

Nonlinear susceptibility of H₂ and D₂ accurately measured over a wide range of wavelengths

Victor Mizrahi and D. P. Shelton

Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7

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We have accurately measured the dispersion properties of the nonlinear susceptibilities of H₂ and D₂ over a sufficiently wide range to permit an extrapolation to the static limit, where a comparison is made with theory. The effect of the vibrational resonances is calculated and is shown to be significant.

I. INTRODUCTION

Despite the substantial interest in nonlinear optics in recent years,¹ surprisingly little progress has been made in the problem of accurately calculating nonlinear susceptibilities of free molecules in nonresonant situations, even in the static case. Some calculations exist for helium²⁻⁵ which, at zero frequency, are probably good to about 1%. The best configuration-interaction calculations for hydrogen^{6,7} are, as we will show, good to within about 5%. Beyond this the situation rapidly deteriorates. This is partly due to a lack of reliable experimental data against which the theory may be compared. In this paper we present the first comprehensive test of the *ab initio* results for hydrogen, with sufficient accuracy to draw definite conclusions. In another work we will present similarly accurate results for Ar, N₂, and O₂, but for which, unfortunately, there are not as yet sufficiently accurate calculations to warrant the detailed discussion upon which we embark here.

Accurate absolute measurements of nonlinear susceptibilities are notoriously difficult. We have chosen instead to measure the ratio of the nonlinear susceptibility for H₂ to that of helium over a wide range of optical frequencies (from $\lambda = 700$ to 458 nm), and then extrapolate the results to zero frequency, where the more accurate *ab initio* results for helium may be employed to deduce the absolute value for H₂. In addition, He has the advantage of displaying relatively little dispersion in its nonlinear susceptibility, and of showing absolutely no structure up to and beyond the optical frequencies employed in the experiment. We have also found it useful to measure H₂ directly against D₂.

The experimental technique employed is that of dc electric-field-induced second-harmonic generation (ESHG). We have taken advantage of recent advances⁸ in this technique, which have allowed us readily to make measurements of ratios of susceptibilities to within an accuracy of 0.3%, and typically better than 1%. This is accurate enough to observe the influence of vibrational resonances.

In what follows we first establish the notation, then give details of the experimental procedure, present the results, and finally given an extensive discussion which includes a careful comparison with the theory.

II. NOTATION

ESHG in gases may, for our experimental geometry (optical-field polarization parallel to the static field), be described⁹ by

$$P_z(2\omega) = \frac{3}{2} \chi_{zzzz}^{(3)}(-2\omega; \omega, \omega, 0) E_z(\omega) E_z(\omega) E_z(0), \quad (1)$$

where $E_z(\omega)$ is the macroscopic applied field oscillating at frequency ω and taken to be in the z direction, $P_z(2\omega)$ is the induced macroscopic polarization oscillating at 2ω , and $\chi^{(3)}$ is the macroscopic third-order nonlinear susceptibility, in whose dispersion properties we are interested. Our notation is consistent with that given in detail in Bogaard and Orr,¹⁰ and has the desirable property that

$$\chi^{(3)}(0; 0, 0, 0) = \lim_{\omega \rightarrow 0} \chi^{(3)}(-2\omega; \omega, \omega, 0)$$

without the need for additional numerical factors.

While experimental measurements in the gas phase are, of necessity, macroscopic laboratory-frame measurements, the *ab initio* calculations to which we would like to relate are of the microscopic second hyperpolarizability $\gamma_{ijkl}(-2\omega; \omega, \omega, 0)$ calculated in the molecule-fixed frame. The relationship between them is given⁹ by

$$\chi_{zzzz}^{(3)}(-2\omega; \omega, \omega, 0) = \frac{1}{6} \rho L \langle \Phi_{z\alpha} \Phi_{z\beta} \Phi_{z\gamma} \Phi_{z\delta} \rangle \times \gamma_{\alpha\beta\gamma\delta}(-2\omega; \omega, \omega, 0), \quad (2)$$

where ρ is the number density of the molecules, the $\Phi_{z\alpha}$ represent direction cosines between the laboratory coordinate z and the α molecule-fixed coordinate, the angular brackets signify an isotropic average, and repeated Greek indices are summed over. L represents the local-field correction factor, which in our experiments differs from unity by less than 1%.

We identify

$$\langle \Phi_{z\alpha} \Phi_{z\beta} \Phi_{z\gamma} \Phi_{z\delta} \rangle \gamma_{\alpha\beta\gamma\delta}(-2\omega; \omega, \omega, 0)$$

as the microscopic nonlinear susceptibility, which we will henceforth write in the abbreviated form $\chi^{(3)}(\omega)$. At $\omega = 0$ it may be shown^{10,11} that

$$\chi^{(3)}(0) = \frac{1}{5} \gamma_{\xi\xi\eta\eta}(0; 0, 0, 0), \quad (3)$$

where repeated indices are again summed over. For a closed-shell atom the averaging process is superfluous.

III. EXPERIMENTAL PROCEDURE

The experimental apparatus is similar to that previously described by Shelton and Buckingham.⁸ A cw laser beam is weakly focused through a gas sample subjected to a static electric field. The static field breaks the symmetry of the system, permitting the coherent generation of frequency-doubled photons. The signal is enhanced by means of periodic phase matching, accomplished by the use of an array of electrodes¹² which is designed so as to reverse the polarity of the electric field every coherence length $l_c = \pi / (2k_\omega - k_{2\omega})$, where k_ω is the wave vector at frequency ω in the gas. The resulting periodic phase shift in the generated second harmonic serves to cancel periodically the accumulating phase shift due to normal dispersion, thus allowing the continued growth of the signal throughout the length of the sample. The coherence length of the gas is adjusted to match the fixed spacing of the electrodes by varying the density of the gas until peak signal is achieved.

A schematic diagram of the experimental apparatus is shown in Fig. 1. The laser is either a cw argon-ion laser or a Rhodamine-6G or DCM dye laser pumped by the argon-ion laser. The laser beam, typically 1 W, is redirected and its polarization is rotated by mirrors. Then a well-defined horizontal linear polarization state of the laser beam is selected by a Glan-laser prism polarizer. A filter eliminates unwanted second-harmonic light generated in the birefringent filter of the dye laser. The beam is weakly focused with a confocal parameter of about 20 cm at the center of the electrode array (150 pairs of wires, 1.59 mm in diameter and 2.69 mm center-to-center spacing, giving a horizontal field.) Phase matching for this array typically occurs at a gas pressure of order 1 atm ($T = 22^\circ\text{C}$), except for helium (a low-dispersion medium), where the pressure is of order 100 atm. The applied field is typically 3 kV/mm, adjusted to be safely below breakdown. After transmission through the array and sample cell, the beam is recollimated and sent through a double-prism spectrometer which eliminates most of the visible fundamental while passing the ultraviolet second harmon-

ic. Brewster-angle—dispersing prisms pass the horizontally polarized light with negligible attenuation. A final filter eliminates the residual fundamental. The second harmonic is detected by photon counting with an uncooled EMI 9893 QB/350 photomultiplier tube. The dark count, about 1 count/sec, is usually the only background. When necessary, the background is eliminated by modulating the high voltage applied to the electrodes with a square wave at 10 Hz and subtracting the voltage-off counts from the voltage-on counts.

The second-harmonic count rate $S^{(2\omega)}$, which is typically of order 1000 counts/sec at phase match, is a sharply peaked function of the density ρ with a full width at half maximum signal of about 1% of the optimum density. By accurately measuring this peak count rate and the density at which it occurs for a given gas sample A , and then repeating the process for another gas B without changing any other experimental parameter (e.g., laser power, applied dc field, etc.), the ratio of the microscopic nonlinear susceptibilities of molecules A and B is determined from

$$\frac{\chi_A^{(3)}(\omega)}{\chi_B^{(3)}(\omega)} = \left[\frac{S_A^{(2\omega)}}{S_B^{(2\omega)}} \right]^{1/2} \frac{n_B^{(\omega)} \rho_B}{n_A^{(\omega)} \rho_A} \quad (4)$$

Here, $n^{(\omega)}$, the sample refractive index, serves to incorporate adequately the small local-field correction. Note that it is not necessary to determine the coherence length as, at optimum density, it is automatically locked to the value determined by the electrode spacing, and this is independent of the gas.

The peak signal and optimum density at which it occurs are determined by slowly bleeding out the gas at a constant rate, thus scanning the density over the peak, and measuring the count rate as a function of density. A parabola is fitted to the peak numerically. Care is taken to include only measurements taken symmetrically within 15% of the peak signal, so as to avoid fitting errors.

The density is derived from measurements of the pressure and temperature and includes virial corrections.¹³ The temperature is monitored inside the cell by a thermistor in direct contact with the gas. Pressures of H₂ and D₂

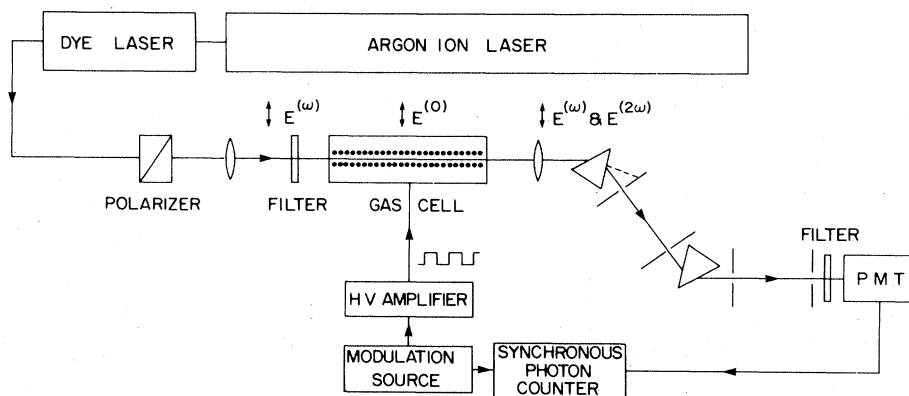


FIG. 1. Schematic diagram of the experimental apparatus showing the lasers and presample optics, the sample cell in which the modulated ESHG beam is produced, the double-Brewster-angle-prism spectrometer which separates the second-harmonic beam, and the photomultiplier tube and associated electronics for synchronous photon counting. The optical field polarization is parallel to the static field.

are measured with a capacitance manometer (MKS Baratron) recently calibrated by the manufacturer and with a stated accuracy of 0.15%. The substantially higher helium pressures are measured with a Bourdon gauge (Heise) accurate to 0.1% of full scale (160 bars). The accuracy with which the optimum density can be determined is generally limited by the pressure gauges.

A detailed discussion of systematic errors which can arise in an experiment of this type has been given elsewhere.¹⁴ Potentially the most important is the effect of beam steering when changing from a low-pressure gas to high-pressure helium. This is avoided by the use of windows at normal incidence on the gas cell and wide pinholes in the spectrometer, so that any residual beam steering when changing gas samples does not cause vignetting of the second-harmonic beam in the spectrometer.

The most significant random error comes from drifts in laser power. To avoid this, care was taken to ensure that the system was well warmed up before use. Further, in measuring gas *A* against gas *B*, triplets of measurements were made, i.e., first *A*, then *B*, and then *A* again, at equally spaced intervals. By averaging the two *A* results together, one obtains significant compensation for residual power drifts. This can be seen by making measurements in coupled triplets (i.e., quintuplets) and noting that the results for each triplet generally agree within the error estimated on the basis of a convolution of counting statistics and the uncertainty involved in density determination. We are satisfied that the errors so determined are a reasonable measure of the total error.

IV. RESULTS

The raw data obtained for $\chi^{(3)}(\omega)$ for H₂, measured as a ratio to $\chi^{(3)}(\omega)$ for He at 19 wavelengths from 700 to 458 nm, are displayed in Table I. Also included are the results of $\chi^{(3)}(\omega)$ for H₂ measured directly against D₂ at 9 wavelengths.

For field frequencies below the lowest resonant frequency of the molecule, we may perform a power-series expansion about $\omega=0$, writing an expression of the form

$$\chi^{(3)}(\omega) = \chi^{(3)}(0)(1 + a\omega^2 + b\omega^4 + \dots) \quad (5)$$

Odd-powered terms are excluded because¹⁵ $\chi^{(3)}(\omega) = \chi^{(3)}(-\omega)$.

In our experiment the second-harmonic frequency is always well below the lowest electronic transition frequency, and so if the vibrational contributions at optical frequencies from low-lying resonances in H₂ and D₂ are small, or can be subtracted out of the raw data, we can expect that such an expansion will hold. In the next section we will calculate this correction and show that it is always less than 2% of the measured $\chi^{(3)}(\omega)$.

In Fig. 2 we have plotted the results for H₂ given as a ratio to $\chi^{(3)}(\omega)$ for He, after the vibrational contribution has been removed, as a function of ω^2 . The excellent fit to a straight line (resulting from a weighted least-squares fit to the corrected data) indicates that terms in ω^4 and higher are small compared to the error bars. This smooth behavior as a function of frequency serves as a stringent test of the experiment, as virtually every significant experimental parameter (e.g., phase-match density, laser power,

TABLE I. Experimental measurements before and after correction for the vibrational (vibr.) resonance contribution. The tabulated values at $\omega=0$ are the result of extrapolating the measurements by means of a weighted least-squares fit with a function of the form $f(\omega) = A(1 + B\omega^2)$. The first line of the table contains the values of *A* for the fits. The corresponding values of *B* (10^{-10} cm²) for the fits are 9.01(22), 8.31(21), 0.47(13), and 0.24(13), respectively.

λ_{air} (nm)	ν_{vac} (cm ⁻¹)	$\chi_{\text{H}_2}^{(3)}/\chi_{\text{He}}^{(3)}$		$\chi_{\text{H}_2}^{(3)}/\chi_{\text{D}_2}^{(3)}$	
		Raw data	Vibr. corrected	Raw data	Vibr. corrected
∞	0	14.72(9)	15.13(9)	1.0125(43)	1.0249(43)
700.0	14282	17.53(11)	17.82(11)		
694.3	14399	17.54(10)	17.82(10)	1.0229(35)	1.0310(35)
690.0	14489	17.61(8)	17.88(8)		
680.0	14702	17.57(9)	17.83(9)		
670.0	14921	17.75(9)	18.00(9)		
660.0	15147	17.67(7)	17.92(7)	1.0221(28)	1.0293(28)
650.0	15380	17.89(8)	18.13(8)		
640.0	15620	17.84(6)	18.07(6)		
632.8	15798	17.88(8)	18.10(8)	1.0223(28)	1.0288(28)
620.0	16124	18.19(8)	18.40(8)		
610.0	16389	18.32(9)	18.52(9)	1.0273(38)	1.0330(38)
600.0	16662	18.37(9)	18.57(9)		
590.0	16944	18.62(7)	18.81(7)	1.0288(29)	1.0340(29)
580.0	17236	18.76(8)	18.94(8)		
514.5	19430	19.81(8)	19.95(8)	1.0315(31)	1.0351(31)
496.5	20135	20.06(13)	20.19(13)	1.0330(34)	1.0362(34)
488.0	20487	20.20(10)	20.32(10)	1.0303(32)	1.0334(32)
476.5	20981	20.55(15)	20.67(15)	1.0307(50)	1.0335(50)
457.9	21831	21.07(25)	21.18(25)		

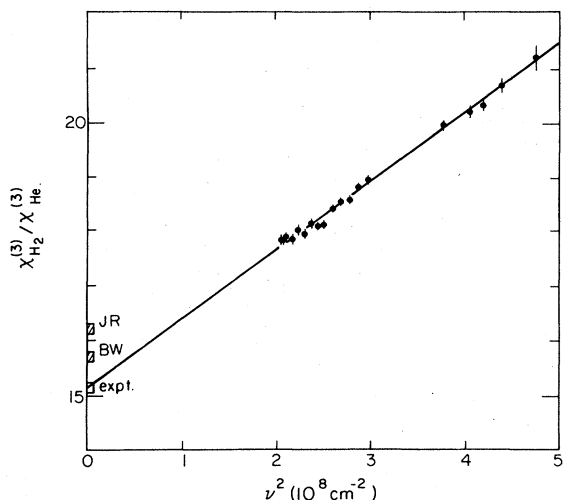


FIG. 2. The susceptibility ratio $\chi_{\text{H}_2}^{(3)}/\chi_{\text{He}}^{(3)}$ plotted as a function of ω^2 . The straight line shown is the weighted least-squares fit to the vibrationally corrected measurements. The uncertainty of the extrapolated ratio at $\omega=0$ is indicated by the open box around the zero intercept of the fitted line. For comparison, the theoretical estimates derived from JR (Ref. 6) and BW (Ref. 7) have also been indicated, in this case by hatched boxes. In order to compare the theoretical results with experiment, the theoretical values of $\chi_{\text{H}_2}^{(3)\text{el}}(0)$ have been divided by $\chi_{\text{He}}^{(3)}(0)$. The height of the hatched boxes represents the full range of the *ab initio* $\chi_{\text{He}}^{(3)}(0)$ values used in this reduction. The zero-frequency results are clearly in disagreement as none of the error boxes overlap.

etc.) changes, often substantially, over the range of wavelengths employed.

The results given in Table I have estimated accuracies ranging between 0.3% and 1.2%. The scatter of the points about the smoothed values, as shown in Fig. 2, is consistent with the indicated error bars. As these results greatly surpass in both frequency range and accuracy most previous experimental results for H₂ (to our knowledge there are no ESHG results for D₂), direct comparison is not generally meaningful. Two exceptions may be noted. Ward and Miller,⁹ using a ruby laser at $\lambda=694.3$ nm, without the benefit of periodic phase matching, were able to obtain an accuracy of 1.2% for the ratio of $\chi_{\text{H}_2}^{(3)}/\chi_{\text{He}}^{(3)}$. Their result is in good agreement with our smoothed value (before vibrational corrections). Shelton and Buckingham⁸ measured H₂ against He at $\lambda=514.5$ nm using the forerunner to this experimental system. Their value, which is 1.9% lower than the present smoothed result, differs by more than the combined error bars of the two measurements, suggesting a possible systematic error. As the present version of the experiment incorporates refinements in the measuring technique, greater attention to possible sources of systematic error, and includes a larger number of measurements with the built-in check of wavelength dependence, we believe that the present results are the more accurate. The probable source of the systematic error in the previous experiment is beam steering. With windows tilted at

$\pm 2^\circ$ to form a gas prism of He at 120 atm, the deflection of the beam would have been 0.3 mrad as He filled the cell. Experience has since shown that such a deflection is quite sufficient to cause a 2% systematic error.¹⁴

V. DISCUSSION

As the best *ab initio* calculations (those which include correlation) of third-order nonlinear susceptibilities of hydrogen to date have only been done in the static limit⁷ ($\omega=0$), or describe processes other than ESHG (Ref. 6) (such as third-harmonic generation), it is necessary first to correctly extrapolate our results to zero frequency, and second to put the theoretical results in a form which is directly comparable to the extrapolated experimental values.

The two *ab initio* calculations at $\omega=0$ to which we will refer are those of Jaszunski and Roos⁶ (JR) and Berns and Wormer⁷ (BW).

JR have done a calculation of all of the independent components of $\gamma_{ijkl}(0;0,0,0)$ at several fixed internuclear separations R , and then averaged over the ground-state ($v=0, J=0$) internuclear probability distribution. Such a calculation does not by its nature include the influence of vibrational resonances, whereas these do affect the experimental results. Following the nomenclature introduced in a previous work,¹⁴ we will refer to the nonlinear susceptibility obtained from a simple internuclear average, as in JR, as the electronic part $\chi^{(3)\text{el}}$, and the contribution coming from the vibrational resonances as $\chi^{(3)\text{vib}}$, so that the total $\chi^{(3)}$, which is measured in the experiment, may be written

$$\chi^{(3)} = \chi^{(3)\text{el}} + \chi^{(3)\text{vib}} \quad (6)$$

Note that for a homonuclear diatomic molecule there is no analogous vibrational resonance contribution to the linear polarizability α , and hence there is no need to distinguish between α and α^{el} .

We have shown elsewhere¹⁴ how to calculate $\chi^{(3)\text{vib}}$ in general. At the optical frequencies employed by us, the only significant contribution comes from the $v=1$ vibrational state. Also, it is adequate to assume that all of the ground-state population is in the $J=1$ rotational state for H₂, or $J=2$ for D₂. Finally, we only consider the $\Delta J=0$ contribution, which dominates the $\Delta J=\pm 2$ contributions. With these simplifications we may write, in atomic units,

$$\chi^{(3)\text{vib}}(\omega) = \omega_{0J,1J}^2 (2\alpha_{0J,1J}^2 + \frac{8}{45}\gamma_{0J,1J}^2) \times \left[\frac{2}{\omega_{0J,1J}^2 - \omega^2} + \frac{1}{\omega_{0J,1J}^2 - 4\omega^2} \right], \quad (7)$$

where $\alpha = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$ and $\gamma = \alpha_{\parallel} - \alpha_{\perp}$ are the transition polarizability and transition anisotropy, respectively, for the $Q_{01}(J)$ vibrational transition. ω is the optical frequency and $\omega_{0J,1J}$ is the fundamental vibrational transition frequency of the molecule.

The vibrational contributions have been calculated using the parameter values¹⁶ given in Table II. A basis for comparison of the calculated $\chi^{(3)\text{vib}}$ with the measured $\chi^{(3)}/\chi_{\text{He}}^{(3)}$ is established by the expression

TABLE II. Calculation of vibrational resonance contribution to $\chi^{(3)}$. The values given are *ab initio* results from Hunt *et al.* (Ref. 16) and are given in atomic units unless otherwise indicated. Expressed in terms of $\chi^{(3)\text{vib}}(\omega)$ and the ratio $x = \omega/\omega_{0J,1J}$, Eq. (7) for the vibrational contribution has the form

$$\chi^{(3)\text{vib}}(x) = \chi^{(3)\text{vib}}(0) [2(1-x^2)^{-1} + (1-4x^2)^{-1}] / 3,$$

where

$$\chi^{(3)\text{vib}}(0) = (6\alpha_{0J,1J}^2 + \frac{8}{15}\gamma_{0J,1J}^2) / \omega_{0J,1J}.$$

H ₂	D ₂
$\alpha_{01,11} = 0.740\ 27$	$\alpha_{02,12} = 0.617\ 65$
$\gamma_{01,11} = 0.611\ 75$	$\gamma_{02,12} = 0.502\ 24$
$\omega_{01,11} = 0.018\ 94$ (= 4156 cm ⁻¹)	$\omega_{02,12} = 0.013\ 61$ (= 2988 cm ⁻¹)
$\chi_{\text{H}_2}^{(3)\text{vib}}(0) = 184$	$\chi_{\text{D}_2}^{(3)\text{vib}}(0) = 178$

$$\chi_{\text{He}}^{(3)}(\omega) = 42.6 \{ 1 + [\omega / (58\ 300\ \text{cm}^{-1})]^2 \}, \quad (8)$$

where $\chi_{\text{He}}^{(3)}(\omega)$ is in a.u. This expression adequately represents the *ab initio* results of Sitz and Yaris⁴ over the frequency range considered in this work. They consider their calculation to be accurate to within a few percent at low frequencies [this is the sole accurate calculation of $\chi_{\text{He}}^{(3)}(\omega)$ for ESHG, but perhaps not the best one at $\omega=0$]. The electronic part of the susceptibility is obtained from the raw data by subtracting the calculated vibrational contribution. The ratios $\chi_{\text{H}_2}^{(3)\text{el}}/\chi_{\text{He}}^{(3)}$ and $\chi_{\text{D}_2}^{(3)\text{el}}/\chi_{\text{D}_2}^{(3)\text{el}}$ obtained by making vibrational corrections to the raw data are given in Table I. The corrections for H₂ vary between 1.7% and 0.5%, while the corrections for D₂ are about half as large. Since the corrections are small, the correction procedure is insensitive to errors in the calculation of $\chi^{(3)\text{vib}}$ due to, for example, errors in the *ab initio* values of $\chi_{\text{He}}^{(3)}(\omega)$. In passing, we note that, in contrast with the situation at optical frequencies, the vibrational contributions at $\omega=0$ are large, nearly 30% of $\chi^{(3)\text{el}}(0)$ for both H₂ and D₂ (see Table II). Also, the near equality of $\chi^{(3)\text{vib}}(0)$ for H₂ and D₂ is not a coincidence, but arises because $\alpha_{0,1}$ and $\gamma_{0,1}$ scale as $(\omega_{0,1})^{1/2}$ in the harmonic approximation, as expressed through Placzek theory.¹⁷

Having made the vibrational corrections, the extrapolation to $\omega=0$ is straightforward. Figure 2 shows the corrected values of $\chi_{\text{H}_2}^{(3)\text{el}}(\omega)/\chi_{\text{He}}^{(3)}(\omega)$ plotted as a function of ω^2 , along with the weighted least-squares straight line whose intercept at $\omega=0$ is the desired experimental estimate of $\chi_{\text{H}_2}^{(3)\text{el}}(0)/\chi_{\text{He}}^{(3)}(0)$. The resulting value (see Table I) is 2.7% higher than would have been obtained by extrapolating the raw data. Similarly, Fig. 3 shows $\chi_{\text{H}_2}^{(3)\text{el}}(\omega)/\chi_{\text{D}_2}^{(3)\text{el}}(\omega)$ plotted as a function of ω^2 , along with the straight-line fit used in the extrapolation to $\omega=0$. Also illustrated in Fig. 3 is the analogous extrapolation of the raw data. At $\omega=0$ the vibrationally corrected extrapolation (see Table I) is 1.2% higher than the result of extrapolating the raw data.

The final step in the reduction of our data involves putting the extrapolated value of $\chi_{\text{H}_2}^{(3)\text{el}}(0)/\chi_{\text{He}}^{(3)}(0)$ into absolute terms, by multiplying it with $\chi_{\text{He}}^{(3)}(0)$. The values of

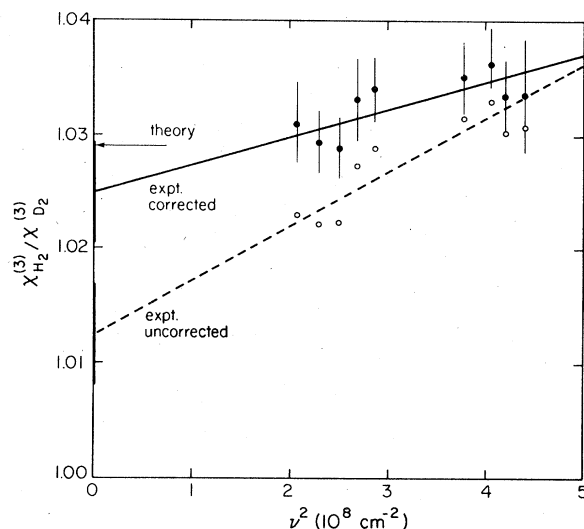


FIG. 3. The susceptibility ratios $\chi_{\text{H}_2}^{(3)\text{el}}(\omega)/\chi_{\text{D}_2}^{(3)\text{el}}(\omega)$ (solid circles) and $\chi_{\text{H}_2}^{(3)}(\omega)/\chi_{\text{D}_2}^{(3)}(\omega)$ (open circles with error bars omitted for clarity) plotted as functions of ω^2 . The solid and dashed straight lines are the weighted least-squares fits to the vibrationally corrected and raw data, respectively. The heavy bars show the experimental uncertainties of the extrapolated ratios at $\omega=0$. The theoretical estimate of $\chi_{\text{H}_2}^{(3)\text{el}}(0)/\chi_{\text{D}_2}^{(3)\text{el}}(0)$ has the value indicated by the arrow. The theoretical value falls within the error bar of the vibrationally corrected experimental result, but does not agree with the uncorrected extrapolation.

$\chi_{\text{He}}^{(3)}(0)$ obtained from the four best calculations (those employing explicitly correlated wave functions) are 43.10 a.u. (Buckingham and Hibbard²), 42.81 a.u. (Grasso, Chung, and Hurst⁵), 42.8 a.u. (Klingbeil³), and 42.6 a.u. (Sitz and Yaris⁴). The spread from highest to lowest is only 1% for these calculations, and as will be seen later, the conclusions of our comparison of theory with experiment will be unaffected by any choice of $\chi_{\text{He}}^{(3)}(0)$ in this range.¹⁸ Using the value $\chi_{\text{He}}^{(3)}(0) = 42.8$ a.u., which is about midrange, we at last obtain the experimental estimate of $\chi_{\text{H}_2}^{(3)\text{el}}(0) = 647 \pm 4$ a.u.

Before making our comparison with theory, we must extract the relevant information from the *ab initio* calculations of JR and BW. JR provide us with the necessary internuclear average for $v=0, J=0$, but we must perform an isotropic average according to Eq. (3), to obtain the value $\chi_{\text{H}_2}^{(3)\text{el}}(0) = 691.2$ a.u. BW provide us with isotropically averaged values at a series of fixed internuclear separations, leaving us to perform the internuclear average. To do this we fit a polynomial of the form

$$\chi_{\text{H}_2}^{(3)\text{el}}(R) = a + bR + cR^2 + dR^3 \quad (9)$$

to the *ab initio* results, where R is the internuclear separation. We find it sufficient to use the values calculated at $R = 0.20, 1.00, 1.40$, and 2.40 a.u., and solve for a, b, c , and d (see Fig. 4).

The internuclear average is then performed by using the published moments²¹ of the ground-state ($v=0, J=0$) distribution for H₂ ($\langle R \rangle = 1.4487$ a.u., $\langle R^2 \rangle = 2.1271$ a.u., and $\langle R^3 \rangle = 3.1642$ a.u.). In this way we obtain

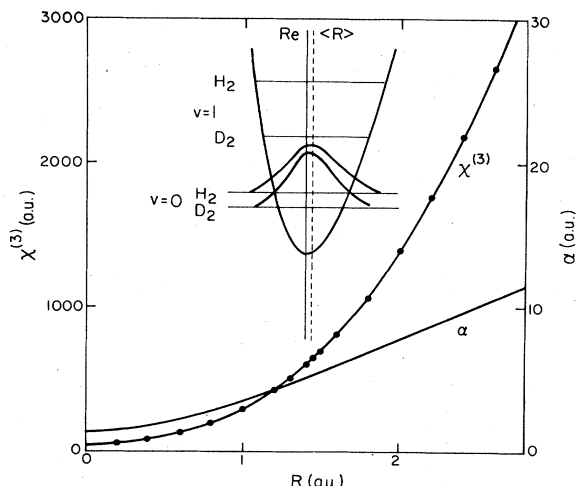


FIG. 4. The relations between the linear (Ref. 19) and nonlinear (Ref. 7) susceptibility functions, the ground vibrational probability distributions (Ref. 20), and the internuclear potential functions (Ref. 20) are illustrated for H₂ and D₂ by plotting them together versus internuclear separation R . Both $\chi^{(3)}(R)$ and $\alpha(R)$ are smoothly increasing functions of R in the region of appreciable probability density for the vibrational wave functions, with the fractional slope of $\chi^{(3)}(R)$ about twice that of $\alpha(R)$ for R near the equilibrium internuclear separation R_e . Due to the effect of the anharmonicity of the potential well, the mean internuclear separation $\langle R \rangle$ is significantly larger than the equilibrium separation R_e . The small increase in $\langle R \rangle$ for H₂ as compared to D₂ (imperceptible on this scale) largely accounts for the differences between the susceptibilities of the two molecules. The curves shown for $\chi^{(3)}$ and α are actually functions with the form of Eq. (9), fitted to the tabulated *ab initio* results (shown as dots for the BW values) and used in the internuclear averaging.

$\chi_{\text{H}_2}^{(3)\text{el}}(0) = 667.0$ a.u. from BW. We may check our averaging procedure by performing the same calculation for JR. From their published data,²² we can only deduce the values of $\chi_{\text{H}_2}^{(3)\text{el}}(R)$ at $R = 0.0, 1.0, 1.4,$ and 2.4 a.u. [note that $\chi_{\text{H}_2}^{(3)\text{el}}(R=0) = \chi_{\text{He}}^{(3)}$; the value at $R=0$ is actually $\chi_{\text{He}}^{(3)}$ for JR]. Fitting a polynomial to these points and averaging using the moments, we obtain 689.5 a.u., in excellent agreement with the averaged value of 691.2 a.u. given in JR.

In fact, as the experiment is performed at $T = 22^\circ\text{C}$, it is necessary to thermally average the nonlinear susceptibilities over the correct distribution of J values. The J dependence comes about because the moments $\langle R^n \rangle$ increase with increasing J .²³ Recalculating, we obtain the thermally averaged value of $\chi_{\text{H}_2}^{(3)\text{el}}(0) = 670.7$ a.u. from BW and $\chi_{\text{H}_2}^{(3)\text{el}}(0) = 693.2$ a.u. from JR, an increase of 0.5% over the $J=0$ results.

By employing the moments²³ appropriate to D₂, we calculate the thermally averaged result $\chi_{\text{H}_2}^{(3)\text{el}}/\chi_{\text{D}_2}^{(3)\text{el}} = 1.029$ for both JR and BW.

The comparison of theory with experiment for H₂ and D₂ is presented in Table III. The main results of the comparison are as follows. First, although the results for $\chi_{\text{H}_2}^{(3)\text{el}}(0)$ derived from JR and BW differ by more than

TABLE III. Comparison of experimental and thermally averaged (at $T = 22^\circ\text{C}$) theoretical results for $\chi^{(3)\text{el}}(0)$ of H₂ and D₂.

	$\chi_{\text{H}_2}^{(3)\text{el}}(0)^a$ (a.u.)	$\chi_{\text{H}_2}^{(3)\text{el}}(0)/\chi_{\text{D}_2}^{(3)\text{el}}(0)$
Theory ^b	693	1.029
Theory ^c	671	1.029
Experiment	647 ± 4^d	1.025 ± 0.004

^aThe conversion to SI units is 1 a.u. = $6.2353 \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$. The conversion to esu is 1 a.u. = 5.0366×10^{-40} esu.

^bDerived from the results of Jaszunski and Roos, Ref. 6.

^cDerived from the results of Berns and Wormer, Ref. 7.

^dObtained assuming $\chi_{\text{He}}^{(3)}(0) = 42.8$ a.u. The assigned uncertainty does not include a contribution due to the uncertainty of $\chi_{\text{He}}^{(3)}(0)$.

3%, their results for $\chi_{\text{H}_2}^{(3)\text{el}}(0)/\chi_{\text{D}_2}^{(3)\text{el}}(0)$ are identical at the 0.1% level. We feel, therefore, that this insensitivity of $\chi_{\text{H}_2}^{(3)\text{el}}(0)/\chi_{\text{D}_2}^{(3)\text{el}}(0)$ to the details of the theory provides us with a stringent test of the experimental results as corrected for the influence of the vibrational resonances. The experimental ratio is in good agreement with the theoretical value, as is most clearly illustrated in Fig. 3. Note that the experimental results agree only after the vibrational correction has been made. The approximations underlying this correction¹⁴ are therefore seen to be justified.

The second result of our comparison is that both theoretical calculations overestimate the value of $\chi_{\text{H}_2}^{(3)\text{el}}(0)$ by an amount much larger than the estimated experimental uncertainty of $\pm 0.6\%$ (7% for JR and 4% for BW). The accuracy of the $\chi_{\text{He}}^{(3)}(0)$ used to calibrate the experiment is probably better than 1% and so cannot account for the discrepancy. The situation is illustrated in Fig. 2, where it is seen that the experimental and two theoretical values of $\chi_{\text{H}_2}^{(3)\text{el}}(0)$ are mutually incompatible.

Finally, the origin of the isotopic shift in the values of $\chi^{(3)\text{el}}$, and also α , for H₂ and D₂, is readily understood by reference to Fig. 4. Both $\chi^{(3)\text{el}}(R)$ and $\alpha(R)$ are monotonically increasing functions of R in the region of significant probability density. Due to the anharmonicity of the potential well, the lighter H₂ has a greater mean separation than D₂ ($\langle R \rangle_{\text{H}_2} = 1.01 \langle R \rangle_{\text{D}_2}$). As a result, both $\chi_{\text{H}_2}^{(3)\text{el}}/\chi_{\text{D}_2}^{(3)\text{el}}$ and $\alpha_{\text{H}_2}/\alpha_{\text{D}_2}$ are larger than 1, with the larger ratio in the nonlinear case arising because $\chi^{(3)\text{el}}(R)$ is a stronger function of R than $\alpha(R)$. Similarly, centrifugal distortion results in both $\chi^{(3)\text{el}}$ and α being (weakly) increasing functions of J .

VI. CONCLUSIONS

We have accurately measured both $\chi_{\text{H}_2}^{(3)}(\omega)/\chi_{\text{D}_2}^{(3)}(\omega)$ and $\chi_{\text{H}_2}^{(3)}(\omega)/\chi_{\text{He}}^{(3)}(\omega)$ over a wide range of optical frequencies. The results were corrected for the vibrational resonance contribution and then extrapolated to $\omega=0$, where a comparison was made with the best *ab initio* calculations available at the time. We find that the theoretical values are several percent too high, at best. While this is still reasonable agreement, we note that these calculations are

for the simplest molecule and include the effects of correlations through configuration interaction. It would be interesting to see if better agreement can be obtained with explicitly correlated wave functions. As far as larger molecules are concerned, we must agree with JR that calculations for them are very much in doubt as to reliability. We have also demonstrated that, for hydrogen, the effect of vibrational resonances at optical frequencies is small but not negligible.

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