Coupled cluster investigation of the electric-field-gradient-induced birefringence of H_2, N_2, C_2H_2, and CH_4

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An *ab initio* investigation of the electric-field-gradient-induced birefringence of H_2, N_2, C_2H_2, and CH_4 is presented. All linear and nonlinear optical properties contributing to the induced anisotropy of the refractive index are computed by means of coupled cluster singles and doubles response theory. For systems of cubic or icosahedral symmetry, the only nonvanishing contribution to the induced birefringence within the semiclassical approach is due to the frequency-dependent dipole–dipole–quadrupole and dipole–dipole–magnetic dipole hyperpolarizabilities. These hyperpolarizabilities are important for accurate experimental determinations of the molecular quadrupole moment from electric-field-gradient-induced birefringence measurements. © *1998 American Institute of Physics.* [S0021-9606(98)30241-X]

I. INTRODUCTION

The electric-field-gradient-induced birefringence (EFGB) is the anisotropy of the refractive index observed when plane-polarized light passes through a medium in a direction perpendicular to an external electric field gradient. The EFGB, which was originally predicted by Debye,[1] has similarities to optical effects like the Kerr,[2,3] the Cotton–Mouton,[4] and the Faraday[5,6] effects. The EFGB originates (primarily) from the interaction of the electric field gradient with the molecular quadrupole moment, resulting in a partial orientation of the molecules in the sample, and (secondarily) from changes in the effective polarizability induced by the field gradient. The first effect is temperature dependent and it can be expressed in terms of the molecular quadrupole moment and the molecular electric-dipole polarizability. The second contribution is temperature independent and determined by higher-order polarizabilities.

For quadrupolar systems, EFGB measurements can be used to determine the molecular quadrupole moment as suggested by Buckingham in 1959.[7] The first experiment was carried out in 1963 by Buckingham and Disch,[8] who determined the quadrupole moment of CO_2. Since then, EFGB measurements have been used as an accurate tool for determining molecular quadrupole moments (see, for instance, Refs. 9–15). The theoretical foundations of the EFGB effect in gases have been discussed by Buckingham and Longuet-Higgins[16] and Buckingham and Jamieson,[17] and the theory has been extended to compressed gas mixtures by Kielich.[18] The general theory has been revisited by Imrie and Raab[19] using the semiclassical approach also employed by Buckingham and Longuet-Higgins. Recently, a quantum theory of EFGB based on a finite-temperature perturbation approach to molecular light scattering was presented by Dumitru and Woolley.[20,21] An account of the historical developments of EFGB was given in a recent review by Ritchie.[22]

In the past, EFGB measurements were often performed at a fixed temperature and the hyperpolarizability contribution was neglected due to its smallness compared to the temperature-dependent term. In some cases, theoretical results for the hyperpolarizability term have been used to obtain the molecular quadrupole moment from the EFGB experiment (see, for example, Refs. 23 and 24). By performing measurements at different temperatures, the temperature-dependent and temperature-independent terms can be separated by linear regression, and the quadrupole moment extracted provided that the electric-dipole polarizability tensor is known.[25] The experimental procedure is nevertheless difficult and cannot easily be applied for all systems. For instance, the difficulties of handling compressed acetylene gas over a wide range of temperatures prevented an analysis of the temperature dependence of the EFGB in a recent experimental study by Keir *et al.*[23] In non-quadrupolar systems, measurements of EFGB give the hyperpolarizability terms directly.

Buckingham and Longuet-Higgins[16] computed, in the static limit, the anisotropy of the refractive index induced by an electric field gradient analytically for the hydrogen atom, and Buckingham and Jamieson[17] estimated the temperature-independent contribution to the EFGB for rare gases, H_2 and

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CH_4, using the approximate relationship that exists between this term and the Verdet constant in the static limit and for ''spherical'' systems.

Today, sophisticated and reliable techniques are available for accurate calculations of the molecular quadrupole moment, the electric-dipole polarizability anisotropy, and the hyperpolarizabilities contributing to the anisotropy of the refractive index. Whereas there is a large number of studies of the first two properties in the literature, calculations of the frequency-dependent hyperpolarizabilities characterizing the temperature-independent term have been scarce. To our knowledge, the only *ab initio* study dedicated to the calculation of the hyperpolarizability contribution to the EFGB is that of Amos,[26] who, at the most advanced level, calculated the hyperpolarizability contribution to the EFGB of nitrogen in the low-frequency limit by a coupled Hartree–Fock (CHF) approach.

In this work, we investigate the EFGB of H_2, N_2, C_2H_2, and CH_4. Quadrupole moments are computed as analytical derivatives of the coupled cluster singles and doubles (CCSD) Lagrangian as described in Ref. 27. For the linear and nonlinear polarizabilities, the recently implemented linear[28] and quadratic[29] CCSD response approach is employed.

II. THEORY

For an ideal gas at the absolute temperature T, the relationship between the microscopic properties and the observed EFGB Δn is (in SI units)[16,17]

$$\Delta n = n_x - n_y = \frac{2\pi N q}{(4\pi\epsilon_0)} \left\{ b + \frac{2}{15kT} \left[\Theta_{\alpha\beta}\alpha_{\alpha\beta} - \mu_\alpha \left(A_{\beta,\alpha\beta} + \frac{5}{\omega}\epsilon_{\alpha\beta\gamma}G_{\beta,\gamma} \right) \right] \right\}, \tag{1}$$

where Einstein's convention for implicit summation over repeated indices is used. Here n is the refractive index, N the number density, q the laboratory field gradient (a diagonal traceless tensor, $q = q_{xx} = -q_{yy}$; $q_{zz} = 0$), Θ the permanent molecular quadrupole moment, and μ the permanent electric dipole moment. Also, α, A and G are the frequency-dependent electric dipole–electric dipole, electric dipole–electric quadrupole, and electric dipole–magnetic dipole polarizabilities. The frequency-dependent polarizabilities A and G can be written as sum-over-states expressions[30]

$$A_{\alpha,\beta\gamma}(-\omega;\omega) = \frac{1}{\hbar} \sum_P \sum_{m\neq g} \frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle m|\hat{\Theta}_{\beta\gamma}|g\rangle}{(\omega_{mg}-\omega)}, \tag{2}$$

$$G_{\alpha,\beta}(-\omega;\omega) = \frac{1}{\hbar} \sum_P \sum_{m\neq g} \frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle m|\hat{m}_\beta|g\rangle}{(\omega_{mg}-\omega)}, \tag{3}$$

and they describe the dipole moment induced by the electric-field gradient and the time-dependent magnetic field associated with the propagating wave, respectively. Here $\hat{\mu}$, $\hat{m}$, and $\hat{\Theta}$ represent the electric dipole, magnetic dipole, and electric quadrupole operators

$$\hat{\mu}_\alpha = \sum_i q_i \hat{r}_{i,\alpha}, \tag{4}$$

$$\hat{m}_\alpha = \sum_i \frac{q_i}{2m_i} \hat{l}_{i,\alpha}, \tag{5}$$

$$\hat{\Theta}_{\alpha\beta} = \frac{1}{2} \sum_i q_i (3\hat{r}_{i,\alpha}\hat{r}_{i,\beta} - \hat{r}_i^2 \delta_{\alpha,\beta}), \tag{6}$$

with $\hat{r}_{\alpha,i}$ and $\hat{l}_{\alpha,i}$ indicating the α Cartesian component of the position and angular momentum operators for a particle of charge q_i and mass m_i. In Eqs. (2) and (3), Σ_P indicates summation over all permutations of the pairs $(\hat{\mu}_\alpha/-\omega)$, $(\hat{\Theta}_{\beta\gamma}/\omega)$, and of the pairs $(\hat{\mu}_\alpha/-\omega)$, $(\hat{m}_\beta/\omega)$, respectively. Here $\hbar\omega_{ij} = E_i - E_j$, and $|g\rangle$ is the electronic ground state.

The temperature-independent term is a combination of higher-order polarizabilities[16,17]

$$b = \frac{2}{15}[B_{\alpha,\beta,\alpha\beta}(-\omega;\omega,0) - B_{\alpha,\beta,\alpha\beta}(-\omega;0,\omega)] - \frac{2}{3\omega}\epsilon_{\alpha\beta\gamma}J_{\alpha,\beta,\gamma}(-\omega;\omega,0), \tag{7}$$

where[31]

$$B_{\alpha,\beta,\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2) = \frac{1}{\hbar^2} \sum_P \sum_{m\neq g} \sum_{n\neq g} \frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle m|\overline{\hat{\mu}_\beta}|n\rangle\langle n|\hat{\Theta}_{\gamma\delta}|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_2)} \tag{8}$$

and

$$J_{\alpha,\beta,\gamma}(-\omega_\sigma;\omega_1,\omega_2) = \frac{1}{\hbar^2} \sum_P \sum_{m\neq g} \sum_{n\neq g} \frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle m|\overline{\hat{m}_\beta}|n\rangle\langle n|\hat{\mu}_\gamma|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_2)}, \tag{9}$$

where ϵ is the Levi-Civita tensor, $\omega_\sigma = \omega_1 + \omega_2$, Σ_P indicates here summation over all permutations of the pairs $(\hat{\mu}_\alpha/-\omega_\sigma)$, $(\hat{\mu}_\beta/\omega_1)$ and $(\hat{\Theta}_{\gamma\delta}/\omega_2)$ for B, and of the pairs $(\hat{\mu}_\alpha/-\omega_\sigma)$, $(\hat{m}_\beta/\omega_1)$ and $(\hat{\mu}_\gamma/\omega_2)$ for J. $\langle i|\overline{\hat{O}}|j\rangle = \langle i|\hat{O}|j\rangle - \delta_{ij}\langle g|\hat{O}|g\rangle$. Equivalent expressions for B and J were given in Refs. 16 and 17.

For the temperature-independent contribution to the EFGB we employ the symbol ''b,'' as introduced by Buckingham and Jamieson.[17] The relationship between b and the dipole–dipole–quadrupole hyperpolarizability B is given in Eq. (7). In the original paper of Buckingham and Longuet-Higgins[16] the symbol ''B'' was used instead of ''b.'' This still continues to be done in the literature and it may be a source of misunderstanding, as the temperature-independent contribution to the EFGB has been associated with a ''molecular dipole–dipole–quadrupole'' hyperpolarizability B, and then erroneously identified with the dipole–dipole–quadrupole hyperpolarizability introduced by Buckingham[30] (see, for instance, Refs. 10, 23, 25, 32, and 24). This may lead to serious problems when theoretical estimates of B (instead of b) are used to extract the molecular quadrupole moment from measurement of the EFGB (*vide infra*).

Imrie and Raab[19] have discussed the implications of using the primitive quadrupole moment operator in the derivation of the expression for the anisotropy of the refractive index induced by an electric field gradient. The general form of the equations remains unchanged in their approach, although the particular combination of higher-order polarizabilities differs from that of Ref. 16. Still, Eq. (1) is identical to that obtained by Imrie and Raab[19] for nonpolar molecules.

Both $\Theta_{\alpha\beta}$ and the term in round parentheses in Eq. (1) depend on the choice of origin for polar molecules. However, the origin independence of the temperature-dependent contribution in Eq. (1) has been proven.[16] Imrie and Raab[19] derived a general expression for the anisotropy of the refractive index which is independent of the choice of origin when the traced form of the quadrupole moment operator is employed. Origin independence can be shown for the b term alone in the approach of Imrie and Raab,[19] as is also easily demonstrated for nonpolar systems, regardless of the choice of quadrupole moment operator. In polar molecules, an *effective quadrupolar center*—in general depending on the frequency used in the experiment—can be determined as the choice of origin for which the term in round parentheses in Eq. (1) vanishes.[16]

For molecules with an n-fold rotation axis with $n \geqslant 3$, $\alpha_{xx}=\alpha_{yy}\neq\alpha_{zz}$, and $\Theta_{zz}=-2\Theta_{yy}=-2\Theta_{xx}\equiv\Theta$, Eq. (1) simplifies to

$$\Delta n = n_x - n_y = \frac{2\pi Nq}{(4\pi\epsilon_0)}\left\{ b + \frac{2}{15kT} \times \left[\Theta\Delta\alpha - \mu\left(A_{\parallel} + 2A_{\perp} + \frac{10}{\omega} G \right) \right] \right\}, \quad (10)$$

where $\Delta\alpha=\alpha_{zz}-\alpha_{xx}$. With the rotation axis along the z direction, $A_{\parallel}=A_{z,zz}=-2A_{z,xx}=-2A_{z,yy}$, $A_{\perp}=A_{x,zx}=A_{x,xz}=A_{y,zy}=A_{y,yz}$, and $G=G_{x,y}=-G_{y,x}$. For nonpolar species, as those studied here,

$$\Delta n = n_x - n_y = \frac{2\pi Nq}{(4\pi\epsilon_0)}\left\{ b + \frac{2}{15kT}\Theta\Delta\alpha \right\} = \frac{2\pi Nq}{(4\pi\epsilon_0)}\left\{ b + \frac{F}{T} \right\} = {}_mQ(T)Nq. \quad (11)$$

For spherical top molecules, i.e., for systems of cubic or icosahedral symmetry, $F=0$ and only the temperature-independent term is nonvanishing.

Assuming ideal gas behavior, Eq. (11) becomes

$$\Delta n = n_x - n_y = \frac{2\pi Pq}{(4\pi\epsilon_0)}\left\{ \frac{1}{kT} b + \frac{2}{15(kT)^2}\Theta\Delta\alpha \right\}, \quad (12)$$

where P is the pressure. The electric-field-gradient-induced retardation or retardance ϕ associated to the anisotropy of the refractive index is[8]

$$\phi = \frac{2\pi l}{\lambda}\Delta n, \quad (13)$$

where l is the path length and λ is the vacuum wavelength of the radiation.

In the derivation of Eq. (1), the molecular rotation has been treated classically. A quantal treatment of the rotational motion—which is important for a molecule with a small moment of inertia such as H_2—leads, within some approximations, to a slightly modified version of Eq. (11):[33]

$$\Delta n = n_x - n_y = \frac{2\pi Nq}{(4\pi\epsilon_0)}\left[b' + \frac{2}{15}\frac{\Theta\Delta\alpha}{kT} f(T) \right], \quad (14)$$

where $f(T)=1-\sigma+\frac{8}{15}\sigma^2-\cdots$, with $\sigma=hcB_0/kT$, B_0 being the rotational constant. At room temperature, $f(T)$ has been estimated to be 0.75 for H_2.[9,33] At lower temperatures the correction becomes larger. For CO_2, quantum corrections have been found to be unimportant at room temperature.[33] In Eq. (14) b' differs from b in Eq. (11) by the effects of centrifugal distortions.[33]

The frequency-dependent polarizabilities and hyperpolarizabilities of Eqs. (2), (3), (8), and (9) can be expressed in terms of linear and quadratic response functions:

$$A_{\alpha,\beta\gamma} = \langle\langle \hat{\mu}_\alpha ; \hat{\Theta}_{\beta\gamma} \rangle\rangle_\omega, \quad (15)$$

$$G_{\alpha,\beta} = \langle\langle \hat{\mu}_\alpha ; \hat{m}_\beta \rangle\rangle_\omega, \quad (16)$$

and

$$b = \frac{2}{15}\left(\langle\langle \hat{\mu}_\alpha ; \hat{\mu}_\beta, \hat{\Theta}_{\alpha\beta} \rangle\rangle_{\omega,0} - \langle\langle \hat{\mu}_\alpha ; \hat{\mu}_\beta, \hat{\Theta}_{\alpha\beta} \rangle\rangle_{0,\omega} \right) - \frac{2}{3\omega}\epsilon_{\alpha\beta\gamma}\langle\langle \hat{\mu}_\alpha ; \hat{m}_\beta, \hat{\mu}_\gamma \rangle\rangle_{\omega,0}. \quad (17)$$

In the limit of zero frequency, the last term in Eq. (17) is related to the Verdet constant $V(\omega) \propto \omega\epsilon_{\alpha\beta\gamma}\langle\langle \hat{\mu}_\alpha ; \hat{m}_\beta, \hat{\mu}_\gamma \rangle\rangle_{0,\omega}$, and the two dipole–dipole–quadrupole hyperpolarizabilities cancel. For spherical-top systems in the zero-frequency limit, J is determined by the single constant, $J_{\alpha,\beta,\gamma}=J\epsilon_{\alpha\beta\gamma}$,[16] and b can, in these cases, be deduced from measurements of the Verdet constant $V(\omega)$ at low frequencies:[17]

$$b_0 = \lim_{\omega\to 0} b = -\lim_{\omega\to 0}\left(\frac{4J}{\omega} \right), \quad (18)$$

$$\lim_{\omega\to 0}\left(\frac{V}{\omega^2} \right) = -\frac{1}{2c}\lim_{\omega\to 0}\left(\frac{n_x - n_y}{q} \right) = -\frac{\pi N}{(4\pi\epsilon_0)c} b_0. \quad (19)$$

The systems studied in this work are all nonpolar, and we therefore focus on the calculation of the hyperpolarizabilities in Eq. (17), the molecular quadrupole moment, and the anisotropy of the electric-dipole polarizability, all of which enter Eq. (11).

For the linear and nonlinear polarizabilities we have employed the recently developed response approach for a CCSD wave function as described in Refs. 29 and 34.

The linear and quadratic coupled cluster response functions are obtained as derivatives of the time-averaged quasi-energy Lagrangian

$$\{L(t,\epsilon)\}_T = \left\{ \langle \mathrm{HF}|\hat{H}(t,\epsilon)e^{\hat{T}(t,\epsilon)}|\mathrm{HF}\rangle + \sum_\mu \overline{t}_\mu(t,\epsilon) \times \langle \mu|e^{-\hat{T}(t,\epsilon)}\left(\hat{H}(t,\epsilon) - i\frac{\partial}{\partial t} \right)e^{\hat{T}(t,\epsilon)}|\mathrm{HF}\rangle \right\}_T, \quad (20)$$

where $\hat{H}(t,\epsilon)=\hat{H}_0+\hat{V}(t,\epsilon)$, and $\hat{V}(t,\epsilon)$ describes the time-dependent perturbation by the external electric and magnetic fields

$$\hat{V}(t,\epsilon)=\sum_X \hat{H}^X \epsilon_X(\omega_X)e^{-i\omega_X t}. \tag{21}$$

For homogeneous electric or magnetic fields $\hat{H}^X$ is a component of, respectively, $\hat{\mu}$ and $\hat{m}$; the interaction with the gradient of the electric field is described by the quadrupole operator $\hat{\Theta}$. In Eq. (20), $\hat{T}(t,\epsilon)$ is the field- and time-dependent cluster operator $\hat{T}(t,\epsilon)=\Sigma_\nu t_\nu(t,\epsilon)\hat{\tau}_\nu$, where $\hat{\tau}_\nu$ are the excitation operators and $t_\nu(t,\epsilon)$ the corresponding field- and time-dependent amplitudes. Here $|\mathrm{HF}\rangle$ is the unperturbed Hartree–Fock state, and $\langle\mu|=\langle\mathrm{HF}|\hat{\tau}^\dagger$. $\overline{t}_\mu(t,\epsilon)$ are the field- and time-dependent Lagrangian multipliers, which are multiplied with the time-dependent equations for the CC parameters. The $\{\}_T$ indicates the time-averaging over the shortest common multiple period T of the perturbations in Eq. (21). The linear and quadratic response functions are calculated as second and third derivatives of the real part of the time-averaged quasi-energy Lagrangian with respect to the strengths ϵ of the external fields:

$$\langle\langle A;B\rangle\rangle_\omega=\left(\frac{d^2(\frac{1}{2}\{L(t,\epsilon)\}_T+\frac{1}{2}\{L(t,\epsilon)\}_T^*)}{d\epsilon_A(-\omega)d\epsilon_B(\omega)}\right)_{\epsilon=0}, \tag{22}$$

$$\langle\langle A;B,C\rangle\rangle_{\omega_B,\omega_C}=\left(\frac{d^3(\frac{1}{2}\{L(t,\epsilon)\}_T+\frac{1}{2}\{L(t,\epsilon)\}_T^*)}{d\epsilon_A(-\omega_B-\omega_C)d\epsilon_B(\omega_B)d\epsilon_C(\omega_C)}\right)_{\epsilon=0}. \tag{23}$$

As in the time-dependent quasi-energy Lagrangian equation (20)—employed for the calculation of frequency-dependent properties—the unperturbed Hartree–Fock state $|\mathrm{HF}\rangle$ is used as the reference state in the coupled cluster response calculations, relaxation of the SCF canonical orbitals in the presence of external fields is not treated explicitly, but implicitly through the single-excitation part of the cluster operator. For details the reader is referred to Refs. 27, 29, and 35.

The quadrupole moment, a frequency-independent first-order property, is calculated as the analytical first derivative of the static CCSD Lagrangian, as described in Ref. 27.

III. COMPUTATIONAL DETAILS

For hydrogen the equilibrium distance of $1.4a_0$ was used. Experimental geometries were employed for the other molecules with $R_{\mathrm{NN}}=2.07431a_0$ for nitrogen,[36] $R_{\mathrm{CC}}=2.27351a_0$ and $R_{\mathrm{CH}}=2.00719a_0$ for acetylene,[37] and $R_{\mathrm{CH}}=2.05186a_0$ for methane.[38]

Augmented correlation-consistent basis sets of Dunning and co-workers[39–41] x-aug-cc-pVXZ—where x denotes the augmentation level and X the cardinal number—were used throughout. They constitute a well-established hierarchy of basis sets, which allows us to analyze the convergence of the properties with respect to the valence orbital description (X) and the diffuseness (x) of the basis set. To estimate the effects of electron correlation, a Hartree–Fock self-consistent field (SCF) calculation with a relatively large basis set was also performed for each molecule.

TABLE I. H_2. The electric-field-gradient-induced birefringence. Results in a.u. Wavelength 632.8 nm, $T=297.15$ K and $F=2\Theta\Delta\alpha/15k$.

	Basis set	Θ	$\Delta\alpha$	b	$\frac{F}{T}$
SCF	d-aug-cc-pV5Z	0.4934	1.8998	−37.17	132.8
FCI	aug-cc-pVTZ	0.4604	1.8507	−36.72	121.5
	aug-cc-pVQZ	0.4573	1.8624	−36.92	120.7
	aug-cc-pV5Z	0.4563	1.8705	−36.86	120.9
	d-aug-cc-pVTZ	0.4579	1.8695	−37.01	121.3
	d-aug-cc-pVQZ	0.4564	1.8706	−36.84	121.0
	d-aug-cc-pV5Z	0.4561	1.8710	−36.75	120.9
	t-aug-cc-pVTZ	0.4578	1.8704	−37.01	121.3
	t-aug-cc-pVQZ	0.4563	1.8703	−36.83	120.9

For H_2 the CCSD model gives the full configuration interaction (FCI) results within the given orbital basis. For nitrogen, acetylene, and methane, only the valence electrons were correlated in the CCSD calculations since the selected basis sets have only limited flexibility for describing core correlation. All frequency-dependent properties were evaluated at the experimental frequency of 632.8 nm.

The results are presented in atomic units unless otherwise mentioned. Conversion factors from atomic units to SI and e.s.u. for the quantities of interest are

(i) 1 au of $\alpha\equiv e^2a_0^2E_h^{-1}\cong 1.648\,778\times10^{-41}$ C^2 m^2 J^{-1} $\cong 1.48\,185\times10^{-25}\,4\pi\epsilon_0$ cm^3,
(ii) 1 au of $\Theta\equiv ea_0^2\cong 4.486\,554\times10^{-40}$ C m^2 $\cong 1.34503\times10^{-26}$ Fr cm^2,
(iii) 1 au of $b(=B)\equiv e^3a_0^4E_h^{-2}\cong 1.696\,733\times10^{-63}$ C^3 m^4 J$^{-2}\cong 4.57168\times10^{-41}\,4\pi\epsilon_0$ Fr cm^5 erg^{-1},
(iv) 1 au of $J\equiv e^3a_0^4\hbar^{-1}E_h^{-1}\cong 7.01453\times10^{-47}$ C^3 m^4 s^{-1} J$^{-2}\cong 6.30435\times10^{-35}$ Fr^2 cm^2 erg^{-1} G^{-1}, and
(v) 1 au of $q\equiv e^{-1}a_0^{-2}E_h\cong 9.71736\times10^{21}$ V m^{-2} $\cong 3.24136\times10^{15}$ Fr cm^{-3} $(4\pi\epsilon_0)^{-1}$.

To obtain the anisotropy of the refractive index at a pressure of 1 bar and a temperature of 273.15 K ($N=3.92\,931\times10^{-6}a_0^{-3}$, or $N=2.65\,163\times10^{25}$ m^{-3}), from values of the quantity in graph parentheses in Eq. (11) given in a.u. and q given in SI units, the reader should multiply by the factor $2.54\,067\times10^{-27}$.

IV. RESULTS AND DISCUSSION

The results of the basis set investigation for the different contributions to the EFGB for H_2, N_2, and C_2H_2 are collected in Tables I, II, and III, respectively. In Table IV, the results for b of CH_4 can be found. Note that in Tables I, II, and III, the temperature-dependent terms have been evaluated at $T=297.15$ K for hydrogen, at $T=298.15$ K for nitrogen, and at $T=294$ K for acetylene to conform to the experimental conditions. For the different quantities in Eq. (11) we have collected in Table V our best results, which we com-

pare with previous theoretical and experimental results. In this table, our results for the *averaged* dipole–dipole–quadrupole hyperpolarizability $B_\omega = \frac{2}{15} B_{\alpha,\beta,\alpha\beta}(-\omega;\omega,0)$ are also given and compared to previous static and frequency-dependent theoretical values.

A. Basis set study

From the results in Tables I–IV, Θ, $\Delta\alpha$, and b appear to have similar basis set demands. Significant improvements are observed if the cardinal number X is increased successively. The double-zeta basis sets are inadequate, as for all augmentation levels we obtain relatively large changes going from the x-aug-cc-pVDZ to the x-aug-cc-pVTZ sets. In contrast, the changes observed when going to the x-aug-cc-pVQZ sets are small. Significant changes in the properties are also observed when, for a given X, a second set of diffuse functions is added to the aug-cc-pVXZ sets, whereas triple augmentation leads to only minor changes. For CH_4 no significant difference is observed between the d-aug-cc-pVTZ and t-aug-cc-pVTZ results. In some cases the changes introduced by the third augmentation level are in the opposite direction of those obtained by increasing the cardinal number X. The d-aug-cc-pVXZ series seems to be the best choice for b and $\Delta\alpha$, whereas it might suffice to use a single-augmented basis set for Θ.

We note that when the cardinal number is increased, the single- and double-augmented basis set results converge from opposite side toward a common value.

In Table V we have listed the results obtained with the best basis sets used for the different molecules—that is, the d-aug-cc-pV5Z basis for hydrogen, and the d-aug-cc-pVQZ basis sets of N_2, C_2H_2, and CH_4. The basis set saturation errors at the CCSD level are estimated to be less than 1% for all properties. They were obtained by considering the differences between the d-aug-cc-pV5Z and the d-aug-cc-pVQZ results for H_2 and the differences between the d-aug-cc-pVQZ and d-aug-cc-pVTZ results for the other molecules.

B. Effect of electron correlation

Comparing the SCF and CCSD results, electron correlation is seen to have a pronounced effect, in some cases much larger than the changes observed when varying the basis set. For H_2, the most significant change is a reduction of the quadrupole moment by 7.6%. The polarizability anisotropy and b change by about 1%–1.5%. For nitrogen, significant changes are observed for Θ (−21%) and $\Delta\alpha$ (−14%), while the correlation effect on b is rather small, less than 0.5%. For acetylene, the main changes are for Θ (−11%) and b (−15%). In methane, a decrease of b by about 11% due to electron correlation is observed.

TABLE II. N_2. The electric-field-gradient-induced birefringence. Results in a.u. Wavelength 632.8 nm, $T = 298.15$ K, and $F = 2\Theta\Delta\alpha/15k$.

	Basis set	Θ	$\Delta\alpha$	b	$\frac{F}{T}$
SCF	t-aug-cc-pVTZ	−0.9299	5.3236	−36.74	−699.1
CCSD	aug-cc-pVDZ	−1.1223	4.7324	−32.65	−750.0
	aug-cc-pVTZ	−1.1205	4.4921	−35.35	−710.8
	aug-cc-pVQZ	−1.1162	4.5475	−36.07	−716.8
	d-aug-cc-pVDZ	−1.1530	4.6636	−37.58	−750.3
	d-aug-cc-pVTZ	−1.1263	4.5665	−36.49	−726.3
	d-aug-cc-pVQZ	−1.1186	4.5536	−36.13	−719.3
	t-aug-cc-pVDZ	−1.1550	4.6576	−37.63	−759.7
	t-aug-cc-pVTZ	−1.1280	4.5658	−36.58	−727.3

C. Comparison with other theoretical estimates

It is beyond the scope of the present paper to discuss in detail our results for the quadrupole moment and the anisotropy of the electric-dipole polarizability. Our best results are collected in Table V together with those extracted from experiment.

Previous *ab initio* estimates of b are limited to the work of Amos,[26] who computed the low-frequency limit of b as the dipole–dipole–magnetic dipole hyperpolarizability $\omega^{-1}\epsilon_{\alpha\beta\gamma}J_{\alpha,\beta,\gamma}$ for a few molecular systems, including N_2, C_2H_2, and CH_4. This approximation was motivated by the fact that in the zero-frequency limit, the difference $[B_{\alpha,\beta,\alpha\beta}(-\omega;\omega,0) - B_{\alpha,\beta,\alpha\beta}(-\omega;0,\omega)]$ vanishes. For nonzero frequencies the contribution from this difference is, in our case, much smaller than that from $\omega^{-1}\epsilon_{\alpha\beta\gamma}J_{\alpha,\beta,\gamma}$. Comparing the best basis set results at the CCSD level for nitrogen, acetylene, and methane with those of Amos,[26] we observe that the sum-over-states techniques used either with canonical SCF orbitals or with field-perturbed orbitals strongly underestimate b for all three molecules. The coupled Hartree–Fock result of −34.18 au obtained in Ref. 26 for nitrogen is, on the other hand, in rather good agreement with both our SCF and CCSD values, in spite of the fact that the term $[B_{\alpha,\beta,\alpha\beta}(-\omega;\omega,0) - B_{\alpha,\beta,\alpha\beta}(-\omega;0,\omega)]$ was neglected and a small basis set was used.

We are not aware of other *ab initio* studies of the J hyperpolarizability. The literature on *ab initio* calculations of the frequency-dependent dipole-dipole-quadrupole hyperpolarizability B is also limited. For H_2, accurate calculations have been done by Bishop and co-workers.[42–45] In Ref. 45, the individual tensor elements and appropriate averages of $B_{\alpha,\beta,\gamma\delta}(-\omega;\omega,0)$, obtained using a sum-over-states technique with extended basis sets and explicitly correlated wave functions, are reported for several frequencies. The pure electronic contribution to $B_\omega(-78.07$ a.u.) of Ref. 45 is very close to our best result (−78.46 a.u.). Note that rovibrational averaging decreases the value of B_ω by more than 10% (to −85.73 a.u.).[45]

No results seem to be available for the frequency-dependent dipole–dipole–quadrupole hyperpolarizabilities of N_2, C_2H_2, and CH_4. For these molecules, we compare in Table V with the static results of Maroulis and Thakkar.[46–48]

D. *T*-independent versus *T*-dependent contribution to Δn

The importance of b compared to that of the temperature-dependent contribution to the EFGB varies from molecule to molecule. As observed by Buckingham,[9] mol-

TABLE III. C_2H_2. Electric-field-gradient-induced birefringence. Results in a.u. Wavelength 632.8 nm, $T=294$ K, and $F=2\Theta\Delta\alpha/15k$.

	Basis set	Θ	$\Delta\alpha$	b	$\frac{F}{T}$
SCF	d-aug-cc-pVTZ	5.4509	12.453	−203.8	9721
CCSD	aug-cc-pVDZ	4.7900	12.784	−164.8	8769
	aug-cc-pVTZ	4.8823	12.170	−184.8	8509
	d-aug-cc-pVDZ	4.7766	12.076	−198.9	8261
	d-aug-cc-pVTZ	4.8701	12.093	−195.9	8434
	d-aug-cc-pVQZ	4.8950	12.098	−193.3	8481
	t-aug-cc-pVDZ	4.7727	12.070	−198.7	8250
	t-aug-cc-pVTZ	4.8692	12.089	−195.5	8430

TABLE IV. CH_4. Electric-field-gradient-induced birefringence. Results in a.u. Wavelength 632.8 nm.

	Basis set	b
SCF	d-aug-cc-pVTZ	−88.44
CCSD	aug-cc-pVDZ	−90.86
	aug-cc-pVTZ	−96.26
	d-aug-cc-pVDZ	−98.83
	d-aug-cc-pVTZ	−98.10
	d-aug-cc-pVQZ	−97.32
	t-aug-cc-pVDZ	−98.98
	t-aug-cc-pVTZ	−98.10

ecules with a small quadrupole moment may have a relatively large b contribution. For hydrogen, b decreases the observed birefringence by as much as 30%. If the effects of molecular vibration on b are neglected, and if the temperature-dependent term is multiplied with the factor of 0.75—as estimated from the quantum treatment of Buckingham and Pariseau[33]—the relative contribution of the temperature-independent term increases to 41% of the total anisotropy. For nitrogen and acetylene, the relative contribution of b is much smaller, about +5% and −2%, respectively. The importance of b appears therefore to decrease in the series hydrogen, nitrogen, acetylene, that is, as the axial character of the system increases. Similar observations were made for the magnetic-field-induced birefringence (the Cotton–Mouton effect), where also the orientational effect increases in the order $H_2<N_2<C_2H_2$.[49]

E. *Ab initio* versus experiment

Assuming an ideal gas behavior at STP, the anisotropies Δn obtained from our calculated values of ${}_mQ$—using a field gradient intensity of 1×10^9 Vm^{-2} ($\approx1\times10^{-13}$ au), which is the largest field-gradient strength commonly used in experiment[22]—range from about 2×10^{-16} for H_2 and CH_4 to about 2×10^{-14} for acetylene—that is, an order of magnitude smaller than the anisotropies observed in standard Cotton–Mouton experiments[49] and several order of magnitude smaller than those due to Faraday effect.[50] As an example, and also to compare directly to the quantity actually observed in the laboratory, we estimate an induced retardance of about 35 nrad for H_2 at a pressure of 10^3 kPa, $T=300$ K, and for a path length of 1.8 m by using Eqs. (12) and (13) and the data in Table V. If molecular rotation is treated quantum mechanically and Eq. (14) is used—that is, the temperature-dependent term for the hydrogen molecule is multiplied by the factor 0.75—our estimated retardation reduces to approximately 22 nrad. Experiment observes in the same conditions a retardance of about 60 nrad.[22]

It is not uncommon for experimentalists to resort to values for b obtained from theoretical calculations to improve the accuracy in their determination of the molecular quadrupole moment. This was recently done for example by Graham *et al.*[24] In an attempt to obtain a more reliable estimate of the quadrupole moment of N_2, Graham *et al.* employed as b the average of the CHF value for the dipole–dipole–magnetic dipole hyperpolarizability contribution of Amos[26] and the static dipole–dipole–quadrupole hyperpolarizability $\underline{\underline{B}}=\frac{2}{15}B_{\alpha,\beta,\alpha\beta}(0;0,0)$ calculated at the MP4 level by Maroulis and Thakkar.[46] As mentioned in Sec. II, the misuse of $\underline{\underline{B}}$ as the theoretical estimate for b might, to some extent, find its roots in the use of the symbol B instead of b for the temperature-independent contribution in the early days of EFGB.[16,17] The final b value obtained from this averaging—which mixes different quantities calculated at different levels of theory—is strongly overestimated, as $\underline{\underline{B}}$ is more than an order of magnitude larger than the low-frequency value for b obtained by Amos, and it leads to an estimate of (-1.04 ± 0.02) a.u. for the quadrupole moment of N_2.[24] Correcting the experimental datum in Ref. 24 with our CCSD/d-aug-cc-pVQZ b term, we obtain instead (-1.116 ± 0.02) a.u. in very satisfactory agreement with our best CCSD equilibrium geometry result 1.119 a.u. In a recent theoretical investigation,[51] the rovibrationally averaged coupled cluster singles and doubles with perturbative corrections for connected triple excitations—CCSD(T)—basis set limit result including estimates of relativity and correlation beyond CCSD(T) was determined to be (-1.099 ± 0.007) a.u.

In an experimental investigation by Keir *et al.*,[23] a low-density molar field-gradient birefringence constant ${}_mQ=(4.97\pm0.15)\times10^4$ a.u. was measured at $T=294$ K for acetylene. Ignoring the b correction term, these authors deduced a value of (4.55 ± 0.2) a.u. for the molecular quadrupole moment. Our estimate for the ${}_mQ$ constant at the same temperature as obtained from the computed Θ, $\Delta\alpha$, and b employing a d-aug-cc-pVQZ basis is 5.207×10^4 a.u. (see Table V). The agreement is quite satisfactory, considering the neglect of vibrational effects and correlation effects beyond the CCSD approximation used in our calculations.

If we employ our calculated b term from Table V, together with the experimental data for ${}_mQ$, a value of 4.66 a.u. is obtained for the quadrupole moment of acetylene. Russell and Spackman[32] employed an *ab initio* static value of the average dipole–dipole–quadrupole hyperpolarizability $\underline{\underline{B}}$ (Ref. 47)—incurring in the same misunderstanding as the authors of Ref. 24—to estimate a quadrupole moment of (4.70 ± 0.1)a.u. from the experimental data for ${}_mQ$.

Due to symmetry, the temperature-dependent term of the EFGB vanishes for CH_4. Direct comparison with experiment

TABLE V. Electric-field-gradient-induced birefringence. Summary of theoretical and experimental results. $F=2\Theta\Delta\alpha/15k$, and see text for other definitions. $T=297.15$ K (H_2), $T=298.15$ K (N_2), $T=294.0$ K (C_2H_2). Results labeled ''CCSD'' are our best basis set results obtained with basis d-aug-cc-pV5Z (H_2) and d-aug-cc-pVQZ (N_2, C_2H_2, CH_4). Results labeled ''Others'' are previous theoretical results for the property.

	H_2			N_2			C_2H_2			CH_4		
Property	CCSD	Others	Experimental	CCSD	Others	Experimental	CCSD	Others	Experimental	CCSD	Others	Experimental
b	−36.75		−46±15[a]	−36.13	−17.09[b] −26.52[c] −34.18[d]		−193.3	−76[b] −107[c]		−97.32	−31.83[b] −41.85[c]	−262±66[a]
$\frac{F}{T}$	120.9		145[e]	−719.3		−700[a]	8481					
$mQ(T)$[f]	528.7			−4747			5.207×10^4		$(4.97\pm0.15)\times10^4$[g]	−611.5		
Θ	0.4561		0.484[h]	−1.119		−1.09±0.07[i] −1.04±0.02[k]	4.869		4.55±0.2[j] 4.57±0.1[l]			
					−1.099±0.007[m]	−1.12±0.02[n]			4.66[o]			
$\Delta\alpha$	1.8710		2.12[p]	4.554		4.749[q]	12.09		12.13±0.24[g]			
$\overline{B_\omega}$[r]	−78.46	−78.07[s]		−151.53	−149[t]		−576.62	−582[u]		−317.79	−278[v]	

[a]Reference 9.
[b]Reference 26. Sum-over-states with SCF canonical orbitals.
[c]Reference 26. Sum-over-states with field perturbed orbitals.
[d]Reference 26. Coupled Hartree–Fock.
[e]From the value of 110.0 a.u. (which allows for a 25% quantum correction) tabulated in Ref. 9.
[f]$_m Q(T)=2\pi/4\pi\epsilon_0\{b+F/T\}$. See Eq. (11).
[g]Reference 23.
[h]Reference 57.
[i]Reference 14, ignoring the b term correction.
[j]Reference 23. EFGB measurements.
[k]Reference 24.
[l]Reference 23. Cotton–Mouton measurements.
[m]Reference 51. Rovibrationally averaged CCSD(T) basis set limit result including estimates of relativity and correlation beyond CCSD(T).
[n]As obtained from correction of the experimental result for the ''effective quadrupole moment'' in Ref. 24 with our ''best'' b.
[o]As obtained from correction of the experimental EFGB result in Ref. 23 with our ''best'' b.
[p]Reference 58. From light scattering measurements.
[q]Reference 59.
[r]$\overline{B_\omega}=\frac{2}{15}B_{\alpha,\beta,\alpha\beta}(-\omega,\omega,0)$.
[s]Reference 45. Frequency-dependent (632.8 nm) result with explicitly correlated wave functions. The zero-point and thermally averaged value was −85.73 at 295 K.
[t]Reference 46. MP4 static value.
[u]Reference 47. SCF static value.
[v]Reference 48. SCF static value.

is still difficult, since vibrational corrections have to be taken into account. Our best result is far outside the experimental error bars, and, even by taking into account the uncertainty on our results arising from basis set incompleteness and correlation effects beyond the CCSD model, it seems unlikely that theory and experiment can be brought into agreement.

F. Vibrational effects

In order to compare theory and experiment, the computed electronic properties—obtained at a fixed internuclear distance—should be corrected for rovibrational effects.[31] In general, the importance of the vibrational corrections varies from molecule to molecule and from property to property. While zero-point vibrational averaging can easily be done for diatomic molecules, the procedure becomes time consuming for molecules with more than one vibrational degree of freedom. A study of the vibrational effects for the properties computed here is, however, beyond the purpose of this investigation.

The (ro)vibrational effects on both the quadrupole moment and the static polarizability of hydrogen and nitrogen have been the subject of an investigation by Bishop and Cybulski.[52] For hydrogen, the authors found changes of about +6% for Θ and α_{zz}, and by about +4% for α_{xx}, all calculated at the MP2 level. A rovibrational effect of approximately 10% was found for the frequency-dependent dipole–dipole–quadrupole polarizability $B(-\omega,\omega,0)$ of H_2 at 632.8 nm (Ref. 45) and for the Verdet constant.[53] In the static limit, the latter is related to the main contribution to b. For a discussion of rovibrational effects on the quadrupole moment of nitrogen, we refer to Ref. 51, where the effect was estimated to be around 1%. Vibrational effects have been shown to be about 0.4%[52] for the static polarizability. In a previous investigation,[54] we calculated the rovibrational correction for the Verdet constant of N_2 at the CCSD level to be about 1.5%. For an analysis of rovibrational effects on the quadrupole moment and polarizability of acetylene, the reader is referred to Ref. 32. No vibrational study is available for the electric field gradient birefringence of methane.

No pure vibrational corrections have so far been computed for the hyperpolarizabilities entering the b term. Perturbation theory expressions for the static vibrational dipole–dipole–quadrupole hyperpolarizabilities are given, for instance, in Ref. 31. They were used by Bishop and Lam to estimate the importance of pure vibrational contributions to the static value of B in hydrogen and nitrogen.[42–44] The au-

thors found the effect ''quite significant.'' One would expect such a contribution to be less important at a finite frequency in analogy with the electric-dipole hyperpolarizabilities in electro-optic Pockels effect and dc–Kerr optical processes (see for instance, Ref. 55). According to Ref. 53, pure vibrational contributions to the Verdet constant are zero for molecules without a permanent magnetic moment.

V. SUMMARY AND CONCLUSIONS

We have presented the first comprehensive *ab initio* study of electric-field-gradient-induced birefringence for the set of nonpolar molecules H_2, N_2, C_2H_2, and CH_4. The effects of basis set extension and electron correlation have been investigated within a hierarchy of augmented correlation-consistent basis sets, and employing a CCSD wave function. For all frequency-dependent properties coupled cluster response theory—a state-of-the-art approach for the calculation of molecular linear and nonlinear frequency dependent properties—has been employed. The investigation shows that to obtain accurate results for the temperature-independent hyperpolarizability contribution *b* to the EFGB of N_2, C_2H_2, and CH_4 a basis set of at least d-aug-cc-pVTZ quality is required. With our largest sets, saturation errors are estimated to be less than 1%. For H_2 we present FCI, that is ''benchmark quality,'' results. Whereas for C_2H_2 and CH_4 correlation appears to have a pronounced effect on *b*, the effect of electron correlation on this property in N_2 is quite small. This was hardly unexpected since a previous study on these systems had led to the conclusions that apparently dynamical correlation played a minor role in the study of the Faraday effect[54] of N_2. Comparison with experiment is rather satisfactory for H_2, N_2, and C_2H_2, in spite of neglecting of rovibrational correction and—for the last two molecules—of correlation effects beyond CCSD. A marked disagreement is found when comparing *ab initio* and experimental predictions for *b* in methane. Note, though, that the experimental datum carries a quite large error bar, whereas recent evidence of a large zero-point vibrational correction for the frequency-dependent electric dipole second hyperpolarizability[56] shows that the possibility of strong vibrational effects, unaccounted for in our approach, cannot be entirely ruled out. The EFGB measurements are carried out more and more often to determine accurate values of molecular quadrupole moments. We have shown that in some cases an incorrect use of *ab initio* data for the *b* correction in the process of extracting the molecular quadrupole moment from EFGB measurements may lead to quite severe loss of accuracy.

The present study further demonstrates the strengths of current highly correlated response theory approaches for the calculation of molecular nonlinear properties, and their applicability to the study of sophisticated optical processes. A major advantage of these techniques lies in their computational efficiency, which allows the use of increasingly larger basis sets and more and more accurate wave functions. We believe that the benefits of theoretical studies for understanding experimental data have been clearly illustrated by the present study.

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