

Hyperpolarizability dispersion measured for CO₂

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The frequency dependence of the second hyperpolarizability (γ) of CO₂ has been measured in the visible ($488 < \lambda < 693$ nm) by means of gas phase electric-field-induced second-harmonic generation (ESHG). Comparison of these results with the results for several other third-order nonlinear optical processes suggests that there are significant vibrational contributions to γ_{CO_2} .

INTRODUCTION

The third-order nonlinear susceptibility $\chi^{(3)}$ mediates a wide range of nonlinear optical processes, with applications ranging from femtosecond optical pulse generation and manipulation, to combustion diagnostics through coherent anti-Stokes Raman scattering (CARS).¹⁻⁵ The diverse manifestations of the macroscopic susceptibility $\chi^{(3)}$ and its underlying microscopic molecular second hyperpolarizability tensor γ , is to be contrasted with the single theoretical expression which describes γ in all cases.⁶⁻⁸ The essential unity of the fundamental theoretical description is obscured because the γ for each nonlinear optical process has a characteristically different balance of contributions from the electronic, vibrational, and rotational degrees of freedom of each molecule.⁹⁻¹² However, since the particular γ tensors mediating the various processes (e.g., dc Kerr effect, electric-field-induced second-harmonic generation (ESHG), third-harmonic generation (THG), and four wave mixing (FWM)) are merely instances of a general γ tensor, differing only in their frequency arguments, it should be possible to disentangle the contributions of the various molecular mechanisms by studying the frequency dependence of γ . Below are presented experimental measurements of the dispersion of γ for CO₂ made using ESHG, and a comparison of these results with the measurements from several other nonlinear optics experiments with the same molecule.

EXPERIMENT

The experimental technique has been described in detail elsewhere.^{10,11,13-16} A cw laser beam from an argon-ion laser pumped dye laser, or from the argon-ion laser directly, is weakly focused through a sample cell containing the gas in which second-harmonic generation takes place. This is made possible by a symmetry breaking dc electric field. By arranging the electrodes so that the field alternates in direction every coherence length (adjusted by varying the gas density) periodic phase matching results, enhancing the second-harmonic signal generated. The electrode spacing is 2.69 mm, resulting in optimal pressures in the range of 1.2-6.5 atm (at 19-22 °C) in the experiments reported here. A double prism spectrometer and glass filters serve to separate the second harmonic from the fundamental beam, and a photomultiplier tube is used to count signal photons. The dye laser wavelengths were set to match those of Na or Ne atomic emission lines using spectral lamps and a Jarrell-Ash 1 m spectrometer.

The ratio of hyperpolarizabilities for a sample gas B and a reference gas A is obtained from the relation^{10,13}

$$\frac{\gamma_B}{\gamma_A} = \left[\frac{S_B^{(2\omega)}}{S_A^{(2\omega)}} \right]^{1/2} \left[\frac{\rho_B n'_B}{\rho_A n'_A} \right]^{-1}, \quad (1)$$

where $S^{(2\omega)}$ is the peak signal, ρ is the number density, and $n' = (n_0^4 n_\omega^3 n_{2\omega})^{1/6}$ with n_ω the refractive index of the gas at phase match. In the present case B = CO₂ and A = N₂. Since the optical and static field polarizations are parallel, the experiment measures the ZZZZ component of the orientationally averaged tensor $\gamma_{\alpha\beta\gamma\delta}$.^{11,15} The laser power at the sample was 0.2-1.0 W, and the signals $S^{(2\omega)}$ were in the range 50-800 cps against a background of 0.4 cps. Sample densities were computed from the measured pressures and temperatures using the virial equation of state.¹⁷ Refractive indices were calculated from tables^{4,18} using the measured densities. High purity gases were used (CO₂, 99.99%; N₂, 99.999%). Measurements were made in triplets (ABA) or coupled triplets (ABABA...) in order to cancel drifts. The estimated total experimental uncertainty of a hyperpolarizability ratio measurement is obtained by convolving the statistical uncertainty for an average of five triplets of runs with the uncertainty of the density determinations due to the limited accuracy of the pressure gauge. The accuracy of the ratio is about $\pm 0.3\%$.

In the course of the hyperpolarizability ratio measurements one also obtains the ratio of linear polarizability dispersion $\Delta\alpha_{\text{CO}_2}/\Delta\alpha_{\text{N}_2}$, where $\Delta\alpha(\omega) = \alpha(2\omega) - \alpha(\omega)$, since $\Delta\alpha$ is just proportional to ρ^{-1} , the inverse phase match density.^{13,19} The accuracy of the polarizability dispersion ratio has been given as $\pm 0.20\%$, a conservative estimate based on the absolute pressure gauge accuracy of $\pm 0.15\%$. If the gauge is linear, the dispersion ratio accuracy will instead be set by the $\pm 0.04\%$ density ratio reproducibility. The correct value for the error bar is probably intermediate between these two bounds.

RESULTS AND DISCUSSION

The ratios $\gamma_{\text{CO}_2}/\gamma_{\text{N}_2}$ measured at five wavelengths in this ESHG experiment are given in Table I. In order to extract γ_{CO_2} from the ratio, use has been made of the previous measurements of $\gamma_{\text{N}_2}/\gamma_{\text{He}}$,¹⁴ and the *ab initio* results of Sitz and Yaris for γ_{He} .²⁰ Over the range of frequencies employed in the present measurements, the calibration results are adequately represented by¹⁴

$$\gamma_{\text{N}_2}/\gamma_{\text{He}} = 20.30 [1 + (6.55 \times 10^{-10} \text{ cm}^2) \nu^2] \quad (2)$$

TABLE I. Experimental results for γ_{CO_2} measured by ESHG.

λ^a (nm)	ν^b (cm ⁻¹)	$\Delta\alpha_{\text{CO}_2}/\Delta\alpha_{\text{N}_2}^c$	$\gamma_{\text{CO}_2}/\gamma_{\text{N}_2}$	$\gamma_{\text{CO}_2}^d$ (10 ⁻⁶³ C ⁴ m ⁴ J ⁻³)
692.9	14427.1	1.7689 ± 0.0036	1.294 ± 0.005	84.1 ± 0.5
650.7	15368.9	1.7603 ± 0.0036	1.301 ± 0.004	86.6 ± 0.4
616.1	16227.3	1.7573 ± 0.0036	1.308 ± 0.005	89.1 ± 0.5
514.5	19429.8	1.7593 ± 0.0036	1.331 ± 0.003	99.4 ± 0.5
488.0	20486.7	1.7654 ± 0.0036	1.341 ± 0.005	103.5 ± 0.6

^a Wavelength in air.

^b Frequency in cm⁻¹ in vacuum.

^c The tabulated error bars may be too pessimistic by as much as a factor of 5.

^d Obtained using Refs. 14 and 20 for calibration.

and²⁰

$$\gamma_{\text{He}} = 42.6 \text{ a.u.} [1 + (2.94 \times 10^{-10} \text{ cm}^2) \nu^2], \quad (3)$$

where ν is given in cm⁻¹ and 1 a.u. = 6.2360 × 10⁻⁶⁵ C⁴ m⁴ J⁻³. An uncertainty of ± 0.4% due to the $\gamma_{\text{N}_2}/\gamma_{\text{He}}$ calibration has been assumed in assigning the error bars for γ_{CO_2} . The *ab initio* result for γ_{He} is thought to be accurate to 1%. No allowance has been made for the uncertainty of γ_{He} in arriving at the experimental results for γ_{CO_2} given in Table I. Also given in Table I are the experimentally measured values of the linear polarizability dispersion ratio $\Delta\alpha_{\text{CO}_2}/\Delta\alpha_{\text{N}_2}$.

The experimental ESHG results for γ_{CO_2} are plotted as a function of ν^2 in Fig. 1, where it is seen that the data is accurately represented by a straight line. Such a result is expected if γ_{CO_2} is dominated by the contributions from high frequency electronic transitions.¹¹⁻¹⁵ It has been suggested that the electronic contribution to γ for the various third-order nonlinear optical processes (at frequencies well below

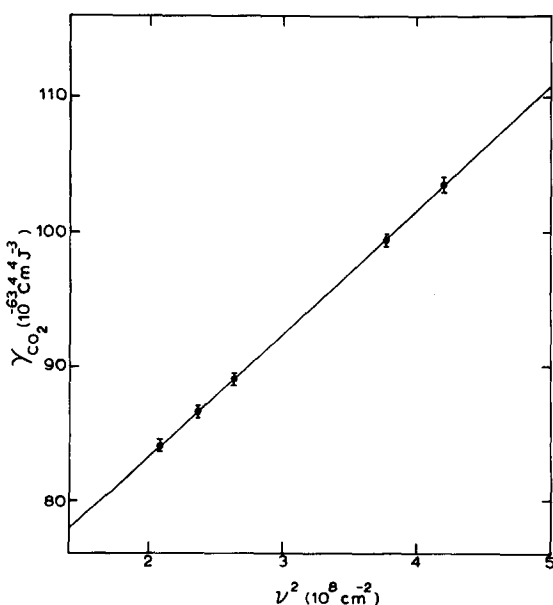


FIG. 1. Dispersion of the experimental results for γ_{CO_2} measured by ESHG. The straight line is a least squares fit of the function $\gamma = A[1 + B\nu^2]$ to the data. The coefficients of the fit are $A = 65.0 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ and $B = 14.07 \times 10^{-10} \text{ cm}^2$, where ν is given in cm⁻¹.

TABLE II. Hyperpolarizability of CO₂ measured by several nonlinear optical processes.

Process	λ (nm)	ν_L^2 ^a (10 ⁸ cm ⁻²)	$\gamma_{\text{CO}_2}^b$ (10 ⁻⁶³ C ⁴ m ⁴ J ⁻³)
dc Kerr ^c	632.8	4.99	558 ± 120
FWM ^d	694, 975	8.64	114 ± 17
FWM ^e	532, 683	14.47	114 ± 17
ESHG ^f	694.3	12.44	83.1 ± 1.0
ESHG ^g	514.5	22.65	99.0 ± 0.5
THG ^h	694.3	24.88	116 ± 17

^a Defined by Eq. (5); $\nu_L^2 = 6\nu^2$ for ESHG, etc.

^b Conversion factor 1 esu = 7.4279 × 10⁻²⁵ C⁴ m⁴ J⁻³ has been used.

^c $\gamma(-\omega; 0, 0, \omega)$, from Ref. 21.

^d $\gamma(-2\omega_1 + \omega_2; \omega_1, \omega_1, -\omega_2)$, from Ref. 23, as corrected and given in Ref. 24.

^e From Ref. 24.

^f $\gamma(-2\omega; \omega, \omega, 0)$, from Ref. 22.

^g From Ref. 13.

^h $\gamma(-3\omega; \omega, \omega, \omega)$, from Ref. 25.

the electronic resonance frequencies of the molecule) will obey the relation¹²

$$\gamma^e(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \gamma^e(0; 0, 0, 0) [1 + C\omega_L^2], \quad (4)$$

where the effective laser frequency ω_L is defined by

$$\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 + \omega_3^2. \quad (5)$$

If it is the case that the electronic contributions to γ_{CO_2} are dominant, Eqs. (4) and (5) indicate that the values of γ_{CO_2}

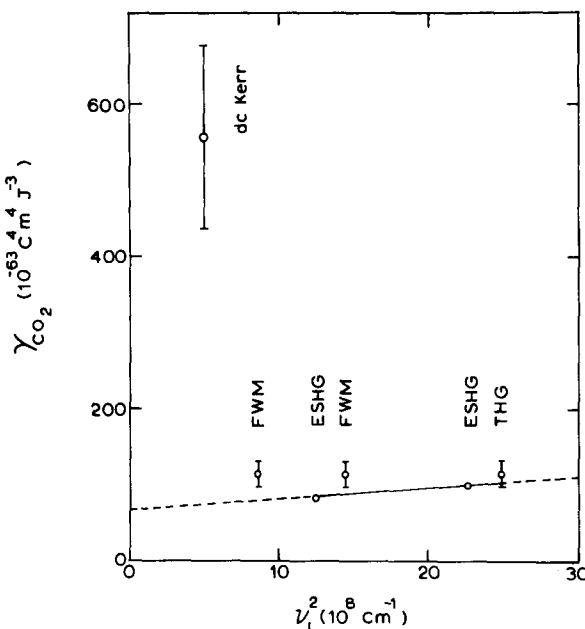


FIG. 2. Comparison of the hyperpolarizability of CO₂ measured by several nonlinear optical processes: dc Kerr effect, electric-field-induced second-harmonic generation (ESHG), four wave mixing (FWM), and third-harmonic generation (THG). The straight line is the ESHG result of Fig. 1 replotted vs ν_L^2 . The effective laser frequency ν_L is defined by Eq. (5). The dashed portions of the line indicate extrapolation outside the frequency interval containing the actual measurements. The open circles are the data of Table II. The error bars of the ESHG measurements are smaller than the circles. All the results should fall on the line if electronic contributions are dominant.

experimentally determined using different nonlinear optical processes should all fall on the same straight line when plotted vs ν_L^2 . Conversely, deviations from a common line will indicate significant vibrational or rotational contributions to γ_{CO_2} .

The values of γ_{CO_2} obtained from dc Kerr,²¹ ESHG,^{13,22} four wave mixing (FWM),^{23,24} and third-harmonic generation (THG)²⁵ experiments have been collected in Table II, and this data has been plotted vs ν_L^2 in Fig. 2. As may be seen from Fig. 2, the experimental results for ESHG and THG agree well with the prediction of Eqs. (4) and (5), while the FWM results fall significantly above the predicted line. Furthermore, the measured dc Kerr value is a factor of 7 larger than the value predicted on the basis of purely electronic contributions to γ_{CO_2} . These results are consistent with the presence of vibrational contributions to γ_{CO_2} . Elliott and Ward⁹ have shown that enhanced vibrational contributions

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \hbar^{-3} \sum_P \left\{ \sum'_m \sum'_n \sum'_p \frac{\langle g|\mu_\alpha|m\rangle \langle m|\mu_\delta|n\rangle \langle n|\mu_\gamma|p\rangle \langle p|\mu_\beta|g\rangle}{(\Omega_{mg} - \omega_\sigma)(\Omega_{ng} - \omega_1 - \omega_2)(\Omega_{pg} - \omega_1)} - \sum'_m \sum'_n \frac{\langle g|\mu_\alpha|m\rangle \langle m|\mu_\delta|g\rangle \langle g|\mu_\gamma|n\rangle \langle n|\mu_\beta|g\rangle}{(\Omega_{mg} - \omega_\sigma)(\Omega_{ng} - \omega_1)(\Omega_{ng} + \omega_2)} \right\}, \quad (6)$$

where $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$, and Σ_P denotes the sum over terms obtained by permuting the frequencies $-\omega_\sigma, \omega_1, \omega_2, \omega_3$ together with their associated spatial subscripts $\alpha, \beta, \gamma, \delta$. The primed sums over intermediate states exclude the ground state $|g\rangle$. This expression is valid for nondipolar molecules.

The vibrational contribution to the total γ is the sum of all those terms for which at least one of the intermediate states m, n, p is a vibrationally excited state of the ground electronic manifold. To evaluate γ_{Kerr}^ν we begin by substituting $(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = (-\omega; 0, 0, \omega)$, writing out the 24 frequency permuted terms, and regrouping the terms according to whether 0, 1, or 2 of the factors $(\Omega_{mg} - \omega')$ in the denominator have $\omega' = 0$. Since $\Omega_{mg} \ll \omega$ for typical vibrational and optical frequencies, terms with two factors of the form $(\Omega_{mg} - 0)$ in the denominator will be strongly enhanced over all the other terms. Retaining only the doubly enhanced terms one obtains the following expressions for the relevant tensor components of γ^ν :

$$\gamma_{\alpha\beta\beta\alpha}^\nu(-\omega; 0, 0, \omega) = \hbar^{-2} \left\{ 4 \sum'_m \sum'_n \frac{\alpha_{gm}^{\alpha\alpha} \mu_{mn}^\beta \mu_{ng}^\beta}{\Omega_{mg} \Omega_{ng}} + 2 \sum'_m \sum'_n \frac{\mu_{gm}^\beta \alpha_{mn}^{\alpha\alpha} \mu_{ng}^\beta}{\Omega_{mg} \Omega_{ng}} - 2 \sum'_m \frac{\alpha_{gg}^{\alpha\alpha} \mu_{gm}^\beta \mu_{mg}^\beta}{\Omega_{mg} \Omega_{mg}} \right\} \quad (7a)$$

and

$$\gamma_{\alpha\beta\alpha\beta}^\nu(-\omega; 0, 0, \omega) = \gamma_{\alpha\alpha\beta\beta}^\nu(-\omega; 0, 0, \omega) = 0, \quad (7b)$$

$$\gamma_{\text{Kerr}}^\nu = \hbar^{-2} \left\{ \frac{4}{5} \sum'_m \sum'_n \frac{(\alpha_{gm}^{zz} - \alpha_{gm}^{xx})(\mu_{mn}^z \mu_{ng}^z - \mu_{mn}^x \mu_{ng}^x)}{\Omega_{mg} \Omega_{ng}} + \frac{2}{5} \sum'_m \sum'_n \frac{\mu_{gm}^z (\alpha_{mn}^{zz} - \alpha_{mn}^{xx}) \mu_{ng}^z - \mu_{gm}^x (\alpha_{mn}^{zz} - \alpha_{mn}^{xx}) \mu_{ng}^x}{\Omega_{mg} \Omega_{ng}} - \frac{2}{5} \sum'_m \frac{(\alpha_{gg}^{zz} - \alpha_{gg}^{xx})(\mu_{gm}^z \mu_{mg}^z - \mu_{gm}^x \mu_{mg}^x)}{\Omega_{mg} \Omega_{mg}} \right\}. \quad (11)$$

to γ will occur when subsets of the applied field frequency arguments sum to zero. Thus, one may expect the size of vibrational contributions to γ to follow the order $\gamma_{\text{Kerr}}^\nu > \gamma_{\text{FWM}}^\nu > \gamma_{\text{ESHG}}^\nu > \gamma_{\text{THG}}^\nu$, where the appearance of two static field arguments in γ_{Kerr}^ν results in a double enhancement of γ_{Kerr}^ν . The size of the deviations of the γ_{CO_2} measurements from the straight line in Fig. 2 follows the predicted order. There is also similar evidence for a vibrational contribution to $\gamma_{\text{SF}_6}^\nu$,¹⁰ where for that molecule the dc Kerr result is nearly twice as large as predicted from the ESHG measurements.

The outstanding feature in the above comparison for CO₂ is that the dc Kerr result is so much larger than the ESHG result. In order to better understand the origin of this difference, we have calculated γ_{Kerr}^ν for CO₂ following the outline given by Elliott and Ward.⁹ The starting point is the expression⁶

where $|m\rangle, |n\rangle$ are vibrationally excited states of the ground electronic manifold, and where $\alpha_{mn}^{\alpha\beta}$ is the Raman transition polarizability defined by

$$\alpha_{mn}^{\alpha\beta} = \hbar^{-1} \sum'_p \langle m|\mu_\alpha|p\rangle \langle p|\mu_\beta|n\rangle \left(\frac{2\Omega_{pg}}{\Omega_{pg}^2 - \omega^2} \right). \quad (8)$$

To obtain Eq. (7b) we have also made the assumption that $\alpha_{gn}^{\alpha\beta}$ is diagonal for all transitions $g \rightarrow n$ of significant strength, which is valid for a centrosymmetric linear molecule such as CO₂. Equation (7a) with $\alpha = \beta$ is essentially the same as Eq. (17) of Ref. 9, except for the third group of terms and an overall factor of 6 arising from the definition $6\chi^{(3)} = \gamma$.

The dc Kerr effect birefringence measured in the lab is related to the isotropically averaged molecular hyperpolarizability tensor through the definition

$$\gamma_{\text{Kerr}} = \frac{3}{2} [\langle \gamma \rangle_{zzzz} - \langle \gamma \rangle_{zzxx}], \quad (9)$$

where $\langle \rangle$ denotes the isotropic average and the upper case spatial indices refer to the lab frame. From Eq. (7), the only non vanishing components of γ^ν contributing to $\langle \gamma^\nu \rangle$ are $\gamma_{\alpha\beta\beta\alpha}^\nu$. Evaluating Eq. (9) and making use of the axial symmetry of CO₂ one gets

$$\gamma_{\text{Kerr}}^\nu = \frac{1}{2} [(\gamma_{xxxx}^\nu - \gamma_{zzzz}^\nu) + (\gamma_{zzzz}^\nu - \gamma_{zzxx}^\nu)], \quad (10)$$

where the lower case indices denote components in the molecule fixed frame and z is the molecular symmetry axis. Substituting Eq. (7) into Eq. (10) one obtains an explicit expression for γ_{Kerr}^ν for CO₂ [the degeneracy of the bending vibration is accounted for in Eq. (10)],

TABLE III. Transition matrix elements for the ¹²C¹⁶O₂ molecule, used in the calculation of $\gamma_{\text{Kerr}}^{\nu}$. The notation for the vibrational state of the molecule is $v_1v_2l_2v_3r$, where r labels the members of a Fermi resonance polyad in order of decreasing transition frequency (Refs. 30 and 31). The fundamental infrared and Raman transitions have been marked with a star. Only transitions for which the changes in each quantum number are at most ± 1 have been included. Missing entries in the table are zero by symmetry.

$\nu_{\nu' \nu''}$ (cm ⁻¹)	ν'	ν''	$ \mu_{\nu' \nu''}^z ^a$ (10 ⁻³² C m)	$ \mu_{\nu' \nu''}^x ^a$ (10 ⁻³² C m)	$\frac{1}{2} \alpha_{\nu' \nu''}^{zz} + 2\alpha_{\nu' \nu''}^{xx} $ (10 ⁻⁴² C ² m ² J ⁻¹)	$ \alpha_{\nu' \nu''}^{zz} - \alpha_{\nu' \nu''}^{xx} $ (10 ⁻⁴² C ² m ² J ⁻¹)
0	00001	00001			293.3 ^b	235 ^c
544.283	11102	10001		7.55		
618.033	10002	01101		28.22		
647.058	11102	10002		48.70		
667.379*	01101	00001		40.67		
688.678	11101	10001		49.61		
720.808	10001	01101		29.68		
791.452	11101	10002		9.90		
960.959	00011	10001	12.76			
1063.734	00011	10002	10.83			
1263.689	10012	00011			5 ^d	4 ^d
1265.091	11102	01101			4.4 ^e	7.2 ^e
1285.412*	10002	00001			5.10 ^f	4.26 ^f
1365.640	10011	00011			6 ^d	4 ^d
1388.187*	10001	00001			6.46 ^f	4.24 ^f
1409.470	11101	01101			5.5 ^e	6.5 ^e
1932.470	11102	00001		0.168		
2076.865	11101	00001		0.481		
2224.657	10012	10001	3.61			
2326.594	10011	10001	107.63			
2327.432	10012	10002	107.17			
2349.146*	00011	00001	104.50			
2429.369	10011	10002	2.45			
3612.844	10012	00001	8.75			
3714.781	10011	00001	10.39			

^a The dipole matrix elements are computed from infrared absorption intensities of Ref. 32, by the method outlined in the Appendix of Ref. 9.

^b From the refractive index, $\lambda = 632.8$ nm, Refs. 4 and 18.

^c From depolarized light scattering, $\lambda = 632.8$ nm, Refs. 4, 26, and 27.

^d Estimated to be equal to the transition polarizability of the corresponding fundamental.

^e Computed from data in Ref. 33 normalized to the measured cross sections for the fundamentals as given in Ref. 34.

^f Computed from cross sections of Ref. 34 and depolarization ratios of Ref. 33, by essentially the methods outlined in the Appendix of Ref. 9.

Note that the third group of terms in Eq. (11) is canceled by the $m = n$ subset of the second group of terms. This follows because $\partial\alpha/\partial Q = 0$ and $\alpha_{mm} = \alpha_{gg}$, for the bending and asymmetric stretching vibrational modes for which $\mu_{gm} \neq 0$. The remaining terms all contain at least one transition dipole or polarizability corresponding to an overtone or combination band, which makes them much smaller than if they contained only fundamentals.

The transition dipole moments and polarizabilities needed to evaluate Eq. (11) for the ¹²C¹⁶O₂ molecule have been collected in Table III. Assuming all matrix elements are positive, one obtains $\gamma_{\text{Kerr}}^{\nu} = -1.1 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ for CO₂. This result is not very much larger than the terms which were ignored in writing Eq. (7). Terms of the type $\alpha^2/\hbar\Omega$ (previously considered for H₂)¹⁵ give a contribution $+0.4 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$. Of the other terms omitted, those of the type $\mu^4/(\hbar\omega)^3$ are negligible (contribution of order $10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$), while those of the type $\mu\beta/\hbar\Omega$ will give a contribution $2 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ if one takes the hyper-Raman polarizability β of CO₂ to be as large as that of CH₄.⁹ Thus, retaining only double enhanced terms in Eq. (7) does not select a clearly dominant set of terms. Our best estimate of $\gamma_{\text{Kerr}}^{\nu}$ from the incomplete data at our disposal is

$$0 \pm 2 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}.$$

The measured γ_{Kerr} is the sum of $\gamma_{\text{Kerr}}^{\nu}$ and γ_{Kerr}^e . Equation (4) and our measurements of γ_{ESHG} may be combined to estimate $\gamma_{\text{Kerr}}^e = +72.6 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ at $\lambda = 632.8$ nm for CO₂. Adding γ_{Kerr}^e to $\gamma_{\text{Kerr}}^{\nu}$ gives the prediction $\gamma_{\text{Kerr}} = +73 \pm 2 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$, to be compared with the experimentally measured result $\gamma_{\text{Kerr}} = +558 \pm 120 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$. The value of γ_{Kerr} calculated above is unlikely to be in error by an amount as large as the difference between the calculated and measured values. Therefore, the next step is to review the published results of the dc Kerr experiment in an attempt to resolve the discrepancy.

The value of γ_{Kerr} is obtained from the dc Kerr effect measurements of Buckingham *et al.*,²¹ as the zero intercept of a straight line fit to the first Kerr virial coefficient vs T^{-1} . Nine measurements were made over the temperature range $T = 252\text{--}337$ K. Inspecting a graph of this data, one sees that the lowest temperature data point disagrees with the trend of the other eight points. Furthermore, excluding this single point from the fit reduces the standard deviation of the fit by nearly a factor of 3. The slopes of the lines fitted to either eight or nine points agree equally well with the slope

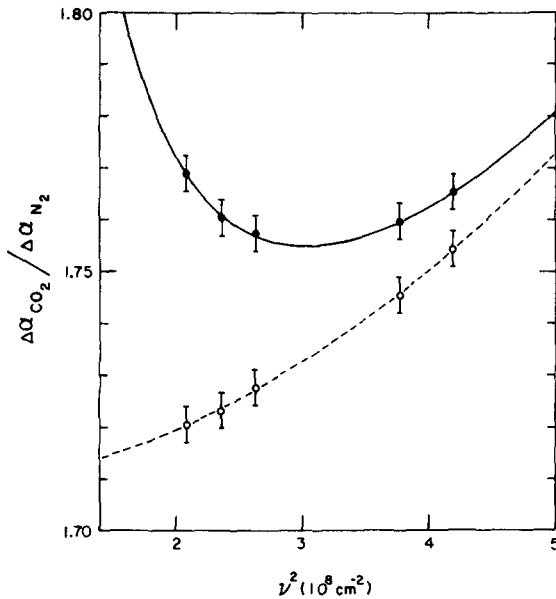


FIG. 3. Variation of the linear polarizability dispersion ratio $\Delta\alpha_{\text{CO}_2}/\Delta\alpha_{\text{N}_2}$, where $\Delta\alpha(\omega) = \alpha(2\omega) - \alpha(\omega)$, plotted as a function of ν^2 . The dashed curve is a least squares fit of the function $\Delta\alpha_{\text{CO}_2}^e/\Delta\alpha_{\text{N}_2} = A[1 + B\nu^2 + C\nu^4]$ to the vibrationally corrected data ($\Delta\alpha_{\text{CO}_2}^e/\Delta\alpha_{\text{N}_2} = \text{Eq. (14)}/\text{Eq. (15)}$ has been subtracted). The coefficients of the fit are $A = 1.7087$, $B = 0.0266 \times 10^{-10} \text{ cm}^2$, and $C = 14.5 \times 10^{-20} \text{ cm}^4$, where ν is given in cm^{-1} . Adding back the vibrational contribution gives the solid curve through the original data points. The dispersion ratio is expected to be monotonic in ν^2 if electronic contributions are dominant.

calculated from the classical orientational dc Kerr effect, but excluding the single lowest temperature data point changes the intercept from $\gamma_{\text{Kerr}} = 558 \times 10^{-63}$ to $-61 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$. The indications are that the lowest temperature point should be rejected, giving the revised estimate $\gamma_{\text{Kerr}} = -61 \pm 200 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ (our error estimate is obtained by adding the statistical uncertainty of the fit and the systematic uncertainty of the total measured birefringence). This revised experimental estimate of γ_{Kerr} is in agreement with our estimate of $\gamma_{\text{Kerr}}^e + \gamma_{\text{Kerr}}^v$, so it would seem that the large and discrepant value of γ_{Kerr} given in the literature is spurious, the result of a single bad data point. In fact γ_{Kerr} for CO₂ is only about 3% different from γ_{Kerr}^e alone, due to the vibrational contribution γ_{Kerr}^v .

There are also vibrational contributions to the linear polarizability of CO₂,^{9,28} as may be seen in Fig. 3 where the polarizability dispersion ratio $\Delta\alpha_{\text{CO}_2}/\Delta\alpha_{\text{N}_2}$ has been plotted vs ν^2 (filled circles, solid line). When α is dominated by high frequency electronic resonance contributions such a plot results in a monotonic increasing line, such as is the case for CH₄.²⁹ However, in the case of CO₂ this plot exhibits a pronounced minimum, indicating that in the red end of the visible the dispersion due to low frequency vibrational resonances becomes comparable to that due to high frequency electronic resonances. For CO₂ the vibrational contribution to the isotropic polarizability α may be calculated from the expression^{4,9}

$$\alpha^v(\omega) = (3\hbar)^{-1} \sum'_m [|\mu_{mg}^z|^2 + 2|\mu_{mg}^x|^2] \left(\frac{2\Omega_{mg}}{\Omega_{mg}^2 - \omega^2} \right). \quad (12)$$

At optical frequencies one may make the approximation $\Omega_{mg}^2 - \omega^2 \approx -\omega^2$, obtaining the simple result

$$\Delta\alpha^v(\omega) = (2\hbar\omega^2)^{-1} \sum'_m \Omega_{mg} [|\mu_{mg}^z|^2 + 2|\mu_{mg}^x|^2]. \quad (13)$$

Including just the two fundamental infrared active modes in the evaluation of Eq. (13) gives

$$\Delta\alpha_{\text{CO}_2}^v (\text{C}^2 \text{ m}^2 \text{ J}^{-1}) = +0.70 \times 10^{-34} \nu^{-2}, \quad (14)$$

where ν is given in cm^{-1} .

Equation (14) for $\Delta\alpha_{\text{CO}_2}^v$ allows one to extract $\Delta\alpha_{\text{CO}_2}^e$, by multiplying the experimental values of $\Delta\alpha_{\text{CO}_2}/\Delta\alpha_{\text{N}_2}$ by $\Delta\alpha_{\text{N}_2}$, where¹⁹

$$\begin{aligned} \Delta\alpha_{\text{N}_2} (\text{C}^2 \text{ m}^2 \text{ J}^{-1}) \\ = 3.117 \times 10^{-50} \nu^2 [1 + 3.076 \times 10^{-10} \nu^2 \\ + 17.58 \times 10^{-20} \nu^4], \end{aligned} \quad (15)$$

and subtracting the calculated values of $\Delta\alpha_{\text{CO}_2}^v$. The resulting plot of $\Delta\alpha_{\text{CO}_2}^e/\Delta\alpha_{\text{N}_2}$ vs ν^2 in Fig. 3 (open circles, dashed line) shows the expected monotonic increasing variation. As a check, one may derive an estimate of $\Delta\alpha_{\text{CO}_2}$ from the measurements of the refractive index of CO₂, over the wavelength range $\lambda = 237.9\text{--}546.2 \text{ nm}$, as given in Landolt-Bornstein tables.¹⁸ This result, $\Delta\alpha_{\text{CO}_2}^{\text{LB}}$, should be directly comparable to our $\Delta\alpha_{\text{CO}_2}^e$, since $\Delta\alpha_{\text{CO}_2}^v$ becomes small enough to neglect at ultraviolet wavelengths. The two results

$$\begin{aligned} \Delta\alpha_{\text{CO}_2}^e (\text{C}^2 \text{ m}^2 \text{ J}^{-1}) \\ = 5.33 \times 10^{-50} \nu^2 [1 + 3.1 \times 10^{-10} \nu^2 \\ + 32 \times 10^{-20} \nu^4] \end{aligned} \quad (16a)$$

and

$$\begin{aligned} \Delta\alpha_{\text{CO}_2}^{\text{LB}} (\text{C}^2 \text{ m}^2 \text{ J}^{-1}) \\ = 5.37 \times 10^{-50} \nu^2 [1 + 3.6 \times 10^{-10} \nu^2 \\ + 16 \times 10^{-20} \nu^4] \end{aligned} \quad (16b)$$

are in good agreement, which confirms the adequacy of our calculation for $\Delta\alpha_{\text{CO}_2}^e$.

In summary, the vibrational contributions to γ_{CO_2} appear to be insignificant for ESHG and THG, but not for FWM and the dc Kerr effect. The published dc Kerr effect result is incorrect and far too large. More accurate dc Kerr effect measurements would be interesting as a test of the calculated value of γ_{Kerr}^v . The present calculation of γ_{Kerr}^v seems to indicate that the vibrational contribution γ_{Kerr}^v for spherical top molecules will be about the same as that for CO₂ because the terms which contribute are essentially the same. This result is somewhat at odds with the result of a previous calculation which estimates $\gamma_{\text{Kerr}}^v > \gamma_{\text{Kerr}}^e$ for CF₄.⁹ However, in the last step of the previous calculation [Eq. (17') of Ref. 9] all transition moments were replaced by the fundamental vibrational transition moment for a given mode, so one may expect the numerical result of that calculation to be an overestimate.

Note added in proof: As yet unpublished measurements by I. R. Gentle, D. R. Laver, and G. L. D. Ritchie have been brought to the author's attention. These measurements give $\gamma_{\text{Kerr}} = +110 \pm 39 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$, supporting the present results.

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