϵ_8	8.689487				

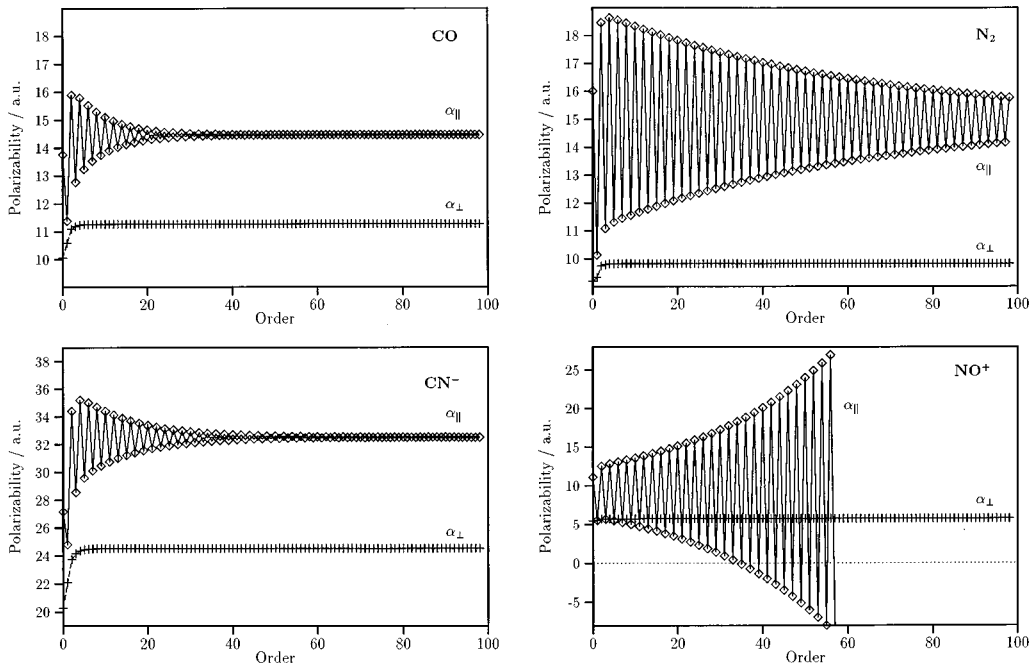


FIG. 5. MBPT expansion of the CHF approximation for the static dipole polarizabilities.

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