NON-RESONANT THIRD-ORDER SUSCEPTIBILITIES
MEASURED FOR ETHANE, PROPANE AND n-BUTANE

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Third-order non-linear susceptibilities have been measured for ethane, propane and n-butane at three wavelengths in the visible region by means of gas-phase electric-field-induced second-harmonic generation (ESHG). The susceptibilities are found to be large and strongly frequency dependent. The possible application of these results to the calibration of the non-resonant background in coherent anti-Stokes Raman scattering (CARS) measurements is discussed.

1. Introduction

Of the various third-order non-linear optical processes, coherent anti-Stokes Raman scattering (CARS) has found the most widespread applications, ranging from fundamental spectroscopic investigations to combustion diagnostics [1,2]. The quantitative analysis of a CARS measurement is complicated because the non-resonant susceptibility makes a significant or even dominant contribution to the observed signal, particularly when the molecule of interest is present at low concentration in a mixed gas sample. In principle, it should be possible to evaluate the non-resonant susceptibility by means of any of the various third-order non-linear optical processes, such as the dc Kerr effect or electric-field-induced second-harmonic generation (ESHG). However, the frequency dependence of the susceptibility must be considered if such an attempt is to be valid. The susceptibility $\chi^{(3)}$ is the macroscopic expression of the microscopic molecular second hyperpolarizability tensor $\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$, and it is just differences in the frequency arguments of γ that distinguish the various non-linear optical processes [3]. In what follows we present measurements of $\chi^{(3)}$ (and hence γ) made by ESHG, and a comparison of these results with those from several other processes. The molecules studied are of particular interest in the context of combustion research.

2. Experiment

The ESHG measurements reported here were made using a cw argon-ion laser and a dye laser, employing the technique of periodic phase matching [4], with N_2 as the reference gas. The experimental method follows closely that of the previous work for CH_4 [5], so mainly the points of difference will be indicated here. Phase match occurred at gas pressures of 0.25–1.20 atm (at 21–24°C) for the n-alkanes in these experiments. Thus, the breakdown field strength and allowable cell voltage were reduced, as was the signal (30–250 cps in these experiments). Since the N_2 reference gas phase matches at much higher density than the sample gas, the signal in the reference measurements was increased by a factor of four by applying twice as large a voltage to the N_2 as to the sample, thus improving the precision of the ratio measurements. The quadratic voltage dependence of the signal was verified in a separate set of measurements; because of the limited accuracy of our test, the uncertainty of the hyperpolarizability ratio has an additional $\pm 0.3\%$ contribution included. The virial and local field corrections that were made are small, less than 2% at most [6,7]. Each ratio measurement is the average of three or four runs using high-purity gases (N_2, 99.999%; C_2H_6, C_3H_8, 99.99%; n-C_4H_{10}, 99.96%). The overall accuracy of the final results is about $\pm 1\%$.

3. Results and discussion

The results of the ESHG measurements made for ethane, propane and n-butane are presented in table 1. The molecular hyperpolarizabilities γ given in table 1 are obtained from the measured susceptibility ratios using the previously measured ratio γ_{N_2}/γ_{He} [8] and the ab initio value of γ_{He} [9] for calibration, as detailed in ref. [5]. Having obtained values of γ at three wavelengths by ESHG for these n-alkanes, it remains to relate these measurements to the value of the non-resonant susceptibility in CARS. There are several aspects which must be considered. First of all, intrinsically first- and second-order processes can also contribute to the third-order susceptibility $\chi^{(3)}$, as is the case for the dc Kerr effect [3]. Second, even the intrinsically third-order contributions have components of both electronic and vibrational origin, and the relative size of these γ^e and γ^v terms differs for each particular non-linear optical process [11]. Finally, even if one were to deal with only the electronic part of $\gamma(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$, there are still three frequency arguments to be considered when trying to compare different optical processes measured at different wavelengths.

As a first approximation, one may consider that the non-linear response is dominated by γ^e arising from high-frequency electronic resonances. In that case, one may analyze the measurements employing the following simple result derived from a single-resonance-frequency model [12]:

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

where

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

In accordance with eqs. (1) and (2), the results given in table 1 have been plotted versus ν_L^2 in fig. 1. A least-squares fit of eq. (1) to the ESHG data for each gas has been performed, giving the solid lines drawn in fig. 1 and the coefficients recorded in table 2. Eq. (1) is seen to be a good representation of the data, at least over a limited frequency range for a single process. Examining table 2 and fig. 1, one observes that the magnitude of γ increases approximately in proportion to the molecular size, while the relative dispersion increases more slowly. In every case, γ varies significantly over the visible spectrum.

Eqs. (1) and (2) also allow us to attempt a quantitative comparison of the experimental results for different non-linear optical processes. The available gas-phase measurements of γ for ethane, propane and n-butane, obtained using the dc Kerr effect [13,14] or four-wave mixing (FWM) [15,16], have been collected in table 3 and plotted versus ν_L^2 in fig. 1. The agreement of these measurements with the dispersion equations predicted from the ESHG measurements (solid lines in fig. 1) is not uniformly good. This discrepancy prompts a further examination of the possible contributions to the hyperpolarizabilities of these molecules.

First consider the vibrational contributions to γ.

Table 1

Results of ESHG measurements for ethane, propane and n-butane at three wavelengths in the visible region. The values of the hyperpolarizability γ in the last column are obtained using the results of refs. [8,9] for calibration

Gas	λ (nm)	$\Delta\alpha/\Delta\alpha_{N_2}$ [a]	γ/γ_{N_2}	γ $(10^{-63}\ C^4\ m^4\ J^{-3})$
C_2H_6	616.1	3.84 ± 0.01	6.27 ± 0.03	427 ± 3
	514.5	3.90 ± 0.01	6.66 ± 0.04	498 ± 4
	488.0	3.96 ± 0.01	6.97 ± 0.06	538 ± 5
C_3H_8	616.1	5.66 ± 0.01	10.84 ± 0.08	739 ± 6
	514.5	5.76 ± 0.02	11.78 ± 0.08	880 ± 7
	488.0	5.83 ± 0.02	12.23 ± 0.09	945 ± 8
n-C_4H_{10}	616.1	7.43 ± 0.03	14.08 ± 0.21	959 ± 15
	514.5	7.56 ± 0.02	15.56 ± 0.17	1162 ± 13
	488.0	7.65 ± 0.03	16.32 ± 0.18	1260 ± 14

[a] Polarizability dispersion ratio obtained from phase match densities, where $\Delta\alpha=\alpha(2\omega)-\alpha(\omega)$; see ref. [10] for further details.
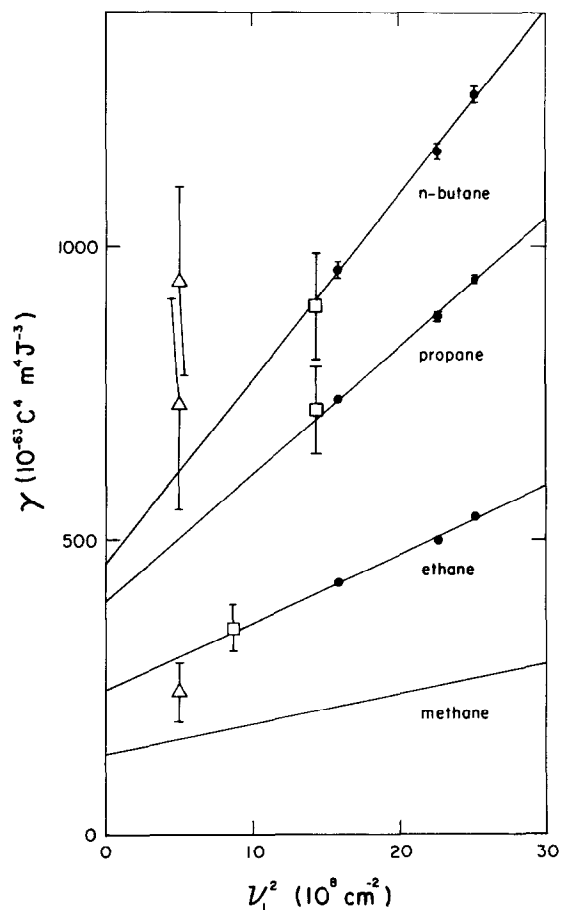
Fig. 1. Experimental measurements of the hyperpolarizabilities of n-alkanes made by means of ESHG (filled circles, present work), non-resonant CARS (open squares) and the dc Kerr effect (open triangles, n-butane, propane and ethane from top to bottom, respectively) are plotted versus ν_L^2 (see eq. (2)). The error bars are smaller than the drawn symbols for some of the ethane and propane ESHG measurements. The solid lines are least-squares fits of eq. (1) to the ESHG data, with coefficients as given in table 2. The corresponding line for methane has been drawn for comparison, using the results of ref. [5]. If γ is dominated by electronic contributions, the results of all the measurements for a given gas should fall on the same straight line.

Previous calculations [11] and measurements [5] for methane seem to indicate that γ^v contributes less than 10% of the total hyperpolarizability. However, ethane and propane have more vibrational degrees of freedom, and for n-butane one should also consider conformational degrees of freedom. The calculation of γ^v is not a simple matter for a large molecule, because the required data are not available and

Table 2
Coefficients of the least squares fit of $\gamma = A(1 + B\nu_L^2)$ to the data presented in table 1. The effective laser frequency for ESHG is given by $\nu_L^2 = 6\,\nu^2$, where ν is given in cm^{-1} (in vacuum). For comparison, the corresponding results for methane from ref. [5] have been included

Gas	A $(10^{-63}$ C^4 m^4 J$^{-3})$	B $(10^{-10}$ cm$^2)$
CH$_4$	136.3	3.718
C$_2$H$_6$	242.9	4.749
C$_3$H$_8$	394.2	5.504
n-C$_4$H$_{10}$	457.9	6.891

because the expressions become quite complicated (note that the expression used by Lundeen et al. [15] is inadequate except for homonuclear diatomic molecules). However, γ^v is expected to be about the same for ESHG and FWM but larger for dc Kerr, and essentially constant at optical frequencies for all three processes [11]. The data in fig. 1 are consistent with these expectations, with the FWM results falling on the ESHG lines for each of the n-alkanes, but with the dc Kerr results lying mostly above the ESHG results. To be of use in calibrating the non-resonant CARS susceptibility, it is sufficient that vibrational contributions are the same for ESHG and FWM (non-resonant CARS). Furthermore, vibrational contributions to the linear polarizability are small for these molecules at optical frequencies, as evidenced by the monotonic increase of $\Delta\alpha$ with ω (table 1; see refs. [5,10] for more details), so it is not unreasonable to expect γ^v to be relatively small as well.

A possible difficulty in the interpretation of the experimental ESHG results arises because the static dipole moments, μ, of propane and n-butane are not zero by symmetry, so that a contribution $\mu\beta/3kT$, where β is the first hyperpolarizability, may contaminate the measured γ [3]. To properly evaluate this contribution, the experimental measurements should be made over a range of temperatures. However, the measured dipole moments are small for these molecules (propane: 0.086 ± 0.010 D; n-butane: $\leqslant 0.05\pm0.05$ D) [17]. From the measured μ, and assuming that β is about the same as that measured for various fluoromethanes and other small dipolar molecules ($\beta \approx \pm 1 \times 10^{-51}$ C^3 m^3 J^{-2}) [18,19], one obtains $\mu\beta/3kT \approx \pm 23 \times 10^{-63}$ C^4 m^4 J^{-3} at $T = 300$ K for propane, < 3% of the measured value of γ. For

Table 3
Hyperpolarizabilities of n-alkanes, from gas phase measurements by means of several non-linear optical processes

Process	Gas	λ (nm)	ν_L^2 [a] (10^8 cm^{-2})	γ (10^{-63} C^4 m^4 J^{-3})
dc Kerr [b]	C_2H_6	632.8	4.99	240 ± 50 [c]
	C_3H_8	632.8	4.99	730 ± 180 [d]
	n-C_4H_{10}	632.8	4.99	940 ± 160 [d]
FWM [e]	C_2H_6	694975	8.64	350 ± 40 [f]
	C_3H_8	532607	14.24	719 ± 74 [g]
	n-C_4H_{10}	532607	14.24	897 ± 92 [g]

[a] Defined by eq. (2).   [b] $\gamma(-\omega;0,0,\omega)$.   [c] Ref. [13].   [d] Ref. [14].   [e] $\gamma(-2\omega_1+\omega_2;\omega_1,\omega_1,-\omega_2)$.
[f] Ref. [15], uncorrected for vibrational contribution.
[g] Ref. [16], including off-resonance vibrational contributions, and using the conventions of ref. [3] when converting from bulk suscep-
tibility to molecular hyperpolarizability.

n-butane the corresponding contribution is $< 1\%$ of γ. According to these estimates the $\mu\beta/3kT$ contribution is small or negligible compared to γ. It is interesting at this point to consider the additivity of γ. The bond additivity approximation [20–22] predicts equal differences between γ for the successive molecular pairs CH_4 and C_2H_6, C_2H_6 and C_3H_8, and C_3H_8 and n-C_4H_{10}. Clearly the curves in fig. 1 are not equally spaced, but by simply assuming the static limiting value $\mu\beta/3kT = 43\times10^{-63}$ C^4 m^4 J^{-3} for propane and then correcting that curve, all the curves are made to fit the prediction of the bond additivity approximation. So it seems that either the $\mu\beta/3kT$ contribution is significant for propane or else the bond additivity approximation fails for the n-alkanes. A measurement of the temperature dependence of the susceptibility of propane would resolve this matter.

The large discrepancies seen in fig. 1 between the dc Kerr and ESHG measurements for propane and n-butane should not be given too much weight. Reliable dc Kerr measurements of γ are difficult, because γ is not the dominant contribution to $\chi^{(3)}$ and because the Kerr birefringence is very sensitive to intermolecular interactions. In contrast, γ may be measured routinely to 1% accuracy by ESHG, and provided γ^v is small compared to γ^e, the γ for ESHG is very simply related to that for non-resonant CARS (FWM). Simply extending the wavelength range of the ESHG measurements to 650 nm, the values of ν_L^2 for ESHG may be made to overlap with the ν_L^2 for a typical CARS measurement made using a doubled Nd:YAG pump laser, removing the need to extrapolate and

further improving the reliability of the calibration of γ_{CARS} in terms of γ_{ESHG}.

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