Kleinman symmetry deviations for hydrogen

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The frequency dependence of the deviation from Kleinman symmetry for the electronic part of the third-order nonlinear susceptibility tensor $\chi^{(3)}$ has been experimentally determined for H_2 and D_2. The electronic contribution is extracted from the measured Kleinman symmetry deviation, obtained by means of an electric-field-induced second-harmonic-generation experiment, by making a correction for the vibrational and rotational contributions. The deviation measured at $\lambda = 1064$ nm where the vibrational contribution is dominant provides a test of the adequacy of the calculated corrections.

Kleinman symmetry is a relation between the tensor components of the third-order nonlinear-optical susceptibility $\chi^{(3)}$. For an isotropic medium such as a gas Kleinman symmetry implies the relation $\chi^{(3)}_{zxxz} = \chi^{(3)}_{zxzx} = \chi^{(3)}_{zzxx} = \chi^{(3)}_{zzzz}/3$, where the subscripts indicate the polarizations of the scattered and applied fields.[1] Kleinman symmetry is exact in the static limit but holds only approximately for applied fields of nonzero frequency, and is of interest because the deviations are due solely to the dynamics of the interaction of the molecular system with the applied fields. Accurate measurements of deviations from Kleinman symmetry have been made for a number of molecules, including H_2 and D_2, but at the time of the previous measurements the analysis was impeded by the absence of accurate data on the dispersion of $\chi^{(3)}_{zzzz}$.[1] Such accurate data is now available for H_2 and D_2,[2] and in the light of the recent elaborate *ab initio* calculations[3] of $\chi^{(3)}_{H_2}$ and $\chi^{(3)}_{D_2}$ for which there are few stringent experimental tests, it is now appropriate to reanalyze the previous measurements of Kleinman symmetry deviations for H_2 and D_2. The analysis of the measurements entails a substantial correction for the vibrational[1,2,4] and rotational[5] susceptibilities $\chi^{(3)v}$ and $\chi^{(3)r}$ in order to extract the Kleinman symmetry deviation that is due to the electronic contribution $\chi^{(3)e}$ (it is the electronic contribution to the Kleinman symmetry deviation that is useful in testing the *ab initio* calculations). Accordingly, we have also made a measurement for H_2 at $\lambda = 1064$ nm, where the vibrational contribution to the deviation should be large and dominant, so that the accuracy of the calculated correction may be assessed.

Kleinman symmetry deviations are measured by means of an electric-field-induced second-harmonic-generation (ESHG) experiment as previously described.[1] For ESHG there are only two independent tensor components of $\chi^{(3)}$ and the experiment measures the ratio of the two independent tensor components

$$R(\omega) \equiv \chi^{(3)}_{zzzz}(-2\omega;\omega,\omega,0)/\chi^{(3)}_{zxxz}(-2\omega;\omega,\omega,0) . \quad (1)$$

When Kleinman symmetry holds it follows that $R = 3$, so it is just the deviations from $R = 3$ that are of interest to us. The apparatus used for the present measurement is very similar to that previously used. The output beam of a cw Nd:yttrium aluminium garnet laser (CVI 210 PT) operating at $\lambda = 1064$ nm was passed through a Glan-laser prism polarizer, followed by a Soleil-Babinet compensator (Special Optics 8-400-IR) by means of which the polarization state of the laser beam could be manipulated. The beam was weakly focused into a gas cell containing an electrode array with a spacing of 2.69 mm. The beam power at the sample was 0.5 W, and with a Schott RG-780 glass filter before the sample cell and a double prism spectrometer and $Ni(NO_3)_2$ solution filter before the detector, the background count rate was 2.5 counts/sec. Periodic phase match for H_2 occurred at a gas pressure of 39 bar at $T = 24\,^{\circ}C$ (pressure ten times higher than that for the previous measurements[1]), giving a second-harmonic signal of 500 counts/sec with parallel optical and static fields. Previous measurements[1] had demonstrated insignificant deviations from Kleinman symmetry for Ar over the visible, so R for Ar was also measured (phase match at 27 bar, maximum signal 200 counts/sec). By using the Ar measurement (3.002 ± 0.004) to normalize the raw H_2 measurement (2.893 ± 0.006), possible residual systematic errors are removed at the expense of slightly increasing the statistical uncertainty of the final result ($R = 2.891 \pm 0.007$). The results of this and the previous experimental measurements of R for H_2 and D_2 are collected in Table I.[1,6]

The Kleinman symmetry deviation due to the electronic susceptibility contribution alone is quantified by the ratio $R^e = \chi^{(3)e}_{zzzz}/\chi^{(3)e}_{zxxz}$, where the value of R^e may be extracted from the experimentally measured value of R by applying the expression

$$R^e = R[1 + (\chi^{(3)vr}_{zzzz} - R\chi^{(3)vr}_{zxxz})/\chi^{(3)e}_{zzzz}]^{-1} . \quad (2)$$

An accurate value of R^e may be obtained from Eq. (2) using approximate values for the components of $\chi^{(3)}$ provided that $\chi^{(3)e} \gg \chi^{(3)vr}$. It is expected that the frequency dependence of R^e in the visible will be adequately represented by the simple, one-parameter expression,[1,7,8]

$$R^e = 3(1 + A\nu^2) . \quad (3)$$

TABLE I. Measured deviations from Kleinman symmetry, which appear as deviations from 3 of the ratio $R=\chi^{(3)}_{zzzz}/\chi^{(3)}_{zxxz}$, are listed for H_2 and D_2. The ratio $R^e=\chi^{(3)e}_{zzzz}/\chi^{(3)e}_{zxxz}$, obtained from R by accounting for the vibrational and rotational contributions to $\chi^{(3)}$, expresses the deviation from Kleinman symmetry due to the electronic part of the susceptibility alone. The uncertainty of the last digit is given in parentheses. For H_2 Ref. 6 gives $R=2.86\pm0.03$, measured at $\lambda=694.3$ nm by ESHG, but because of the large statistical error bar and because it is not clear how possible systematic errors were dealt with, we have not included this point in our analysis.

λ (nm)	ν (cm^{-1})	R_{H_2}	$R^e_{H_2}$	R_{D_2}	$R^e_{D_2}$
1064	9396	2.891(7)	2.978(7)		
590.0	16944	2.890(4)[a]	2.907(4)	2.909(6)[a]	2.918(6)
514.5	19430	2.867(2)[a]	2.879(2)	2.881(3)[a]	2.887(3)
488.0	20487	2.858(3)[a]	2.868(3)	2.872(4)[a]	2.877(4)

[a]From Ref. 1.

The values of $\chi^{(3)e}_{zzzz}$ needed to evaluate Eq. (2) are obtained using the experimental ratios (for ESHG, *zzzz* component)[2]

$$\chi^{(3)e}_{H_2}/\chi^{(3)e}_{D_2}=1.0249[1+(0.24\times10^{-10}\ \mathrm{cm}^2)\nu^2] \quad (4)$$

and

$$\chi^{(3)e}_{H_2}/\chi^{(3)}_{He}=15.13[1+(8.31\times10^{-10}\ \mathrm{cm}^2)\nu^2]\ , \quad (5)$$

and the recent, accurate ($\pm0.1\%$) *ab initio* result for He (for ESHG, *zzzz* component),[8]

$$\gamma_{He}=2.613\times10^{-63}\mathrm{C}^4\,\mathrm{m}^4\,\mathrm{J}^{-3}\times[1+(2.709\times10^{-10}\mathrm{cm}^2)\nu^2+(7.37\times10^{-20}\mathrm{cm}^4)\nu^4]\ , \quad (6)$$

TABLE II. Molecular parameter values used in the calculation of $\chi^{(3)vr}$ for H_2 and D_2. The frequency of the $vJ\rightarrow v'J'$ transition is denoted $\nu_{vJ,v'J'}$. For rotational transitions $\nu_{0J,0J+2}=(6+4J)B_0$. Except for the rotational transition frequency, we have ignored the small J dependence of the parameters and taken the values for the most populated rotational level, $J=1$ for H_2 or $J=2$ for D_2, to be representative. The static values of the mean Raman transition polarizability and anisotropy are denoted by $\alpha_{vJ,v'J'}$ and $\Delta\alpha_{vJ,v'J'}$. The data is from the *ab initio* results of Ref. 9, except for the overtone transition polarizabilities which are adjusted to conform to the experimental measurements of Ref. 10.

	H_2	D_2
Fundamental vibration		
$\nu_{0J,1J}$ (cm^{-1})	4156	2988
$\alpha_{0J,1J}$ ($10^{-42}\ \mathrm{C}^2\,\mathrm{m}^2\,\mathrm{J}^{-1}$)	12.21	10.18
$\Delta\alpha_{0J,1J}$ ($10^{-42}\ \mathrm{C}^2\,\mathrm{m}^2\,\mathrm{J}^{-1}$)	10.09	8.28
Overtone vibration		
$\nu_{0J,2J}$ (cm^{-1})	8077	5856
$\alpha_{0J,2J}$ ($10^{-42}\,\mathrm{C}^2\,\mathrm{m}^2\,\mathrm{J}^{-1}$)	$-0.06\alpha_{0J,1J}$	$-0.05\alpha_{0J,1J}$
$\Delta\alpha_{0J,2J}$ ($10^{-42}\,\mathrm{C}^2\,\mathrm{m}^2\,\mathrm{J}^{-1}$)	$-0.06\Delta\alpha_{0J,1J}$	$-0.05\Delta\alpha_{0J,1J}$
Rotation		
B_0 (cm^{-1})	59.3	29.9
$g_{ns}(J=\mathrm{even})$	1	2
$g_{ns}(J=\mathrm{odd})$	3	1
$\Delta\alpha_{0J,0J+2}$ ($10^{-42}\ \mathrm{C}^2\,\mathrm{m}^2\,\mathrm{J}^{-1}$)	33.8	32.7

where ν is given in cm^{-1} and the relation between the susceptibility per molecule and the isotropically averaged hyperpolarizability is $\chi^{(3)}=\langle\gamma\rangle/6$. The calculation of $\chi^{(3)vr}$ is essentially the same as previously described, but with the contributions of rotations and the first vibrational overtone included in addition to the contribution of the fundamental vibration. The present calculations of $\chi^{(3)v}$ and $\chi^{(3)r}$ make use of Eq. (18) of Ref. 4 and Eq. (5) of Ref. 5, respectively. The molecular data employed in these calculations is given in Table II.[9,10] At $\lambda=1064$ nm for H_2, one calculates $6\chi^{(3)e}_{zzzz}$, $6\chi^{(3)vr}_{zzzz}$, and $6\chi^{(3)vr}_{zxxz}$ to be 42.08, -3.62, and $-0.51\times10^{-63}\ \mathrm{C}^4\mathrm{m}^4\ \mathrm{J}^{-3}$. At $\lambda=1064$ nm for H_2, the contributions to the difference (R^e-R) due to the vibrational fundamental, the vibrational overtone, and the rotations are $+0.090$, $+0.002$, and -0.005, respectively. At higher frequencies $\chi^{(3)vr}$ and the difference (R^e-R) rapidly decrease in magnitude.

The values of R^e obtained by applying Eq. (2) to the experimentally measured R values for H_2 and D_2 are listed in Table I. A least-squares fit of Eq. (3) to the R^e values for H_2 and D_2 gives the dispersion coefficients

$$A_{H_2}=(-1.062\pm0.010)\times10^{-10}\ \mathrm{cm}^2 \quad (7)$$

and

$$A_{D_2}=(-0.986\pm0.014)\times10^{-10}\ \mathrm{cm}^2\ . \quad (8)$$

With explicit expressions now available for R^e, $\chi^{(3)e}$, and $\chi^{(3)vr}$, one may express R as

$$R=R^e(\chi^{(3)e}_{zzzz}+\chi^{(3)vr}_{zzzz})/(\chi^{(3)e}_{zzzz}+R^e\chi^{(3)vr}_{zxxz})\ . \quad (9)$$

The data points and the fitted curves for R and R^e are plotted in Fig. 1 for H_2 and in Fig. 2 for D_2. The high quality of the fits, especially for H_2, supports the adequacy of our analysis. However, even though a straight-line fit adequately represents R^e versus ν^2 for our measurements, it does not rule out the possibility of significant higher-order terms; for the hydrogen atom the ν^4 terms contribute nearly 10% of the deviation at $R^e=2.85$.[7]

Unfortunately only six of the seven independent tensor elements of γ needed to calculate R^e have so far been obtained in the most recent *ab initio* calculation for H_2,[3] so we cannot yet use our results to test this calculation. However, it is interesting to compare the dispersion

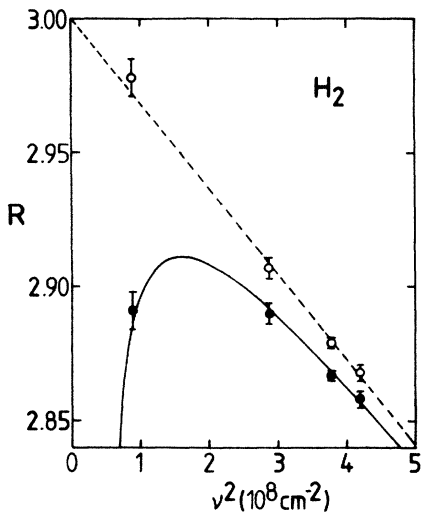

FIG. 1. Deviation from Kleinman symmetry, appearing as the deviation from $R=3$, is shown as a function of ν^2 for H_2. The fits to the directly measured R (solid line, closed circles) and to the vibrationally corrected R^e (dashed line, open circles) are shown.

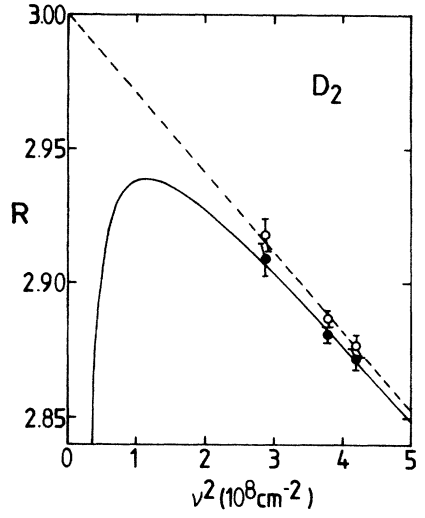

FIG. 2. Deviation from Kleinman symmetry, appearing as the deviation from $R=3$, is shown as a function of ν^2 for D_2. The fits to the directly measured R (solid line, closed circles) and to the vibrationally corrected R^e (dashed line, open circles) are shown.

coefficients obtained for the sequence of two-electron systems 2H, H_2, D_2, He in which the internuclear distance varies from ∞ to 0. The Kleinman symmetry deviations for these systems have dispersion coefficients $A=-1.810$, -1.062, -0.986, -0.405×10^{-10} cm^2, which decrease in magnitude as the nuclei are brought together.[3,7,8] The low-frequency dispersion of $\chi^{(3)e}_{zzzz}$ obeys $\chi^{(3)e}=\chi^{(3)e}_{\text{static}}(1+B\nu^2)$, where the coefficients $B=12.11$, 11.02, 10.78, 2.709×10^{-10} cm^2 also decrease with decreasing internuclear separation.[2,3,7,8] The ratios of coefficients $B/A=-6.69$, -10.38, -10.93, -6.69 behave differently. The value of B/A is the same for the atomic systems 2H and He, but has a peak at an internuclear separation near that of H_2 or D_2. Perhaps this is an indication that the calculated deviations from Kleinman symmetry will be more sensitive to details of the electronic structure for a molecule than for an atom.

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