The electric-field-gradient-induced birefringence of Helium, Neon, Argon, and SF_6

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(Received 8 June 1999; accepted 11 August 1999)

The results of an investigation of the electric-field-gradient-induced birefringence of the noble gases He, Ne, Ar and of the octahedral system SF_6 are presented. For all these systems the induced anisotropy of the refractive index is related to the sole temperature-independent contribution $b(\omega)$, a combination of quadratic response functions. These hyperpolarizabilities, as well as their dispersion coefficients to seventh order, are calculated at the optical experimental frequency by the CCSD response approach. The dispersion coefficients are used to determine the curve of $b(\omega)$ in the normal dispersion region. We show that for atoms the dipole–dipole–quadrupole and the dipole–dipole–magnetic dipole contributions to the dispersion coefficients of $b(\omega)$ have intimate relations to the Cauchy moments and to the dispersion coefficients for the Verdet and the Cotton–Mouton constants. © *1999 American Institute of Physics.* [S0021-9606(99)30441-4]

I. INTRODUCTION

An isotropic substance exhibits linear birefringence when plane polarized light propagates through it at right angles with respect to an external perturbation. The focus here is on the electric-field-gradient-induced birefringence (EFGB)—that is, the linear birefringence induced by a uniform electric field gradient. The effect has been known for quite a long time, having been predicted by Debye in the 1920s,[1] and it started to become of some importance in the sixties, when Buckingham proposed its application to the experimental determination of molecular quadrupole moments.[2] Basically, a phase difference is induced between the two coherent resolved components of the light beam linearly polarized in the X and Y directions, and the phase difference is proportional to the difference of the refractive indices $n_{XX}-n_{YY}$. This anisotropy is interpretable in terms of microscopic properties, such as dipole and quadrupole moments, polarizabilities, and hyperpolarizabilities. The equations connecting the anisotropy to these microscopic properties have been first derived by Buckingham and Longuet-Higgins,[3,4] and re-derived using different approaches by Imrie and Raab[5] and more recently by Dumitru and Woolley.[6,7] Special interest has been raised by the still open question of origin dependence of the equations, in connection with the use of a traced or traceless form for the quadrupole moment. The subject is of relevance for dipolar species, whereas agreement between different derivations of the expression of the birefringence exists for nonpolar systems.

In analogy to other optical effects as Kerr[8,9] or Cotton–Mouton,[10] the (generally) dominant contribution to the EFGB arises from a temperature dependent, orientational term, which in this case is mainly due to the interaction of the external field gradient with the molecular quadrupole moment.[3,5]

A secondary, temperature-independent, contribution arises from the changes in the effective polarizability induced by the EFG, and is given by a combination of dipole–dipole–quadrupole and dipole–dipole–magnetic dipole hyperpolarizabilities. This is known as $b(\omega)$.[3,5,11] For highly symmetric systems, e.g., atoms, tetrahedral or octahedral molecules, the orientational contribution vanishes, and the resulting birefringence is thus related only to the hyperpolarizability term $b(\omega)$.[4,11]

We have recently presented a systematic investigation of the EFGB of H_2, N_2, C_2H_2, and CH_4,[11,12] where accurate values for both the orientational term and the temperature-independent hyperpolarizability contribution $b(\omega)$ to the observed anisotropy were calculated at the coupled cluster singles and doubles (CCSD) level of approximation, and at the experimental optical wavelength 632.8 nm. The study also pointed out a misuse of calculated results for an averaged static dipole–dipole–quadrupole hyperpolarizability $\bar{B}$—erroneously identified with $b(\omega)$—in the derivation of molecular quadrupole moments from EFGB measurements in some experimental work, which can compromise the accuracy of the experimentally derived values.[11,13,14]

In the following we present an investigation of the EFGB dispersion for He, Ne, Ar, and the octahedral molecule SF_6. For all these systems the EFGB effect is related only to the hyperpolarizability contribution $b(\omega)$. Dated experimental measures at 632.8 nm are available only for Ar and SF_6,[15] and they bear a very large uncertainty, such that even the sign of the measured effect is undetermined. *Ab initio* results—in particular for atoms, where there are no

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TABLE I. Helium. Hyperpolarizability contributions and total $b(\omega)$ at 632.8 nm (a.u.); FCI.

Basis	B	$\mathcal{B}$ [a]	J	$B-\mathcal{B}$	$-4J/\omega$	b
d-aug-cc-pVQZ	−7.448 88	−7.406 71	0.056 1430	−0.042 172	−3.118 93	−3.161 11
aug-cc-pV5Z	−6.428 21	−6.379 24	0.055 7900	−0.048 963	−3.099 33	−3.148 29
d-aug-cc-pV5Z	−7.477 02	−7.434 78	0.056 0434	−0.042 239	−3.113 40	−3.155 64
t-aug-cc-pV5Z	−7.475 43	−7.433 10	0.056 0285	−0.042 336	−3.112 57	−3.154 91
d-aug-cc-pV6Z	−7.457 15	−7.414 57	0.055 9698	−0.042 582	−3.109 31	−3.151 89

[a] $\mathcal{B}=B(-\omega,0,\omega)$.

vibrational corrections—are thus of great value to direct a revised experimental determination. Using the CCSD response approach, we calculated the dispersion coefficients for the various hyperpolarizabilities entering $b(\omega)$ analytically up to seventh order in the frequency argument. The coefficients allow us to obtain a power series expansion of the dispersion curve of $b(\omega)$ in the normal region, i.e., below the first excitation pole. The expansion is in principle correct in the frequency to the order to which the dispersion coefficients were computed. Its convergence is investigated by comparison with the results of a direct calculation for the typical experimental wavelength of 632.8 nm. It is shown that for atoms the dipole–dipole–magnetic dipole hyperpolarizability $\boldsymbol{J}(-\omega;\omega,0)$, which contributes to $b(\omega)$, is related in a simple way to the frequency-dependent polarizability $\boldsymbol{\alpha}(\omega)$. Moreover, the dispersion coefficients of the contributions $\boldsymbol{J}$ and $\boldsymbol{B}$ to $b(\omega)$ are related closely to those for the Faraday[16,17] (Verdet constant) and Cotton–Mouton effects.[10]

We do not enter here into the details of response theory for a coupled cluster parametrization of the wave function. The reader is referred to Ref. 18 for a general description and to Ref. 19 for the derivation of CCSD quadratic response theory equations. The implementation of the dispersion coefficients for linear and quadratic response properties in coupled cluster response theory is described in Refs. 20 and 21.

II. THEORY

The electric-field-gradient induced anisotropy of the refractive index in an ideal gas is given by (a.u.)

$$\Delta n = n_{XX} - n_{YY} = 2\pi N q \left\{ b(\omega) + \frac{2\Theta_{\alpha\beta}\alpha_{\alpha\beta}(\omega)}{15kT} \right\}, \qquad (1)$$

where n is the refractive index, N the number density, q the laboratory uniform electric field gradient ($q_{XX}=-q_{YY}, q_{ZZ}=0$), $\boldsymbol{\Theta}$ the permanent quadrupole moment tensor, and $\boldsymbol{\alpha}(\omega)$ the electric dipole polarizability tensor. Einstein's summation over repeated indices is assumed here and throughout. Equation (1) applies to both polar and non-polar species. In this last case $\boldsymbol{\Theta}$ refers then to the so-called ''effective quadrupole center,'' as discussed in detail in Refs. 3 and 5. In a parallel study, the analysis of the EFGB in a polar species (carbon monoxide) along these lines has been undertaken.[22] Note that Dumitru and Woolley's approach to EFGB,[6,7] based on the quantum theory of light scattering at finite temperatures and relying on the use of the density current operator, leads to an expression which, analogous to (1), includes both a temperature independent term and a main contribution inversely proportional to the temperature. Their definition of the birefringence is independent of the polarity of the molecules.

For systems of cubic or higher point group symmetry, the orientational contribution $2\Theta_{\alpha\beta}\alpha_{\alpha\beta}(\omega)/15kT$ vanishes, and the observed anisotropy reduces to

$$\Delta n = 2\pi N q b(\omega). \qquad (2)$$

The contribution $b(\omega)$—the temperature-independent term—is a combination of three hyperpolarizabilities[3,4]

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

where $\epsilon_{\alpha\beta\gamma}$ is the Levi–Civita tensor and

$$B_{\alpha,\beta,\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2) = \sum_P \sum_{m\neq g} \sum_{n\neq g} \frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle m|\overline{\hat{\mu}_\beta|n}\rangle\langle n|\hat{\Theta}_{\gamma\delta}|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_2)}, \qquad (4)$$

$$J_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) = i\sum_P \sum_{m\neq g} \sum_{n\neq g} \frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle m|\overline{\hat{m}_\beta|n}\rangle\langle n|\hat{\mu}_\gamma|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_2)}, \qquad (5)$$

or, in terms of response functions,[11]

$$B_{\alpha,\beta,\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2) = \langle\langle \hat{\mu}_\alpha;\hat{\mu}_\beta,\hat{\Theta}_{\gamma\delta}\rangle\rangle_{\omega_1,\omega_2}, \qquad (6)$$

$$J_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) = i\langle\langle \hat{\mu}_\alpha;\hat{m}_\beta,\hat{\mu}_\gamma\rangle\rangle_{\omega_1,\omega_2}. \qquad (7)$$

TABLE II. Neon. Hyperpolarizability contributions and total $b(\omega)$ at 632.8 nm (a.u.); CCSD/frozen core.

Basis	B	$\mathcal{B}$	J	$B-\mathcal{B}$	$-4J/\omega$	b
d-aug-cc-pVTZ	−14.9751	−14.8987	0.106 468	−0.076 4548	−5.914 65	−5.991 10
d-aug-cc-pVQZ	−16.2037	−16.1221	0.105 243	−0.081 5674	−5.846 60	−5.928 16
d-aug-cc-pV5Z	−17.4306	−17.3561	0.104 590	−0.074 5212	−5.810 31	−5.884 83

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TABLE III. Argon. Hyperpolarizability contributions and total $b(\omega)$ at 632.8 nm (a.u.); CCSD/frozen core.

Basis	B	$\mathcal{B}$	J	$B-\mathcal{B}$	$-4J/\omega$	b
d-aug-cc-pVTZ	−151.9051	−150.0022	1.031 221	−1.902 916	−57.287 87	−59.190 78
d-aug-cc-pVQZ	−154.6215	−152.8371	1.013 666	−1.784 401	−56.312 60	−58.097 00
d-aug-cc-pV5Z	−159.0246	−157.3704	1.014 477	−1.654 158	−56.357 65	−58.011 81

In the above equations $\hat{\mu}$, $\hat{\Theta}$ and $\hat{m}$ are the electric dipole, electric quadrupole, and magnetic dipole operators, respectively, g is the ground state, and $\omega_\sigma=\omega_1+\omega_2$. Σ_P indicates 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 $\boldsymbol{B}$, and of the pairs $(\hat{\mu}_\alpha/-\omega_\sigma)$, $(\hat{m}_\beta/\omega_1)$, and $(\hat{\mu}_\gamma/\omega_2)$ for $\boldsymbol{J}$. The ''reduced'' operators in Eqs. (4) and (5) are defined as $\bar{\hat{\mu}}=\hat{\mu}-\delta_{mn}\langle g|\hat{\mu}|g\rangle$, and analogously for $\bar{\hat{m}}$ and $\bar{\hat{\Theta}}$.

The frequency dependence of $b(\omega)$ can be obtained through the dispersion coefficients for the individual hyperpolarizability contributions. As discussed in Ref. 21, quadratic response functions for a finite molecular or atomic system in its electronic ground state are meromorphic in their frequency arguments, the poles occurring when a frequency or a sum of frequencies becomes equal to an excitation energy. Thus, for frequencies below the first pole, a quadratic response function can be expanded in a (convergent) power series in its (independent) frequency arguments as[21]

$$\langle\langle A;B,C\rangle\rangle_{\omega_B,\omega_C}=\sum_{n,m=0}^{\infty}\omega_B^n\,\omega_C^m\,D_{ABC}(n,m). \tag{8}$$

Note that only two of the three frequency arguments are independent due to the matching condition between the frequencies of the response function, $\Sigma_i\omega_i=0$. In Ref. 21 analytical expressions for the expansion (dispersion) coefficients $D_{ABC}(n,m)$ were derived for a general coupled cluster quadratic response function. It was shown that the coefficients with even total order $n+m$ are real, while those with odd total order $n+m$ are pure imaginary. Thus when the (Hermitian) operators A, B, and C are real, the expansion contains only terms of even total order, whereas if exactly one of the operators is pure imaginary, only odd terms are present. For the hyperpolarizabilities $\boldsymbol{B}$ and $\boldsymbol{J}$ entering $b(\omega)$ one of the two frequencies is zero, and the expansion is analogous to that of the first electric dipole hyperpolarizability $\beta_{\alpha\beta\gamma}(-\omega,\omega,0)$ describing the electro-optical Pockels effect [see Eq. (44) in Ref. 21]:

$$B_{\alpha,\beta,\gamma\delta}(-\omega,\omega,0)=\sum_{n=0}^{\infty}\omega^{2n}B_{\alpha,\beta,\gamma\delta}(2n), \tag{9}$$

$$B_{\alpha,\beta,\gamma\delta}(-\omega,0,\omega)=B_{\alpha,\gamma\delta,\beta}(-\omega,\omega,0)=\sum_{n=0}^{\infty}\omega^{2n}B_{\alpha,\gamma\delta,\beta}(2n), \tag{10}$$

$$J_{\alpha\beta\gamma}(-\omega,\omega,0)=\sum_{n=0}^{\infty}\omega^{2n+1}J_{\alpha\beta\gamma}(2n+1). \tag{11}$$

The odd-order expansion for $\boldsymbol{J}$ is due to the imaginary nature of the magnetic dipole operator. At zero frequency the two dipole–dipole–quadrupole contributions cancel each other. The resulting dispersion formula for $b(\omega)$, Eq. (3), can thus be written as

$$b(\omega)=\sum_{n=0}^{\infty}\omega^{2n}\,b(2n) \tag{12}$$

with

$$b(2n)=\begin{cases}-\frac{2}{3}\epsilon_{\alpha\beta\gamma}J_{\alpha\beta\gamma}(1) & \text{for } n=0,\\ \frac{2}{15}[B_{\alpha,\beta,\alpha\beta}(2n)-B_{\alpha,\alpha\beta,\beta}(2n)]\\ -\frac{2}{3}\epsilon_{\alpha\beta\gamma}J_{\alpha\beta\gamma}(2n+1) & \text{for } n>0.\end{cases} \tag{13}$$

III. A SPECIAL CASE: ATOMS

For atoms the tensors $\boldsymbol{B}$ and $\boldsymbol{J}$ are determined each by a single constant[3] (frequency dependence implicit),

$$B_{\alpha,\beta,\gamma\delta}=B[-\tfrac{1}{2}\delta_{\alpha\beta}\delta_{\gamma\delta}+\tfrac{3}{4}(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})],$$

$$J_{\alpha\beta\gamma}=J\epsilon_{\alpha\beta\gamma} \tag{14}$$

and $b(\omega)$ reduces to

$$b(\omega)=B(-\omega;\omega,0)-B(-\omega;0,\omega)-\frac{4}{\omega}J(-\omega;\omega,0). \tag{15}$$

For ease of notation we will use in the following the symbol $\mathcal{B}$ for the $B(-\omega;0,\omega)$ hyperpolarizability of atoms and its dispersion coefficients, reserving B to $B(-\omega;\omega,0)$ and its dispersion coefficients.

For atoms—similar as the paramagnetic hypermagnetizability contribution to the Cotton–Mouton constant[23,24]—the hyperpolarizability $\boldsymbol{J}(-\omega_\sigma;\omega_1,\omega_2)$ can be expanded in terms of the Cauchy moments. This is most easily seen if the electronic part of $\boldsymbol{J}$ in the sum-over-state expression in Eq. (5) is rewritten in terms of the position operator $\hat{r}=-\hat{\mu}$ and the angular momentum operator $\hat{l}=-2\hat{m}$. For an atom in a S state the sum-over-states expression then reduces to

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TABLE IV. Neon. Hyperpolarizability contributions and total $b(\omega)$ at 632.8 nm (a.u.). Comparison of CC models.

Method	B	$\mathcal{B}$	J	$B-\mathcal{B}$	$-4J/\omega$	b
			d-aug-cc-pV5Z/frozen-core			
CCS	−13.527 4	−13.483 4	0.077 498	−0.043 955 1	−4.305 25	−4.349 21
CC2	−17.233 5	−17.152 4	0.105 492	−0.081 067 1	−5.860 41	−5.941 48
CCSD	−17.430 6	−17.356 1	0.104 590	−0.074 521 2	−5.810 31	−5.884 83
			d-aug-cc-pCVQZ/all electrons correlated			
CCS	−12.585 8	−12.537 1	0.077 362	−0.048 723 7	−4.297 71	−4.346 43
CC2	−15.866 8	−15.780 4	0.104 962	−0.086 321 0	−5.830 99	−5.917 31
CCSD	−16.025 8	−15.945 6	0.103 999	−0.080 198 3	−5.777 51	−5.857 71

$$J=J_{xyz}(-\omega_\sigma;\omega_1,\omega_2)=\frac{1}{2}\sum_{m\neq g}\left\{\frac{|\langle g|\hat{r}_z|m\rangle|^2}{(\omega_{mg}-\omega_\sigma)(\omega_{mg}-\omega_2)}-\frac{|\langle g|\hat{r}_z|m\rangle|^2}{(\omega_{mg}+\omega_\sigma)(\omega_{mg}+\omega_2)}\right\}. \tag{16}$$

Using the sum-over-states expression for the Cauchy moments,

$$S(k)=\sum_{m\neq g}2\,\omega_{mg}^{k+1}\langle g|\hat{r}_z|m\rangle\langle m|\hat{r}_z|g\rangle, \tag{17}$$

the right-hand side of Eq. (16) can be expanded in a power series in the frequencies ω_1 and ω_2 as

$$J_{xyz}(-\omega_\sigma;\omega_1,\omega_2)=\frac{1}{2}\sum_{n=0}^{\infty}S(-2n-4)\times\sum_{m=0}^{2n+1}\omega_1^{2n+1-m}\;\omega_2^m\binom{2n+2}{m}. \tag{18}$$

For the dipole–dipole–magnetic dipole hyperpolarizability $\boldsymbol{J}(-\omega;\omega,0)$, which enters the dominant contributions to the temperature-independent term in EFGB, Eq. (18) reduces to

$$J_{xyz}(-\omega;\omega,0)=\frac{1}{2}\sum_{n=0}^{\infty}\omega^{2n+1}S(-2n-4)=\frac{1}{2\omega}[\alpha(\omega)-\alpha(0)] \tag{19}$$

and the dispersion coefficients for the expansion of $b(\omega)$ in Eq. (12) for atoms simply become

$$b(2n)=B(2n)-\mathcal{B}(2n)-2S(-2n-4). \tag{20}$$

Similarly, for the dipole–dipole–magnetic dipole hyperpolarizability $J(-\omega;0,\omega)$, which appears in the expression of the Verdet constant $V(\omega)$, the expansion in Eq. (18) reduces to the well-known Becquerel form:[25]

$$J_{xyz}(-\omega;0,\omega)=\frac{1}{2}\sum_{n=0}^{\infty}\omega^{2n+1}(2n+2)\,S(-2n-4)=\frac{1}{2}\frac{d\alpha(\omega)}{d\omega}, \tag{21}$$

$$V(\omega)=\frac{2\pi N}{c}\;\omega\;\;J_{xyz}(-\omega;0,\omega)=\frac{\pi N}{c}\omega\frac{d\alpha(\omega)}{d\omega}. \tag{22}$$

The dispersion expansion for the Verdet constant can thus be written as

$$V(\omega)=\sum_{n=1}^{\infty}\omega^{2n}V(2n) \tag{23}$$

with

$$V(2n)=\frac{2n\pi N}{c}S(-2n-2). \tag{24}$$

For atoms, one can also compute the Cotton–Mouton constant ${}_mC(\omega)$[26,24] from the Cauchy moments $S(k)$ and the dipole–dipole–quadrupole hyperpolarizability B:

$${}_mC(\omega)=\frac{2\pi N_A}{27}\Delta\eta(\omega)=\frac{2\pi N_A}{27}(\Delta\eta^p(\omega)+\Delta\eta^d(\omega)), \tag{25}$$

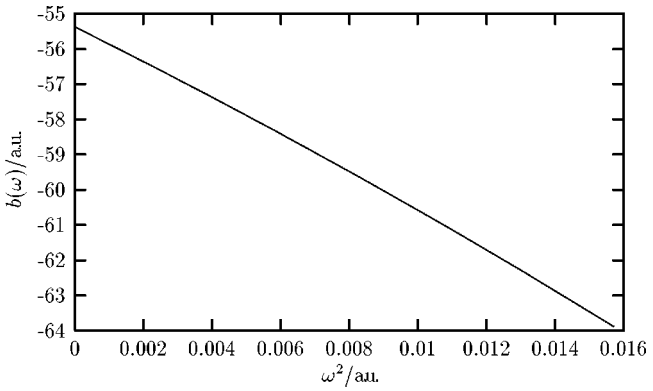


FIG. 1. EFGB dispersion curve for Ar.

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TABLE V. Argon. Hyperpolarizability contributions and total $b(\omega)$ at 632.8 nm (a.u.). Comparison of CC models for the d-aug-cc-pV5Z basis set.

Method	B	$\mathcal{B}$	J	$B-\mathcal{B}$	$-4J/\omega$	b
CCS	−154.4617	−153.0497	0.935 435	−1.411 928	−51.966 63	−53.378 56
CC2	−158.5563	−156.8985	0.999 051	−1.657 829	−55.500 66	−57.158 49
CCSD	−159.0246	−157.3704	1.014 477	−1.654 158	−56.357 65	−58.011 81

$$\Delta\eta^p(\omega) = -\frac{1}{2}\langle\langle r_x; r_x, l_x, l_x\rangle\rangle_{\omega,0,0} + \frac{1}{2}\langle\langle r_x; r_x, l_z, l_z\rangle\rangle_{\omega,0,0} = -\frac{1}{4}\frac{d^2\alpha(-\omega;\omega)}{d\omega^2} = -\frac{1}{4}\sum_{n=0}^{\infty}(2n+1)(2n+2)\,\omega^{2n}S(-2n-4), \tag{26}$$

$$\Delta\eta^d(\omega) = -\frac{1}{4}\left\langle\left\langle r_x; r_x, \frac{1}{2}(3r_x^2 - r^2)\right\rangle\right\rangle_{\omega,0} = -\frac{1}{4}B(-\omega;\omega,0) = -\frac{1}{4}\sum_{n=0}^{\infty}\omega^{2n}B(2n), \tag{27}$$

where N_A is the Avogadro number, $\Delta\eta$ indicates the anisotropy of the hypermagnetizability, and the superscripts p and d distinguish the paramagnetic and diamagnetic contributions (see Ref. 27 for a review of the subject). The dispersion expansion of the Cotton–Mouton constant thus becomes

$${}_mC(\omega) = \sum_{n=0}^{\infty}\omega^{2n}\,{}_mC(2n) \tag{28}$$

with

$${}_mC(2n) = \frac{2\pi N_A}{27}\Delta\eta(2n) = -\frac{2\pi N_A}{108}\{(2n+1)(2n+2)\,S(-2n-4) + B(2n)\} \tag{29}$$

IV. COMPUTATIONAL DETAILS

For the three atomic systems a basis set investigation was performed at the experimental frequency using the doubly augmented correlation consistent sets[28,29] d-aug-cc-pVXZ, with X=Q, 5 and 6 for He and X=T, Q and 5 for Ne and Ar. For Ne calculations were also carried out with the core-valence correlation consistent set d-aug-cc-pCVQZ.[30,31] Only the d-aug-cc-pVDZ set was employed for the calculations on sulphurhexafluoride.

The dispersion coefficients were calculated for each system for the largest (valence only) basis set. Note that the CCSD results for He are full configuration interaction (FCI) results. For Ar and SF_6 only the valence electrons were correlated, while for Ne the d-aug-cc-pCVQZ calculations were performed with all electrons correlated. For SF_6 a S–F bond distance of 1.564 Å was employed.

All calculations have been carried out with a local version of the DALTON program package[32] which includes an integral-direct coupled cluster response program.[33–35,19–21]

V. DISCUSSION OF RESULTS

A. Noble gases

In Tables I–III we report the results for the unique components of the hyperpolarizabilities B, $\mathcal{B}$, and J, the relative contributions to the EFGB $B-\mathcal{B}$ and $-4J/\omega$ and the total $b(\omega)$ at the wavelength 632.8 nm. For helium, all quantities in Table I show a monotonic convergence trend when increasing the polarization level X of the basis set, except for the individual contributions B and $\mathcal{B}$. Due to cancellation, however, the net effect of the anisotropy $B-\mathcal{B}$ is monotonic. The non-monotonic behavior of B and $\mathcal{B}$ of helium with increasing zeta level, which is opposite to that for neon and argon, might be an effect of the different construction schemes for the diffuse functions of helium in the aug-cc-pVXZ basis sets.[28] For neon the convergence of the two dipole–dipole–quadrupole hyperpolarizabilities is mono-

TABLE VI. Helium. Frequency dispersion coefficients (a.u.). FCI/d-aug-cc-pV6Z.

n	$B(2n)$	$\mathcal{B}(2n)$[a]	$S(-2n-4)$	$b(2n)$	$V(2n)/C$[b]	$\Delta\eta(2n)$[c]
0	−7.338 4271	−7.338 4271	1.543 971	−3.087 942[d]		1.062 621
1	−22.614 128	−14.546 605	2.045 665	−12.158 85	3.087 942	−0.483 463
2	−54.647 301	−26.885 345	2.927 773	−33.617 50	8.182 660	−8.296 472
3	−120.773 73	−48.228 122	4.376 326	−81.298 26	17.566 64	−31.075 133
4					35.010 61	

[a] $\mathcal{B}(2n)$ are the dispersion coefficients for $B(-\omega,0,\omega)$.
[b] $\mathcal{C}=0.912\,742\times10^{-7}$.
[c] For the relation between $\Delta\eta(2n)$ and ${}_mC(2n)$, see Eq. (29).
[d] Cfr. Ref. 4: $b(0)=-3.06$ a.u.

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TABLE VII. Ne. Frequency dispersion coefficients (a.u.). CCSD/d-aug-cc-pV5Z/frozen core.

n	$B(2n)$	$\mathcal{B}(2n)$	$S(-2n-4)$ [a]	$b(2n)$	$V(2n)/\mathcal{C}$	$\Delta\eta(2n)$
0	−17.121 356	−17.121 356	2.878 909	−5.757 818[b]		2.840 885
1	−58.725 587	−44.635 636	5.006 371	−24.102 69	5.757 818	−0.337 716
2	−175.014 92	−121.032 06	10.689 49	−75.361 84	20.025 48	−36.417 445
3	−495.687 49	−337.917 27	25.128 57	−208.0274	64.136 94	−227.878 11
4					201.0286	

[a]Cfr. CCSD/q-aug-cc-pV5Z/all electrons correlated (Ref. 20): 2.857, 4.949, 10.54, 24.73. DOSD (Ref. 44): 2.886, 5.063, 10.86, 25.53.
[b]Cfr. Ref. 4: $b(0)=-5.75$ a.u.

tonic, while the total anisotropy $B-\mathcal{B}$ is not. This does not, however, affect the convergence trend for $b(\omega)$. Deviation from a monotonic behavior is observed also for J of argon, but again without effect on the final $b(\omega)$.

The variation between d-aug-cc-pV5Z and d-aug-cc-pV6Z results for $b(\omega)$ of helium is ca. 0.004 a.u. To assess the inaccuracy of the calculated $b(\omega)$ due to basis set incompleteness we have also analyzed the effect of multiple augmentation for the X=5 polarization level. As expected, double augmentation is found to give the largest variation, ca. 0.007 a.u., while the effect of triple augmentation is an order of magnitude smaller. These results suggest that the true value for $b(\omega)$ at 632.8 nm is -3.15 ± 0.01 a.u., where the uncertainty is conservative.

In order to estimate correlation effects beyond CCSD for both Ne and Ar, we carried out calculations for the d-aug-cc-pV5Z basis set in the hierarchy CCS, CC2, and CCSD. The results are shown in Tables IV and V. For Ne, core correlation effects were also investigated performing similar calculations for the d-aug-cc-pVCQZ basis set with all electrons correlated. For Ne the CC2 results for $b(\omega)$ are, in absolute value, larger than the CCSD ones, the difference being ca. 0.06 a.u. at both d-aug-cc-pV5Z/frozen-core and d-aug-cc-pCVQZ/all electrons correlated levels. Higher excitation effects are expected to be smaller, also in view of the results obtained for the static polarizability of Ne by Christiansen *et al.*,[36] and the connection between $b(\omega)$ and $\alpha(\omega)$ of atoms discussed in Sec. III. From a comparison of d-aug-cc-pCVQZ/all electrons correlated and d-aug-cc-pVQZ/frozen-core results at the CCSD level, core correlation appears to reduce $b(\omega)$ by ca. 0.07 a.u. The difference between d-aug-cc-pCVQZ/all electrons correlated and d-aug-cc-pV5Z/frozen-core is ca. 0.03 a.u. For argon, the behavior of the calculated $b(\omega)$ in the CC hierarchy is completely monotonic, with a variation from CC2 to CCSD of 0.85 a.u. Higher excitations are expected to be at most of the same order of magnitude. As no core-valence basis sets are available for argon, we cannot easily determine the effect of core correlation. However, as hyperpolarizabilities are in general not particularly sensitive to the description of the core region, we expect core effects on $b(\omega)$ of Ar to be small.

Thus, with a conservative estimate of all uncertainties, the results of the calculations suggest that the true values for $b(\omega)$ of Ne and Ar at 632.8 nm are -5.9 ± 0.1 a.u. and -58 ± 2 a.u., respectively. This expectation is also supported by the good agreement we obtain between the CCSD values for the Verdet constant and the experimental results for this property (*vide infra*). Experimental results for the EFGB of helium and neon are not available in the literature. The EFGB of Ar at 632.8 nm was measured in 1968 by Buckingham, Dish, and Dunmur,[15] and $b(\omega)$ was found to be 0 ± 109 a.u.

As shown in Sec. III, the dipole–dipole–magnetic dipole hyperpolarizability J for atoms is related to the difference between the frequency dependent and the static dipole polarizability. This means that the dispersion coefficients $J(n)$ are simple multiples of the Cauchy moments. The latter are therefore collected in Tables VI, VII, and VIII, together with the dispersion coefficients for the two hyperpolarizabilities B and $\mathcal{B}$, and those for the derived properties $b(\omega)$, $V(\omega)$, and $\Delta\eta(\omega)$. The quality of the dispersion expansion can be tested against the finite frequency results at 632.8 nm in Tables I–III. For both He and Ne, the dispersion formula results for $b(\omega)$ coincide with the finite frequency results for the number of digits given in Tables I and II. For argon, the expansion-derived value at 632.8 nm is $b=-58.0117$ a.u., against $b=-58.0118$ a.u. from the finite frequency calculation. As an example, the EFGB dispersion curve for Ar is plotted in Fig. 1. The EFGB dispersion curves for the other two atomic systems—as well as SF_6—show similar features and can easily be reproduced from the tabulated coefficients. Buckingham and Jamieson[4] were the first to establish the

TABLE VIII. Argon. Frequency dispersion coefficients (a.u.). CCSD/d-aug-cc-pV5Z/frozen core.

n	$B(2n)$	$\mathcal{B}(2n)$	$S(-2n-4)$ [a]	$b(2n)$	$V(2n)/\mathcal{C}$	$\Delta\eta(2n)$
0	−152.982 20	−152.982 20	27.687 977	−55.375 954[b]		24.401 562
1	−1128.7193	−828.108 53	92.690 288	−485.991 35	55.375 954	4.108 961
2	−6884.1565	−4372.9709	374.428 61	−3260.0428	370.761 15	−1087.175 45
3	−38 331.593	−23 631.673	1688.3217	−18 076.563	2246.5717	−14 053.6055
4					13 506.574	

[a]Cfr. DOSD: (Ref. 44): 27.91, 95.06, 391.5, 1802.
[b]Cfr. Ref. 4: $b(0)=-54.90$ a.u.

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TABLE IX. Comparison of results for the Verdet constant ($V(\omega)\times 10^9$ a.u.) at different frequencies.

	He		Ne				Ar			
ω	This work[a]	Ref. 43[f]	This work[b]	Ref. 20[c]	Ref. 44[d]	Ref. 43[f]	This work[b]	Ref. 39[e]	Ref. 44[d]	Ref. 43[f]
0.125 35	4.6194	4.533	8.7327	8.67	8.76	8.429	88.643		89.54	89.14
0.113 91	3.7865	3.656	7.1402	7.09	7.16	7.071	71.764	73.51	72.46	71.55
0.104 50	3.1691	2.976	5.9649	5.92	5.98	5.968	59.515		60.08	59.68
0.101 25	2.9697	2.893	5.5862	5.54	5.60	5.579	55.606	56.94	56.12	55.78
0.091 13	2.3931	2.307	4.4939	4.46	4.51	4.435	44.432	45.49	44.83	44.62
0.083 45	1.9995	1.919	3.7505	3.72	3.76	3.667	36.912		37.24	37.06
0.082 84	1.9699	1.890	3.6945	3.67	3.70	3.608	36.348	37.21	36.67	36.53
0.078 83	1.7807	1.715	3.3378	3.31	3.35	3.242	32.767		33.05	33.03
0.077 32	1.7120	1.653	3.2085	3.18	3.22	3.106	31.472		31.75	31.71
0.075 594	1.6505	1.595	3.0927	3.07	3.10	2.983	30.314	31.03	30.58	30.45
0.070 510	1.4032	1.362	2.6274	2.61	2.63	2.435	25.680	26.28	25.90	25.53
0.065 09	1.2076	1.175	2.2598	2.24	2.27	1.965	22.037	22.55	22.23	21.80
0.060 75	1.0504	1.022	1.9647	1.95	1.97	1.621	19.125	19.57	19.29	18.96
0.056 95	0.9220	0.890	1.7239	1.71	1.73	1.384	16.756	17.15	16.90	16.68
0.053 60	0.8159	0.799	1.5251	1.51	1.53	1.216	14.805	15.15	14.93	14.73
0.050 63	0.7274	0.734	1.3593	1.35	1.36	1.118	13.182		13.29	13.24
0.046 614	0.6034		1.1272	1.12	1.13	1.018	10.916		11.01	11.20

[a]FCI/d-aug-cc-pV6Z.
[b]CCSD/d-aug-cc-pV5Z/frozen core.
[c]CCSD/q-aug-cc-pV5Z/all electrons correlated.
[d]Values derived from the DOSD Cauchy moments of Ref. 44.
[e]MCSCF.
[f]Experiment.

connection between the zero-frequency limit of $b(\omega)$ and the Verdet constant for atoms

$$\lim_{\omega\to 0} b(\omega) = -C' \lim_{\omega\to 0} \frac{V(\omega)}{\omega^2}, \tag{30}$$

where C' is the appropriate dimensional constant. According to our expansion for b and V, Eq. (30) becomes

$$b(0) = -C'V(2). \tag{31}$$

From this relationship, Buckingham and Jamieson[4] estimated $b(0)$ for the three rare gases considered here from values of the zero frequency limit of $V(\omega)/\omega^2$. For He the latter were taken from a variational calculation of Victor, Dalgarno, and Taylor.[37] For Ne and Ar, they were derived from the expressions for V of Dalgarno and Kingston.[38] The resulting estimates were $b(0) = -3.06$ a.u. for He, $b(0) = -5.75$ a.u. for Ne, and $b(0) = -54.90$ a.u. for Ar, in rather good agreement with our $b(0) = -3.088$ a.u. for He, $b(0) = -5.758$ a.u. for Ne, and $b(0) = -55.376$ a.u. for Ar, respectively.

In Tables IX and X we have collected the results for $V(\omega)$ and the hypermagnetizability anisotropy $\Delta\eta$ obtained from the tabulated dispersion coefficients $V(2n)$ and $\Delta\eta(2n)$ at different frequencies. Other theoretical[20,27,39–42] and experimental[43–47] values are included for comparison. Figure 2 shows the dispersion curves for the Verdet constants of helium, neon, and argon. For all three atoms we obtain a very good agreement between our Verdet CCSD response results and the experimental values from Ref. 43 and also the DOSD derived results from Ref. 44. The largest

TABLE X. Comparison of results for the hypermagnetizability anisotropy $\Delta\eta$ at different frequencies (a.u.).

	ω	This work [a]	Others	Experiment
Helium	0.0	1.0626	1.060 61[b,42]	
	0.072 00	1.0599	1.057 91[b,42,27]	1.1 ± 1.1[c]
	0.088 56	1.0583		0.80 ± 0.16[45]
Neon	0.0	2.841	2.869[d,20], 2.687[e,40], 3.017[f,41]	
	0.072 00	2.838	2.868[d,20], 3.029[f,41]	4.1 ± 3.0[c]
	0.088 56	2.836	2.866[d,20], 2.670[e,40], 3.034[f,41]	1.25 ± 0.07[46]
Argon	0.0	24.40		
	0.072 00	24.39	25.68[f,41]	26.0 ± 1.5[c]
	0.088 556	24.36	25.70[f,41], 24.14[e,39]	30.0 ± 4.5[47]

[a]FCI/d-aug-cc-pV6Z for He, CCSD/d-aug-cc-pV5Z/frozen-core for Ne and Ar.
[b]Explicitly correlated wave function.
[c]W. Hüttner. Results cited in Refs. 27, 40, and 42 as private communication.
[d]CCSD/q-aug-cc-pV5Z/all electrons correlated.
[e]MCSCF.
[f]Pseudo-energy MP2.

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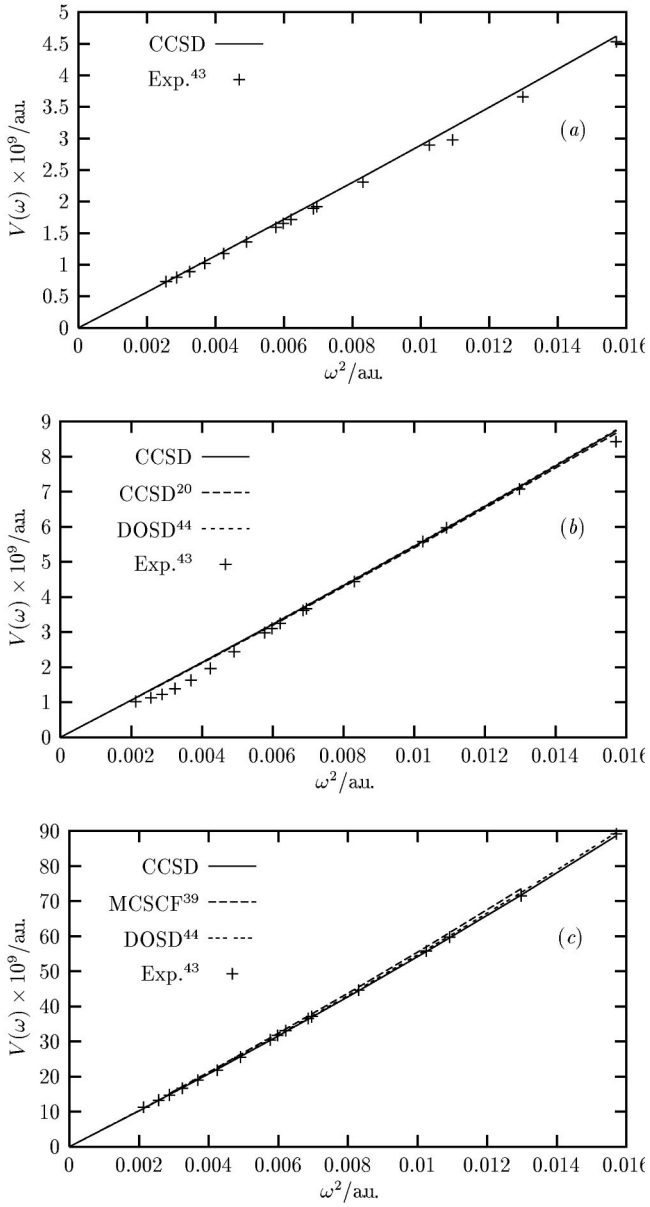


FIG. 2. Verdet constant dispersion curves for He (a), Ne (b), and Ar (c).

deviations are observed for neon for small frequencies ($\lambda > 600$ nm), where obviously the experiment encounters problems as the experimental curve does not follow the asymptotic quadratic dependency on ω predicted by the theory for ideal gases, and which is also observed for helium and argon. Since—at least for the systems studied here—$b(\omega)$ is dominated by the contribution from $J(-\omega;\omega,0)$, which apart from a permutation of the frequency arguments is the same response property as the one from which the Verdet constant $V(\omega)$ is calculated, one can expect similar accuracy for the CCSD response results of both properties $V(\omega)$ and $b(\omega)$.

TABLE XI. SF_6. Symmetry-unique hyperpolarizability contributions and total $b(\omega)$ at 632.8 nm (a.u.). CCSD/d-aug-cc-pVDZ/frozen core.

$B_{z,z,zz}$	−231.4842
$B_{x,z,xz}$	−230.6594
$B_{z,zz,z}$	−229.5050
$B_{x,xz,z}$	−229.5207
J_{xyz}	1.680 05
$b^{a,b}$	−95.035 17

[a] $b(\omega)=\frac{2}{5}[B_{z,z,zz}-B_{z,zz,z}+2(B_{x,z,xz}-B_{x,xz,z})]-4\omega^{-1}J_{xyz}$.
[b] Experiment (Ref. 15): $b=0\pm109$ a.u.

The hypermagnetizabilities of Table X are essentially in line with previous *ab initio* results. That for argon is apparently more or less within the experimental bounds. The numbers for helium are very close to the explicitly correlated wave function estimates of Ref. 42, which can be considered as a benchmark reference for Cotton–Mouton measurements in gases.[27] Those for neon provide further confirmation that the error bars associated to the experiment discussed in Ref. 46 are too small.

B. Sulphurhexafluoride SF_6

The results for the symmetry unique components of the hyperpolarizabilities entering the EFGB and of the final $b(\omega)$ at the experimental frequency are collected in Table XI. The corresponding dispersion coefficients are collected in Table XII. From the tabulated dispersion coefficients, the dispersion curve for $b(\omega)$ in the frequency region below the first pole can readily be obtained according to Eq. (12). At 632.8 the value of $b(\omega)$ derived from the dispersion expansion is -95.0350 a.u., to be compared with -95.0352 a.u. from the finite frequency calculation. The quality of the only experimental result[15] available in the literature is rather poor: 0 ± 109 a.u. Even though the calculated results were obtained with a relatively small basis set and do not include vibrational correction, they can serve as indication for a new experimental determination of the electric-field-induced birefringence of SF_6.

VI. CONCLUSIONS

We have presented an investigation of the EFGB dispersion of the first three rare gases and of SF_6. For all these systems the EFGB is related to the sole hyperpolarizability contribution $b(\omega)$, which has been expanded analytically up to sixth order in the frequency argument, for the frequency

TABLE XII. SF_6. Frequency dispersion coefficients (a.u.). CCSD/d-aug-cc-pVDZ/frozen core.

n	$B_{z,z,zz}(2n)$	$B_{x,z,xz}(2n)$	$B_{z,zz,z}(2n)$	$B_{x,xz,z}(2n)$	$J_{xyz}(2n+1)$	$b(2n)$
0	−224.752 55	−224.243 44	−224.752 55	−224.243 44	22.877 043	−91.508 172
1	−1266.6758	−1208.2538	−897.104 08	−994.096 89	84.454 650	−656.972 82
2	−5978.6227	−5518.9203	−3695.5921	−4484.0315	650.094 10	−4341.4997
3	−27 963.924	−24 701.274	−15 154.425	−20 781.642	5364.3440	−29 716.881

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region below the first pole. At 632.8 nm, a typical wavelength for the EFGB experiment, our best-basis-set results for $b(\omega)$ are -3.152 a.u. (He), -5.885 a.u. (Ne), -58.01 a.u. (Ar), and -95.04 a.u. (SF_6). Including conservative estimates of residual inaccuracies due to higher order excitations and/or basis set incompleteness the results suggest that the true values for the three atoms are -3.15 ± 0.01 a.u., -5.9 ± 0.1 a.u., and -58 ± 2 a.u.

The only experimental measurements of the EFGB on the systems here considered are those for Ar and SF_6 by Buckingham, Dish, and Dunmur,[15] whose large uncertainty makes it impossible even to assess the sign of the effect. The calculated results thus provide an excellent indication for a revised experimental determination of the induced birefringence on these systems. This is in particular true for the atoms, where vibrational contributions are not present. These results, with estimated uncertainties between 0.3% and 3.5%, might even be accurate enough to be useful for calibration of future EFGB experiments.

For atoms we have moreover shown the connection between the J contribution to b and the Cauchy moments. From the calculated Cauchy moments and dipole–dipole–quadrupole hyperpolarizability dispersion coefficients the Verdet constant and hypermagnetizability anisotropy (Cotton–Mouton) dispersion coefficients have also been obtained.

ACKNOWLEDGMENTS

S.C. thanks A. Halkier for useful discussions. This work was supported by the Danish Natural Council (Grant No. 9600856). S.C. and C.H. acknowledge financial support from the Training and Mobility of Researchers (TMR) program of the European Commission through Marie Curie Fellowships.

APPENDIX

Conversion factors for the quantities discussed throughout the paper are given in the following:[48]

(a) 1 a.u. of $b(=B)\equiv e^3a_0^4E_h^{-2}\cong 1.696\,733\times10^{-63}$ C^3 m^4 J$^{-2}\cong 4.571\,68\times10^{-41}$ $4\pi\epsilon_0$ Fr cm^5 erg^{-1}.

(b) 1 a.u. of $J\equiv e^3a_0^4\hbar^{-1}E_h^{-1}\cong 7.014\,53\times10^{-47}$ C^3 m^4 s^{-1} J$^{-2}\cong 6.304\,35\times10^{-35}$ Fr^2 cm^2 erg^{-1} G^{-1}.

(c) 1 a.u. of $V(\omega)\equiv$ rad $ea_0\hbar\cong 2.763\,816\times10^2$ min G^{-1} cm^{-1} $\cong 8.039\,624\times10^4$ rad T^{-1} m^{-1}.

(d) 1 a.u. of $\eta\equiv e^4a_0^4m_e^-1E_h^{-2}\cong 2.984\,25\times10^{-52}$ C^2 m^2 J^{-1} T$^{-2}\cong 2.682\,11\times10^{-44}(4\pi\epsilon_0)$ cm^3 G^{-2}.

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