Calculation of frequency-dependent polarizabilities using the approximate coupled-cluster triples model CC3

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The calculation of frequency-dependent polarizabilities is discussed for the iterative approximate coupled-cluster singles, doubles and triples model CC3. A new implementation of the linear response functions is reported, which has the same computational $\mathcal{O}(N^7)$ scaling as CC3 ground state calculations and uses an explicitly spin-coupled excitation space. Sample calculations are presented for the static and frequency-dependent polarizabilities of Ne and ethylene, as well as for the static polarizabilities of HF. The largest calculation employs the t-aug-cc-pVTZ basis set for ethylene giving a total of 328 basis functions. The results obtained agree well with the experimental data. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1523905]

I. INTRODUCTION

During the last decade the coupled-cluster model has evolved to the method of choice for the calculation of molecular properties for smaller single configuration dominated systems. When triple excitations are accounted for the electronic structure problem is solved for many molecular properties to an accuracy that is comparable to or even surpasses the one that is obtained in experimental studies. The full relaxation of the triples in the coupled-cluster singles, doubles and triples (CCSDT) model[1,2] has a computational scaling of $\mathcal{O}(N^8)$, where N is the number of basis functions, and is too costly for routine applications. Many models have been suggested where the triples are treated in an approximate fashion, and where the computational scaling thereby has been reduced to $\mathcal{O}(N^7)$. The most favored approach is the noniterative triples model CCSD(T) (see Ref. 3) where the triples contribution is added perturbatively to the coupled-cluster singles and doubles (CCSD) energy. The CCSD(T) model has successfully been used to calculate many molecular properties[4,5] such as equilibrium geometries,[6] atomization energies,[7–9] and vibrational frequencies.[10]

In the noniterative triples models the response functions have poles that are not affected by the triples excitation space and frequency-dependent molecular properties are therefore not determined with the same accuracy as static molecular properties. On the contrary, in iterative triples models the poles are relaxed to the triples excitation space and static and frequency-dependent molecular properties are obtained with a similar quality.[11] In this paper we consider the calculation of the frequency-dependent polarizability using the iterative triples model CC3,[12,13] which as the CCSD(T) model has a computational scaling of (N^7).

CC3 is a member of the coupled-cluster model hierarchy CCS, CC2, CCSD, CC3, and CCSDT which is especially designed to describe frequency-dependent properties. CCS is the coupled-cluster singles model, in CCSD doubles are added and in CC2 the doubles of the CCSD model are approximated using the same strategy as for triples when CCSDT is approximated to give CC3. Excitation energies have been calculated successfully using this hierarchy. The error in the excitation energies is reduced by about a factor 3 at each level for the models CCS, CC2, CCSD, and CC3, and the CC3 excitation energies closely approximate the ones of the CCSDT model.[14] Calculation of frequency-dependent polarizabilities and hyperpolarizabilities have shown similar systematic improvements to the excitation energies.[15–17]

In this paper we describe a new implementation of the CC3 frequency-dependent polarizability, which uses an excitation space that is explicitly spin coupled and has a computational scaling of V^4O^3, where O and V denote the number of occupied and virtual orbitals in the Hartree–Fock (HF) calculation, respectively. CC3 frequency-dependent molecular properties have previously been implemented using a spin-orbital based formalism and with a non-iterative V^4O^4 scaling.[15]

In Sec. II we briefly describe the CC3 model and the determination of frequency-dependent polarizabilities. In Sec. III we discuss the strategy used in our implementation and in Sec. IV some results are reported for the static and frequency-dependent polarizabilities of neon and ethylene and the static polarizability of hydrogenfluoride. In the last section we give some concluding remarks.

II. THE CC3 LINEAR RESPONSE FUNCTION

A. Coupled-cluster theory

In response theory we consider the response of a system described by the Hamiltonian H_0 to a time-dependent perturbation $V(t)$. The full time-dependent Hamiltonian is given as

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$$H(t)=H_0+V(t), \tag{1}$$

where $V(t)$ is Hermitian and can be expanded as a sum over Fourier components

$$V(t)=\sum_{k=-N}^{N} \exp(-i\omega_k t)\sum_X \varepsilon_X(\omega_k)X, \tag{2}$$

where X may be any time-independent Hermitian one-electron operator. To ensure hermiticity of $V(t)$, we require that $\omega_{-k}=-\omega_k$ and $\varepsilon_X(\omega_{-k})=\varepsilon_X(\omega_k)^*$. For the coupled-cluster wave function we use a phase-isolated parametrization, where the oscillating phase factor caused by the so-called level-shift or time-dependent quasienergy $\mathcal{W}(t)$ is explicitly isolated:[11,18–20]

$$|\mathrm{CC}(t)\rangle=\exp\left(-i\int_{t_0}^{t}\mathcal{W}(t')dt'\right)\exp(T(t))|\mathrm{HF}\rangle. \tag{3}$$

In the latter equation $T(t)$ is the field- and time-dependent cluster operator $T(t)=\Sigma_i\Sigma_{\mu_i}t_{\mu_i}(t)\tau_{\mu_i}$—the index $i=1,2,3,...$ denotes the excitation level—and $|\mathrm{HF}\rangle$ is the Hartree–Fock reference for the unperturbed molecule. Orbital relaxation is not treated explicitly, but only approximately through the single excitation manifold of the cluster operator. This avoids a two step approach which would introduce artifacts into the response functions as, e.g., a pole structure incompatible with the exact response function.

The quasienergy $\mathcal{W}(t)$ and the time-dependent cluster equations—which determine the cluster amplitudes t_μ—are obtained by projecting the time-dependent Schrödinger equation onto the Hartree–Fock reference $\langle\mathrm{HF}|$ and the excitation manifold $\langle\mathrm{HF}|\tau_\mu^\dagger\exp(-T(t))$, respectively:

$$\mathcal{W}(t)=\langle\mathrm{HF}|H(t)\exp(T(t))|\mathrm{HF}\rangle, \tag{4}$$

$$\langle\mathrm{HF}|\tau_\mu^\dagger\exp(-T(t))H(t)\exp(T(t))|\mathrm{HF}\rangle-i\dot{t}_\mu(t)=0, \tag{5}$$

where $\dot{t}_\mu(t)$ are the derivatives of the cluster amplitudes with respect to time. The coupled-cluster methods CCS, CCSD, and CCSDT are obtained from the above-given equations by truncating the cluster operator $T(t)$ after, respectively, the single, double or triple excitation level.

B. The CC3 linear response function

The CC3 method is obtained as an approximation to CCSDT by truncating the triples equations at second order in the fluctuation potential.[13] The CC3 model gives linear response properties as, e.g., frequency-dependent polarizabilities—similar as for CCSDT—correct through third order in the fluctuation potential. The response functions for CC3 are most conveniently derived if the quasienergy is combined with the cluster equations to a quasienergy Lagrangian:[12]

$$\begin{aligned}L(t)=&\langle\mathrm{HF}|\hat{H}+[H_0,T_2(t)]|\mathrm{HF}\rangle+\sum_{\mu_1}\bar{t}_{\mu_1}(t)(\langle\mu_1|\hat{H}\\&+[\hat{H},T_2(t)]+[H_0,T_3(t)]|\mathrm{HF}\rangle-i\dot{t}_{\mu_1}(t))\\&+\sum_{\mu_2}\bar{t}_{\mu_2}(t)\Big(\langle\mu_2|\hat{H}_0+[\hat{H},T_2(t)]\\&+\frac{1}{2}[[H_0,T_2(t)],T_2(t)]\\&+[\hat{H},T_3(t)]|\mathrm{HF}\rangle-i\dot{t}_{\mu_2}(t)\Big)\\&+\sum_{\mu_3}\bar{t}_{\mu_3}(t)\Big(\langle\mu_3|[F+\hat{V}(t),T_3(t)]+[\hat{H},T_2(t)]\\&+\frac{1}{2}[[V(t),T_2(t)],T_2(t)]|\mathrm{HF}\rangle-i\dot{t}_{\mu_3}(t)\Big),\end{aligned} \tag{6}$$

where F is the Fock operator. In Eq. (6) we have introduced the similarity transformed operators

$$\hat{O}=\exp(-T_1)O\exp(T_1). \tag{7}$$

The time average of the quasienergy Lagrangian, defined as

$$\{L(t)\}_T=\frac{1}{T}\int_{-T/2}^{T/2}L(t)dt, \tag{8}$$

where T is the least common multiple of periods of the frequencies ω_k of the perturbations in Eq. (2), is variational with respect to the cluster amplitudes t_μ and the Lagrangian multipliers $\bar{t}_\mu$ and thus $2n+1$- and $2n+2$-rules[21,22] can be exploited to calculate derivatives of $\{L(t)\}_T$. The linear response function is obtained as the second derivative of the *real part* of the time-averaged quasienergy Lagrangian,[11,23,24]

$$\langle\langle X;Y\rangle\rangle_\omega=\frac{1}{2}\frac{d^2(\{L(t)\}_T+\{L(t)\}_T^*)}{d\varepsilon_X(-\omega)d\varepsilon_Y(\omega)} \tag{9}$$

$$=\frac{1}{2}\hat{C}^{\pm\omega}\hat{P}(X(-\omega),Y(\omega))\times\left\{\eta^X+\frac{1}{2}\mathbf{F}t^X(-\omega)\right\}t^Y(\omega), \tag{10}$$

where the operator $\hat{P}(X(-\omega),Y(\omega))$ symmetries with respect to a simultaneous permutation of the operators X and Y and the accompanied frequencies and the action of $\hat{C}^{\pm\omega}$ is defined by:

$$C^{\pm\omega}f^{XY}(\omega_X,\omega_Y)=f^{XY}(\omega_X,\omega_Y)+f^{XY}(-\omega_X,-\omega_Y)^*. \tag{11}$$

The elements of the vector η^X and the matrix $\mathbf{F}$ are defined as:

$$\eta_\nu^X=\left(\frac{\partial^2\{L\}_T}{\partial t_\nu\partial\varepsilon_X(\omega_X)}\right)_0, \tag{12}$$

and

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$$F_{\nu\lambda}=\left(\frac{\partial^2\{L\}_T}{\partial t_\nu \partial t_\lambda}\right)_0, \tag{13}$$

where the derivatives are taken at zero perturbation strength, i.e., for the unperturbed system. The vector η^X and the matrix $\mathbf{F}$ contain terms which refer only to the singles and doubles space and are similar in structure to the ones that are obtained in the CCSD model differing only in the way the parameters have been determined. Some contributions to η^X and $\mathbf{F}$, however, refer explicitly to the triples space. We focus in the following on these terms and refer the reader to previous publications on the CCSD linear response function[25] for a detailed description of the terms depending only on the singles and doubles space.

For CC3, η^X may be expressed as

$$\eta^X=\begin{pmatrix}\eta^{X,\mathrm{CCSD}}_{\nu_1}\\ \eta^{X,\mathrm{CCSD}}_{\nu_2}\\ 0\end{pmatrix}+\begin{pmatrix}\eta^{X,\mathrm{CC3}}_{\nu_1}\\ \eta^{X,\mathrm{CC3}}_{\nu_2}\\ \eta^{X,\mathrm{CC3}}_{\nu_3}\end{pmatrix}, \tag{14}$$

where $\eta^{X,\mathrm{CCSD}}$ has the same structure as η^X in the CCSD model, but is calculated from different amplitudes and multipliers, and the second contributions contain the terms originating from triples amplitudes and multipliers. Introducing the short-hand notation $\langle\overline{T}^{(0)}_i|=\Sigma_{\mu_i}\overline{t}^{(0)}_{\mu_i}\langle\mu_i|$, the latter contribution can be written as

$$\eta^{X,\mathrm{CC3}}=\begin{pmatrix}\langle\overline{T}^{(0)}_3|[[X,\tau_{\nu_1}],T^{(0)}_3]|\mathrm{HF}\rangle\\ \langle\overline{T}^{(0)}_3|[[X,\tau_{\nu_2}],T^{(0)}_2]|\mathrm{HF}\rangle\\ \langle\overline{T}^{(0)}_2|[X,\tau_{\nu_3}]|\mathrm{HF}\rangle+\langle\overline{T}^{(0)}_3|[\hat{X},\tau_{\nu_3}]|\mathrm{HF}\rangle\end{pmatrix}. \tag{15}$$

Similarly, the transformed vector $\mathbf{F}t^Y$ has the form:

$$\mathbf{F}t^Y=\begin{pmatrix}(\mathbf{F}^{\mathrm{CCSD}}t^Y)_{\nu_1}\\ (\mathbf{F}^{\mathrm{CCSD}}t^Y)_{\nu_2}\\ 0\end{pmatrix}+\begin{pmatrix}(\mathbf{F}^{\mathrm{CC3}}t^Y)_{\nu_1}\\ (\mathbf{F}^{\mathrm{CC3}}t^Y)_{\nu_2}\\ (\mathbf{F}^{\mathrm{CC3}}t^Y)_{\nu_3}\end{pmatrix}, \tag{16}$$

where the first contribution again has the same structure as in the CCSD model, but is now calculated from the CC3 single and double excitation amplitudes and multipliers. The second contribution contains all terms dealing with triple excitations:

$$\mathbf{F}^{\mathrm{CC3}}t^Y=\begin{pmatrix}\langle\overline{T}^{(0)}_3|[([\tilde{H}^Y,T^{(0)}_2]+[\hat{H}_0,T^Y_2]),\tau_{\nu_1}]|\mathrm{HF}\rangle+\langle\overline{T}^{(0)}_2|[[H_0,T^Y_3],\tau_{\nu_1}]|\mathrm{HF}\rangle\\ \langle\overline{T}^{(0)}_3|[\tilde{H}^Y,\tau_{\nu_2}]|\mathrm{HF}\rangle\\ \langle\overline{T}^{(0)}_2|[\tilde{H}^Y,\tau_{\nu_3}]|\mathrm{HF}\rangle\end{pmatrix}, \tag{17}$$

where we introduced the one-index transformed Hamiltonian $\tilde{H}^Y=[\hat{H}_0,T^Y_1]$. Using Eq. (10) and the above-given expressions for η^X and $\mathbf{F}t^Y$ we may write the CC3 linear response function as

$$\langle\langle X;Y\rangle\rangle^{\mathrm{CC3}}_\omega=\langle\langle X;Y\rangle\rangle^{\mathrm{CCSD}}_\omega+\frac{1}{2}C^{\pm\omega}P(X(-\omega),Y(\omega))\times\left\{\eta^{X,\mathrm{CC3}}t^Y(\omega)+\frac{1}{2}\mathbf{F}^{\mathrm{CC3}}t^X(-\omega)t^Y(\omega)\right\} \tag{18}$$

$$\begin{aligned}=\langle\langle X,Y\rangle\rangle^{\mathrm{CCSD}}_{\omega_Y}&+\frac{1}{2}C^{\pm\omega}P(X(-\omega),Y(\omega))\\ &\times\Big\{\langle\overline{T}^{(0)}_3|[\tilde{X}^Y,T^{(0)}_3]|\mathrm{HF}\rangle\\ &+\langle\overline{T}^{(0)}_3|[\hat{X},T^Y_3(\omega)]|\mathrm{HF}\rangle\\ &+\langle\overline{T}^{(0)}_3|[[X,T^Y_2(\omega)],T^{(0)}_2]|\mathrm{HF}\rangle\\ &+\langle\overline{T}^{(0)}_2|[X,T^Y_3(\omega)]|\mathrm{HF}\rangle+\frac{1}{2}\langle\overline{T}^{(0)}_3|[\tilde{\tilde{H}}^{XY},T^{(0)}_2]\\ &+[\tilde{H}^X,T^Y_2(\omega)]|\mathrm{HF}\rangle\\ &+\langle\overline{T}^{(0)}_2|[\tilde{H}^X,T^Y_3(\omega)]|\mathrm{HF}\rangle\Big\},\end{aligned} \tag{19}$$

where we introduced the one-index transformed one-electron operator $\tilde{X}^Y=[X,T^Y_1(\omega)]$ and the double one-index transformed Hamiltonian $\tilde{\tilde{H}}^{X,Y}=[[\hat{H}_0,T^X_1(-\omega)],T^Y_1(\omega)]$. The contribution $\langle\langle X;Y\rangle\rangle^{\mathrm{CCSD}}_\omega$ has the same structure as the CCSD linear response function, but is now calculated from the CC3 singles and doubles amplitudes and multipliers. All contributions arising from triples amplitudes or multipliers are contained in the second contribution. Explicit formulas for the triples contributions to the CC3 linear response function are given in Table I. Note that the first and second triples term in Eq. (19) are both evaluated from the expression in the first row of Table I; for the first term one-index transformed integrals $\tilde{X}^Y$ and zeroth-order amplitudes are used, whereas the second term is evaluated with the similarity transformed integrals $\hat{X}$ and first-order amplitudes. Likewise the two contributions to the fifth triples term in Eq. (19) are both evaluated from the expression given in the fourth row in Table I using the double one-index transformed Hamiltonian $\tilde{\tilde{H}}^{XY}$ and zeroth-order amplitudes or the single one-index transformed Hamiltonian $\tilde{H}^X$ and first-order amplitudes. The one-index transformed integrals can easily be obtained. The single one-index transformed integrals can be found in Ref. 26. The double one-index transformed integrals are obtained in a similar manner. The formulas needed in order to calculate the single and double one-index transformed integrals can be found in Table II.

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TABLE I. Formulas for the CC3 linear response function.

$\Sigma_{\mu_3}\bar{t}^{(0)}_{\mu_3}\langle\mu_3\vert[X,T_3]\vert\mathrm{HF}\rangle$	$=\frac{1}{2}\Sigma_{abdlemn}\bar{t}^{dea}_{lmn}t^{deb}_{lmn}X_{ab}-\frac{1}{2}\Sigma_{ijdlemf}\bar{t}^{def}_{lmj}t^{def}_{lmi}X_{ij}$
$\Sigma_{\mu_3}\bar{t}^{(0)}_{\mu_3}\langle\mu_3\vert[[X,T^Y_2(\omega_Y)],T^{(0)}_2]\vert\mathrm{HF}\rangle$	$=-\Sigma_{aibjckdl}(\bar{t}^{abc}_{ilk}t^{Yab}_{ij}t^{cd}_{kl}X_{jd}+\bar{t}^{adc}_{ijk}t^{Yab}_{ij}t^{cd}_{kl}X_{lb})$
$\Sigma_{\mu_2}\bar{t}^{(0)}_{\mu_2}\langle\mu_2\vert[X,T^Y_3(\omega_Y)]\vert\mathrm{HF}\rangle$	$2\Sigma_{aibjck}\bar{t}^{ab}_{ij}[(t^{Yabc}_{ijk}-t^{Yabc}_{kji})X_{kc}]$
$\Sigma_{\mu_3}\bar{t}^{(0)}_{\mu_3}\langle\mu_3\vert[\hat{H},T_2]\vert\mathrm{HF}\rangle$	$=2\Sigma_{aibjck}t^{ab}_{ij}(\Sigma_d\bar{t}^{acd}_{ikj}\hat{g}_{ckdb}-\Sigma_l\bar{t}^{acb}_{ikl}\hat{g}_{dljm})$
$\Sigma_{\mu_2}\bar{t}^{(0)}_{\mu_2}\langle\mu_2\vert[\hat{H}^X,T^Y_3(\omega_Y)]\vert\mathrm{HF}\rangle$	$=\Sigma_{abijck}\bar{t}^{ab}_{ij}[(t^{Yabc}_{ijk}-t^{Yabc}_{kji})\tilde{F}^X_{kc}$ $+\Sigma_d(2t^{Ybcd}_{jik}-t^{Ybcd}_{kij}-t^{Ybcd}_{jki})\tilde{g}^X_{dckd}$ $-\Sigma_l(2t^{Ybac}_{jkl}-t^{Ybac}_{lkj}-t^{Ybac}_{jlk})\tilde{g}^X_{kilc}]$

C. The CC3 first-order amplitude equation

In order to determine the linear response function in Eq. (19) we need to solve equations for the zeroth-order amplitudes and multipliers as well as for the first-order amplitudes. The zeroth-order equations have been solved as described in Refs. 12, 13, and 27 for the amplitudes and in Ref. 28 for the multipliers. The first-order amplitudes may be determined from

$$(\mathbf{A}-\omega\mathbf{1})t^Y=-\xi^Y, \tag{20}$$

where the components of the vector ξ^Y are defined as

$$\xi^Y_\mu=\left(\frac{\partial^2\{L\}_T}{\partial\bar{t}_\mu\partial\varepsilon_Y(\omega_Y)}\right)_0 \tag{21}$$

giving

$$\xi^Y=\begin{pmatrix}\xi^{Y_{\mathrm{CCSD}}}_{\nu_1}\\ \xi^{Y_{\mathrm{CCSD}}}_{\nu_2}\\ 0\end{pmatrix}+\begin{pmatrix}0\\ \xi^{Y_{\mathrm{CC3}}}_{\nu_2}\\ \xi^{Y_{\mathrm{CC3}}}_{\nu_3}\end{pmatrix}. \tag{22}$$

The last term which contains the contributions originating from the triples amplitudes is given by

$$\xi^{Y,\mathrm{CC3}}=\begin{pmatrix}0\\ \langle\mu_2\vert[Y,T^{(0)}_3]\vert\mathrm{HF}\rangle\\ \langle\mu_3\vert[\hat{Y},T^{(0)}_3]+\frac{1}{2}[[Y,T^{(0)}_2],T^{(0)}_2]\vert\mathrm{HF}\rangle\end{pmatrix}. \tag{23}$$

The CC3 Jacobian is

$$\mathbf{A}=\begin{pmatrix}\langle\mu_1\vert[\hat{H}_0+[H_0,T^{(0)}_2],\tau_{\nu_1}]\vert\mathrm{HF}\rangle & \langle\mu_1\vert[\hat{H}_0,\tau_{\nu_2}]\vert\mathrm{HF}\rangle & \langle\mu_1\vert[H_0,\tau_{\nu_3}]\vert\mathrm{HF}\rangle\\ \langle\mu_2\vert[\hat{H}_0+[\hat{H}_0,T^{(0)}_2+T^{(0)}_3],\tau_{\nu_1}]\vert\mathrm{HF}\rangle & \langle\mu_2\vert[\hat{H}_0+[H_0,T^{(0)}_2],\tau_{\nu_2}]\vert\mathrm{HF}\rangle & \langle\mu_2\vert[\hat{H}_0,\tau_{\nu_3}]\vert\mathrm{HF}\rangle\\ \langle\mu_3\vert[[\hat{H}_0,T_2],\tau_{\nu_1}]\vert\mathrm{HF}\rangle & \langle\mu_3\vert[\hat{H}_0,\tau_{\nu_2}]\vert\mathrm{HF}\rangle & \varepsilon_{\mu_3}\delta_{\mu_3\nu_3}\end{pmatrix}.$$

The solution to the first-order amplitude equations can be obtained using iterative algorithms where explicit reference is made only to the subspace of all singles and doubles excitations.

The inverse of a general matrix may be expressed as

$$\begin{pmatrix}N & P\\ Q & S\end{pmatrix}^{-1}=\begin{pmatrix}T^{-1} & -T^{-1}PS^{-1}\\ -S^{-1}QT^{-1} & S^{-1}+S^{-1}QT^{-1}PS^{-1}\end{pmatrix}, \tag{24}$$

where

$$T=N-PS^{-1}Q. \tag{25}$$

TABLE II. Formulas for single and double one-index transformed integrals.

$\tilde{h}^X_{pq}=\hat{h}^X_{pq}+\hat{h}^X_{p\bar{q}}$
$\tilde{g}^X_{pqrs}=\hat{g}^X_{pqrs}+\hat{g}^X_{p\bar{q}rs}+\hat{g}^X_{pq\bar{r}s}+\hat{g}^X_{pqr\bar{s}}$
$\hat{h}^{X,Y}_{\bar{a}\bar{i}}=-\Sigma_{bj}\hat{h}_{jb}t^{Xa}_jt^{Yb}_i$
$\hat{g}^{X,Y}_{\bar{a}\bar{i}rs}=-\Sigma_{bj}\hat{g}_{jbrs}t^{Xa}_jt^{Yb}_i$
$\hat{g}^{X,Y}_{ar\bar{s}\bar{i}}=-\Sigma_{bj}\hat{g}_{jrsb}t^{Xa}_jt^{Yb}_i$

Identifying all single and double excitations with the first component of Eq. (24) and the triples excitations with the second component of Eq. (24), the singles and doubles component of the first-order amplitude equation can be expressed as

$$(\mathbf{A}^{\mathrm{eff}}(\omega)-\omega\mathbf{1})t^Y_{\mathrm{SD}}=-\xi^{Y,\mathrm{eff}}_{\mathrm{SD}}, \tag{26}$$

where

$$\xi^{Y,\mathrm{eff}}_{\mathrm{SD}}=\xi^{Y_{\mathrm{CCSD}}}+\begin{pmatrix}0\\ \langle\mu_2\vert[Y,T_3]\vert\mathrm{HF}\rangle\end{pmatrix}-\sum_{\mu_3}\begin{pmatrix}\langle\mu_1\vert[H_0,\tau_{\mu_3}]\vert\mathrm{HF}\rangle\\ \langle\mu_2\vert[\hat{H}_0,\tau_{\mu_3}]\vert\mathrm{HF}\rangle\end{pmatrix}(\varepsilon_{\mu_3}-\omega)^{-1}\times\left\langle\mu_3\left\vert[\hat{Y},T_3]+\frac{1}{2}[[Y,T_2],T_2]\right\vert\mathrm{HF}\right\rangle, \tag{27}$$

and

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$$\mathbf{A}^{\mathrm{eff}}(\omega)=\mathbf{A}^{\mathrm{CCSD}}+\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ \langle\mu_2|[[H_0,T_3],\tau_{\nu_1}]|\mathrm{HF}\rangle & \mathbf{0}\end{pmatrix}$$
$$-\sum_{\mu_3}\begin{pmatrix}\langle\mu_1|[H_0,\tau_{\mu_3}]|\mathrm{HF}\rangle\\ \langle\mu_2|[\hat{H}_0,\tau_{\mu_3}]|\mathrm{HF}\rangle\end{pmatrix}(\varepsilon_{\mu_3}-\omega)^{-1}$$
$$\times(\langle\mu_3|[[\hat{H}_0,T_2],\tau_{\nu_1}]|\mathrm{HF}\rangle,$$
$$\langle\mu_3|[\hat{H}_0,\tau_{\nu_2}]|\mathrm{HF}\rangle). \quad (28)$$

Again, $\mathbf{A}^{\mathrm{CCSD}}$ has the same structure as the Jacobian in the CCSD model, but differs in the amplitudes. The linear transformation of a trial vector containing singles and doubles components with $\mathbf{A}^{\mathrm{eff}}(\omega)$ has been described in detail in Refs. 12, 13, and 27.

The right-hand side consists of the term that has the same structure as the vector ξ^Y in the CCSD model (but different amplitudes) and two correction terms. The first correction term is the triples contribution which enters directly into the doubles component of the ξ^Y and the second correction term arises from the partitioning of the triples into the singles and doubles space. Let us consider evaluating the last term in more detail. The singles component of this term can be rewritten as

$$\left\langle {a \atop i}|[H_0,\tau_{\mu_3}]|\mathrm{HF}\right\rangle(\varepsilon_{\mu_3}-\omega)^{-1}\langle\mu_3|[\hat{Y},T_3]$$
$$+\tfrac{1}{2}[[Y,T_2],T_2]|\mathrm{HF}\rangle=-\left\langle {a \atop i}|[H_0,\check{T}_3^Y]|\mathrm{HF}\right\rangle \quad (29)$$

and the doubles component as

$$\left\langle {ab \atop ij}|[\hat{H}_0,\tau_{\mu_3}]|\mathrm{HF}\right\rangle(\varepsilon_{\mu_3}-\omega)^{-1}\left\langle \mu_3|[\hat{Y},T_3]\right.$$
$$\left.+\frac{1}{2}[[Y,T_2],T_2]|\mathrm{HF}\right\rangle=-\left\langle {ab \atop ij}|[\hat{H}_0,\check{T}_3^Y]|\mathrm{HF}\right\rangle, \quad (30)$$

where

$$\check{T}_3^Y=\frac{1}{G}\sum_{\substack{abc\\ijk}}\check{T}_{ijk}^{Y^{abc}}\tau_{ai,bj,ck} \quad (31)$$

and

$$\check{T}_{ijk}^{Y^{abc}}=-\frac{1}{\varepsilon_{ai,bj,ck}-\omega}P_{ijk}^{abc}\left\langle {abc \atop ijk}\right|[\hat{Y},T_3]$$
$$\left.+\frac{1}{2}[[Y,T_2],T_2]\right|\mathrm{HF}\right\rangle=P_{ijk}^{abc}\check{t}_{ijk}^{Y^{abc}}. \quad (32)$$

In the evaluation of Eq. (19) we need the triples component of the solution vector in Eq. (20). This vector is obtained as

$$t_{\mu_3}^Y=-(\varepsilon_{\mu_3}-\omega)^{-1}\times(\langle\mu_3|[\hat{Y},T_3]+\tfrac{1}{2}[[Y,T_2],T_2]|\mathrm{HF}\rangle$$
$$+\langle\mu_3|[[\hat{H}_0,T_1^Y(\omega_Y)],T_2]+[\hat{H}_0,T_2^Y(\omega_Y)]|\mathrm{HF}\rangle). \quad (33)$$

Each term in Eq. (33) has been evaluated in Table III. It should be noted that the third and fourth terms in Eq. (33) are both evaluated from the fourth term in Table III. For the third term we use one-index transformed integrals and zeroth-order amplitudes whereas we use the normal similarity transformed integrals and first-order amplitudes in the fourth term. The exact form for $t_{\mu_3}^Y$ is

$$T_{ijk}^{Y^{abc}}=-\frac{1}{\varepsilon_{ijk}^{abc}-\omega}P_{ijk}^{abc}\Big[\frac{1}{2}\sum_d t_{ijk}^{dbc}\hat{Y}_{ad}-\frac{1}{2}\sum_l t_{ljk}^{abc}\hat{Y}_{li}$$
$$-\sum_{ld}t_{il}^{ac}t_{jk}^{bd}Y_{ld}+\sum_d t_{ij}^{ad}\tilde{g}_{ckbd}^Y-\sum_l t_{il}^{ab}\tilde{g}_{cklj}^Y$$
$$+\sum_d t_{ij}^{Y^{ad}}\hat{g}_{ckbd}-\sum_l t_{il}^{Y^{ab}}\hat{g}_{cklj}\Big]=P_{ijk}^{abc}t_{ijk}^{Y^{abc}}, \quad (34)$$

where $\tilde{g}^Y$ refers to one-index transformed two-electron integrals.

TABLE III. Various formulas used in the first-order amplitudes equation.

$\langle {ij}^{ab}\|[X,T_3]\|\mathrm{HF}\rangle$	$=2P_{ij}^{ab}\Sigma_{kc}(t_{ijk}^{abc}-{}_{kji}^{abc})X_{kc}$
$\langle {ijk}^{abc}\|[\hat{X},T_3]\|\mathrm{HF}\rangle$	$\frac{1}{2}P_{ijk}^{abc}(\Sigma_d t_{ijk}^{dbc}\hat{X}_{ad}-\Sigma_l t_{ljk}^{abc}\hat{X}_{li})$
$\frac{1}{2}\langle {ijk}^{abc}\|[[X,T_2],T_2]\|\mathrm{HF}\rangle$	$=-P_{ijk}^{abc}\Sigma_{ld}t_{il}^{ac}t_{jk}^{bd}X_{ld}$
$\langle {ijk}^{abc}\|[\hat{H},T_2]\|\mathrm{HF}\rangle$	$=\Sigma_d t_{ij}^{ad}\hat{g}_{ckbd}-\Sigma_l t_{il}^{ab}\hat{g}_{cklj}$

III. IMPLEMENTATION

The CC3 linear response function has been implemented in a local version of the DALTON[29] program package. In the following, we briefly describe the algorithms used to obtain a $\mathcal{O}(O^4V^3)$ scaling.

A. Implementation of the first-order amplitude equations

To solve the first-order amplitude equations, we need to implement the different terms on the right-hand side of Eq. (26) as an efficient right-hand side ξ_{eff}^Y. The contribution in the doubles space is identical to the Fock matrix contribution in a ground state energy calculation and details about the implementation can be found in Ref. 27. The partitioning of the triples component of the vector ξ^Y into the singles and doubles space (the last term in Eq. (27)) is given in detailed form in Eqs. (29) and (30).

We use the strategy proposed in Ref. 27 where the triples amplitudes are calculated for two fixed virtual indices. Since we need the zeroth-order amplitudes t_3 to calculate the $\check{t}_3^Y$ amplitudes in Eq. (32) and the first-order triples amplitudes t_3^Y in Eq. (34) we cannot use the usual S and Q intermediates from Ref. 27. Instead we introduce the intermediates $\check{W}^Y$ and W^Y as

$$\check{W}^{Y^{bc}}(aikj)=\check{t}_{ijk}^{Y^{abc}}+\check{t}_{ikj}^{Y^{acb}}, \quad (35)$$

$$W^{Y^{bc}}(aikj)=t_{ijk}^{Y^{abc}}+t_{ikj}^{Y^{acb}}. \quad (36)$$

It should be noted that

$$\check{T}_{ijk}^{Y^{abc}}=P_{ijk}^{abc}\check{t}_{ijk}^{Y^{abc}}=\check{W}^{Y^{bc}}(aikj)+\check{W}^{Y^{ab}}(ckji)$$
$$+\check{W}^{Y^{ac}}(bjki), \quad (37)$$

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$$T_{ijk}^{Y^{abc}} = P_{ijk}^{abc} t_{ijk}^{Y^{abc}} = W^{Y^{bc}}(aikj) + W^{Y^{ab}}(ckji) + W^{Y^{ac}}(bjki). \quad (38)$$

Using the formulas from Table III we obtain that

$$\check{W}^{Y^{bc}}(aikj) = -\frac{1}{\varepsilon_{ijk}^{abc} - \omega} P_{jk}^{bc} \left(\frac{1}{2} \sum_d t_{ijk}^{dbc} Y_{ad} - \frac{1}{2} \sum_l t_{ljk}^{abc} Y_{li} - \sum_{ld} t_{il}^{ac} t_{jk}^{bd} Y_{ld} \right) \quad (39)$$

and

$$W^{Y^{bc}}(aikj) = \check{W}^{bc}(aikj) - \frac{1}{\varepsilon_{ijk}^{abc} - \omega} P_{jk}^{bc} \left(\sum_d t_{ij}^{ad} \tilde{g}_{ckbd}^{Y} - \sum_l t_{il}^{ab} \tilde{g}_{cklj}^{Y} + \sum_d t_{ij}^{Y^{ad}} \hat{g}_{ckbd} - \sum_l t_{il}^{Y^{ab}} \hat{g}_{cklj} \right) \quad (40)$$

and Eqs. (29) and (30) may be evaluated using the conventional CC3 energy expression in Eqs. (100) and (101) of Ref. 13 where the zeroth-order amplitudes are replaced by the $\check{T}$ intermediates in Eq. (37). The calculation can therefore be summarized as follows.

Sum over C

Sum over B

Construct $\check{W}^{Y^{BC}}(aikj)$

$\Omega_{ai} \leftarrow \Omega_{ai} + \check{W}^{Y^{BC}}(aikj) L_{jBkC}$

$\Omega_{Bj} \leftarrow \Omega_{Bj} + 2\check{W}^{Y^{BC}}(aikj) L_{kCia}$

$\Omega_{ai,Bj} \leftarrow \Omega_{ai,Bj} + 2\check{W}^{Y^{BC}}(aikj) \hat{F}_{kC}$

$\Omega_{Bj,Ck} \leftarrow \Omega_{Bj,Ck} + \check{W}^{Y^{BC}}(aikj) \hat{F}_{ia}$

$\Omega_{dj,ai} \leftarrow \Omega_{dj,ai} + 4\sum_d \check{W}^{Y^{BC}}(aikj) \hat{g}_{dBkC}$

$\Omega_{dj,Bk} \leftarrow \Omega_{dj,Bk} + 4\sum_d \check{W}^{Y^{BC}}(aikj) \hat{g}_{dCia}$

$\Omega_{di,Bj} \leftarrow \Omega_{di,Bj} + 4\sum_d \check{W}^{Y^{BC}}(aikj) \hat{g}_{dakC}$

$\Omega_{Bl,ai} \leftarrow \Omega_{Bl,ai} + 4\sum_l \check{W}^{Y^{BC}}(aikj) \hat{g}_{jlkC}$

$\Omega_{Cl,Bk} \leftarrow \Omega_{Cl,Bk} + 4\sum_l \check{W}^{Y^{BC}}(aikj) \hat{g}_{jlia}$

$\Omega_{al,Bj} \leftarrow \Omega_{al,Bj} + 4\sum_l \check{W}^{Y^{BC}}(aikj) \hat{g}_{ilkC}$

End sum over B

End sum over C

We have for each term only shown the calculation of the first triples amplitude, but the remaining contributions are trivially obtained by substituting $\check{W}^{Y}$ in each contribution by a sum of $\check{W}^{Y}$'s where the occupied indices have been permuted in accordance with the formulas in Ref. 13.

B. Implementation of the linear response function

The fifth and sixth terms in the linear response function in Eq. (19) are equal to terms in the calculation of CC3 first-order properties[28] but with a different mix of integrals and amplitudes, and these terms will therefore not be discussed in the following. In the linear response function we also see that the first term is equal to the densities used in the calculation of first-order properties (D^0) but multiplied by T_1^Y transformed integrals. The implementation of these "zeroth-order" densities are described in Ref. 28 and are available on disk. The only conceptually new terms that we need to implement are the second, third, fourth, and the last term in Eq. (19).

The last term in Eq. (19) can be seen to be identical to Eq. (30) multiplied with the doubles multipliers and the triples amplitudes $T_{ijk}^{Y^{abc}}$ replaced by $\check{T}_{ijk}^{Y^{abc}}$. The last term of Eq. (19) is therefore implemented in a similar fashion as Eq. (30).

The second, third, and fourth terms in Eq. (19) are calculated as follows:

Sum over D

Sum over L

Calculate $W_{Lmn}^{Y^{\mathrm{Deb}}}$

Calculate $\tilde{W}_{Lmn}^{Y^{\mathrm{Deb}}} = W_{Lmn}^{Y^{\mathrm{Deb}}} + \frac{1}{2} W_{Lnm}^{Y^{Dbe}}$

Calculate $\bar{t}_{Lmn}^{Def}$

$D_{fb} \leftarrow D_{fb} + \sum_{emn} \bar{t}_{Lmn}^{Def} \tilde{W}_{Lmn}^{Y^{Deb}}$

Sum over N

$D_{iN} \leftarrow D_{iN} - \sum_{emf} \bar{t}_{Lmn}^{Def} \tilde{W}_{Lmi}^{Y^{Def}}$

$M_{im,fN} \leftarrow M_{im,fN} + \sum_e \bar{t}_{LmN}^{Def} t_{Li}^{De}$

$M_{im,fN} \leftarrow M_{im,fN} + \sum_e \bar{t}_{LmN}^{Def} t_{Li}^{Y^{De}}$

End sum over N

$D_{Lb} \leftarrow D_{Lb} - \sum_{emn} \bar{t}_{nm}^{De} \tilde{W}_{Lmn}^{Y^{\mathrm{Deb}}}$

$D_{mb} \leftarrow D_{mb} - \sum_{en} \bar{t}_{Ln}^{De} \tilde{W}_{Lmn}^{Y^{\mathrm{Deb}}}$

$D_{ia} \leftarrow D_{ia} + \sum_{en} \bar{t}_{Lm}^{De} \tilde{W}_{Lmi}^{Y^{Dea}}$

End sum over L

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TABLE IV. Polarizability of Ne.

	α			
Basis set	$\omega=0.0$	$\omega=0.1$	$\omega=0.2$	$\omega=0.3$
aug-cc-pVDZ	1.981	1.998	2.053	2.158
d-aug-cc-pVDZ	2.676	2.705	2.798	2.978
t-aug-cc-pVDZ	2.684	2.714	2.810	2.999
aug-cc-pVTZ	2.421	2.443	2.512	2.647
d-aug-cc-pVTZ	2.691	2.721	2.816	3.003
t-aug-cc-pVTZ	2.693	2.723	2.819	3.008
aug-cc-pVQZ	2.594	2.619	2.700	2.856
d-aug-cc-pVQZ	2.680	2.709	2.804	2.989
t-aug-cc-pVQZ	2.680	2.709	2.804	2.990
aug-cc-pV5Z	2.643	2.671	2.758	2.928
d-aug-cc-pV5Z	2.670	2.699	2.793	2.978
t-aug-cc-pV5Z	2.670	2.699	2.793	2.978
aug-cc-pV6Z	2.652	2.680	2.771	2.945
d-aug-cc-pV6Z	2.665	2.694	2.788	2.972
Experiment[a]	2.663	⋯	⋯	⋯
Empirical	2.669[b]	2.699[c]	2.794[c]	2.980[c]

[a]Reference 36.
[b]Reference 37. The result are derived from dipole oscillator strength distributions.
[c]Calculated from the empirical dipole oscillator strength distributions from Ref. 37.

End sum over D

$$D_{ia} \leftarrow D_{ia} + \sum_{fnm} M_{im,fn} t_{mn}^{Yaf}$$

$$D_{ia} \leftarrow D_{ia} + \sum_{fnm} M_{im,fn} t_{mn}^{af}$$

$$D_{ia} \leftarrow D_{ia} - \sum_{b} t_i^{Yb} D_{ba}^0$$

$$D_{ia} \leftarrow D_{ia} + \sum_{j} t_j^{Ya} D_{ij}^0$$

and the total contribution is then obtained by contracting the densities D_{ab}, D_{ij}, and D_{ia} with the T_1-transformed one-electron integrals.

IV. RESULTS

We have calculated the frequency-dependent polarizabilities of Ne for the frequencies 0.1, 0.2, and 0.3 and for ethylene for the wavelength $\lambda = 632.8$ nm. In addition, we calculated the static polarizabilities for Ne, HF, and ethylene. Besides reporting the individual polarizability components $(\alpha_{xx}, \alpha_{yy}, \alpha_{zz})$ we give for HF the anisotropy $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$. All the calculations were carried out using the correlation-consistent basis sets of Dunning and co-workers augmented with diffuse functions,[30,31] n-aug-cc-pVXZ, where X is the cardinal number of the basis set and n is the augmentation level.

A. Ne

In Table IV we listed the calculated polarizabilities for the neon atom. Single, double, and triple augmented basis sets have been used up to d-aug-cc-pV6Z. The results in Table IV converge nicely toward the basis set limit and we have changes of about 0.005–0.006 a.u. when we go from d-aug-cc-pV5Z to d-aug-cc-pV6Z. Note that double augmentation is sufficient to saturate the calculation in the diffuse region already from the TZ level. In a previous study it was found that the CC3 polarizability for Ne in the d-aug-cc-pVDZ basis set differed from the full configuration interaction (FCI) polarizability by less than 0.004 a.u. for frequencies up to 0.3 a.u.[17] Comparing the experimental and the empirical values of the static polarizability with the CC3/d-aug-cc-pV6Z result we see a good agreement as should be expected since correlation effects beyond CC3 are small. The frequency-dependent polarizabilities are also close to the empirical numbers.

TABLE V. Static polarizability of HF.

Basis set	α_{xx}	α_{zz}	$\Delta\alpha$
aug-cc-pVDZ	4.29	6.22	1.93
d-aug-cc-pVDZ	5.23	6.40	1.17
t-aug-cc-pVDZ	5.25	6.38	1.13
aug-cc-pVTZ	4.89	6.33	1.44
d-aug-cc-pVTZ	5.26	6.38	1.12
t-aug-cc-pVTZ	5.25	6.39	1.14
aug-cc-pVQZ	5.09	6.33	1.24
d-aug-cc-pVQZ	5.21	6.34	1.13
t-aug-cc-pVQZ	5.21	6.35	1.14
aug-cc-pV5Z	5.14	6.32	1.18
d-aug-cc-pV5Z	5.19	6.33	1.14
Estimate[a]	5.23	6.73	1.50
Experiment[b]	⋯	⋯	1.49

[a]d-aug-cc-pV5Z polarizability + vibrational contributions (see the text).
[b]From Ref. 33. From Stark effect measurements.

B. HF

The calculations on the polarizability of HF were carried out at the internuclear distance $R_e = 1.732\,879\,5$ a.u. which is the distance used in a previous polarizability calculation.[17] In Table V the individual components of the polarizability of HF—α_{xx} and α_{zz}—are presented along with the anisotropy. In a previous study the difference between the FCI results and the CC3 results using the aug-cc-pVDZ basis set were found to be 0.006 and 0.011 a.u. for the α_{xx} and α_{zz} components, respectively.[17] The N-electron error in the CC3 calculations of the polarizability of HF with the basis sets that we use may therefore be expected not to significantly exceed these values. Looking at the basis set convergence of the CC calculations in Table V it is clear that adding diffuse functions beyond double augmentation has only a very little effect, which decreases with increasing cardinal number. Looking at the convergence of the results obtained in the d-aug-cc-pVXZ basis sets with increasing cardinal number, the d-aug-cc-pV5Z results may be expected to be within 0.01 a.u. of the basis set limit. In Ref. 32 the vibrational average and the pure vibrational contribution was calculated at the CCSD(T)/aug-cc-pVQZ level. Adding these corrections to the CC3/d-aug-cc-pV5Z results we obtain our best estimates for the static polarizability of HF, denoted ''Estimate'' in Table V. Our best estimate for the anisotropy is nearly identical with the experimental result obtained in Ref. 33 from Stark effect measurements.

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TABLE VI. Static polarizability of C_2H_4.

Basis set	α_{xx}	α_{yy}	α_{zz}
aug-cc-pVDZ	24.38	21.80	34.14
d-aug-cc-pVDZ	24.89	22.26	34.12
t-aug-cc-pVDZ	24.92	22.25	34.13
aug-cc-pVTZ	24.73	21.89	34.03
d-aug-cc-pVTZ	24.88	21.93	34.04
t-aug-cc-pVTZ	24.88	21.93	34.04
Estimate[a]	26.05	22.37	35.21
Experiment[b]	26.02(24)	22.38(18)	35.06(12)

[a]t-aug-cc-pVTZ polarizability+ZPVC (see the text).
[b]From Ref. 38. Static polarizability tensor component from the Kerr effect.

C. Ethylene

The static polarizability and the frequency-dependent polarizability at $\lambda = 632.8$ nm have been calculated for ethylene, using the equilibrium geometry in Ref. 34, where experimental rotational constants and calculated vibration–rotation interaction constants have been combined to give highly accurate equilibrium geometries. The static polarizabilities are presented in Table VI and the frequency-dependent polarizabilities in Table VII. The largest basis set employed is t-aug-cc-pVTZ, which was seen to give reasonable basis set saturation in the Ne and HF calculations. The results in Tables VI and VII support that the one-electron basis set error in the t-aug-cc-pVTZ calculation is small. In Ref. 35 the zero point vibrational correction (ZPVC) was calculated at the MP2/DZP-ANO2 level of theory. Adding the ZPVC to the polarizabilities obtained using the t-aug-cc-pVTZ basis set we obtain a best estimates for the polarizabilities of ethylene, denoted ''Estimate'' in Tables VI and VII. These estimates are very close to the experimental values for α_{xx} and α_{yy}, whereas α_{zz} falls just outside the experimental uncertainty.

V. SUMMARY

We have in this article presented the implementation of frequency-dependent polarizabilities in the approximate coupled-cluster singles, doubles, and triples model CC3. The implementation scales as $\mathcal{O}(V^4O^3)$ and the triples amplitudes are calculated ''on-the-fly'' whenever they are needed, ensuring that an appropriate balance between operation count, I/O and storage requirements is obtained. Sample calculations have been performed for the frequency-dependent polarizabilities of neon and ethylene and the static polarizabilities for hydrogenfluoride. The results compare favorable with experimental data.

TABLE VII. Frequency-dependent polarizability for C_2H_4 for the wavelength $\lambda = 632.8$ nm.

Basis set	α_{xx}	α_{yy}	α_{zz}
aug-cc-pVDZ	4.088	3.690	5.820
d-aug-cc-pVDZ	4.181	3.772	5.817
t-aug-cc-pVDZ	4.185	3.770	5.819
aug-cc-pVTZ	4.151	3.706	5.803
d-aug-cc-pVTZ	4.179	3.714	5.804
t-aug-cc-pVTZ	4.179	3.714	5.804
Estimate[a]	4.372	3.787	5.997
Experiment[b]	4.41±0.04	3.79±0.03	5.94±0.02
Experiment[c]	4.34±0.15	3.78±0.13	6.02±0.20

[a]t-aug-cc-pVTZ polarizability+ZPVC (see the text).
[b]From Ref. 38. Derived from the Cotton–Mouton effect mean polarizability and Kerr effect.
[c]From Ref. 39. Derived from the Cotton–Mouton effect Rayleigh depolarization ratio and mean polarizability.

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