Anomalous Hyperpolarizability Dispersion Measured for Neon

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(Received 7 December 1988)

Measurements of electric-field–induced second-harmonic generation are presented which show that the hyperpolarizability (γ) of the Ne atom decreases with increasing frequency at infrared frequencies. Such negative dispersion of γ at frequencies far below the first resonance is unprecedented. The new data, when combined with the results of *ab initio* calculations, indicate that the electron-correlation contribution is 40% of γ_{Ne}. This raises the question of the adequacy of Hartree-Fock calculations of the nonlinear optical properties of other atoms and molecules.

The third-order nonlinear optical response of atoms and molecules is a rich field of study, as well as having applications ranging from testing *ab initio* wave functions to optical signal processing and combustion diagnostics.[1] A wide range of third-order nonlinear optical processes such as the dc Kerr effect, electric-field–induced second-harmonic generation (ESHG), and third-harmonic generation (THG) are mediated by the molecular second hyperpolarizability γ.[2] Quantum-mechanical expressions for γ are well established[3-5] and inter-relationships between the various third-order nonlinear optical processes have been explored.[6-9] Calculations and measurements have been performed for many atoms and molecules,[2,7-11] and recently there have been systematic measurements of the frequency dependence of γ.[12-14] Since γ is a delicate and difficult property to calculate, experimental checks on the adequacy of the available calculational techniques for γ of multielectron systems are important. The near-infrared ESHG measurements of γ for the Ne atom reported below were undertaken to allow reliable extrapolation of the γ_{Ne} dispersion curve to the static limit, where unequivocal comparison with the results of static *ab initio* calculations would be possible.

The hyperpolarizability of Ne was measured at $\lambda = 1064$ and 1319 nm by gas-phase ESHG using periodic

TABLE I. The results of several nonlinear optical measurements for Ne. The linear polarizability dispersion values $\Delta\alpha = \alpha(2\nu) - \alpha(\nu)$ were determined from phase-match density measurements, except for the result given by Ref. 18 which was calculated from refractive index data in the literature. All experiments measure the ratio γ_{Ne}/γ_{He}, except the dc Kerr effect experiment in which γ_{Ne} was measured directly. The ratio γ_{Ne}/γ_{He} for the dc Kerr effect has been evaluated in two ways. The first of the tabulated numbers is obtained by dividing γ_{Ne} by the experimental value for γ_{He} also measured in the same experiments (Ref. 17). This is done in the hope that systematic errors will cancel out; however, since the signal for Ne in the dc Kerr effect experiment would have been 2.5 times larger than that for He under the same conditions it is likely that some systematic errors were relatively much larger for He than for Ne, probably precluding the desired cancellation. The second number for γ_{Ne}/γ_{He} is obtained by dividing γ_{Ne} by the accurate *ab initio* value of γ_{He} (Ref. 8). The wide discrepency between these two numbers reflects the fact that the dc-Kerr experimental value for γ_{He} is 30% larger than the accurate *ab initio* result.

Expt.	Ref.	λ (nm)	ν (cm^{-1})	ν_L^2 (10^8 cm^{-2})	$\Delta\alpha_{Ne}/\Delta\alpha_{He}$	γ_{Ne}/γ_{He}
Kerr	17	632.8	15798	4.992	$\cdots$	1.91 ± 0.20
	17	632.8	15798	4.992	$\cdots$	2.38 ± 0.20
ESHG	a	1319	7581	3.448	1.853 ± 0.004	2.534 ± 0.019
	a	1064	9395	5.296	1.850 ± 0.007	2.487 ± 0.011
	18	694.3	14399	12.440	1.87 ± 0.01	2.77 ± 0.09
	15	594.5	16817	16.969	1.864 ± 0.008	2.20 ± 0.03
	15	514.5	19430	22.651	1.881 ± 0.012	2.28 ± 0.02
	15	488.8	20487	25.183	1.872 ± 0.014	2.36 ± 0.03
THG	19	1055	9480	10.784	$\cdots$	1.80 ± 0.18
	20	694.3	14399	24.849	$\cdots$	2.23 ± 0.38

[a]The present work.

phase matching. The experimental technique is essentially the same as previously reported,[15] but with the continuous-wave (cw) argon-ion and dye lasers replaced by a cw Nd-doped yttrium-aluminum-garnet laser Q switched at 5 kHz to give a train of 1-kW pulses. Because of the longer laser wavelength the longitudinal spacing of the cell electrodes was increased by about 6 or 9 times to keep the phase-match pressure below 60 atm for the Ne sample gas and 110 atm for the He reference gas. The voltage applied to the electrodes was adjusted so that about one second-harmonic photon was counted for every ten laser pulses. Sources of systematic errors such as dead time, window birefringence, and coherent background were carefully considered and dealt with. A more complete account of the experimental methods will be presented in a future publication reporting the larger study from which these γ_{Ne} measurements are drawn.[16]

The results of the present ESHG experiment and also the previous dc Kerr effect,[17] ESHG,[15,18] and THG[19,20] measurements for Ne are presented in Table I and in Fig. 1. In order to combine data from several nonlinear optical processes the measured γ_{Ne}/γ_{He} values have been plotted versus $v_L^2 = v_\sigma^2 + v_1^2 + v_2^2 + v_3^2$, where v_1, v_2, and v_3 are the applied field frequencies and $v_\sigma = v_1 + v_2 + v_3$.[7-9,13,14] A function of the form $\gamma_{Ne}/\gamma_{He} = A[1 + Bv_L^2 + Cv_L^4]$ fitted to the five most recent ESHG measurements is shown by the curve in Fig. 1. The striking feature of these measurements is that γ_{Ne}/γ_{He} vs v_L^2 is *not* monotonic. Furthermore, using the accurate *ab initio* results for γ_{He} to deduce γ_{Ne} from the measured ratios,[8] one also finds that γ_{Ne} itself has a pronounced minimum and shows strong negative dispersion at $v = 0$. The magnitude of the relative dispersion $\gamma^{-1}(d\gamma/dv_L^2)$ at $v_L^2 = 0$ is larger for Ne than for He, Ar, Kr, or Xe. These results are most unusual and unexpected. Nevertheless, we believe that the error bars on our data points properly reflect their accuracy. The reliability of the near-infrared ESHG data which reveal the negative dispersion of γ_{Ne} may be checked in several ways. First, one may eliminate the possibility of significant impurities in the sample since $\Delta\alpha_{Ne}/\Delta\alpha_{He}$ [where $\Delta\alpha = \alpha(2v) - \alpha(v)$, see Table I] shows the expected slow monotonic increase with v.[21] Second, ESHG measurements for Ar, Kr, and Xe, made on the same apparatus, fall on smooth monotonically increasing dispersion curves.[16] Finally, the older nonlinear optical measurements for Ne are consistent with the five most recent ESHG measurements (see Fig. 1). The collision-induced contributions to the measured values of γ for Ne and He due to interatomic interactions have been calculated and are found to increase γ_{Ne}/γ_{He} by 0.6% at the highest sample densities employed.[17,22]

Since there is no previous experimental or theoretical evidence for negative dispersion of γ at incident light frequencies below the lowest resonance frequency of an atom or molecule, the first question to address is the
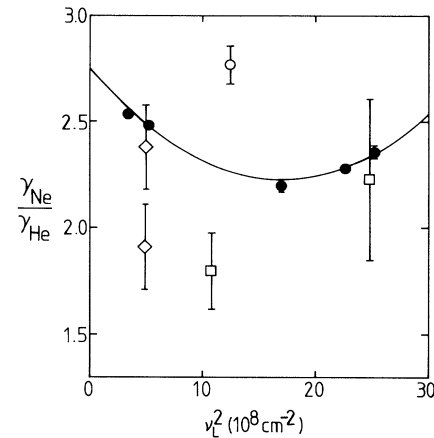

FIG. 1. The measured ratios of hyperpolarizabilities for Ne and He plotted vs the effective laser frequency v_L^2 (see text). The data measured by the dc Kerr effect (diamonds) (Ref. 17), ESHG (circles) (Refs. 15 and 18), and THG (squares) (Refs. 19 and 20) should all fall on the same dispersion curve when plotted vs v_L^2 (Refs. 7-9, 13, and 14). A curve of the form $\gamma_{Ne}/\gamma_{He} = A[1 + Bv_L^2 + Cv_L^4]$ satisfactorily fits the ESHG measurements made in the author's laboratory (filled circles, error bars are smaller than the drawn circles for three of the points). The earlier nonlinear optical measurements (open symbols) (Refs. 17-20) are in adequate agreement with the fitted curve, despite the apparently significant deviation of three of the points, since the error bars on those points have most likely been underestimated. The coefficients of the weighted least-squares fit for γ_{Ne}/γ_{He} are $A = 2.753$, $B = -2.251 \times 10^{-10}$ cm^2, and $C = 6.609 \times 10^{-20}$ cm^4, where v_L is given in cm^{-1}. Using the *ab initio* results for γ_{He} for calibration (Ref. 8) one also obtains $\gamma_{Ne} = A^*[1 + B^* v_L^2 + C^* v_L^4]$, where $A^* = 115.8$ a.u., $B^* = -1.923 \times 10^{-10}$ cm^2, and $C^* = 6.924 \times 10^{-20}$ cm^4 (one atomic unit equals 6.23538×10^{-65} C^{4}m^{4}J^{-3} for γ). The curve for γ_{Ne} has a minimum of 100.4 a.u. at $v_L^2 = 13.9 \times 10^8$ cm^{-2} ($\omega = 0.069$ a.u. for ESHG).

theoretical possibility of such an observation. The expression for γ derived by means of quantum-mechanical perturbation theory by Orr and Ward[3] contains two groups of terms, where each term is the product of four dipole transition matrix elements divided by the product of three frequency differences.[3,9,13] The first group of terms involves sequences of transitions $g \rightarrow m \rightarrow n \rightarrow p \rightarrow g$, where g is the ground state and m, n, and p are excited states. The second group of terms, which is subtracted from the first group, involves sequences $g \rightarrow m \rightarrow g \rightarrow n \rightarrow g$. In order that γ be positive while its dispersion is negative, a fine balance between these two groups of terms must be struck. The two groups of terms must partially cancel, with the first group having a larger magnitude and the second group having a larger dispersion. Consideration of the explicit dispersion formulas given by Bishop for atoms[9] shows that such a balance is possible, but that the near complete cancellation

required should make γ itself anomalously small. Evidence that γ for Ne actually is anomalously small compared to γ for other atoms and molecules is provided by the study of a recently proposed scaling law for hyperpolarizabilities.[2,3] The experimental results for fifteen other atoms and molecules are found to agree with the predictions of this scaling law, whereas the experimental result for Ne is 5 times smaller than predicted.

To better understand the origin of the negative dispersion seen for γ_{Ne} we may study the results of *ab initio* calculations.[24-32] Most calculations have been done within the self-consistent-field Hartree-Fock (SCF-HF) approximation and also in the static limit. The calculated static values of γ_{Ne} for the SCF calculations fall in the range 42-84 a.u.[24-30] The HF limit probably lies near 70 a.u.[15,32] The two SCF calculations which have considered dispersion give a monotonically increasing function for γ_{Ne}.[26,27] Electron-correlation effects, which are not included in the HF approximation, have been addressed by a static many-body perturbation-theory (MBPT) calculation of γ_{Ne},[31] and also by a more recent coupled-clusters-doubles (CCD) calculation which takes better account of correlations and uses a better basis set.[32] The MBPT calculation (complete to fourth order in the electron-correlation perturbation but still incompletely converged) gives $\gamma_{Ne} = 105$ a.u., which is only 10% smaller than the present experimental result of 116 ± 2 a.u. The CCD calculation gives $\gamma_{Ne} = 114 \pm 9$ a.u., in excellent agreement with the present experimental result. Thus, it appears that a calculation of γ_{Ne} at the HF limit accounts for only 60% of the total γ_{Ne}, and the rest must be attributed to the electron-correlation contribution. Furthermore, since negative dispersion does not arise in the SCF calculations, it seems as though the negative dispersion is in some way due to the electron correlations. It would be most interesting to see whether a calculation including correlation effects can correctly account for the negative dispersion of γ_{Ne}.

If Ne is typical of multielectron atoms and molecules, then one should not expect HF calculations to give reliable results for γ. But is Ne typical? The electron-correlation contribution is 40% of γ_{Ne}, while for the He atom it is only 16% of the total.[15] An indication that the size of the correlation contribution seen for γ_{Ne} may in fact be typical of the correlation contributions for other multielectron atoms and molecules comes from recent calculations for the Ar atom[33] and the F_2 molecule[34] which estimate the correlation contributions to γ as 25% and 50% of the total, respectively. The trend of these results for the correlation contributions to γ is qualitatively similar to that seen previously for the correlation contributions to the linear polarizability α for F, Ne, and Ar atoms.[35]

In summary, we have found that the dispersion curve for γ_{Ne} is not monotonic. Consequently our extrapolation to the static limit of γ_{Ne} differs markedly from the estimate made in a previous publication based on incomplete data and radically alters most of the conclusions reached therein.[15] It is now apparent that the electron-correlation contribution to γ_{Ne} is very large, and that it can be accurately calculated by MBPT or CCD techniques, at least in the static limit. The present experimental estimate of the static value of γ_{Ne} is probably reliable to about $\pm 2\%$. Further experimental and theoretical investigations of γ_{Ne} are clearly indicated to confirm and refine the present observations, and to help determine the implications for calculations of γ for other atoms and molecules.

[1]Y. R. Shen, *Principles of Nonlinear Optics* (Wiley, New York, 1984).

[2]M. P. Bogaard and B. J. Orr, in *International Review of Science, Physical Chemistry, Molecular Structure and Properties*, edited by A. D. Buckingham (Butterworths, London, 1975), Ser. 2, Vol. 2, p. 149.

[3]B. J. Orr and J. F. Ward, Mol. Phys. **20**, 513 (1971).

[4]N. Bloembergen, H. Lotem, and R. T. Lynch, Ind. J. Pure Appl. Phys. **16**, 151 (1978).

[5]Y. Prior, IEEE J. Quantum Electron. **20**, 37 (1984).

[6]D. S. Elliott and J. F. Ward, Mol. Phys. **51**, 45 (1984).

[7]D. P. Shelton, Phys. Rev. A **36**, 3032 (1987).

[8]D. M. Bishop and B. Lam, Phys. Rev. A **37**, 464 (1988).

[9]D. M. Bishop, Phys. Rev. Lett. **61**, 322 (1988); D. M. Bishop, Chem. Phys. Lett. **153**, 441 (1988).

[10]D. C. Hanna, M. A. Yuratich, and D. Cotter, *Nonlinear Optics of Free Atoms and Molecules* (Springer-Verlag, Berlin, 1979).

[11]T. Lundeen, S.-Y. Hou, and J. W. Nibler, J. Chem. Phys. **79**, 6301 (1983).

[12]V. Mizrahi and D. P. Shelton, Phys. Rev. A **32**, 3454 (1985).

[13]D. P. Shelton, J. Chem. Phys. **84**, 404 (1986).

[14]D. P. Shelton, Phys. Rev. A **34**, 304 (1986).

[15]D. P. Shelton and Z. Lu, Phys. Rev. A **37**, 3813 (1988).

[16]D. P. Shelton (unpublished).

[17]A. D. Buckingham and D. A. Dunmur, Trans. Faraday Soc. **64**, 1776 (1968).

[18]R. S. Finn and J. F. Ward, Phys. Rev. Lett. **26**, 285 (1971).

[19]H. J. Lehmeier, W. Leupaucher, and A. Penzkofer, Opt. Commun. **56**, 67 (1985).

[20]J. F. Ward and G. H. C. New, Phys. Rev. **185**, 57 (1969).

[21]D. P. Shelton and V. Mizrahi, Phys. Rev. A **33**, 72 (1986).

[22]M. G. Papadopoulos and J. Waite, Chem. Phys. Lett. **135**, 361 (1987); D. P. Shelton, Phys. Rev. A **36**, 3461 (1987).

[23]D. P. Shelton, in *Topical Meeting on Nonlinear Optical Properties of Materials*, 1988 Technical Digest Series, Vol. 9 (Optical Society of America, Washington, 1988), p. 16; D. P. Shelton, J. Opt. Soc. Am. B **6**, 830 (1989).

[24]H. D. Cohen, J. Chem. Phys. **45**, 10 (1966).

[25]R. E. Sitter and R. P. Hurst, Phys. Rev. A **5**, 5 (1972).

[26]E. Leuliette-Devin and R. Locqueneux, Chem. Phys. Lett.

19, 497 (1973).

[27]R. Klingbeil, Phys. Rev. A **7**, 376 (1973).

[28]T. Voegel, J. Hinze, and F. Tobin, J. Chem. Phys. **70**, 1107 (1979).

[29]P. Dacre, Can. J. Phys. **60**, 963 (1982).

[30]G. Maroulis and D. M. Bishop, Chem. Phys. Lett. **114**, 182 (1985).

[31]I. Cernusak, G. H. F. Diercksen, and A. J. Sadlej, Phys. Rev. A **33**, 814 (1986).

[32]G. Maroulis and A. J. Thakkar, Chem. Phys. Lett. **156**, 87 (1989).

[33]I. Cernusak, G. H. F. Diercksen, and A. J. Sadlej, Chem. Phys. Lett. **128**, 18 (1986).

[34]G. Maroulis and A. J. Thakkar, J. Chem. Phys. **90**, 366 (1989).

[35]E.-A. Reinsch and W. Meyer, Phys. Rev. A **14**, 915 (1976).