Ab initio study of the electric-field-gradient-induced birefringence of a polar molecule: CO

Antonio Rizzo
Istituto di Chimica Quantistica ed Energetica Molecolare del Consiglio Nazionale delle Ricerche, Area della Ricerca di Pisa, loc. San Cataldo, Via Alfieri 1, I-56010 Ghezzano, San Giuliano Terme, Pisa, Italy

Sonia Coriani,[a] Asger Halkier,[b] and Christof Hättig[c]
Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Denmark

(Received 24 March 2000; accepted 25 May 2000)

An *ab initio* coupled cluster singles and doubles (CCSD) investigation of the electric-field-gradient-induced birefringence (EFGB) of a polar molecule, CO, is presented. The so-called ''effective quadrupole center'' (EQC), the origin to which the quadrupole moment deduced from EFGB experiments refers for dipolar molecules and which experimentalists cannot determine directly, is computed within two different semiclassical theories of the EFGB. The temperature independent frequency dependent contribution to the birefringence is determined as well. The molecular electric quadrupole moment with the origin at the EQC is determined within the two theories via an accurate value of the quadrupole moment referring to the center of mass, obtained using well-established hierarchies of basis sets and wave function models, and the calculated EQCs. The final theoretical values result as the basis set limit at the CCSD(T) level completed with estimates for relativistic effects, correlation contributions beyond CCSD(T), rovibrational effects, and residual errors in the EQC. The comparison of the theoretical results with the corresponding experimentally deduced values sheds some light on the differences between the two semiclassical approaches to the EFGB. © *2000 American Institute of Physics.* [S0021-9606(00)30332-4]

I. INTRODUCTION

Molecular electric quadrupole moments are often determined from measurements of the birefringence induced by an electric field gradient (EFG) with a component perpendicular to the direction of propagation of the beam.[1]

For a linear molecule, the resulting anisotropy of the refractive index Δn at constant pressure can be written as

$$\Delta n \propto \left(b + \frac{2}{15kT} q \Delta\alpha \right) \nabla E, \tag{1}$$

where ∇E indicates the component of the EFG, T is the temperature, and k is the Boltzmann constant. The quantity b is a combination of frequency dependent (quadratic) response properties, $\Delta\alpha$ the anisotropy of the electric dipole polarizability, and q represents the permanent molecular electric quadrupole moment.

Since the first experiment carried out by Buckingham and Disch in 1963,[2] the technique has been widely employed to determine molecular electric quadrupole moments for both nondipolar and dipolar molecules.[3–10] The interpretation of the measurement in dipolar gases has been difficult, due to the dependence of q on the origin in molecules possessing a permanent electric dipole moment. Theories have been developed by Buckingham and Longuet-Higgins,[11] by Imrie and Raab,[12] and by Dumitru and Woolley.[13,14]

Recently, we have completed studies of the electric field gradient induced birefringence (EFGB) in atoms[15] and nonpolar molecules.[16] Here we present the first *ab initio* study of the EFGB of a polar molecule. More specifically, we perform a coupled cluster singles and doubles (CCSD) (Ref. 17) investigation of the EFGB of carbon monoxide (CO), carried out within the frameworks of the semiclassical approaches of Imrie and Raab,[12] and of Buckingham and Longuet-Higgins.[11] The so-called effective quadrupole center (EQC)—the origin to which the quadrupole moment deduced from the EFGB experiment via Eq. (1) refers—is determined as a function of the frequency through the dispersion coefficients of the appropriate linear response functions. The quadrupole moment q at the EQC as well as $\Delta\alpha$ and the quantity b, which for constant pressure is temperature-independent, are also computed. In the experimental studies of the EFGB in CO (Refs. 3, 10) the contribution from b has always been neglected, and we shall test the validity of this approximation. For this investigation, the hierarchies of augmented correlation-consistent valence basis sets[18–20]—denoted aug-cc-pVXZ, d-aug-cc-pVXZ, and t-aug-cc-pVXZ for single, double, and triple augmentation with diffuse functions, respectively—are employed, as our previous studies of the EFGB of nonpolar systems[15,16] have shown the importance of inclusion of diffuse functions in the basis set in *ab initio* studies of EFGB.

The two semiclassical formulations of the EFGB for a polar molecule—one authored by Buckingham and Longuet-

[a]Permanent address: Dipartimento di Scienze Chimiche, Università degli studi di Trieste, via Giorgieri 1, I-34127 Trieste, Italy.
[b]Present address: Theoretical Chemistry Group, Debye Institute, Utrecht University, P.O. Box 80052, NL-3508 TB Utrecht, The Netherlands.
[c]Permanent address: Forschungszentrum Karlsruhe, Institute of Nanotechnology, P.O. Box 3640, D-76021 Karlsruhe, Germany.

 © 2000 American Institute of Physics

Higgins, Ref. 11, and one formulated by Imrie and Raab, Ref. 12—differ, among other things, in the use of a traceless[11] vs a traced[12] form of the quadrupole moment operator. The observable is in both approaches independent of the origin, as it must be, and the two approaches have been said to ''agree'' in the limiting case of nondipolar molecules.[12,10] Although it has been stated that direct comparison of the results for the quadrupole moment with respect to the EQC of polar molecules is possible (see Refs. 10, 12) this is a matter of some debate.

In this paper we follow closely the more recent approach of Imrie and Raab and compare the results with those obtained with the formulation of Buckingham and Longuet-Higgins to investigate the difference between the two approaches numerically.

Finally, a high-level *ab initio* investigation of q referring to the center of mass is performed, and used—together with the two calculated EQC's—to obtain final theoretical values for the quadrupole moment refering to the EQC, which are compared with experimentally deduced values. For this end, calculations in well-established hierarchies of basis sets and wave function models are performed. Regarding the latter, the following sequence of models is employed: Hartree–Fock self-consistent field (SCF), second-order Møller–Plesset perturbation theory (MP2),[21] CCSD, and CCSD augmented by a perturbational correction for connected triple excitations (CCSD(T)).[22] This hierarchy of wave function models has proven to be very useful for accurate calculations of q,[23–25] and the accuracy of the CCSD(T) results is comparable to that of experiment when sufficiently large basis sets are employed. Regarding basis-set demands, the inclusion of diffuse functions in the basis set has been found to be very important because of the quadratic dependence of the electric quadrupole moment operator on the electronic coordinates.[26] Accordingly, we shall employ the above-mentioned series of diffusely augmented correlation-consistent valence basis sets and the corresponding series of singly augmented core-valence basis sets, denoted aug-cc-pCVXZ.[27] Relativistic effects on q of CO are expected to be small, as no heavy nuclei are present. Nevertheless, some semirelativistic calculations that take the effect of the mass-velocity and one-electron Darwin terms into account are performed to estimate the effect of relativity. To interface our theoretical value with the experimentally deduced one a rovibrational averaging is finally performed.

We do not discuss the details of response theory for a coupled cluster parameterization of the wave function here. A general description of the method is given in Ref. 28, whereas the derivation of the CCSD quadratic response theory equations can be found in Ref. 29. The implementation of the dispersion coefficients for linear and quadratic response properties in coupled cluster response theory is described in Refs. 30 and 31.

II. THEORY

A. Basic theory

The electric-field-gradient induced anisotropy Δn of the refractive index n for an ideal gas of a polar species and for light propagating along the Z axis is given by[11,12,32]

$$\Delta n = n_X - n_Y = \frac{1}{\epsilon_0} N s \nabla E \tag{2}$$

in atomic units, where N is the number density and, in the formulation of Imrie and Raab,[12]

$$s = \frac{1}{60}\Big\{ 6B_{\alpha,\beta,\alpha\beta} - 2B_{\alpha,\alpha,\beta\beta} - ß_{\alpha,\alpha\beta,\beta} - 3ß_{\alpha,\beta\beta,\alpha} - \frac{10}{\omega}\varepsilon_{\alpha\beta\gamma} J'_{\alpha,\beta,\gamma} + \frac{1}{kT}\Big[6q_{\alpha\beta}\alpha_{\alpha\beta} - 2q_{\alpha\alpha}\alpha_{\beta\beta} - \mu_\alpha\Big(3a_{\alpha,\beta\beta} + a_{\beta,\beta\alpha} + \frac{10}{\omega}\varepsilon_{\alpha\beta\gamma} G'_{\beta,\gamma}\Big)\Big]\Big\}. \tag{3}$$

Here $q_{\alpha\beta}$ denotes the components of the permanent electric quadrupole moment tensor, μ_α the components of the permanent electric dipole moment vector and $\varepsilon_{\alpha\beta\gamma}$ the components of the Levi–Civita tensor. Einstein implicit summation over repeated indices is assumed here and throughout. The remaining tensor elements indicate frequency dependent linear or quadratic response properties. Thus, in the notation of e.g., Ref. 33 (see also Ref. 34),

$$\alpha_{\alpha\beta}(-\omega;\omega) = \alpha_{\beta\alpha}(-\omega;\omega) = -\langle\langle \hat{\mu}_\alpha;\hat{\mu}_\beta\rangle\rangle_\omega \tag{4}$$

denotes the usual electric dipole polarizability, and

$$a_{\alpha,\beta\gamma}(-\omega;\omega) = a_{\alpha,\gamma\beta}(-\omega;\omega) = -\langle\langle \hat{\mu}_\alpha;\hat{q}_{\beta\gamma}\rangle\rangle_\omega \tag{5}$$

and

$$G'_{\alpha,\beta}(-\omega;\omega) = -i\langle\langle \hat{\mu}_\alpha;\hat{m}_\beta\rangle\rangle_\omega \tag{6}$$

describe the response of the electric dipole moment to the gradient of the electric field and to the time derivative of the magnetic field associated with the radiation, respectively.[35] The frequency dependent quadratic response properties are the dipole–dipole–quadrupole

$$\begin{aligned} B_{\alpha,\beta,\gamma\delta}(-\omega;\omega,0) &= B_{\beta,\alpha,\gamma\delta}(-\omega;\omega,0) \\ &= B_{\alpha,\beta,\delta\gamma}(-\omega;\omega,0) \\ &= \langle\langle \hat{\mu}_\alpha;\hat{\mu}_\beta,\hat{q}_{\gamma\delta}\rangle\rangle_{\alpha,0}, \end{aligned} \tag{7}$$

the dipole–quadrupole–dipole

$$\begin{aligned} ß_{\alpha,\beta\gamma,\delta}(-\omega;\omega,0) &= ß_{\alpha,\gamma\beta,\delta}(-\omega;\omega,0) \\ &= \langle\langle \hat{\mu}_\alpha;\hat{q}_{\beta\gamma},\hat{\mu}_\delta\rangle\rangle_{\omega,0} \\ &= B_{\alpha,\delta,\beta\gamma}(-\omega;0,\omega), \end{aligned} \tag{8}$$

and the dipole-magnetic dipole–dipole

$$J'_{\alpha,\beta,\gamma}(-\omega;\omega,0) = i\langle\langle \hat{\mu}_\alpha;\hat{m}_\beta,\hat{\mu}_\gamma\rangle\rangle_{\omega,0} \tag{9}$$

hyperpolarizabilities.

The electric dipole, magnetic dipole, and electric quadrupole moment operators in the above equations are defined as follows:

$$\hat{\mu}_\alpha = \sum_i q_i \hat{r}_{i\alpha}, \tag{10}$$

$$\hat{m}_\alpha = \sum_i \frac{q_i}{2m_i}(\hat{\mathbf{r}}_i \times \hat{\mathbf{p}}_i)_\alpha, \tag{11}$$

$$\hat{q}_{\alpha\beta}=\sum_i q_i \hat{r}_{i\alpha}\hat{r}_{i\beta}, \tag{12}$$

where the summation extends over all particles i with position vector $\mathbf{r}_i$, momentum $\mathbf{p}_i=-i\hbar\nabla_i$, and mass m_i. Note the choice of the *traced* form for the electric quadrupole moment operator, as suggested by Imrie and Raab,[12] see also Refs. 10, 36–38.

B. Effective quadrupole center

Again, following Imrie and Raab,[12] in the case of a linear molecule with the z axis as the molecular axis, Eq. (2) becomes

$$\Delta n=\frac{N\nabla E}{2\epsilon_0}\left\{b+\frac{2}{15kT}\left[q\Delta\alpha-\frac{\mu}{2}\left(2a_1+a_2+3a_3+\frac{10}{\omega}G'\right)\right]\right\}, \tag{13}$$

where $\mu=\mu_z$, $q=q_{zz}-q_{xx}$, $\Delta\alpha=\alpha_{zz}-\alpha_{xx}$ and $a_1=a_{z,zz}$, $a_2=a_{x,xz}=a_{y,yz}$, $a_3=a_{z,xx}=a_{z,yy}$ and $G'=G'_{x,y}=-G'_{y,x}$ (the dependence on the frequency parameters has been left out for ease of notation). Also

$$b_{\mathrm{IR}}=\left(\overline{B}-\overline{\beta}_{\mathrm{IR}}+\frac{\overline{J'}_{\mathrm{IR}}}{\omega}\right), \tag{14}$$

where, in detail,

$$\begin{aligned}\overline{B}=&\tfrac{2}{15}[-B_{z,z,xx}(-\omega;\omega,0)+B_{z,z,zz}(-\omega;\omega,0)\\&+B_{x,x,yy}(-\omega;\omega,0)-B_{x,x,zz}(-\omega,\omega,0)\\&+6B_{x,z,xz}(-\omega;\omega,0)+7B_{x,y,xy}(-\omega;\omega,0)],\end{aligned} \tag{15}$$

$$\begin{aligned}\overline{\beta}_{\mathrm{IR}}=&\tfrac{1}{5}[3B_{z,z,xx}(-\omega;0,\omega)+2B_{z,z,zz}(-\omega;0,\omega)\\&+B_{x,z,xz}(-\omega;0,\omega)+7B_{x,x,yy}(-\omega;0,\omega)\\&+3B_{x,x,zz}(-\omega;0,\omega)+B_{z,x,xz}(-\omega;0,\omega)\\&+9B_{x,y,xy}(-\omega;0,\omega)],\end{aligned} \tag{16}$$

and

$$\begin{aligned}\overline{J'}_{\mathrm{IR}}=&-\tfrac{2}{3}[J'_{x,y,z}(-\omega;\omega,0)+J'_{z,x,y}(-\omega;\omega,0)\\&+J'_{y,z,x}(-\omega;\omega,0)].\end{aligned} \tag{17}$$

The subscript ''IR'' indicates here and below that we are following the formulation of Imrie and Raab,[12] and it will be used when we want to distinguish quantities for which the expressions differ from those arising in the approach by Buckingham and Longuet-Higgins,[11] for which we will use the subscript ''BLH.'' Measurements of the EFGB of a linear dipolar molecule over a range of temperatures thus yield information about the term in square brackets in Eq. (13), which is a definite property of the molecule not depending on the choice of the origin. The individual terms within square brackets, however, do depend on this choice. The shift of origin which brings the term in round brackets to vanish defines the EQC.[11,12] Let us indicate with a superscript (or) a given origin, e.g., the center of the nuclear masses. With a shift R_z along the z axis, for a neutral linear molecule

$$a_1\rightarrow a_1^{(\mathrm{or})}-2R_z\alpha_{zz}, \tag{18}$$

$$a_2\rightarrow a_2^{(\mathrm{or})}-R_z\alpha_{xx}, \tag{19}$$

$$a_3\rightarrow a_3^{(\mathrm{or})}, \tag{20}$$

$$G'\rightarrow G'^{(\mathrm{or})}+\frac{\omega}{2}R_z\alpha_{xx}^{\mathrm{Mixed}}, \tag{21}$$

where we have introduced the electric dipole polarizability in the mixed length-velocity form, $\alpha_{\alpha,\beta}^{\mathrm{Mixed}}(-\omega;\omega)$, defined as

$$\alpha_{\alpha,\beta}^{\mathrm{Mixed}}(-\omega;\omega)=\frac{i}{\omega}\langle\langle\hat{\mu}_\alpha;\hat{\mu}_\beta^p\rangle\rangle_\omega, \tag{22}$$

with

$$\hat{\mu}_\alpha^p=\sum_i\frac{q_i}{m_i}\hat{p}_{i,\alpha}. \tag{23}$$

Equating the quantity in round brackets in Eq. (13) to zero, one obtains for the shift of origin defining the EQC,

$$R_{z,\mathrm{IR}}=\frac{2a_1^{(\mathrm{or})}+a_2^{(\mathrm{or})}+3a_3^{(\mathrm{or})}+10\omega^{-1}G'^{(\mathrm{or})}}{4\Delta\alpha_{\mathrm{IR}}^{\mathrm{Mixed}}}=\frac{W_{\mathrm{IR}}(\omega)}{4\Delta\alpha_{\mathrm{IR}}^{\mathrm{Mixed}}}, \tag{24}$$

where

$$\Delta\alpha_{\mathrm{IR}}^{\mathrm{Mixed}}=\alpha_{zz}+\frac{\alpha_{xx}}{4}-\frac{5\alpha_{xx}^{\mathrm{Mixed}}}{4}. \tag{25}$$

Besides for the factor $10/\omega$, this shift depends on ω through the ω-dependence of the linear response properties in the right-hand side of Eq. (24). This equation holds rigorous even for approximate *ab initio* methods employing nonvariational wave functions—as in our case—and/or finite basis sets. In the case of an exact wave function, or of a variational wave function expanded in a complete (infinite) basis set, both the Ehrenfest theorem and the operator identity $[\hat{r},\hat{\mathcal{H}}]=i\hat{p}$ hold (or, equivalently, the hypervirial relationship is fulfilled), and one obtains

$$R_{z,\mathrm{IR}}^{\mathrm{Hyp}}=\frac{2a_1^{(\mathrm{or})}+a_2^{(\mathrm{or})}+3a_3^{(\mathrm{or})}+10\omega^{-1}G'^{(\mathrm{or})}}{4\Delta\alpha}=\frac{W_{\mathrm{IR}}(\omega)}{4\Delta\alpha}. \tag{26}$$

The superscript ''Hyp'' refers to this situation. Equation (26) can also be obtained by imposing the condition that in absence of approximations the quantity in square brackets in Eq. (13) must not depend on the origin. Note that in approximate calculations, independence on the origin of the quadrupole moment is thus *not* guaranteed for both the temperature dependent and temperature independent contributions to the EFGB in Eq. (1).

In the formulation of Buckingham and Longuet-Higgins,[11] the traceless form of the quadrupole moment operator is employed, and an analysis similar to the one above yields

$$R_{z,\mathrm{BLH}}=\frac{2A_{x,xz}^{(\mathrm{or})}+A_{z,zz}^{(\mathrm{or})}+10\omega^{-1}G'^{(\mathrm{or})}}{2\Delta\alpha_{\mathrm{BLH}}^{\mathrm{Mixed}}} \tag{27}$$

for the EQC for a linear molecule, where

$$\Delta\alpha_{\mathrm{BLH}}^{\mathrm{Mixed}}=\alpha_{zz}+\frac{3\alpha_{xx}}{2}-\frac{5\alpha_{xx}^{\mathrm{Mixed}}}{2}. \tag{28}$$

The tensor elements in Eq. (27) are the linear responses

$$A_{\alpha,\beta\gamma}(-\omega;\omega)=A_{\alpha,\gamma\beta}(-\omega;\omega)=-\langle\langle\hat{\mu}_\alpha;\hat{\Theta}_{\beta\gamma}\rangle\rangle_\omega, \tag{29}$$

where $\hat{\Theta}_{\alpha\beta}=\frac{1}{2}(3\hat{q}_{\alpha\beta}-\hat{q}_{\gamma\gamma}\delta_{\alpha\beta})$ indicates the traceless quadrupole moment operator. Note especially that $\hat{\Theta}_{zz}=\hat{q}_{zz}-\hat{q}_{xx}$ for linear molecules. The use of the relationships

$$A_{x,xz}=\tfrac{3}{2}a_2, \tag{30}$$

$$A_{z,zz}=a_1-a_3, \tag{31}$$

leads to

$$R_{z,\mathrm{BLH}}=\frac{3a_2^{(\mathrm{or})}+a_1^{(\mathrm{or})}-a_3^{(\mathrm{or})}+10\omega^{-1}G'^{(\mathrm{or})}}{2\Delta\alpha_{\mathrm{BLH}}^{\mathrm{Mixed}}}=\frac{W_{\mathrm{BLH}}(\omega)}{2\Delta\alpha_{\mathrm{BLH}}^{\mathrm{Mixed}}} \tag{32}$$

and for an exact wave function, or for a variational wave function expanded on an infinite basis set

$$R_{z,\mathrm{BLH}}^{\mathrm{Hyp}}=\frac{3a_2^{(\mathrm{or})}+a_1^{(\mathrm{or})}-a_3^{(\mathrm{or})}+10\omega^{-1}G'^{(\mathrm{or})}}{2\Delta\alpha}=\frac{W_{\mathrm{BLH}}(\omega)}{2\Delta\alpha}. \tag{33}$$

Equation (32) provides the EQC estimate in the formulation of Buckingham and Longuet-Higgins. In the Results section below, the differences between the two formulations will be discussed in some detail. Note that the differences between the two approaches also extend to the temperature-independent term b in Eq. (13). Working out the expressions given in Refs. 11 and 32 it is possible to show that

$$b_{\mathrm{BLH}}=\left(\overline{B}-\overline{\beta}_{\mathrm{BLH}}+\frac{\overline{J'}_{\mathrm{BLH}}}{\omega}\right), \tag{34}$$

where

$$\overline{J'}_{\mathrm{BLH}}=2\overline{J'}_{\mathrm{IR}} \tag{35}$$

and

$$\begin{aligned}\overline{\beta}_{\mathrm{BLH}}=\tfrac{2}{15}[&-B_{z,z,xx}(-\omega;0,\omega)+B_{z,z,zz}(-\omega;0,\omega)\\&+3B_{x,z,xz}(-\omega;0,\omega)+B_{x,x,yy}(-\omega;0,\omega)\\&-B_{x,x,zz}(-\omega;0,\omega)+3B_{z,x,xz}(-\omega;0,\omega)\\&+7B_{y,x,xy}(-\omega;0,\omega)].\end{aligned} \tag{36}$$

In the static limit, $b_{\mathrm{BLH}}=\overline{J'}_{\mathrm{BLH}}/\omega$. Note also that the differences which clearly exist between b_{IR} [Eq. (14)] and b_{BLH} [Eq. (34)] lead as a consequence to the conclusion that the two formulations of the EFGB are *not* equivalent and *do not* lead to the same result in the case of nondipolar systems.

C. The EFGB at the EQC

Choosing the effective quadrupole center as given by R_z [see Eq. (24) or Eq. (32)], Eq. (13) can be rewritten as follows:

$$n_X-n_Y=\frac{N\nabla E}{2\epsilon_0}\left\{b^{(R_z)}+\frac{2}{15kT}q^{(R_z)}\Delta\alpha\right\}, \tag{37}$$

where $q^{(R_z)}$ denotes the molecular quadrupole moment referring to the EQC,

$$q^{(R_z)}=q^{(\mathrm{or})}-2R_z\mu, \tag{38}$$

and

$$b_{\mathrm{IR}}^{(R_z)}=b_{\mathrm{IR}}^{(\mathrm{or})}+R_{z,\mathrm{IR}}b', \tag{39}$$

$$b_{\mathrm{BLH}}^{(R_z)}=b_{\mathrm{BLH}}^{(\mathrm{or})}+2R_{z,\mathrm{BLH}}b', \tag{40}$$

where

$$\begin{aligned}b'=&\frac{\beta_{xxz}(-\omega;\omega,0)-\beta_{zxx}(-\omega;\omega,0)}{3}\\&-\frac{\beta_{x,x,z}^{\mathrm{Mixed}}(-\omega;\omega,0)-\beta_{z,x,x}^{\mathrm{Mixed}}(-\omega;\omega,0)}{3}.\end{aligned} \tag{41}$$

We have here introduced the first hyperpolarizabilities,

$$\beta_{\alpha\beta\gamma}(-\omega;\omega,0)=\beta_{\beta\alpha\gamma}(-\omega;\omega,0)=\langle\langle\hat{\mu}_\alpha;\hat{\mu}_\beta,\hat{\mu}_\gamma\rangle\rangle_{\omega,0}, \tag{42}$$

$$\beta_{\alpha,\beta,\gamma}^{\mathrm{Mixed}}(-\omega;\omega,0)=-\frac{i}{\omega}\langle\langle\hat{\mu}_\alpha;\hat{\mu}_\beta^p,\hat{\mu}_\gamma\rangle\rangle_{\omega,0}. \tag{43}$$

Using the hypervirial relationship it is easy to prove that, as expected, the temperature-independent contribution to Δn does not depend on the choice of origin (*in the ''exact'' case*), whereas the quadrupole moment does, as indicated in Eq. (38). The dependence of $b^{(R_z)}$ in approximate calculations is given explicitly in Eqs. (39) and (40).

D. Effects of rotation and molecular vibration

We briefly discuss here the effect of molecular vibration and of quantized rotation on the anisotropy of the refractive index induced by an electric field gradient. The matter has been given attention by Buckingham and Pariseau,[39] who derived a fully quantum mechanical expression for the observable, and discussed the consequences in the case of diatomic (nonpolar) molecules. The authors have shown that quantization of molecular rotation modifies the classical expression Eq. (13) by reducing the alignment of the quadrupolar molecule in the field gradient, i.e., by reducing the inverse-temperature term, and by introducing an extra contribution arising from centrifugal distortion. Also, both the temperature independent term b and the properties entering the inverse-temperature term should be zero-point vibrationally averaged. Equation (13), under the assumption that only the ground vibrational state $|v\rangle$ of the electronic ground state is populated, would then become [cf. Eq. (22) in Ref. 39],

$$\Delta n = \frac{N\nabla E}{2\epsilon_0}\left\{\langle v|b|v\rangle + \frac{2}{15kT}\left[\langle v|q|v\rangle\langle v|\Delta\alpha|v\rangle - \frac{\langle v|\mu|v\rangle}{2}\left(2\langle v|a_1|v\rangle + \langle v|a_2|v\rangle + 3\langle v|a_3|v\rangle + \frac{10}{\omega}\langle v|G'|v\rangle\right)\right]F(T) + C(T)\right\}. \quad (44)$$

In Eq. (44), $\langle v|P|v\rangle$ indicates the average over the vibrational ground state of the electronic property P (for the electronic ground state), a function of the nuclear displacement. The function $F(T)$ has the form

$$F(T) = 1 - \sigma + \tfrac{8}{15}\sigma^2 + \cdots, \quad (45)$$

where $\sigma = hc_0 B_v/kT$ involves the rotational term B_v. The centrifugal term $C(T)$ is in good approximation independent of the temperature, and its magnitude is proportional to B_v/ω_e, the ratio of the rotational term and the vibrational frequency ω_e.

Buckingham and Pariseau[39] have shown that quantized rotation effects are negligible for CO_2, but that they are substantial for molecular hydrogen, where they lead to a 25% reduction of the T-dependent term. Centrifugal distortion was found in both cases rather unimportant. We will discuss the effects of vibrational zero-point average and of quantized rotation of carbon monoxide in the following.

We shall pay special attention to the description of the effect of coupling of electronic polarization and nuclear coordinates, which in general also involves, besides the so-called zero-point vibrational average of the properties, the contribution due to the excited vibrational states, generally identified as pure-vibrational contribution.[40] The effect of excited vibrational states on electronic properties is often huge for static properties, but it becomes much less important at optical frequencies. In our study we follow the approach of Bishop and Kirtman[41] to derive expressions for the vibrational dipole–quadrupole and dipole-magnetic dipole polarizabilities which determine the EQC and for the dipole–dipole–quadrupole and dipole–dipole-magnetic dipole hyperpolarizabilities entering the definition of b. Using the notations of Ref. 41 we can write

$$a^v_{\alpha,\beta\gamma}(-\omega;\omega) = [\text{``}\mu q\text{''}], \quad (46)$$

$$G'^v_{\alpha,\beta}(-\omega;\omega) = [\text{``}\mu m\text{''}], \quad (47)$$

$$\alpha^v_{\alpha\beta}(-\omega;\omega) = [\text{``}\mu^2\text{''}], \quad (48)$$

$$B^v_{\alpha,\beta,\gamma\delta}(\omega_\sigma;\omega_1,\omega_2) = [\text{``}\mu^2 q\text{''}] + [\text{``}\mu a\text{''}] + [\text{``}\alpha q\text{''}], \quad (49)$$

$$J'^v_{\alpha,\beta,\gamma}(\omega_\sigma;\omega_1,\omega_2) = [\text{``}\mu^2 m\text{''}] + [\text{``}\alpha m\text{''}] + [\text{``}\mu G'\text{''}]. \quad (50)$$

Detailed expressions will be given elsewhere.[42] Equation (47) and the first and second term on the right-hand side of Eq. (50) involve matrix elements between vibrational states of the magnetic dipole moment function and thus vanish in our approximation. We will discuss below the magnitude of the pure vibrational contribution—computed employing Eqs. (46)–(50)—and its effect on both the effective quadrupole center and the temperature independent term b of carbon monoxide.

E. Frequency dependence and dispersion

The frequency dependence of the different response properties above can be obtained through frequency dispersion coefficients. Linear and quadratic response functions for a finite molecular or atomic system in its electronic ground state are analytical in the frequency arguments, except at the poles, which occur when a frequency or a sum of frequencies is equal to an excitation energy. Thus for frequencies below the first pole, the linear and quadratic response functions can be expanded in power series as[15,30,31]

$$\langle\langle\hat{A};\hat{B}\rangle\rangle_{\omega_B} = \sum_{n=0}^{\infty}\omega_B^n D_{AB}(n), \quad (51)$$

$$\langle\langle\hat{A};\hat{B},\hat{C}\rangle\rangle_{\omega_B,\omega_C} = \sum_{n,m=0}^{\infty}\omega_B^n\omega_C^m D_{ABC}(n,m). \quad (52)$$

Analytical expressions for the expansion (dispersion) coefficients $D_{AB}(n)$ and $D_{ABC}(n,m)$ have been derived for a general coupled cluster quadratic response function.[31] The coefficients with even total order n and $(n+m)$—in Eqs. (32) and (33), respectively—are real, while those with odd total order are purely imaginary. Thus when the (Hermitian) operators $\hat{A}$, $\hat{B}$ and $\hat{C}$ are real, the expansion contains only terms of even total order, whereas if exactly one of the operators is purely imaginary (as in G', α^{Mixed} and β^{Mixed} defined above), only odd terms are present.

Using the dispersion relationships, Eq. (24) [or the analogous Eq. (26)] takes the general form

$$R_z = \frac{\Sigma^{\infty}_{n(\text{even})=0}\omega^n P(n)}{\Sigma^{\infty}_{n(\text{even})=0}\omega^n Q(n)}, \quad (53)$$

where $P(n)$ and $Q(n)$ are the coefficients of order n in the polynomial expansion. In the present case we will truncate the two series in Eq. (53) after $n=4$, so we will include the first three terms in the expansion of all the response functions.

III. COMPUTATIONAL DETAILS

All the calculations have been carried out at the experimentally derived equilibrium bond distance $R_{\text{CO}} = 2.1322$ a.u.,[43] which is only negligibly different from the state-of-the-art *ab initio* value of 2.1331 a.u. obtained at the full coupled cluster singles, doubles, and triples level in the cc-pVQZ basis set.[44] The molecule is placed on the z-axis, which is directed from the oxygen to the carbon atom. The reference origin—labeled with the superscript ''(or)'' above—was taken at the center of the nuclear masses (CM). Thus R_z has positive values for displacements from the CM toward the C atom. The frequency dependent response properties have been computed at the CCSD level employing the aug-cc-pVXZ (X=D–Q), d-aug-cc-pVXZ (X=D–Q), and t-aug-cc-pVDZ basis sets with only the valence electrons correlated.

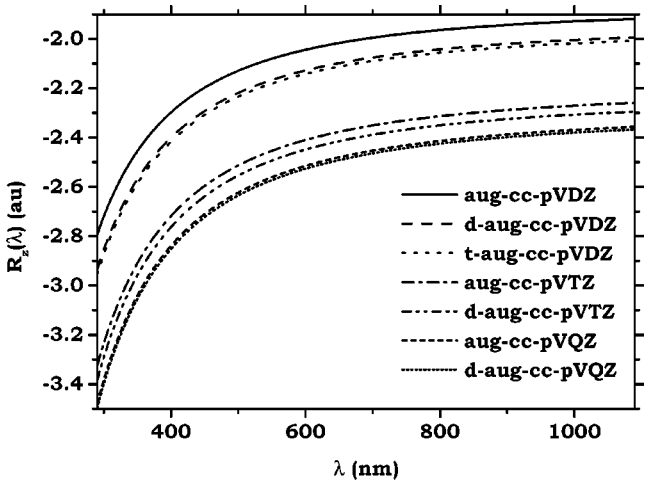


FIG. 1. CO. The effective quadrupole center R_z as a function of the wavelength λ in the 290–1090 nm range for different correlation-consistent basis sets in the formulation of Imrie and Raab, see Ref. 12. Atomic units.

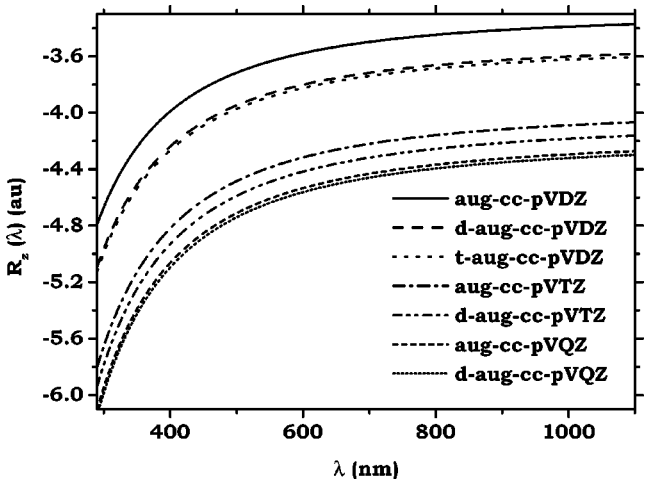


FIG. 2. CO. The effective quadrupole center R_z as a function of the wavelength λ in the 290–1090 nm range for different correlation-consistent basis sets in the formulation of Buckingham and Longuet-Higgins, see Ref. 11. Atomic units.

For the investigation of $q_e^{(\mathrm{CM})}$ (where the subscript ''*e*'' designates the equilibrium value), SCF, MP2, CCSD, and CCSD(T) calculations have been performed employing the aug-cc-pVXZ (X=D–6), d-aug-cc-pVXZ (X=D–6), t-aug-cc-pVXZ (X=D–Q), and aug-cc-pCVXZ (X=D–5) basis sets. In the valence basis sets, only the valence electrons have been correlated, whereas in the core-valence basis sets all the electrons have been correlated.

All the *ab initio* calculations presented in this study have been performed with a development version of the DALTON program[45] that contains the integral-direct coupled cluster code of Koch and co-workers.[26,30,31,46–48] This program does not have analytical evaluation of q at the CCSD(T) level. However, it is possible to add an external perturbation to the Hamiltonian explicitly, so q at this level is obtained from the total energy by central differences numerical differentiation—the accuracy of the numerical differentiation has been checked at the MP2 and CCSD level where calculations based both on analytical and numerical differentiation have been performed. At the CCSD level, the mass-velocity and Darwin terms can be calculated in the presence of an external perturbation and added to the nonrelativistic CCSD energy obtained in the presence of the perturbation. From this ''total semirelativistic energy'' a semirelativistic quadrupole moment may then be obtained by numerical differentiation. This has been done for the aug-cc-pCVXZ (X=D–Q) basis sets with all electrons correlated.

For the rovibrational averaging of the quadrupole moment, we calculated $q^{(\mathrm{CM})}$ and the total electronic energy at ten different geometries at the CCSD(T)/aug-cc-pV5Z level with only the valence electrons correlated to obtain the potential energy curve and quadrupole moment function. The actual rovibrational averaging based on these results was performed, as for the averaging of the properties as discussed below, with the VIBROT module of the MOLCAS-4 program.[49]

To compute vibrational corrections to R_z and b, consisting of a zero-point vibrational (ZPV) average and a pure vibrational (PV) contribution (see Sec. II D) the relevant electronic properties have been computed at the CCSD level using the d-aug-ccpVTZ basis for a total of twelve internuclear distances equally spaced by $0.1a_0$ around the equilibrium geometry. Vibrational averages have been calculated for the first eight vibrational states employing the above mentioned CCSD(T)/aug-cc-pV5Z potential energy curve, following closely the procedure adopted in Ref. 50. Finally, the conversion factors given in the Appendix are used when converting from a.u. to SI and esu units.

IV. RESULTS AND DISCUSSION

A. The effective quadrupole center

To compute R_z in the formulations of Imrie and Raab[12] (labeled IR) and Buckingham and Longuet-Higgins[11] (BLH), we determined the frequency dispersion coefficients of the linear response functions involved in Eqs. (24) and (32) [see

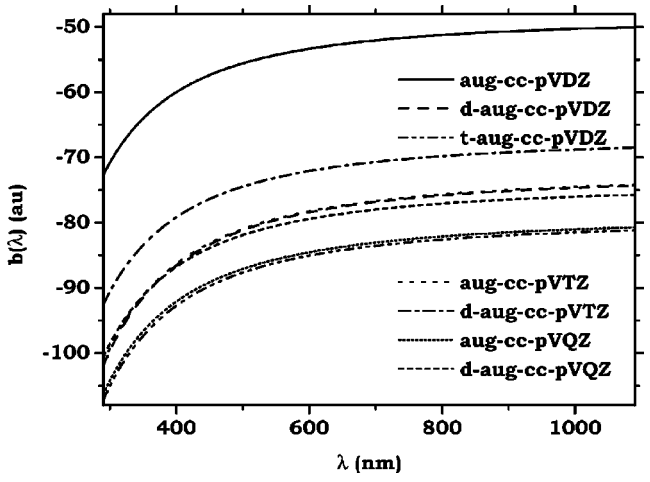


FIG. 3. CO. The temperature-independent contribution to the EFG induced birefringence, computed at the effective quadrupole center R_z, as a function of the wavelength λ in the 290–1090 nm range for different correlation-consistent basis sets in the formulation of Imrie and Raab, see Ref. 12. Atomic units.

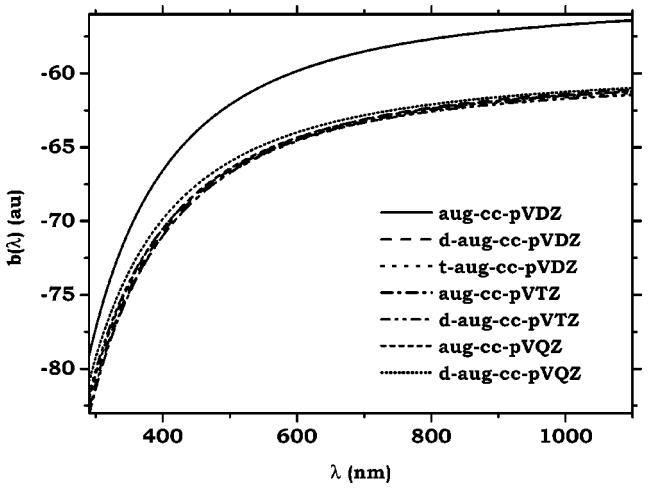


FIG. 4. CO. The temperature-independent contribution to the EFG induced birefringence, computed at the effective quadrupole center R_z, as a function of the wavelength λ in the 290–1090 nm range for different correlation-consistent basis sets in the formulation of Buckingham and Longuet-Higgins, see Ref. 11. Atomic units.

also Eqs. (25) and (28)] using the CCSD model and a variety of correlation-consistent basis sets, see Sec. III. The resulting equilibrium EQC's are shown as a function of the wavelength λ in the range between 290 and 1090 nm in Figs. 1 (IR) and 2 (BLH), respectively. The difference between the two formulations is noticeable, and will be discussed in more detail below. Regardless of the approach, the value of R_z increases in absolute value as the cardinal number (X) of the basis set increases. Furthermore, the difference between the R_z values obtained in a singly augmented and a doubly augmented basis set for a given X decreases significantly as X increases, and the effect of triple augmentation is small—at least at DZ level. The convergence pattern of the property with respect to extension of the basis set is smooth and well defined, and we estimate that our best basis set results (d-aug-cc-pVQZ) for the EQC are within one tenth of an atomic unit of the CCSD basis-set limit.

Figures 3 (IR) and 4 (BLH) display the frequency dependence of the equilibrium $b^{(R_z)}$ for the different correlation-consistent basis sets. For b_{IR} the basis-set convergence pattern is not as smooth as that of the EQC, and the changes with the basis are larger, especially from the aug-cc-pVXZ to the d-aug-cc-pVXZ sets. At least double augmentation is needed to obtain a reasonable convergence with the cardinal number for this property. Triple augmentation has no practical effect at least at the double-zeta level. The difference between the d-aug-cc-pVTZ (−84.48 a.u.) and the d-aug-cc-pVQZ (−83.97 a.u.) results, however, is small, indicating that the d-aug-cc-pVQZ value is converged within a few percent of the basis-set limit. Convergence is remarkably fast for b_{BLH}, where, due to the near cancellation of the first two contributions on the left-hand side of Eq. (34), it reflects the surprisingly weak dependence on the details of the basis set of the largely dominating $\overline{J'}$ term, Eq. (35).

The ''best'' CCSD values for R_z (d-aug-cc-pVQZ) at the experimentally relevant wavelength $\lambda = 632.8\,\mathrm{nm}$ are −2.502 a.u. (IR) and −4.523 a.u. (BLH), as obtained from the frequency dispersion function. To check the convergence of the power series, we also determined all response functions, and thus the EQC and $b^{(R_z)}$, analytically at $\lambda = 632.8\,\mathrm{nm}$. The corresponding results are shown in Table I. The direct calculation of R_z at the experimental wavelength in our largest basis set gives values of −2.503 a.u. (IR) and −4.524 a.u. (BLH), negligibly different from those obtained via the power series expansions, and the basis-set convergence pattern displayed for R_z in Table I confirms our estimate given above that the basis-set incompleteness error of the d-aug-cc-pVQZ value is less than 0.1 a.u. Similarly, negligible differences between the dispersion and analytical results are observed for $b^{(R_z)}$ regardless of the formulation.

Table I also allows us to discuss the dependence on the basis set of other relevant quantities at $\lambda = 632.8\,\mathrm{nm}$, such as the combination of linear response functions at the CM labeled $W(\omega)$ in Sec. II B, or that of the equilibrium electric dipole polarizability anisotropy ($\Delta\alpha$). The former is remarkably stable and variations with the basis set are basically negligible. The functions in the two formulations—$W_{\mathrm{IR}}(\omega)$ and $W_{\mathrm{BLH}}(\omega)$ as defined in Eqs. (24) and (32), respectively—differ by about 4%: at the CCSD/d-aug-cc-pVQZ level $W_{\mathrm{IR}}(\omega) = -40.3\,\mathrm{a.u.}$ and $W_{\mathrm{BLH}}(\omega) = -38.5\,\mathrm{a.u.}$ Buckingham, Disch, and Dunmur[3] published a very rough estimate of $-14\times10^{-32}\,\mathrm{esu}$ for $W(\omega)$ at $\lambda = 632.8\,\mathrm{nm}$ (≈ -180 a.u., see the Appendix), associated with a corresponding R_z of ≈ -24 a.u., much larger than our values. $\Delta\alpha$ varies by ≈10% in the range of basis sets in Table I,

TABLE I. CO. Equilibrium values for the $W(\omega)$ function [see Eqs. (24) and (32)], the EQC R_z, the anisotropy of the electric dipole polarizability and the temperature independent contribution to the anisotropy of the refractive index (b) for a series of correlation-consistent basis sets. Results obtained at $\lambda = 632.8\,\mathrm{nm}$ with a direct calculation, i.e, *not* employing the power expansion in Eqs. (51) and (52). Results labeled as ''Hyp'' are those obtained by assuming the fulfillment of the hypervirial relationship, see Eqs. (26), (33), and (39), (40). Atomic units.

		Imrie and Raab					Buckingham and Longuet-Higgins				
	$\Delta\alpha$	$W_{\mathrm{IR}}(\omega)$	$R_{z,\mathrm{IR}}$	$R^{\mathrm{Hyp}}_{z,\mathrm{IR}}$	b_{IR}	$b^{\mathrm{Hyp}}_{\mathrm{IR}}$	$W_{\mathrm{BLH}}(\omega)$	$R_{z,\mathrm{BLH}}$	$R^{\mathrm{Hyp}}_{z,\mathrm{BLH}}$	b_{BLH}	$b^{\mathrm{Hyp}}_{\mathrm{BLH}}$
aug-cc-pVDZ	4.2284	−37.4237	−2.0258	−2.2126	−52.8545	−53.5035	−35.5362	−3.5477	−4.2021	−59.3442	−61.6174
d-aug-cc-pVDZ	4.0131	−36.9732	−2.1084	−2.3033	−77.8299	−78.7012	−35.8485	−3.7696	−4.4665	−63.9047	−67.0204
t-aug-cc-pVDZ	4.0110	−37.1497	−2.1227	−2.3155	−77.6674	−78.5276	−35.9541	−3.7928	−4.4820	−64.1162	−67.1904
aug-cc-pVTZ	3.9014	−39.7242	−2.3880	−2.5455	−71.5603	−71.6436	−37.8055	−4.2804	−4.8451	−64.0492	−64.3477
d-aug-cc-pVTZ	3.8548	−39.7600	−2.4264	−2.5786	−84.4914	−84.8773	−38.0063	−4.3801	−4.9297	−64.0702	−65.4632
aug-cc-pVQZ	3.8187	−40.3214	−2.4918	−2.6397	−78.8904	−79.0952	−38.4163	−4.4962	−5.0300	−63.8946	−64.6340
d-aug-cc-pVQZ	3.8065	−40.3349	−2.5032	−2.6491	−83.9867	−84.3129	−38.4579	−4.5243	−5.0516	−63.5570	−64.7360

and increasing X from D to T and from T to Q for the singly augmented basis sets the incremental changes are about 0.3 a.u. and 0.1 a.u., respectively. The effect of augmentation with diffuse functions decreases as X increases, and the ''best'' d-aug-cc-pVQZ value ($\Delta\alpha = 3.8065$ a.u.) is only 0.01 a.u. lower than the value obtained with the aug-cc-pVQZ basis set. Using the d-aug-cc-pVTZ basis set, the zero-point vibrational correction and the pure vibrational contributions to the polarizability anisotropy were estimated as described above as, respectively, +1.10% and −0.04%, leading to a total increase by 1.07%. Experimental literature references for $\Delta\alpha$ of CO at $\lambda = 632.8$ nm are 3.59 ± 0.07 (Ref. 51) and 3.59 a.u.[52] A rather detailed analysis of the reasons for this discrepancy can be found in Ref. 53.

The data of Table I also allow us to estimate the quality of the approximation made by assuming that the Ehrenfest theorem holds and the basis set is complete. Thus in Table I we included the results obtained for R_z^{Hyp}, Eqs. (26) and (33), and for the corresponding $b^{(R_z^{\mathrm{Hyp}})}$. Under this approximation the (equilibrium) EQC has ''best'' values of −2.649 a.u. (IR) and −5.052 (BLH), respectively, about 5% (IR) and 10% (BLH) more negative than the ''rigorous'' result. The temperature-independent term is much less sensitive; its value (−84.313 a.u. for IR, −64.74 for BLH) is 1%–2% more negative than the one computed assuming basis set completeness and the fulfillment of the Ehrenfest theorem.

Let us now briefly discuss the effect of quantized rotation and of molecular vibration on the EFGB of CO, following the lines drawn in Sec. II D. Our estimate of $B_v = B_0$ from the CCSD(T)/aug-cc-pV5Z(frozen core) potential curve of CO is 8.7204×10^{-6} a.u., which means $\sigma = 0.010\,08$ at $T = 273.15$ K. According to Eqs. (44) and (45) quantized rotation thus reduces the inverse-temperature contribution to the EFGB of CO by ≈1%. The computed equilibrium vibrational frequency is $\omega_e = 2163.7\ \mathrm{cm}^{-1}$, so that the factor B_0/ω_e has a value of 8.85×10^{-4} a.u., approximately three times larger than estimated for carbon dioxide and much smaller than the value computed for molecular hydrogen, see Ref. 39. The centrifugal distortion contribution $C(T)$ in Eq. (44) can thus safely be neglected.

Table II collects the results for the ZPVA and PV corrections to the equilibrium electronic properties, including R_z and b both in the BLH and the IR formulation. The total vibrational corrections to all properties are small, at most 3.4% for $\Delta\alpha$. We account for vibrational effects on R_z and b by adding the calculated corrections to our ''best'' results.

We believe though that the most relevant issue of this section is the large difference which exists between the results in the formulations of Imrie and Raab[12] and of Buckingham and Longuet Higgins.[11] There is a factor of roughly 2 between the two estimates for the EQC, and those for the temperature-independent contribution to the EFG induced birefringence—$b^{(R_z)}$—differ by as much as 25%. In particular, due to Eq. (38), the differences in the EQC affect strongly the theoretical prediction of the molecular quadrupole moment of CO. The consequences of this large disagreement between the two formulations of the same physical process will be discussed in more detail in Sec. IV C.

TABLE II. CO. Equilibrium values, ZPV average contributions, and pure vibrational contributions for the quantities of interest. The results are obtained at the CCSD level using the d-aug-cc-pVTZ basis set, an equilibrium distance of 2.132 a.u. and the CCSD(T)/aug-cc-pV5Z(frozen core) potential curve, as described in the text. Atomic units.

	Equilibrium	ZPVA(0 K)	% (ZPVA)	PV	% (ZPVA+PV)
α_{zz}	15.9805	0.1780	1.1	−0.0069	1.1
α_{xx}	12.1277	0.0386	0.3	0	0.3
$\bar{\alpha}$	13.4119	0.0851	0.6	−0.0023	0.6
$\Delta\alpha$	3.8528	0.1394	3.6	−0.0069	3.4
$a_{z,xx}$	0.9663	0.0045	0.5	0.0101	1.5
$a_{z,zz}$	14.7860	0.0606	0.4	−0.0010	0.4
$a_{x,xz}$	10.2033	−0.0095	−0.1	0	−0.1
$G'_{x,y}$	−0.6019	−0.0060	1.0	0	1.0
$R_{z,\mathrm{IR}}$	−2.6556	0.0482	−1.8	−0.0027	−1.7
$R_{z,\mathrm{BLH}}$	−5.0835	0.0762	−1.5	−0.0101	−1.3
$\bar{B}$	−219.9442	−1.5108	0.7	0.5527	0.4
$\bar{\beta}_{\mathrm{IR}}$	−165.9054	−0.9908	0.6	−0.2190	0.7
$\bar{\beta}_{\mathrm{BLH}}$	−216.1454	−1.4667	0.7	0.4390	0.5
$\bar{J}'_{\mathrm{IR}}$	−2.2198	−0.0215	1.0	−0.0349	2.5
b_{IR}	−84.8680	−0.8189	1.0	0.2867	0.6
b_{BLH}	−65.4572	−0.6418	1.0	−0.8565	2.3

B. High-accuracy *ab initio* value of the quadrupole moment at the center of mass

The calculated $q_e^{(\mathrm{CM})}$ values (origin taken at the center of mass, CM) obtained with the different basis sets and wave function models are given in Table III. We initially note that the effect of augmenting the d-aug-cc-pVXZ basis sets with further diffuse functions is small and becomes negligible as X increases—the difference between the t-aug-cc-pVXZ and d-aug-cc-pVXZ CCSD(T) results decreases from 1.0 milliatomic units (mau) at the double-zeta level to 0.1 mau at the qaudruple-zeta level. Our most accurate result for $q_e^{(\mathrm{CM})}$ is thus obtained from the d-aug-cc-pV6Z valence-only result corrected for core-correlation effects. From the d-aug-cc-

TABLE III. CO. Basis set and wave function model investigation of the equilibrium electric quadrupole moment referring to the center of mass. In the valence basis sets, only the valence electrons have been correlated, whereas in the core-valence basis sets all the electrons have been correlated. Atomic units.

Basis	SCF	MP2	CCSD	CCSD(T)
aug-cc-pVDZ	−1.5820	−1.5715	−1.5341	−1.5402
aug-cc-pVTZ	−1.5457	−1.5093	−1.4764	−1.4807
aug-cc-pVQZ	−1.5302	−1.4923	−1.4591	−1.4626
aug-cc-pV5Z	−1.5302	−1.4905	−1.4576	−1.4608
aug-cc-pV6Z	−1.5300	−1.4897	−1.4569	−1.4599
d-aug-cc-pVDZ	−1.5434	−1.5417	−1.5016	−1.5088
d-aug-cc-pVTZ	−1.5339	−1.4995	−1.4666	−1.4712
d-aug-cc-pVQZ	−1.5297	−1.4917	−1.4590	−1.4625
d-aug-cc-pV5Z	−1.5300	−1.4902	−1.4574	−1.4605
d-aug-cc-pV6Z	−1.5299	−1.4895	−1.4567	−1.4597
t-aug-cc-pVDZ	−1.5410	−1.5406	−1.5006	−1.5078
t-aug-cc-pVTZ	−1.5335	−1.4995	−1.4669	−1.4715
t-aug-cc-pVQZ	−1.5298	−1.4918	−1.4591	−1.4626
aug-cc-pCVDZ	−1.5899	−1.5745	−1.5395	−1.5454
aug-cc-pCVTZ	−1.5401	−1.4998	−1.4707	−1.4752
aug-cc-pCVQZ	−1.5293	−1.4877	−1.4584	−1.4620
aug-cc-pCV5Z	−1.5301	−1.4870	−1.4582	−1.4614

pV6Z CCSD(T) result and the difference between the aug-cc-pCV5Z and aug-cc-pV5Z CCSD(T) results we obtain our best value as -1.460 a.u.

The change in $q_e^{(\mathrm{CM})}$ with each increment in X ($q_{e(X+1)}^{(\mathrm{CM})} - q_{e(X)}^{(\mathrm{CM})}$) decreases steadily as X increases, and from the basis-set convergence within the d-aug-cc-pVXZ series the basis-set incompleteness error on our best value is estimated to be 0.001 a.u. For the d-aug-cc-pV6Z basis set, the change from SCF to CCSD is 0.073 a.u., whereas the change from CCSD to CCSD(T) amounts to 0.003 a.u., thus the effect of triple excitations (as described by CCSD(T)) is only 4% of the effect of single and double excitations. In a recent full configuration interaction (FCI) benchmark study[25] it was found that CCSD(T) recovered about 98.5% of the total FCI correlation contribution for $q_e^{(\mathrm{CM})}$ of BH and HF. The percentage of the effect of triple excitations (as described by CCSD(T)) compared to single and double excitations for $q_e^{(\mathrm{CM})}$ of CO is somewhat smaller than for $q_e^{(\mathrm{CM})}$ of BH (7%) and HF (16%),[25] and a reasonable estimate of the error due to correlation beyond CCSD(T) for $q_e^{(\mathrm{CM})}$ of CO thus appears to be 2% of the CCSD(T) correlation contribution. For the d-aug-cc-pV6Z basis set this amounts to 0.0014 a.u. Finally, we note that the semirelativistic CCSD results differed by less than 0.001 a.u. from their nonrelativistic counterparts in Table III, and the effect of relativity can thus be neglected compared to the error due to the incompleteness of the CCSD(T) model. Taking everything into account, our final best theoretical value for $q_e^{(\mathrm{CM})}$ of CO thus becomes (-1.460 ± 0.002) a.u. $= (-6.550 \pm 0.008) \times 10^{-40}\,\mathrm{C\,m^2}$ (we combine the uncertainties as standard deviations).

The rovibrationally averaged value obtained at the CCSD(T)/aug-cc-pV5Z level, which provides accurate values of $q^{(\mathrm{CM})}$ and the electronic energy at reasonable computational costs, is -1.446 a.u. Compared to the CCSD(T)/aug-cc-pV5Z $q_e^{(\mathrm{CM})}$ value, the rovibrational effect is 0.015 a.u. (1.0%). Correcting our best $q_e^{(\mathrm{CM})}$ value accordingly, we obtain $q_0^{(\mathrm{CM})} = (-1.445 \pm 0.002)$ a.u. $= (-6.483 \pm 0.008) \times 10^{-40}\,\mathrm{C\,m^2}$.

C. Comparison with an experimentally deduced quadrupole moment

In a recent study by Graham *et al.*,[10] $q^{(R_z)}$ of CO was determined from measurements of EFGB at 298 K to be $(-9.47 \pm 0.15) \times 10^{-40}\,\mathrm{C\,m^2}$. In this study the hyperpolarizability correction term b was neglected. Our ''best'' (CCSD/d-aug-cc-pVQZ) values of $b^{(R_z)}$ (ca. -84 a.u. for IR and -65 a.u. for BLH) correspond to roughly 8% and 6% of the temperature dependent term in Eq. (1). Thus, although the b-term is small, it is significant in a comparison with our high-level *ab initio* value, and we shall therefore revise the experimentally derived value of Ref. 10 to take it into account. At the EQC, Eq. (44) may be rearranged as follows:

$$q = q_{\mathrm{app}} - \frac{15bkT}{2\Delta\alpha F(T)}, \tag{54}$$

where we have introduced the apparent quadrupole moment q_{app}, which is the result obtained if b is neglected, and used the fact that $C(T)$ can be neglected. Employing our CCSD/d-aug-cc-pVQZ values of $b^{(R_z)}$ (Table I) corrected for vibrational effects (see Table II) together with the experimental value[52] of $\Delta\alpha = 5.92 \times 10^{-41}\,\mathrm{C^2\,m^2\,J^{-1}}$ and the above-mentioned value of q_{app} we obtain two revised experimentally deduced values, $q_{\mathrm{exp,IR}}^{(R_z)} = (-8.71 \pm 0.15) \times 10^{-40}\,\mathrm{C\,m^2}$ and $q_{\mathrm{exp,BLH}}^{(R_z)} = (-8.89 \pm 0.15) \times 10^{-40}\,\mathrm{C\,m^2}$.

In order to compare our theoretical value for q at the center of mass with these revised experimental values, we need to translate the origin of the former to the EQC. This may be accomplished using Eq. (38), which requires knowledge of the electric dipole moment. The experimentally deduced equilibrium electric dipole moment of CO is $\mu_e = -0.123(2)$ D.[54] Using this value together with the CCSD/d-aug-cc-pVQZ values for R_z in Table I to translate $q_e^{(\mathrm{CM})}$ we obtain $q_{e,\mathrm{IR}}^{(R_z)} = -1.702$ a.u. $= -7.64 \times 10^{-40}\,\mathrm{C\,m^2}$ in the formulation of Imrie and Raab and $q_{e,\mathrm{BLH}}^{(R_z)} = -1.898$ a.u. $= -8.51 \times 10^{-40}\,\mathrm{C\,m^2}$ in the formulation of Buckingham and Longuet-Higgins. Using the experimental value $\mu_0 = -0.1097(1)$ D (Ref. 54) together with the ZPVA- and PV-corrected value for R_z to translate $q_0^{(\mathrm{CM})}$ we obtain $q_{0,\mathrm{IR}}^{(R_z)} = -1.657$ a.u. $= -7.43 \times 10^{-40}\,\mathrm{C\,m^2}$ in the formulation of Imrie and Raab and $q_{0,\mathrm{BLH}}^{(R_z)} = -1.830$ a.u. $= -8.21 \times 10^{-40}\,\mathrm{C\,m^2}$ in the formulation of Buckingham and Longuet-Higgins. It appears immediately that the formulation of Buckingham and Longuet-Higgins gives results that are in better agreement with experiment with respect to those given by the formulation of Imrie and Raab. So far, however, we have not discussed the error in the calculated value of R_z and its influence on $q^{(R_z)}$. As R_z has been determined at the CCSD/d-aug-cc-pVQZ level of theory, an analysis of the indetermination of R_z is needed. It is very difficult to obtain a reliable estimate of the error in R_z due to the incompleteness of the CCSD wave function model and the basis set, as we do not currently have the possibility to increase the level of theory any further. However, a rough estimate of this error in R_z may be obtained from the difference between the R_z and R_z^{Hyp} results, which reduces to zero for the exact wave function. From Table I, this difference is seen to be about 0.5 a.u. at the CCSD/d-aug-cc-pVQZ level in the formulation of Buckingham and Longuet-Higgins and about 0.15 a.u. in that of Imrie of Raab. We shall use the largest of these two values (0.5 a.u.) as a crude (but rather conservative) estimate of the uncertainty on the determined value of R_z. The additional uncertainty in $q^{(R_z)}$ due to this estimated uncertainty in the calculated R_z and the uncertainty on μ_0 can then be obtained via Eq. (38). Combining the relative uncertainties of both quantities, the effect of the indetermination of R_z and μ_0 on $q^{(R_z)}$ is estimated to be 0.05 a.u. Combining this additional uncertainty of ± 0.05 a.u. with our values of $q_0^{R_z}$ we obtain the final theoretical values of $q_{0,\mathrm{IR}}^{(R_z)} = (-1.66 \pm 0.05)$ a.u. $= (-7.43 \pm 0.23) \times 10^{-40}\,\mathrm{C\,m^2}$ and $q_{0,\mathrm{BLH}}^{(R_z)} = (-1.83 \pm 0.05)$ a.u. $= (-8.21 \pm 0.23) \times 10^{-40}\,\mathrm{C\,m^2}$.

Comparing these results with the revised experimental ones, we see that the theoretical and experimental values obtained in the formulation of Imrie and Raab do not overlap even when three times the uncertainty ranges are considered, whereas the theoretical and revised experimental values ob-

tained in the formulation of Buckingham and Longuet-Higgins overlap when two times the uncertainty ranges are considered. Concerning the difference between the two semiclassical interpretations of the EFGB in dipolar molecules it thus appears that in the case of CO, the numerical evidence points in favor of that of Buckingham and Longuet-Higgins. However, further studies to confirm this for other dipolar molecules are certainly desirable. Also a thorough analysis of the recent work of Dumitru and Woolley[13,14] might be worthwhile. Their explicitly origin-independent quantum statistical formulation does not involve a definition of an EQC, and as such it bypasses in principle the difficulties which are apparently encountered when an origin dependent approach to the EFGB of polar molecules is taken.

V. CONCLUDING REMARKS

The first *ab initio* study of the electric-field-gradient-induced birefringence of a polar molecule has been presented. Within two semiclassical formulations of EFGB of dipolar molecules, the effective quadrupole center for CO, which cannot be determined directly experimentally, has been obtained as a function of the frequency at the CCSD level in a variety of correlation-consistent basis sets, and the different contributions to the birefringence at the effective quadrupole center for $\lambda = 632.8$ nm have been determined at the same level of theory. A highly accurate theoretical value of the molecular electric quadrupole moment referring to the center of mass $q_0^{(\mathrm{CM})} = (-6.483 \pm 0.008) \times 10^{-40}\,\mathrm{C\,m^2}$ is obtained as the basis-set limit value at the CCSD(T) level completed with estimates of relativistic effects, correlation effects beyond CCSD(T), and rovibrational effects. This value leads to the theoretical results of $q_{0,\mathrm{IR}}^{(R_z)} = (-7.43 \pm 0.23) \times 10^{-40}\,\mathrm{C\,m^2}$ for the quadrupole moment referring to the effective quadrupole center within the formulation of Imrie and Raab,[12] while the corresponding result within the formulation of Buckingham and Longuet-Higgins[11] is $q_{0,\mathrm{BLH}}^{(R_z)} = (-8.21 \pm 0.23) \times 10^{-40}\,\mathrm{C\,m^2}$. The revised experimentally deduced values within the two theories are $q_{\mathrm{exp,IR}}^{(R_z)} = (-8.71 \pm 0.15) \times 10^{-40}\,\mathrm{C\,m^2}$ and $q_{\mathrm{exp,BLH}}^{(R_z)} = (-8.89 \pm 0.15) \times 10^{-40}\,\mathrm{C\,m^2}$. Comparison of the theoretical and revised experimentally deduced results appears to support the formulation of Buckingham and Longuet-Higgins,[11] but not the one of Imrie and Raab.[12] A renewed effort in the analysis of the reason for the discrepancies between the two formulations seems appropriate.

ACKNOWLEDGMENTS

We would like to thank Guy Woolley for calling our attention to the problem and David Buckingham for his comments and suggestions. This work has been supported by the Danish Research Council (Grant No. 9600856). S.C. and A.H. acknowledge support from the European Community, Marie Curie TMR program Contract No. ERBFMBICT971922, and Marie Curie individual fellowship program Contract No. MCFI-1999-00006, respectively.

APPENDIX: UNITS

1 a.u. of $\mu \equiv e a_0 \cong 8.478\,36 \times 10^{-30}\,\mathrm{C\,m} \cong 2.541\,75\,\mathrm{D} \equiv 2.541\,75 \times 10^{-18}\,\mathrm{Fr\,cm}$;

1 a.u. of $\alpha \equiv e^2 a_0^2 E_h^{-1} \cong 1.648\,778 \times 10^{-41}\,\mathrm{C^2\,m^2\,J^{-1}} \cong 1.481\,85 \times 10^{-25}\,4\pi\epsilon_0\,\mathrm{cm^3}$;

1 a.u. of $q \equiv e a_0^2 \cong 4.486\,554 \times 10^{-40}\,\mathrm{C\,m^2} \cong 1.345\,03 \times 10^{-26}\,\mathrm{Fr\,cm^2}$;

1 a.u. of $a \equiv e^2 a_0^3 E_h^{-1} \cong 8.724\,96 \times 10^{-52}\,\mathrm{C^2\,m^3\,J^{-1}} \cong 7.841\,60 \times 10^{-34}\,4\pi\epsilon_0\,\mathrm{cm^4}$;

1 a.u. of $G' \equiv e^2 a_0^3 \hbar^{-1} \cong 3.607\,02 \times 10^{-35}\,\mathrm{C^2\,m^3\,J^{-1}\,s^{-1}} \cong 1.081\,36 \times 10^{-27}\,\mathrm{Fr\,cm\,G^{-1}}$;

1 a.u. of $b(=B) \equiv e^3 a_0^4 E_h^{-2} \cong 1.696\,733 \times 10^{-63}\,\mathrm{C^3\,m^4\,J^{-2}} \cong 4.571\,68 \times 10^{-41}\,4\pi\epsilon_0\,\mathrm{Fr\,cm^5\,erg^{-1}}$;

1 a.u. of $J' \equiv e^3 a_0^4 \hbar^{-1} E_h^{-1} \cong 7.014\,53 \times 10^{-47}\,\mathrm{C^3\,m^4\,s^{-1}\,J^{-2}} \cong 6.304\,35 \times 10^{-35}\,\mathrm{Fr^2\,cm^2\,erg^{-1}\,G^{-1}}$;

1 a.u. of $\nabla E \equiv e a_0^{-2} E_h \cong 9.717\,36 \times 10^{21}\,\mathrm{V\,m^{-2}} \cong 3.241\,36 \times 10^{15}\,\mathrm{Fr\,cm^{-3}}(4\pi\epsilon_0)^{-1}$.

[1] A. D. Buckingham, J. Chem. Phys. **30**, 1580 (1959).
[2] A. D. Buckingham and R. L. Disch, Proc. R. Soc. London, Ser. A **273**, 275 (1963).
[3] A. D. Buckingham, R. L. Disch, and D. A. Dunmur, J. Am. Chem. Soc. **90**, 3104 (1968).
[4] J. Vrbancich and G. L. D. Ritchie, J. Chem. Soc., Faraday Trans. 2 **76**, 648 (1980).
[5] R. J. Emrich and W. Steele, Mol. Phys. **40**, 469 (1980).
[6] M. R. Battaglia, A. D. Buckingham, and J. H. Williams, Chem. Phys. Lett. **78**, 421 (1981).
[7] M. R. Battaglia, A. D. Buckingham, D. Neumark, R. K. Pierens, and J. H. Williams, Mol. Phys. **43**, 1015 (1981).
[8] A. D. Buckingham, C. Graham, and J. H. Williams, Mol. Phys. **49**, 703 (1983).
[9] C. Graham, J. Pierrus, and R. E. Raab, Mol. Phys. **67**, 939 (1989).
[10] C. Graham, D. A. Imrie, and R. E. Raab, Mol. Phys. **93**, 49 (1998).
[11] A. D. Buckingham and H. C. Longuet-Higgins, Mol. Phys. **14**, 63 (1968).
[12] D. A. Imrie and R. E. Raab, Mol. Phys. **74**, 833 (1991).
[13] A. G. Dumitru and R. G. Woolley, Mol. Phys. **94**, 581 (1998).
[14] A. G. Dumitru and R. G. Woolley, Mol. Phys. **94**, 595 (1998).
[15] S. Coriani, C. Hättig, and A. Rizzo, J. Chem. Phys. **111**, 7828 (1999).
[16] S. Coriani, C. Hättig, P. Jørgensen, A. Rizzo, and K. Ruud, J. Chem. Phys. **109**, 7176 (1998).
[17] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
[18] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[19] R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[20] D. E. Woon and T. H. Dunning, J. Chem. Phys. **100**, 2975 (1994).
[21] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
[22] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[23] A. Halkier, S. Coriani, and P. Jørgensen, Chem. Phys. Lett. **294**, 292 (1998).
[24] A. Halkier and S. Coriani, Chem. Phys. Lett. **303**, 408 (1999).
[25] A. Halkier, H. Larsen, J. Olsen, P. Jørgensen, and J. Gauss, J. Chem. Phys. **110**, 734 (1999).
[26] A. Halkier, H. Koch, O. Christiansen, P. Jørgensen, and T. Helgaker, J. Chem. Phys. **107**, 849 (1997).
[27] D. E. Woon and T. H. Dunning, J. Chem. Phys. **103**, 4572 (1995).
[28] O. Christiansen, C. Hättig, and P. Jørgensen, Int. J. Quantum Chem. **68**, 1 (1998).
[29] C. Hättig, O. Christiansen, H. Koch, and P. Jørgensen, Chem. Phys. Lett. **269**, 428 (1997).
[30] C. Hättig, O. Christiansen, and P. Jørgensen, J. Chem. Phys. **107**, 10592 (1997).
[31] C. Hättig and P. Jørgensen, Theor. Chem. Acc. **100**, 230 (1998).
[32] A. D. Buckingham and M. J. Jamieson, Mol. Phys. **22**, 117 (1971).
[33] J. Olsen and P. Jørgensen, J. Chem. Phys. **82**, 3235 (1985).
[34] J. Olsen and P. Jørgensen, in *Modern Electronic Structure Theory, Part II*, edited by D. R. Yarkony (World Scientific, Singapore, 1995), p. 857.
[35] A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967).

[36] D. E. Logan, Mol. Phys. **46**, 271 (1982).
[37] E. B. Graham, J. Pierrus, and R. E. Raab, J. Phys. B **25**, 4673 (1992).
[38] M. J. Gunning and R. E. Raab, Mol. Phys. **91**, 589 (1997).
[39] A. D. Buckingham and M. Pariseau, Trans. Faraday Soc. **62**, 1 (1966).
[40] D. M. Bishop, Rev. Mod. Phys. **62**, 343 (1990).
[41] D. M. Bishop and B. Kirtman, J. Chem. Phys. **95**, 2646 (1991).
[42] A. Rizzo, S. Coriani, and A. Halkier (unpublished).
[43] K. P. Huber and G. H. Herzberg, *Molecular Spectra and Molecular Structure. Constants of Diatomic Molecules* (Van Nostrand–Reinhold, New York, 1979).
[44] A. Halkier, P. Jørgensen, J. Gauss, and T. Helgaker, Chem. Phys. Lett. **274**, 235 (1997).
[45] T. Helgaker, H. J. A. Jensen, P. Jørgensen, J. Olsen, K. Ruud, H. Ågren, T. Andersen, K. L. Bak, V. Bakken, O. Christiansen, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T. Saue, P. R. Taylor, and O. Vahtras, DALTON, an *ab initio* electronic structure program, Release 1.0 (1997). See http://www.kjemi.uio.no/software/dalton/dalton.html.
[46] H. Koch, O. Christiansen, R. Kobayashi, P. Jørgensen, and T. Helgaker, Chem. Phys. Lett. **228**, 233 (1994).
[47] H. Koch, A. S. de Meras, T. Helgaker, and O. Christiansen, J. Chem. Phys. **104**, 4157 (1996).
[48] H. Koch, P. Jørgensen, and T. Helgaker, J. Chem. Phys. **104**, 9528 (1996).
[49] K. Andersson, M. R. A. Blomberg, M. P. Fülscher, G. Karlström, R. Lindh, P. Å. Malmqvist, J. Olsen, B. O. Roos, A. J. Sadlej, M. Schütz, L. Seijo, L. Serrano-Andrés, P. E. M. Siegbahn, and P. O. Widmark, MOLCAS version 4, Lund University, Sweden, 1997.
[50] S. Coriani, A. Halkier, P. Jørgensen, J. Gauss, O. Christiansen, and A. Rizzo, J. Chem. Phys. **113**, 1688 (2000).
[51] H. Kling and W. Hüttner, Chem. Phys. **90**, 207 (1984).
[52] M. P. Bogaard, A. D. Buckingham, R. K. Pierens, and A. H. White, J. Chem. Soc., Faraday Trans. 1 **74**, 3008 (1978).
[53] O. Christiansen, C. Hättig, and J. Gauss, J. Chem. Phys. **109**, 4745 (1998).
[54] W. L. Meerts, F. H. D. Leeuw, and A. Dymanus, Chem. Phys. **22**, 319 (1977).