The Kerr effect in hydrogen

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The hyperpolarizability of H_2 has been determined from measurements of the dc Kerr effect for H_2 gas at $T=25°C$ and $\lambda=632.8$ nm. The result of these measurements, $\gamma^{ev}=(4.48\pm0.05)\times10^{-62}$ C^4 m^4 J^{-3} ($\gamma^{ev}=719\pm7$ au), is in fair agreement with the result of the most recent ab initio calculation for H_2, $\gamma^{ev}=726$ au. A refinement of the usual expression for the orientational contribution to the Kerr effect for a gas of quantum rotors has been employed in the analysis of the experimental measurements.

1. Introduction

The nonlinear optical (NLO) properties of materials have received much recent attention. The subject is both difficult and interesting because of the complicated interplay of frequency-dependent electronic, vibrational and orientational contributions to the NLO response. Molecular hydrogen has a special status in the study of the NLO properties of materials. Hydrogen is the only molecule for which both very accurate dynamic ab initio calculations [1] and accurate experimental measurements [2–4] of the hyperpolarizability are feasible. The dc Kerr effect (electric-field-induced birefringence) also has a special status since it is essentially the only NLO process for which absolute measurements of NLO properties are possible with an accuracy much better than 10%. However, while there seems to be agreement between theory and experiment for H_2 for all other NLO processes, the dc Kerr effect results appear to be in significant disagreement [1–4]. The purpose of this study is to resolve this discrepancy by means of further accurate measurements of the dc Kerr effect for H_2.

The hyperpolarizability mediating the Kerr effect in a gas of homonuclear diatomic molecules may be written as $\gamma^{evR}=\gamma^{ev}+\gamma^{R}=\gamma^{ev}+(\Delta\alpha_{eff})^2/5kT$, where e, v, R refer to electronic, vibrational and orientational (rotational) degrees of freedom of the molecule, and $\Delta\alpha$ is the molecular polarizability anisotropy [2,5,6]. A recent study has measured the Kerr effect for H_2 over a wide temperature range [2]. The close agreement between the measured and predicted temperature dependence indicates that the molecular orientational contribution to the Kerr effect, γ^R, is accurately represented by the quantum statistical expression for a gas of rotors first derived by Buckingham and Orr [6] and later refined by Tammer and Hüttner [2]. Therefore, in order to extract γ^{ev} from the measured quantity γ^{evR}, it should be sufficient to measure the Kerr effect for H_2 at a single temperature and subtract the calculated value of γ^R. The following paper reports a measurement of the Kerr effect for H_2, analyzed in such fashion, and compared with the result for γ^{ev} recently calculated by Bishop, Pipin and Cybulski [1].

2. Experiment

The apparatus and techniques employed in these dc Kerr effect measurements are a variant of standard methods, and most closely resemble those of Ritchie and co-workers [7]. The methods are fully described elsewhere [8,9], so only the essential features will be sketched here. A gas Kerr cell (GKC) and a liquid Kerr cell (LKC) are placed between crossed polarizers, and ac and dc voltages are applied to the electrodes to induce a modulated retardation (relative phase shift between the orthogonal linear polarization components of the light). The modulated light signal transmitted through the ana-

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lyzing polarizer is measured with a lock-in amplifier. The quantity derived from the experimental measurements is

$$\gamma_{\text{eff}}=\frac{3\epsilon_0\lambda_0\varphi}{\pi\rho\int F^2\,\mathrm{d}z}, \tag{1}$$

where λ_0 is the light wavelength in vacuum, φ is the induced retardation, ρ is the number density of the gas molecules, and F is the transverse electric field along the path of the laser beam in the GKC (z axis). The quantity γ_{eff} may be expressed in terms of measured voltage and signal ratios, the LKC calibration factor and the separation and length of the GKC electrodes. The molecular hyperpolarizability γ^{evR} is the zero density limit of γ_{eff}, where the difference between γ^{evR} and γ_{eff} at finite density is due to local field effects and intermolecular interactions [2,5–7].

There are several potential sources of large systematic errors which have received careful attention. Since a quarter wave plate is not used in our apparatus, accurate calibration of the LKC requires careful control and compensation of stray birefringence (zero stress birefringence windows are used). The effect of space charge in the LKC is measured under operating conditions and is accurately accounted for in the LKC calibration. The scatter of LKC calibration results is ±0.16%, and the estimated systematic uncertainty is ±0.05%. The combined uncertainty due to phase and amplitude errors in the ac voltage measurements is ±0.1%. The measured results have no detectable contribution due to effects such as electrical pick-up or fringing fields at the GKC windows. The statistical uncertainty in the determination of the ratio of the GKC and LKC signals was ±0.2%–0.5% (the retardation induced in the GKC varied over the range 0.1–0.7 μrad as the sample pressure was varied from 1300 to 9900 Torr). The gas density was determined from calibrated pressure (±1 Torr) and temperature (±0.1°C) measurements, using the virial equation of state [10]. To eliminate the effects of impurities, the GKC was baked under vacuum to reduce outgassing and filled with high purity (99.999%) H_2 gas through a 0.5 μm filter and a liquid nitrogen cold trap. The measurements were made with the GKC at room temperature. The GKC temperature drifted within the range 25.1–25.4°C during the course of the experiment, but the drifts were slow enough that the GKC remained isothermal. The temperature coefficient $\gamma_{\text{eff}}^{-1}\,\mathrm{d}\gamma_{\text{eff}}/\mathrm{d}T\approx-0.11\%/{}^\circ\mathrm{C}$ at $T=25.2\,^\circ\mathrm{C}$, estimated from the work of Tammer and Hüttner [2], was used to adjust all the results to a common temperature of $T=25.2\,^\circ\mathrm{C}$.

The largest contribution to the overall uncertainty in the experimental results is due to the uncertainty in the electrode geometry. The electrodes of the GKC were polished rectangular stainless-steel bars 12.7 mm thick, 25.4 mm wide and 456.7 mm long, separated by 36 alumina ceramic spheres with diameter 3.175 mm, placed at 2.5 cm intervals along the edges of the electrodes. The electrodes were pressed together by 5 teflon rings which also served to insulate electrically and support mechanically the electrode assembly inside the GKC. The ends of the electrodes were square (with 45° bevels, 50 μm×50 μm) so as not to introduce significant errors into the determination of the effective length of the electrodes, even though this reduces the maximum permissible voltage because of the field enhancement near sharp corners. Fringing fields were numerically calculated including the effects of the conducting surfaces of the GKC near the ends of the electrodes; the analytical result of Chaumont [11] overestimates the effective length of the electrodes inside the GKC. The electrode surfaces are smooth but not flat. Because of the relatively large departures from flatness, the inter-electrode spacing is not constant and is not equal to the diameter of the spherical insulating spacers. The inter-electrode separation was determined at 18 positions along the centerline of the electrodes, with an accuracy of ±3 μm, by measuring the difference between the thickness of the assembled electrodes and the combined thickness of the individual electrodes. The separation varied from a minimum of 3.171 nm in the central region, where a few heavily loaded spherical spacers indented the electrode surfaces, to a maximum of 3.340 mm at one end of the electrode assembly, where one electrode had a sharp bend. Despite the large variation in spacing, the average effective separation $\langle d^{-2}\rangle^{-1/2}$ was determined with an uncertainty of ±3 μm. After the completion of the H_2 Kerr experiment, a second measurement of the electrode separation profile showed an increase in separation had occurred at the end with the wide gap, due to cold flow of the most heavily loaded teflon clamping ring. Accounting for measurement uncertainty and spacing drift, the electrode separation during the H_2 Kerr measurements was $\langle d^{-2}\rangle^{-1/2} = 3.195 \pm 0.007$ mm. The uncertainty in the geometrical calibration constant of the GKC, including the uncertainty in the electric field azimuthal angle, was ±0.46%.

3. Results and discussion

The experimental results are presented in table 1 and plotted in fig. 1 as a function of gas density. Each point represents at least three complete measurements made on separate days; measurements at different gas densities were interspersed and made in no set order in density. The measurements have been extrapolated to zero gas density by means of a straight line fit to the data, also shown in fig. 1, to obtain the experimental estimate $\gamma^{evR} = (8.827 \pm 0.045) \times 10^{-62}$ $C^4\,m^4\,J^{-3}$ (1415.6±7.2 au). The present result falls within the range of the three previous Kerr effect measurement results, summarized in refs. [1,2]. The assigned error bars for the previous measurements of γ^{evR} range from ±1.5% to ±12%, but the error bars do not overlap for any pair of these measurements, and none of these experimental results agrees with the ab initio result. The present result for γ^{evR} has an uncertainty of ±0.51% and should provide a critical test of the theoretical calculations of γ^{ev} for H_2.

The next step in the analysis is the calculation of γ^{R} in order to extract an experimental estimate of γ^{ev} from γ^{evR}. The expression used to calculate γ^{R} is

$$\gamma^{R} = \sum_J \rho(J)\,\frac{J(J+1)}{(2J-1)(2J+3)}\,\frac{\Delta\alpha^{(0)}_{J,J}\,\Delta\alpha^{(\omega)}_{J,J}}{5kT} + \sum_J \left(\rho(J) - \frac{2J+1}{2J+5}\rho(J+2)\right)\frac{3(J+1)(J+2)}{(2J+1)(2J+3)} \times \frac{\Delta\alpha^{(0)}_{J,J+2}\,\Delta\alpha^{(\omega)}_{J,J+2}}{5hc\Omega_{J,J+2}}\,(1+\Delta)\,, \quad (2)$$

where the normalized population distribution function at thermal equilibrium is

$$\rho(J) = n_J(2J+1)\exp[-E(J)/kT] \left(\sum_J n_J(2J+1)\exp[-E(J)/kT]\right)^{-1}, \quad (3)$$

with $n_J = (1, 3)$ for $J = $ (even, odd), and where the energies of the low-lying rotational levels of the ground vibrational state are given by

$$E(J)/hc = J(J+1)B_0 - J^2(J+1)^2 D_0 \,. \quad (4)$$

The transition frequency and the transition polarizability anisotropy at optical frequency ω, for the

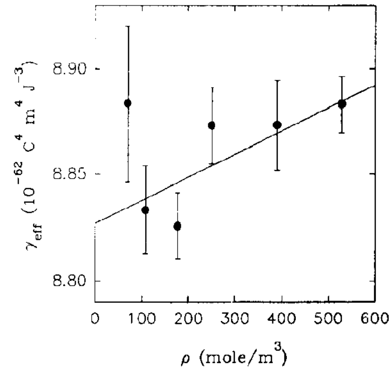

Fig. 1. The Kerr effect measurement results γ_{eff} are plotted versus gas density ρ. A weighted least-squares fir of the data to the function $\gamma_{eff} = \gamma^{evR}(1 + A\rho)$ gives $\gamma^{evR} = (8.827 \pm 0.045) \times 10^{-62}$ $C^4\,m^4\,J^{-3}$ and $A = (1.2 \pm 0.4) \times 10^{-5}$ m^3/mol (for comparison, $A = (1.4 \pm 0.1) \times 10^{-5}$ m^3/mol is obtained from the data in ref. [2]). The dielectric, refractive and Kerr virial coefficients all contribute to the coefficient A. The error bars on the plotted data points, to which the fit has been made, include only the statistical uncertainties. The error bars for the fit coefficients include the 0.48% systematic uncertainty.

Table 1

Summary of experimental Kerr effect results from this work, for H_2 gas at 25.2°C and $\lambda = 632.8$ nm. The zero density limit of the experimentally measured quantity γ_{eff}, defined by eq. (1), is the molecular hyperpolarizability γ^{evR}. The tabulated error bars include only the statistical uncertainties, except for the zero density result which also includes the 0.48% systematic uncertainty added in quadrature

ρ (mol/m^3)	γ_{eff} (10^{-62} $C^4\,m^4\,J^{-3}$)
0.0 [a]	8.827±0.045 [a]
69.6	8.883±0.037
107.5	8.833±0.021
176.7	8.826±0.016
250.1	8.873±0.018
389.8	8.873±0.021
528.8	8.883±0.014

[a] Extrapolated value from least-squares fit in fig. 1.

transition ($v=0$, J)→($v=0$, J'), are denoted by $\Omega_{J,J'}=[E(J')-E(J)]/hc$ and $\Delta\alpha_{J,J'}^{(\omega)}$. The frequency-dependent factor

$$1+\Delta=1+\tfrac{1}{3}[1-(\omega/\Omega_{J,J+2})^2]^{-1}Q \tag{5}$$

contains a rotational resonance term Δ which is small at optical frequencies. The different polarizability dispersion for the Δ term is accounted for by the factor Q

$$Q=\frac{[\Delta\alpha_{J,J+2}^{(0)}+\Delta\alpha_{J,J+2}^{(\omega)}]^2}{4\Delta\alpha_{J,J+2}^{(0)}\Delta\alpha_{J,J+2}^{(\omega)}}\,. \tag{6}$$

The two terms in eq. (2) arise by distinctly different physical mechanisms. The first term of eq. (2) is due to real population redistribution among the M sublevels for molecules in the J rotational level ($\Delta J=0$). The Stark shifts varying as $\Delta\alpha_{J,J}^{(0)}M^2F^2$ determine the deviation from isotropy of the equilibrium orientational distribution, and the optical anisotropy of the gas is then determined by the product of $\Delta\alpha_{J,J}^{(\omega)}$ and the net field-induced orientational anisotropy [6]. Relaxation of the population distribution is due to collisions, since the Stark-split M sublevels of an isolated H_2 molecule are not radiatively coupled. The second term of eq. (2) is due to the virtual rotational Raman transitions ($\Delta J=\pm 2$) in the usual perturbation theory expression for the second hyperpolarizability [12,13]. These transitions occur even for an isolated molecule, and give rise to an effect which has no explicit temperature dependence (though $\rho(J)$ gives an implicit temperature dependence). In the case of the dc Kerr effect the derivation of γ^{R} outlined in ref. [13] can be carried through without neglecting the dispersion of the α matrix elements, to obtain a result in which only the factor Q given by eq. (6) is approximate. The present expression differs from the expressions given in refs. [2,6] in three respects: (i) the effect of centrifugal distortion on the rotational energies has been accounted for in $\Omega_{J,J+2}$ and $\rho(J)$, (ii) an explicitly frequency-dependent factor $1+\Delta$ appears in the second term of eq. (2), and (iii) $\Delta\alpha_{J,J+2}$ rather than $\Delta\alpha_{J,J}$ appears in the second term of eq. (2). If one ignores the J dependence of $\Delta\alpha$, neglects the effect of centrifugal distortion on the rotational energies, and sets $\Omega_{J,J+2}/\omega\to 0$ in Δ, one can show that eq. (2) and the expressions in refs. [2,6] all take the same form.

The molecular property values needed to evaluate γ^{R} at $\lambda=632.8$ nm for H_2 are given in table 2 [14–17]. The result obtained using eq. (2) is $\gamma^{\mathrm{R}}=4.347\times10^{-62}\ \mathrm{C^4\ m^4\ J^{-3}}$ (697.1 au) at 25.2°C. The largest contributions to γ^{R} for H_2 are from the $J=0$ and $J=1$ rotational levels (16% and 70%), and there are about equal contributions to the total from the $\Delta J=0$ and $\Delta J=\pm 2$ terms (42% and 58%); the rotational resonance term Δ is negligible, contributing only 0.03% in the present case. The result for γ^{R} obtained using eq. (6) of ref. [2] instead is significantly different: $\gamma^{\mathrm{R}}=685.3$ au. This result for γ^{R} is 2% smaller because the rotational transition frequencies are overestimated by 1% and because $\Delta\alpha_{J,J}$ is 1% smaller than $\Delta\alpha_{J,J+2}$ (for $J=1$).

Subtracting $\gamma^{\mathrm{R}}=697.1$ au, calculated using eq. (2), from the experimentally determined value for γ^{evR}, gives $\gamma^{\mathrm{ev}}=718.5\pm7.2$ au, in fair agreement with the ab initio value $\gamma^{\mathrm{ev}}=726.2$ au from Bishop et al. [1]. This ab initio result is thought to be accurate to better than 1%, and passes other experimental tests at the 1% level of accuracy. If instead one subtracts $\gamma^{\mathrm{R}}=685.3$ au calculated using the expression in ref. [2], one obtains $\gamma^{\mathrm{ev}}=730.3\ \pm7.2$ au, in somewhat better agreement with the ab initio result.

Table 2
Summary of ab initio values of $\Delta\alpha_{J,J'}^{(\omega)}$ for H_2, in the static limit and for $\lambda=632.8$ nm. The values given below in atomic units are either transcribed or interpolated from tabulated values in refs. [14,16] which have an estimated accuracy of 0.01%. The equivalents for atomic units are E/hc: 1 au=219474.63 cm^{-1}, α: 1 au=$1.648778\times10^{-41}\ \mathrm{C^2\ m^2\ J^{-1}}$, and γ: 1 au=$6.235377\times10^{-65}\ \mathrm{C^4\ m^4\ J^{-3}}$. The rotational and centrifugal distortion constants from ref. [17] are $B_0=59.3392$ cm^{-1} and $D_0=0.04599$ cm^{-1}

J	$\Delta\alpha_{J,J}^{(0)}$ [a] (au)	$\Delta\alpha_{J,J}^{(\omega)}$ [b] (au)	$\Delta\alpha_{J,J+2}^{(0)}$ [c] (au)	$\Delta\alpha_{J,J+2}^{(\omega)}$ [d] (au)
0	2.0293	2.0932	2.0404	2.1043
1	2.0372	2.1014	2.0553	2.1200
2	2.0529	2.1179	2.0778	2.1435
3	2.0764	2.1425	2.1078	2.1750
4	2.1079	2.1755	2.1455	2.2145
5	2.1472	2.217 [e]	2.1908	2.2621
6	2.1946	2.266 [e]	2.2439	2.3178

[a] From ref. [14].

[b] Interpolation of results in ref. [14] using dispersion function from results in table VI of ref. [15].

[c] From table X of ref. [16].

[d] Interpolation of results in table X of ref. [16].

[e] Interpolation of results in ref. [14].

The present best experimental estimate of γ^{ev}, obtained using eq. (2) for γ^R, is significantly below the ab initio result from ref. [1]. This may indicate that the ab initio result for γ^{ev} has not converged, or that eq. (2) is wrong, or that there are unaccounted-for systematic errors in the present experimental result. Further Kerr effect measurements could address the last concern, but it would be difficult to distinguish between the alternative expressions for γ^R by Kerr effect measurements alone. A better assessment of the accuracy of the ab initio results for γ of H_2, by means of some other NLO measurement with 0.1% accuracy for example, may be required to resolve the present discrepancy. However, while there remains a marginally significant disagreement between theory and experiment, the original objective of this work has been met. Either choice of γ^R results in an experimental value of γ^{ev} within 1% of the ab initio value, which indicates that the previously observed discrepancies between theory and experiment for the dc Kerr effect in H_2 were due to systematic errors in the experiments.

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