

The hyperpolarizability dispersion of neon is not anomalous

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Experimental measurements are presented which show that the anomalous hyperpolarizability dispersion previously observed for neon is spurious. The electric-field-induced second harmonic generation measurements of the hyperpolarizability of neon are now in agreement with the best *ab initio* results, both in the static limit and at optical frequencies. This experiment gives $\gamma_{\text{Ne}} = 122.2 \pm 0.4$ and 123.5 ± 0.5 au at $\lambda = 514.5$ and 488.0 nm, respectively. The experimental estimate of the static hyperpolarizability of neon is 108 ± 2 au.

1. Introduction

Nonlinear optical materials have received intense recent study because of their potential application in a wide range of devices, and theoretical calculations play an important role in the endeavor to design and discover better nonlinear optical materials. However, the program to develop effective and accurate methods of calculation requires experimental information to check and guide its development. The comparison of theory and experiment in the case of the neon atom is especially important in assessing the limitations of *ab initio* calculations of hyperpolarizabilities, because neon is the first multielectron atom after helium for which both accurate experimental and theoretical results are presently possible. Basis set and correlation treatment effects can be assessed without the added complication of several nuclei as in a molecule. An inability of theoretical calculations to deal accurately with neon would cast doubt on the possibility of accurate *ab initio* calculations for even the smallest multielectron molecules. It is therefore disturbing to find wide discrepancies between the results of experiments and careful theoretical calculations.

The greatest discrepancy between theory and experiment is the observation of negative hyperpolar-

izability dispersion in neon at frequencies far below the first resonance [1,2]. This anomalous dispersion does not appear in the results of SCF calculations, and also is absent in the results of recent calculations including electron correlation [3–5]. Furthermore, the theoretical bound on the largest possible negative dispersion, determined using sum rules, is inconsistent with the experimental results [6]. It was suggested that the neglect of the contribution of interacting pairs of atoms in the high-pressure gas samples used in the experiments might account for the discrepancy, but the pair contribution to $\chi^{(3)}$ of the sample would have to be at least ten times larger than predicted by theory [7,8]. In view of all the contrary theoretical evidence, it seemed imperative to repeat the previous γ_{Ne} measurements to check their reliability, and also to attempt to assess the effect of pair interactions.

2. Experimental method

The hyperpolarizability of neon is measured relative to helium by means of electric-field induced second harmonic generation (ESHG) with periodic phase matching, as previously described [1,9,10]. An argon-ion laser beam is weakly focused into the sample cell containing an array of electrodes and the sample gas, the periodic phase matching condition is enforced by adjusting the sample gas density, and the

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intensity of the weak frequency-doubled light beam generated in the sample is measured with a photon counting photomultiplier tube. To cancel drifts, sample and reference gases were alternatively measured in two or three coupled triplets (i.e. He:Ne:He:Ne:He:...). The conditions of the previous experiments [9] have been duplicated, except that the laser beam power at the sample has been increased to about 2–3 W, which results in increased second harmonic signals of 100–600 cps. The same electrode array with 2.69 mm inter-electrode spacing and 150 electrode pairs is employed, with phase match for neon occurring at 29 and 24 atmospheres (at 26°C) for $\lambda=514.5$ and 488.0 nm, as before. The laser beam is linearly polarized parallel to the static electric field in the gas cell, and focused with a confocal parameter of 20 cm. High-purity (99.999%) gases are again employed, but with improved sample handling techniques and a more accurate pressure gauge (Paroscientific 1003K, full scale 200 atm, accuracy ± 0.02 atm). To assess the density dependence of $\gamma_{\text{Ne}}/\gamma_{\text{He}}$, measurements have also been made using an array with an electrode spacing of 5.08 mm and 82 electrode pairs. With this array the phase match density of the sample is about half that obtained with the first array.

The measurements were analyzed as previously described [1,9]. A re-examination of the possible sources of systematic errors identified several additional potential problems, which were dealt with as follows. The implicit requirements for accurate final results are that one must maintain very nearly the same laser beam power, pointing and focusing during the sample and reference gas measurements, and then in the analysis, one must account for any remaining small systematic differences between the measurement conditions for the sample and reference gases. Possible systematic errors, due to changes in laser beam parameters when the gas cell is filled, were assessed by conducting measurements of the propagation of fundamental and harmonic light beams into and out of the cell. Corrections due to gas-density-dependent deflection of the beam and change in the Fresnel reflection coefficient of the window-gas interface were made negligible by careful adjustment of the apparatus and by the fortunate near-match of the refractive indices of helium and neon gas at their respective phase-match densities

(e.g. correction to $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ due to window reflectivity change is 0.001%). Direct measurements verified that the corrections due to these effects were negligible. More troublesome are the effects of small residual temperature inhomogeneities in the gas sample (the temperature of a non-ideal gas is changed in the process of filling the measurement cell). Vertical temperature gradients decay slowly in the unstirred gas and result in a detectable downward deflection of the laser beam, but the apparatus has been adjusted to make it insensitive to this effect. The most critical requirement is adequate spatial uniformity of the detector response; the observed beam deflections in our apparatus result in at most 0.01% signal changes. Horizontal temperature gradients (in the direction perpendicular to the long axis of an electrode wire) are expected to be much smaller and shorter lived, but the possible effects of beam focusing or deflection in this direction are not as easily measured or eliminated. However, ESHG measurements on very dissimilar pairs of gases, both with and without stirring of the gas inside the cell, indicate that the effects of thermal gradients on the measured hyperpolarizability ratio have been reduced to the 0.1% level, and the effects are expected to be even smaller in the comparison of neon and helium. The main contributions to the measurement error budget for $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ are $\pm 0.05\%$ – 0.25% for reproducibility and $\pm 0.1\%$ from the density determinations. Pair interaction effects have not been included in our experimental error estimates for the ratio $\gamma_{\text{Ne}}/\gamma_{\text{He}}$.

3. Results and discussion

The results of our measurements of $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ at two argon-ion laser wavelengths are shown in table 1. Also shown are the results of all previous ESHG measurements for neon [1,2,9,11]. The present results for $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ are grossly different from the results previously obtained under the same conditions [9]. However, the phase match density ratios $\rho_{\text{He}}/\rho_{\text{Ne}}$ are in excellent agreement with previous results (see table 1), which indicates that the differences of about 10% between the present and previous hyperpolarizability ratios cannot be attributed to contamination. The discrepancy in the ESHG signal ratios is about 20%, so although the absolute ESHG signal is

Table 1

Summary of experimental results from this work and from all previous ESHG experiments with neon. The values of γ_{Ne} are obtained from the measured ratios using accurate ab initio values of γ_{He} . The experimental dispersion curve for γ_{Ne} is based on just the first four hyperpolarizability values in this table, since the fifth value has large uncertainty and the last three values are spurious (see text). The only other measurements of γ_{Ne} are from one dc Kerr effect experiment and two third harmonic generation experiments (error bars $\pm 8\%$ – 17% , see ref. [2] for discussion)

λ ^{a)} (nm)	ν ^{b)} (cm^{-1})	$\rho_{\text{He}}/\rho_{\text{Ne}}$	$\gamma_{\text{Ne}}/\gamma_{\text{He}}$	γ_{Ne} (au)
514.5 ^{c)}	19430	1.879 ± 0.002	2.550 ± 0.003	122.2 ± 0.4
488.0 ^{c)}	20487	1.882 ± 0.002	2.546 ± 0.007	123.5 ± 0.5
1319 ^{d)}	7581	1.853 ± 0.004	2.534 ± 0.019	111.0 ± 0.8
1064 ^{d)}	9395	1.850 ± 0.007	2.487 ± 0.011	109.9 ± 0.5
694.3 ^{e)}	14399	1.87 ± 0.01	2.77 ± 0.09	126.5 ± 4.1
594.5 ^{f)}	16817	1.864 ± 0.008	2.20 ± 0.03	102.6 ± 1.4
514.5 ^{f)}	19430	1.881 ± 0.012	2.28 ± 0.02	109.4 ± 1.0
488.0 ^{f)}	20487	1.872 ± 0.014	2.36 ± 0.03	114.5 ± 1.5

^{a)} In air. ^{b)} In vacuum. ^{c)} Present work. ^{d)} Refs. [1,2]. ^{e)} Ref. [11]. ^{f)} Ref. [9].

not usually reproducible to better than 10%, in this instance a comparison of the present and the previous values of the absolute ESHG signals for each gas separately is a useful diagnostic. Inspection of the original data shows that the signal previously measured for neon agrees with the present results when scaled to the same applied voltage and laser beam power, but the signal for helium was too large. To account for the too-large signal for helium, one infers that the electrode voltage present during the helium measurements must have been larger than the recorded value, and in fact very close to the breakdown voltage measured for neon. The previous observations can be reconciled if, in those experiments, the output voltage of the high voltage power supply was set to a value at or above breakdown for neon but below breakdown for helium (quite possible since the breakdown voltage for helium at its phase match density is more than five times higher than that for neon). Since the actual electrode voltage was recorded only when the cell was first filled with neon and the voltage set point was chosen, breakdown would result in an uncontrolled and unmeasured difference in the actual electrode voltages during the helium and neon gas measurements. Normally, electrical breakdown is not allowed to occur and this is a perfectly adequate procedure. However, electrical breakdown in neon gas in our apparatus does not result in a spark as is the case with other gases. Instead, breakdown is followed by a steady, electrically quiet

discharge with a slightly decreased but apparently stable voltage across the electrodes (the voltage supply is then operating in current-limit mode). It appears that spurious results were previously obtained for $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ because electrical breakdown, which in all other cases would prevent a measurement, passed unnoticed. This cannot have been the case in any of the subsequent neon versus helium measurements [1,2] because the voltage was set lower and was recorded for every measurement. On the basis of the above argument, the last three measurements of $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ given in table 1 should be discarded.

The experimental results for γ_{Ne} are obtained from the measured ratios $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ using Bishop's accurate ab initio values of γ_{He} for calibration [12]. A dispersion function, fitted to the ab initio results and which takes into account the reduced mass correction for helium, is given in ref. [1] (note that table 2 of ref. [1], which gives the fit coefficients, has a misprint: 10^{-31} in the last line should be 10^{-32}). The ab initio results for γ_{He} are thought to be accurate to better than 0.1%, and no allowance has been made for the possible inaccuracy of the γ_{He} calibration values. The experimental results for γ_{Ne} are most easily compared with ab initio results by expressing them in atomic units, where $1 \text{ au} = 219469 \text{ cm}^{-1}$ for ω and $1 \text{ au} = 6.23656 \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ for γ when reduced mass corrections for neon are incorporated into the conversion factors.

Finally, one must account for possible pair inter-

action effects. The only available theoretical calculation for the pair interaction correction indicates that $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ measured at the highest density in the present work is overestimated by 0.3% [7,8]. A measurement with the coarser electrode array at half the highest sample density yields $\rho_{\text{He}}/\rho_{\text{Ne}} = 1.879 \pm 0.003$ and $\gamma_{\text{Ne}}/\gamma_{\text{He}} = 2.554 \pm 0.010$ at $\lambda = 514.5$ nm. Combined with the result measured at higher density at the same wavelength, this indicates that the pair contribution to the hyperpolarizability ratio is less than about $\pm 1\%$ in these experiments. The error bars on our measurements are wide enough that the data are consistent with either the theoretically estimated density dependence or else simple density independence. The results for γ_{Ne} from the present experiments, given in table 1, include an estimated pair interaction correction of $0.0 \pm 0.3\%$.

The experimental dispersion curve for γ_{Ne} is based on just the first four measurements of γ_{Ne} given in table 1, since the other measurements are either too inaccurate or are simply invalid. The experimental results may be compared with the results of two, electron-correlated ab initio calculations of the frequency dependence of γ_{Ne} for ESHG [3,4]. To make the comparison, a power series dispersion function $\gamma = \gamma_0(1 + A\omega_L^2 + B\omega_L^4)$, where $\omega_L^2 = 6\omega^2$ for ESHG, was fitted to the experimental and theoretical results to give the coefficients shown in table 2. Fitted curves and the experimental data points are plotted in fig. 1. It is immediately apparent that the experimental and theoretical estimates of the dispersion of γ_{Ne} are in good agreement. Table 1 shows that the dispersion coefficients A determined by experiment and by the two, electron-correlated calculations all fall within a 6% range, and fig. 1 shows that the experimental and theoretical dispersion curves lie nearly parallel. The dispersion is only slightly larger for γ_{Ne} than for γ_{He} ($A = 2.5$ au versus $A = 2.191$ au [1,12]). The results in table 1 indicate that the shape of the dispersion curve is relatively insensitive to electron-correlation effects: including correlations increases γ_0 to 1.6 times the SCF result but only increases A by 5% [3]. The parallel displacement of the theoretical curves in fig. 1 reflects the relatively greater sensitivity to correlation treatment and basis set of γ_0 as compared to A . The effects of basis set selection and correlation treatment have been more thoroughly investigated

Table 2

Comparison of measured and calculated dispersion of γ_{Ne} . A function of the form $\gamma = \gamma_0(1 + A\omega_L^2 + B\omega_L^4)$, where $\omega_L^2 = 6\omega^2$ for ESHG and ω and γ are expressed in au, has been least-squares fitted to measured and calculated values of γ_{Ne} for $\omega = 0.0-0.1$ au. The results of a calculation at the SCF level of approximation are also shown for comparison. The B coefficient in the fit to the experimental measurement is arbitrarily set to a value between the values given by the electron-correlated calculations (fitted A depends only weakly on B : ± 0.5 in B gives ± 0.03 in A). This allows a consistent comparison for γ_0 and A even though the experimental data are too limited to reliably determine the small curvature due to the B term. The statistical uncertainties in the experimental fit coefficients are $\pm 1\%$ for γ_0 and $\pm 10\%$ for A

Source	γ_0	A	B
expt. ^{a)}	108.1	2.47	5.50
MP2 ^{b)}	110.4	2.40	5.33
CASSCF ^{c)}	94.6	2.55	5.94
SCF ^{b)}	68.7 ^{d)}	2.28	4.72

^{a)} Data from the first four lines of table 1.

^{b)} Ref. [3]. ^{c)} Ref. [4]. ^{d)} SCF limit is 70.0 au; see ref. [17].

for static calculations than for the dynamic calculations.

The experimental estimate of static γ_{Ne} that is obtained from the fitted dispersion curve is $\gamma_{\text{Ne}} = 108 \pm 2$ au, where a conservative error bar has been assigned because the scatter about the fitted curve is greater than the stated error bars for the two infrared measurements, and this warns of possible unaccounted for systematic errors in those measurements. The values of static γ_{Ne} from various ab initio calculations which include electron correlation, but which differ in terms of basis set and method of treatment of electron correlation, lie in the range 81–123 au [3–5,13–19]. However, the best estimates from the most recent calculations are more tightly grouped: Rice et al., CCSD(T), 110 ± 3 au [13]; Jensen et al., RASSCF, 99 ± 6 au [4]; Chong and Langhoff, CCSD(T), 111.0 au [16]; and Maroulis and Thakkar, CCD+ST(CCD), 114 ± 9 au [17]. The stated uncertainties are based on estimates of the contribution to γ due to terms which could not be directly calculated. The calculations employing coupled-cluster methods show good agreement with experiment. The best static value given by Jensen et al. [4] includes an adjustment based on the estimated effect of adding more correlating orbitals; the difference between their stated best static value of γ and the

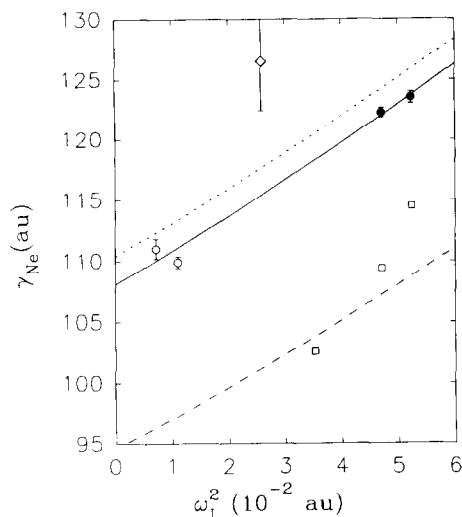


Fig. 1. The hyperpolarizability of neon measured by ESHG is plotted versus $\omega_L^2 = 6\omega^2$, where ω is the laser frequency. The dispersion curves from the two most recent dynamic, electron-correlated ab initio calculations of γ_{Ne} are also shown (dotted line, ref. [3]; dashed line, ref. [4]). The experimental dispersion curve (solid line) is a least-squares fit to the present results (filled circles) and the previous infrared results (open circles, refs. [1,2]). The other experimental points (open diamond, ref. [11]; open squares, ref. [9]) are not included in the fit. Error bars have not been plotted for the open squares since those data are shown to be invalid (see text). Even though the three dispersion curves have different static intercepts, they all show the same frequency dependence for γ_{Ne} .

static intercept of the dispersion curve given in table 2 and fig. 1 is due to this adjustment.

One of the very few other experimental determinations of γ_{Ne} to which one may compare the present results comes from a dc Kerr effect experiment [20]. The Kerr measurement at $\lambda = 632.8$ nm ($\omega_L^2 = 1.036 \times 10^{-2}$ au) gives $\gamma_{\text{Ne}} = 101 \pm 8$ au, in fair agreement with $\gamma_{\text{Ne}} = 111 \pm 2$ au predicted from the ESHG experimental dispersion curve (the two experiments measure slightly different quantities; a 0.1 au correction based on the measured deviation from Kleinman symmetry [9] is included in our estimate to account for this difference). Kerr measurements of higher accuracy should be possible for neon and would be effective for testing and refining the low-frequency end of the dispersion curve for γ_{Ne} .

The results may be summarized as follows. There is no valid evidence for negative dispersion for γ_{Ne} .

The experimental and ab initio results are in quantitative agreement for both the dispersion and the static value of γ_{Ne} . The best experimental and ab initio estimates of the static value of γ_{Ne} and the first dispersion coefficient have uncertainties in the range from 2% to 10%. Further low-frequency measurements are needed to improve the experimental extrapolation to the static limit. Reliable ab initio results for dispersion seems to be relatively easier to calculate than reliable results for the static hyperpolarizability.

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