

Hyperpolarizability dispersion measured for CH₄

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The frequency dependence of the second hyperpolarizability (γ) of CH₄ has been measured in the visible ($477 < \lambda < 672$ nm) by means of gas-phase electric-field-induced second-harmonic generation (ESHG). No resonances due to vibrational overtones are observed. Comparison of the ESHG results with the results of several other third-order nonlinear-optics experiments indicates that vibrational contributions to γ_{CH_4} are negligible.

INTRODUCTION

The third-order nonlinear susceptibility $\chi^{(3)}$, which mediates a wide range of nonlinear-optical processes, is the macroscopic expression of the microscopic molecular second hyperpolarizability tensor γ .¹⁻⁴ Perturbation theory gives a single expression for γ , and the hyperpolarizabilities corresponding to each of the various nonlinear optical processes are just special cases of this general expression.⁵⁻⁷ The underlying unity of the fundamental theoretical description is obscured in practice 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.⁸⁻¹¹ 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 CH₄ 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.^{9,10,12-15} 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 occurs, enhancing the second-harmonic signal generated. The electrode spacing is 2.69 mm, resulting in optimal pressures in the range of 0.9–5.9 atm (at 20–27°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 using a Jarrell-Ash 1-m spectrometer calibrated by Na and Ne spectral lamps.

The ratio of hyperpolarizabilities for a sample gas B and a reference gas A is obtained from the relation^{9,12}

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

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 $B = \text{CH}_4$ and $A = \text{N}_2$. Since the optical- and static-field polarizations are parallel, the experiment measures the $zzzz$ component of the orientationally averaged tensor $\gamma_{\alpha\beta\gamma\delta}$.^{10,14} The laser power at the sample was 0.3–3.0 W, and the signals $S^{(2\omega)}$ were in the range 45–4500 Hz against a typical background of 0.6 Hz (except at the shortest wavelength employed, where the available glass filter was barely adequate and the background was about 5 Hz). Sample densities were computed from the measured pressures and temperatures using the virial equation of state.¹⁶ Refractive indices were calculated from tables^{4,17} using the measured densities. High-purity gases were used (CH₄, 99.97%; N₂, 99.999%). Measurements were made in triplets (ABA) or coupled triplets ($ABABA \dots$) 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 $\pm 0.3\%$, while the reproducibility is about $\pm 0.1\%$.

In the course of the hyperpolarizability-ratio measurements one also obtains as a by product the ratio of linear polarizability dispersion $\Delta\alpha_{\text{CH}_4}/\Delta\alpha_{\text{N}_2}$, where $\Delta\alpha(\omega) = \alpha(2\omega) - \alpha(\omega)$, since $\Delta\alpha$ is just proportional to ρ^{-1} , the inverse phase-match density.^{12,18} 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 $\pm 0.03\%$ density ratio reproducibility. The correct value for the error bar is probably intermediate between these two bounds.

TABLE I. Experimental results for γ_{CH_4} measured by ESHG.

λ^a (nm)	ν^b (cm ⁻¹)	$\Delta\alpha_{\text{CH}_4}/\Delta\alpha_{\text{N}_2}^c$	$\gamma_{\text{CH}_4}/\gamma_{\text{N}_2}$	$\gamma_{\text{CH}_4}^d$ (10 ⁻⁶³ C ⁴ m ⁴ J ⁻³)	γ_{CH_4} (10 ⁻⁶³ C ⁴ m ⁴ J ⁻³)
694.3	14399				195±2 ^e
671.7	14883	2.1634±0.0043	3.105±0.007	204.1±0.9	
671.5	14888	2.1632±0.0043	3.100±0.009	204.2±1.0	
667.8	14970	2.1633±0.0043	3.103±0.007	204.5±0.9	
650.7	15369	2.1684±0.0044	3.134±0.008	208.6±1.0	
619.0	16151	2.1776±0.0046	3.169±0.008	215.4±1.0	
616.1	16227	2.1781±0.0044	3.168±0.008	215.8±1.0	
589.0	16973	2.1874±0.0044	3.209±0.008	223.1±1.1	
514.5	19430	2.2274±0.0045	3.350±0.019	250.3±1.7	248.2±0.4 ^f
501.7	19926	2.2366±0.0045	3.388±0.010	257.1±1.3	250.8±1.1 ^f
496.5	20135	2.2381±0.0045	3.400±0.012	259.7±1.4	259.2±2.0 ^f
488.0	20487	2.2446±0.0046	3.426±0.010	264.6±1.3	267.4±1.6 ^f
476.5	20981	2.2577±0.0046	3.454±0.019	271.0±1.8	269.7±1.0 ^f
457.9	21831				279.5±0.9 ^f

^aWavelength in air.

^bFrequency in cm⁻¹ in vacuum.

^cThe tabulated error bars may be too pessimistic by as much as a factor of 7.

^dObtained using Refs. 13 and 19 for calibration.

^eFrom Ref. 20.

^fFrom Ref. 12.

RESULTS AND DISCUSSION

The ratios $\gamma_{\text{CH}_4}/\gamma_{\text{N}_2}$ measured at 12 wavelengths in this ESHG experiment are given in Table I. In order to extract γ_{CH_4} from the ratio, use has been made of the previous measurements of $\gamma_{\text{N}_2}/\gamma_{\text{He}}$ ¹³ and the *ab initio* results of Sitz and Yaris for γ_{He} ¹⁹. Over the range of frequencies employed in the present measurements, the calibration results are adequately represented by¹³

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

and¹⁹

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

where ν is given in cm⁻¹ and 1 a.u. = $6.2360 \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$. 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_{CH_4} . 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_{CH_4} given in Table I.

The experimental ESHG results for γ_{CH_4} are plotted as a function of ν^2 in Fig. 1. While the data is adequately represented by a straight line, the fit is improved by the inclusion of a small term quadratic in ν^2 . The same situation is obtained when the data for the polarizability-dispersion ratio $\Delta\alpha_{\text{CH}_4}/\Delta\alpha_{\text{N}_2}$ is considered. This data is also given in Table I, and is plotted versus ν^2 in Fig. 2. In both Figs. 1 and 2 a straight line will fall within all the error bars, but the scatter of data points about the quadratic curve is in better agreement with the statistical estimate of the measurement reproducibility. If contributions from

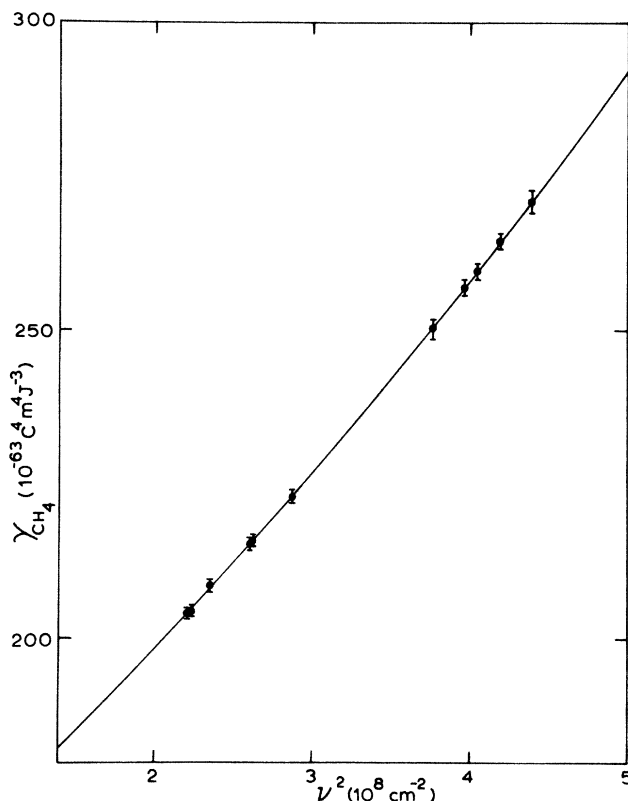


FIG. 1. Dispersion of the experimental results for γ_{CH_4} measured by ESHG. The curve drawn through the points is a least-squares fit of the function $\gamma = A(1 + B\nu^2 + C\nu^4)$ to the data. The coefficients of the fit are $A = 149.1 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$, $B = 14.70 \times 10^{-10} \text{ cm}^2$ and $C = 89.1 \times 10^{-20} \text{ cm}^4$, where ν is given in cm⁻¹. A straight-line least squares fitted to the data will also pass through all the error bars, and is given by $\gamma = A'(1 + B'\nu^2)$ with $A' = 136.3 \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ and $B' = 22.31 \times 10^{-10} \text{ cm}^2$.

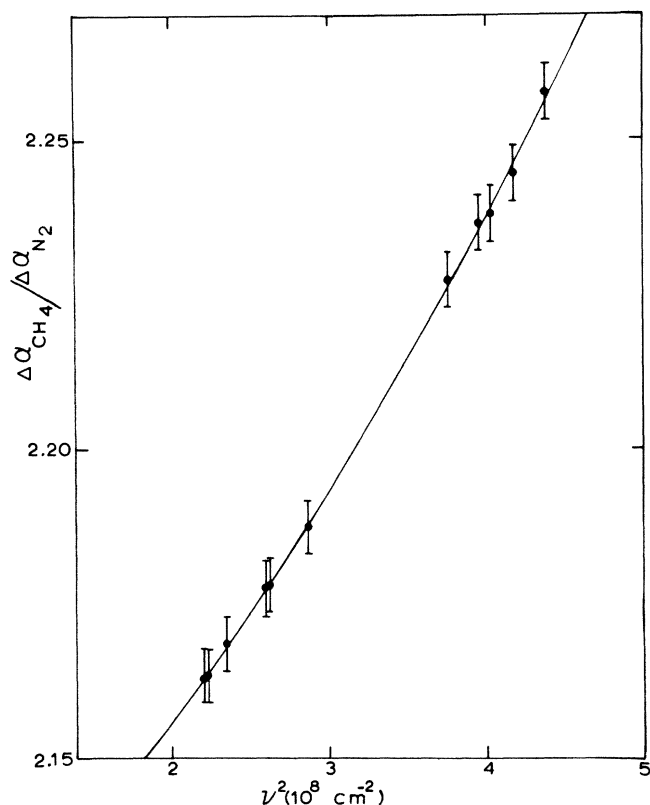


FIG. 2. Variation of the linear polarizability dispersion ratio $\Delta\alpha_{\text{CH}_4}/\Delta\alpha_{\text{N}_2}$, plotted as a function of ν^2 . The error bars shown are probably too conservative. The curve is a least-squares fit of the function $\Delta\alpha_{\text{CH}_4}/\Delta\alpha_{\text{N}_2} = A(1 + B\nu^2 + C\nu^4)$ to the data. The coefficients of the fit are $A = 2.1029$, $B = 0.916 \times 10^{-10} \text{ cm}^2$ and $C = 1.69 \times 10^{-20} \text{ cm}^4$, where ν is given in cm^{-1} .

high-frequency electronic resonances dominate γ (and $\Delta\alpha$) one expects that the frequency dependence of γ (and $\Delta\alpha$) will be expressible as a series in even powers of ν , with the ν^2 term dominating at frequencies far below the electronic resonance frequencies of the molecule.^{10-14,18} The data for γ_{CH_4} and $\Delta\alpha_{\text{CH}_4}$ are consistent with such a dispersion

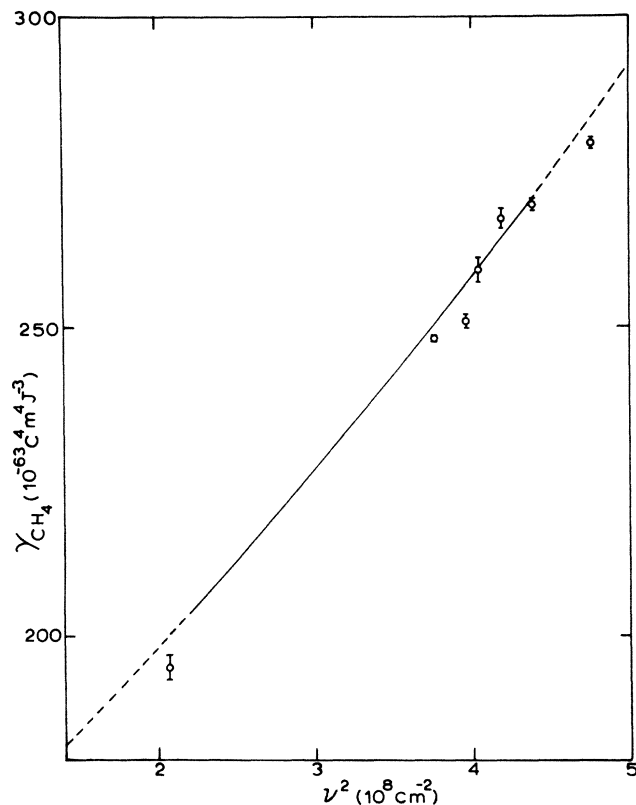


FIG. 3. Comparison of previous ESHG measurements of γ_{CH_4} (open circles) with the results of the present measurements. The curve is the three-parameter fit to the data in Fig. 1, and is shown dashed outside the interval containing the actual data points.

relation.

The results of previous ESHG experiments^{12,20} have been collected in Table I, and are plotted versus ν^2 in Fig. 3 for comparison with the results of the present experiment. As may be seen from Fig. 3, the previous results agree well with the curve fitted to the present results. The scatter of the previous results about this curve indicates

TABLE II. Hyperpolarizability of CH_4 measured by several nonlinear-optical processes.

Process	λ (nm)	ν_L^2 ^a (10^8 cm^{-2})	γ_{CH_4} ^b ($10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$)
dc Kerr ^c	632.8	4.99	180 ± 9
FWM ^d	694,975	8.64	200 ± 30
FWM ^e	694,975	8.64	167 ± 20
FWM ^f	532,683	14.47	208 ± 12
THG ^g	694.3	24.88	245 ± 7

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

^bConversion factor $1 \text{ esu} = 7.4279 \times 10^{-25} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ 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. 22.

^eFrom Ref. 23, as corrected and given in Ref. 24, but with their vibrational correction removed.

^fFrom Ref. 24, with their vibrational correction removed.

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

that their error bars had been underestimated by about a factor of 2 or more.

In order to assess the relative size of the vibrational and electronic contributions to γ_{CH_4} , the values of γ_{CH_4} measured for several nonlinear-optical processes have been compared. It has been suggested that the electronic contribution to γ for the various third-order nonlinear-optical processes (at frequencies well below the electronic resonance frequencies of the molecule) will obey the relation¹¹

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

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_{CH_4} are dominant, then the values of γ_{CH_4} experimentally determined using different nonlinear-optical processes should all fall on the same straight line when plotted versus ν_L^2 . The values of γ_{CH_4} obtained from dc-Kerr,²¹ FWM (Refs. 22–24), and THG (Ref. 25) experiments have been collected in Table II, and this data has been plotted versus ν_L^2 in Fig. 4. The straight line with the form given by Eq. (4) and fitted to the ESHG measurements of Fig. 1 has also been plotted in Fig. 3. The FWM results are in good agreement with this line, which is the prediction of the ESHG measurements assuming only electronic contributions to γ_{CH_4} . The dc Kerr and THG measurements fall about 10% above and below the predicted line. If the error bars of the dc Kerr and THG measurements were underestimated by as much as those of the ESHG measurements in Fig. 3, then their deviations from the predicted line would not be significant. The result of the comparison made in Fig. 4 seems to be that the vibrational contribution to γ_{CH_4} is small. This assessment is supported by the results of a calculation by Elliot and Ward.⁸ They have estimated that the vibrational contribution to γ_{CH_4} is 3% or less for dc Kerr and an order of magnitude smaller still for ESHG. Since the vibrational contributions for all the processes under consideration except dc Kerr are expected to be less than or about equal to that for ESHG, the available data indicate that the vibrational contribution to γ_{CH_4} is negligible. Further dc Kerr and THG measurements would be most useful, both as a check on the accuracy of the previous measurements, and also to test the possibility that the discrepancies seen in Fig. 4 arise because some aspect of the relationship between the various hyperpolarizabilities is not fully understood.

On the basis of previous ESHG measurements it was suggested that resonance with vibrational overtones might

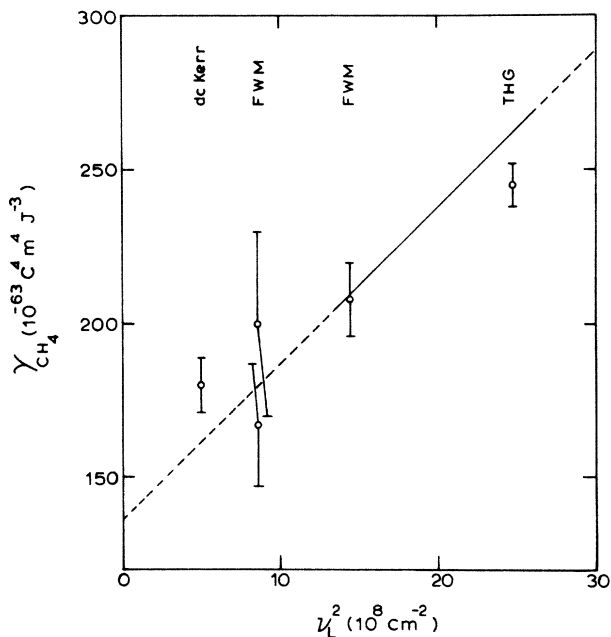


FIG. 4. Comparison of the hyperpolarizability of CH₄ measured by several nonlinear-optical processes: dc Kerr effect, four-wave mixing (FWM), and third-harmonic generation (THG). The straight line is the two-parameter fit to the data of Fig. 1 replotted versus ν_L^2 . The effective laser frequency ν_L 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. All the results should fall on the line if electronic contributions are dominant.

contribute significantly to γ_{CH_4} .¹² However, the present measured values of the ratio $\gamma_{\text{CH}_4}/\gamma_{\text{N}_2}$ (given in Table I) follow a smooth curve when plotted versus ν^2 and examined for deviations at the 0.1% level. Vibrational overtone transition frequencies for levels with quantum number $\nu \leq 5$ have been calculated for CH₄.²⁶ The measurement of γ_{CH_4} at $\lambda = 667.8$ nm falls within 10 cm^{-1} of the calculated position of a $5\nu_3$ resonance but shows no significant deviation from a smooth curve. Since the strength of vibrational overtone resonances increases as the upper-vibrational-level quantum number decreases, detection of a vibrational overtone resonance seems more likely in the near infrared than in the visible. Though it is clear that vibrations make only a minor contribution to γ_{CH_4} , intensity measurements of vibrational overtones would provide valuable information bearing on the nature of highly excited molecular vibrations.²⁶

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