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# Measurements of nonlinear optical polarizabilities for twelve small molecules

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Second- and third-order nonlinear optical polarizabilities for a number of small molecules— $H_2$, $N_2$, $O_2$, CO, NO, $CO_2$, $H_2O$, $H_2S$, $NH_3$, $SF_6$, $(CH_3)_2O$, and $CH_3OH$—are derived from measurements of the temperature dependence of dc-electric-field-induced optical second-harmonic generation in the gas phase. Agreement with related measurements (where available) is generally adequate, but the results of theoretical calculations taken from the literature are in poor agreement with the experimental data. Consideration of the present results for $H_2O$ together with liquid-phase measurements by Levine and Bethea offers a means of investigating intermolecular interactions in liquid water. The bond-additivity approximation applied to $H_2O$, $(CH_3)_2O$, and $CH_3OH$ yields surprisingly good fits of the dipole moment, linear polarizabilities, and second- and third-order nonlinear polarizabilities to experimental data.

## I. INTRODUCTION

We have measured second- and third-order molecular electric polarizabilities (hyperpolarizabilities) for a number of small molecules. The hyperpolarizabilities are deduced from studies of the temperature dependence of dc-electric-field-induced optical second-harmonic generation (dcSHG) in gases or vapors of the molecules at temperatures up to 250 °C, and intermolecular interactions are unimportant.

The data are compared with results of various other experiments in both gases and liquids, and with values from molecular orbital calculations. Points of interest are discussed for several of the molecules, including application of the bond-additivity approximation (BAA) to correlation of dipole electric tensor properties of a subset of them. Notation is similar to that of Ref. 1, and is reviewed briefly here.

Molecules in a gas subjected to a dc electric field and an optical electric field at frequency $\omega$ develop an induced dipole moment at the second-harmonic frequency. The average induced dipole moment amplitude per molecule $\bar{p}^{2\omega}$ may be written

$$\bar{p}_F^{2\omega} = \tfrac{3}{2}\chi^e_{FGHM}(-2\omega;0,\omega,\omega)E_G^0E_H^\omega E_M^\omega, \tag{1}$$

where $\chi^e_{FGHM}(-2\omega;0,\omega,\omega)$ is an effective molecular hyperpolarizability, the $E$'s are electric-field amplitudes at frequencies indicated by superscripts, and $F$, $G$, $H$, $M$ stand for $X$, $Y$, or $Z$ in the laboratory coordinate frame. These hyperpolarizabilities are subject to symmetry restrictions appropriate to the macroscopic isotropy of the gas.[2] We designate $FGHM = YYYY$ by $\parallel$ and $FGHM = YYXX$ by $\perp$, referring to components measured with optical field respectively parallel to and perpendicular to the dc field; there are no other independent components. The effective hyperpolarizability includes, in addition to the intrinsic molecular third-order polarizability, a contribution from the second-order polarizability. This additional term is nonzero in the case of molecules with permanent electric dipole moments ($\mu$) which undergo temperature-dependent partial alignment by the dc field. The two contributions can be written explicity for both $\parallel$ and $\perp$ geometries

$$\chi^e_{\parallel,\perp} = \chi^{(3)}_{\parallel,\perp}(-2\omega;0,\omega,\omega) + (\mu/9kT)\chi^{(2)}_{\parallel,\perp}(-2\omega;\omega,\omega), \tag{2}$$

where each of these laboratory-frame hyperpolarizabilities is an orientational average of molecular hyperpolarizabilities

$$\chi^{(3)}_{\parallel}(-2\omega;0,\omega,\omega) = \langle\Phi_{Yi}\Phi_{Yj}\Phi_{Yk}\Phi_{Yl}\rangle \times\chi^{(3)}_{ijkl}(-2\omega;0,\omega,\omega), \tag{3}$$

$$\chi^{(3)}_{\perp}(-2\omega;0,\omega,\omega) = \langle\Phi_{Yi}\Phi_{Yj}\Phi_{Xk}\Phi_{Xl}\rangle \times\chi^{(3)}_{ijkl}(-2\omega;0,\omega,\omega), \tag{4}$$

$$\mu\chi^{(2)}_{\parallel}(-2\omega;\omega,\omega) = 3\langle\Phi_{Yi}\Phi_{Yz}\Phi_{Yk}\Phi_{Yl}\rangle \times\mu_z\chi^{(2)}_{ikl}(-2\omega;\omega,\omega), \tag{5}$$

$$\mu\chi^{(2)}_{\perp}(-2\omega;\omega,\omega) = 3\langle\Phi_{Yi}\Phi_{Yz}\Phi_{Xk}\Phi_{Xl}\rangle \times\mu_z\chi^{(2)}_{ikl}(-2\omega;\omega,\omega), \tag{6}$$

where each of $i$, $j$, $k$, $l$, can stand for $x$, $y$, or $z$ in the molecular coordinate frame. The sign of $\mu\chi^{(2)}_{\parallel}$ is unambiguously determined by the experiment and is independent of the sense chosen for the $z$ axis. We further *ascribe* to $\chi^{(2)}_{\parallel}$ the sign *measured* for $\mu\chi^{(2)}_{\parallel}$ which implies that the sense of the molecular $z$ axis has been chosen to be along the permanent dipole moment. The expressions in angular brackets in Eqs. (3)–(6) are isotropic averages of products of direction cosines which have been tabulated by Cyvin *et al.*[3] Details of conventions used here in defining molecular hyperpolarizabilities are discussed in Refs. 4 and 5. The apparatus and experiments are discussed briefly in Sec. II, and the results are presented in Sec. III.

## II. EXPERIMENTAL

The experimental apparatus has been described in detail previously.[1,6] Basically, the beam from a 1-MW pulsed, $Q$-switched ruby laser is focused in the gas of density $\rho_{\text{opt}}$ in the presence of a dc electric field $\vec{E}_0$ produced by electrodes at potential difference $V_0$. The dipoles induced at the second-harmonic frequency radiate coherently,[7] and this second-harmonic light is detected by a photomultiplier and associated electronics to produce a voltage $V_S$ proportional to the second-harmonic intensity. A portion of the ruby laser beam is reflected through a quartz crystal, and the second-harmonic so generated is similarly detected to yield a voltage $V_M$ which serves as a monitor of fundamental beam intensity. A quantity $S$ (called the "signal") is then defined in terms of measured quantities

$$S \equiv V_S/(V_M V_0^2). \tag{7}$$

It can be shown (see Ref. 8) that with the gas density adjusted to yield maximum harmonic, the hyperpolarizability is related to the signal by

$$S = (\text{const}) \times |\chi^e/\Delta k_0|^2, \tag{8}$$

where $\chi^e$ is $\chi_\parallel^e$ or $\chi_\perp^e$ depending on the polarization of the incident laser beam relative to $\vec{E}_0$, and the constant is independent of the gas used. $\Delta k_0$ is a measure of the optical dispersion of the gas and is related to the wave vectors for the fundamental, $k_0^\omega$, and harmonic, $k_0^{2\omega}$, by

$$\Delta k_0 = 2k_0^\omega - k_0^{2\omega}. \tag{9}$$

The subscripts zero here indicate quantities evaluated for a gas at a molecular number density of Loschmidt's number per cm$^3$. The data are derived from the results of several different experiments described in Ref. 6. These experiments are described briefly now.

### A. $|\chi_\parallel^e|$

The signal $S$ is measured at a single temperature with the gas of interest in the cell at density $\rho_{\text{opt}}$ and with the optical electric field parallel to $\vec{E}_0$. Such measurements are alternated with measurements of $S$ with helium in the cell. Equation (8) is then used to determine the ratio of $|\chi_\parallel^e|$ for the gas to that of helium. The coefficient is then put on an absolute scale by using the value for helium calculated by Sitz and Yaris,[9] which is thought to be good to 1%;

$$\chi_\parallel^e = \chi_\parallel^{(3)}(-2\omega; 0, \omega, \omega) = 3.79 \times 10^{-39} \text{ esu/atom}. \tag{10}$$

### B. Sign of $\chi_\parallel^e$

The relative signs of $\chi_\parallel^e$ for two gases can be determined by measuring $|\chi_\parallel^e|$ for mixtures of the gases.[8] In particular, if the coefficients are of opposite sign, cancellation will lead to zero signal for a mixture of appropriate proportions. The absolute sign can be determined by using the (positive) sign of the calculated value for helium[9] or, with equivalent result, by assuming that the experimentally determined (positive) sign of the Kerr coefficient for argon[10] is the same as that of the dcSHG coefficient.

### C. $\chi_\perp$

Information about the perpendicular components of hyperpolarizabilities is obtained by first carefully measuring the ratio

$$R^e = \chi_\parallel^e/\chi_\perp^e \tag{11}$$

at a single temperature. The technique involves measuring $S$ at various relative orientations of optical and dc fields, and is described in Ref. 11. Second, relative measurements of $S$ are made at several temperatures (for polar molecules) with fixed density of gas, and with the optical field both parallel and perpendicular to the dc field. Finally, these measurements combined with $\chi_\parallel^e$ obtained in $A$ and $B$ above yield, by means of Eq. (2), the quantities $\chi_{\parallel,\perp}^{(3)}$ and $\chi_{\parallel,\perp}^{(2)}$. Rather than expressing our results in terms of $\chi_\perp^{(3)}$ and $\chi_\perp^{(2)}$ directly, we have found it convenient to deal with $\chi_\parallel^{(3)}$ and $\chi_\parallel^{(2)}$, and with the ratios $R^{(3)}$ and $R^{(2)}$, defined by

$$R^{(3)} = \chi_\parallel^{(3)}/\chi_\perp^{(3)}, \tag{12}$$

$$R^{(2)} = \chi_\parallel^{(2)}/\chi_\perp^{(2)}. \tag{13}$$

If there is no dispersion (dependence of $\chi$ on the frequencies involved) of $\chi^{(3)}$ or $\chi^{(2)}$, then as a result of Eqs. (3)–(6), $R^{(3)}$ or $R^{(2)}$, respectively, will be identically equal to 3.0. Thus, it is the deviation of these quantities from 3.0 which is of interest.

### D. $\Delta k_0$

The wave-vector mismatch $\Delta k_0$, defined by Eq. (9), is required for determination of the optimum density $\rho_{\text{opt}}$ for maximum harmonic generation, as well as for deducing hyperpolarizability ratios from signal ratios using Eq. (8). This quantity is determined by studying the interference between harmonic generated in two quartz plates as the density of experimental gas is changed in a cell located between the plates. The procedure is described in Ref. 12; however, in our measurements, account is taken of the nonideal nature of the gases.

## III. RESULTS

Experimental parameters and data for the molecules lacking a permanent electric dipole moment are displayed in Table I. The values of $E_0$ are typical dc field strengths on the axis of the laser beam between the electrodes. Wave-vector mismatches $\Delta k_0$ were obtained from our experimental data with the aid of the virial data referenced in the table. $\chi_\parallel^e$ and $R^e$ were measured at room temperature (~ 20 °C) and at optimum density $\rho_{\mathrm{opt}}$. Measurement at other temperatures was unnecessary since $\chi_{\parallel,\perp}^e$ do not depend on temperature for these molecules. The uncertainties listed for $\Delta k_0$, $\chi^e$, and $R^e$ are standard deviations.

Similar parameters and data for the polar molecules are presented in Table II. The temperature $T_0$ at which $R^e$ was measured is also listed for each molecule. In addition, since $\chi_{\parallel,\perp}^e$ are functions of temperature, their slopes with respect to $T^{-1}$ and their infinite-temperature limits are indicated. In the cases of CO, NO, and $H_2S$, there was insufficient signal to allow statistically meaningful measurements of $\chi_\perp^e$; however, $R^e$ did not differ significantly from 3.0 at room temperature, so there was no evidence of unusual behavior of $\chi_\perp^e$ (see discussion of $NH_3$ in Sec. IV).

TABLE I. Experimental parameters—dc electric field $E_0$ and optimum density $\rho_{\mathrm{opt}}$ in units of Loschmidt's number per cm$^3$—and experimental data on dispersion and hyperpolarizabilities as discussed in the text, for molecules lacking a permanent electric dipole moment.

| | $E_0$ (esu) | $\rho_{\mathrm{opt}}$ | $-\Delta k_0$ [a] (cm$^{-1}$) | $10^{39}\chi_\parallel^e$ (esu) | $R^e$ |
|---|---|---|---|---|---|
| $H_2$ | 35 | 2.97 | $1.27\pm0.01$ | $65.2\pm0.8$ | $2.86\pm0.03$ |
| $N_2$ | 36 | 1.86 | $1.89\pm0.02$ | $86.6\pm1.0$ | $3.00\pm0.06$ |
| $O_2$ | 48 | 1.46 | $2.41\pm0.02$ | $95.3\pm1.6$ | $2.97\pm0.07$ |
| $CO_2$ | 43 | 1.05 | $3.36\pm0.03$ | $111.9\pm1.3$ | $2.81\pm0.06$ |
| $SF_6$ | 58 | 1.08 | $3.47\pm0.03$ | $130\ \ \pm2$ | $2.97\pm0.07$ |

[a] Using virial data from: Reference 13 ($H_2$, $N_2$, $O_2$); K. E. MacCormack and W. G. Schneider, J. Chem. Phys. 18, 1269 (1950) ($CO_2$); and H. P. Clegg, J. S. Rowlinson, and J. R. Sutton, Trans. Faraday Soc. 51, 1327 (1955) ($SF_6$).

Values of $\chi_\parallel^{(3)}$ and $R^{(3)}$ for both polar and nonpolar molecules, as derived from the experimental data, are shown in Table III, along with results from other gas-phase experiments and with available theoretical estimates. $R^{(3)}$ values do not differ significantly from 3.0, which implies that there is negligible dispersion of $\chi_{ijkl}^{(3)}(-2\omega; 0, \omega, \omega)$. The other experimental gas-phase $\chi_\parallel^{(3)}$ data are from other dcSHG experiments and from three-wave mixing (TWM), Kerr effect, and third-harmonic generation (THG) experiments. These data tend to be slightly larger in magnitude than our values, but not unreasonably so in view of experimental uncertainties and the likelihood of small differen-

TABLE II. Experimental parameters—dc electric field $E_0$, temperature $T_0$, and optimum density $\rho_{\mathrm{opt}}$ in units of Loschmidt's number per cm$^3$—and experimental data on dispersion and hyperpolarizabilities as discussed in the text, for molecules possessing a permanent electric dipole moment.

| | $E_0$ (esu) | $T_0$ (°K) | $\rho_{\mathrm{opt}}$ | $-\Delta k_0$ [a] (cm$^{-1}$) | $10^{39}\lim_{T^{-1}\to 0}\chi_\parallel^e$ (esu) | $10^{36}\frac{d\chi_\parallel^e}{dT^{-1}}$ (esu °K) | $R^e(T_0)$ | $10^{39}\lim_{T^{-1}\to 0}\chi_\perp^e$ [b] (esu) | $10^{36}\frac{d\chi_\perp^e}{dT^{-1}}$ [b] (esu °K) |
|---|---|---|---|---|---|---|---|---|---|
| CO | 43 | 293 | 1.05 | $3.35\pm0.03$ | $144\pm\ 4$ | $+11.6\pm\ 1.2$ | $2.94\pm0.03$ | ⋯ | ⋯ |
| NO | 23 | 293 | 1.29 | $2.72\pm0.03$ | $235\pm\ 7$ | $+18.8\pm\ 2.2$ | $3.24\pm0.06$ | ⋯ | ⋯ |
| $H_2S$ | 29 | 293 | 0.36 | $9.73\pm0.10$ | $865\pm22$ | $-34\ \ \pm\ 7$ | $2.82\pm0.04$ | ⋯ | ⋯ |
| $NH_3$ | 31 | 293 | 0.65 | $5.40\pm0.05$ | $511\pm\ 9$ | $-248\ \ \pm\ 5$ | $2.41\pm0.06$ | $161\pm\ 6$ | $-88\pm4$ |
| $H_2O$ | 23 | 419 | 1.53 | $2.44\pm0.02$ | $194\pm10$ | $-141\ \ \pm\ 5$ | $3.40\pm0.07$ | $60\pm12$ | $-45\pm5$ |
| $(CH_3)_2O$ | 21 | 293 | 0.40 | $8.92\pm0.09$ | $529\pm11$ | $-302\ \ \pm\ 5$ | $3.07\pm0.04$ | $177\pm\ 9$ | $-100\pm4$ |
| $CH_3OH$ | 40 | 393 | 0.73 | $5.02\pm0.07$ | $385\pm11$ | $-207\ \ \pm12$ | $2.98\pm0.06$ | $132\pm\ 9$ | $-71\pm4$ |

[a] Using virial data from: S. H. Maron and D. Turnbull, Ind. Eng. Chem. 33, 408 (1941) ($H_2S$); J. S. Rowlinson, Trans. Faraday Soc. 45, 974 (1949) ($NH_3$); R. M. Kennedy, M. Sagenkahn, and J. G. Aston, J. Am. Chem. Soc. 63, 2267 (1941) [$(CH_3)_2O$]; E. P. Bartlett, H. C. Hetherington, H. K. Kvalnes, and T. H. Tremearne, J. Am. Chem. Soc. 52, 1374 (1930) (CO); Ref. 13 (NO); and L. S. Marks and H. N. Davis, *Tables and Diagrams of the Thermal Properties of Saturated and Superheated Steam* (Longmans, Green and Co., New York, 1929) ($H_2O$).

[b] Measurement of these quantities for $H_2S$, CO, and NO was impractical because of insufficient signal, as discussed in the text.

TABLE III. $R^{(3)}$ and $\chi_{\parallel}^{(3)}$ in units of $10^{-39}$ esu/molecule. Values from other dc-electric-field induced second-harmonic generation (dcSHG), three-wave mixing (TWM), Kerr effect, and third-harmonic generation (THG) experiments, along with theoretical results, are included for comparison.

| | | | Other $\chi_{\parallel}^{(3)}$ data | | | | |
|---|---|---|---|---|---|---|---|
| | $R^{(3)}$ | $\chi_{\parallel}^{(3)}$ | dcSHG [a] | TWM [b] | Kerr | THG [c] | Theory |
| $H_2$ | 2.86<br>±0.03 | 65.2<br>±0.8 | 79 | | 47 [d]<br>±5 | 80<br>±12 | 34 [e] |
| $N_2$ | 3.00<br>±0.06 | 86.6<br>±1.0 | | 104 | 120 [f]<br>±10 | 107<br>±17 | 71 [g] |
| $O_2$ | 3.12<br>±0.07 | 95.3<br>±1.6 | 110 | 100 | | | |
| $SF_6$ | 2.97<br>±0.07 | 130<br>±2 | 200 | 192 | 200 [h]<br>±20 | | |
| $CO_2$ | 2.81<br>±0.08 | 111.9<br>±1.3 | | 192 | 750 [f]<br>±160 | 156<br>±23 | |
| CO | 2.92 [i]<br>±0.15 | 144<br>±4 | | 138 | | | |
| NO | 3.32 [i]<br>±0.15 | 235<br>±7 | | 322 | | | |
| $H_2S$ | 2.84 [i]<br>±0.11 | 865<br>±22 | | | | | |
| $NH_3$ | 3.19<br>±0.11 | 511<br>±9 | | | | | |
| $H_2O$ | 2.94<br>±0.55 | 194<br>±10 | | | | | |
| $(CH_3)_2O$ | 2.99<br>±0.15 | 529<br>±11 | | | | | |
| $CH_3OH$ | 2.90<br>±0.21 | 385<br>±11 | | | | | |

[a] Data from G. Mayer, C. R. Acad. Sci. B 276, 54 (1968) and G. Hauchecorne, F. Kerhervé, and G. Mayer, J. Phys. (Paris) 32, 47 (1971), normalized using the dcSHG coefficient for argon from Ref. 14.

[b] Data from W. G. Rado, Phys. Lett. 11, 123 (1967), normalized using the dcSHG coefficient for argon from Ref. 14.

[c] Reference 4.

[d] A. D. Buckingham and B. J. Orr, Proc. R. Soc. (Lond.) A 305, 259 (1968).

[e] $\chi_{zzzz}(0;0,0,0)$ from Ref. 16.

[f] Reference 15.

[g] $\chi_{zzzz}(0;0,0,0)$ from Ref. 17.

[h] Reference 10.

[i] Derived assuming $R^{(2)} = 3.0 \pm 0.3$.

ces due to dispersion. A possible exception is $\chi^{(3)}$ for $CO_2$, for which the Kerr effect measurement by Buckingham *et al.*[15] is four times larger than other values, whereas their data for $N_2$ and $SF_6$ agree acceptably with ours and those of other workers.

The theoretical values of $\chi_{\parallel}^{(3)}$ listed for $H_2$ and $N_2$ are the molecular $\chi_{zzzz}(0;0,0,0)$ only. The value for $N_2$ is preliminary and it is anticipated[17] that the calculation will be refined and extended to the other components of $\chi_{ijkl}$ for $N_2$ and other molecules investigated here and in Ref. 1.

Values for $\chi^{(2)}$ and $R^{(2)}$, as derived from our experimental data using values from the literature for permanent electric dipole moments, are shown in Table IV. Also shown are available theoretical results and a single other experimental value, a dcSHG measurement in liquid $H_2O$, which is discussed in Sec. IV. The theoretical values are all from molecular orbital calculations, and are classified broadly according to computational scheme, either "semiempirical" (SE), uncoupled Hartree-

TABLE IV. $R^{(2)}$ and $\chi_{\parallel}^{(2)}$ in units of $10^{-33}$ esu/molecule. Theoretical values from various molecular orbital calculations—semiempirical (SE), uncoupled Hartree-Fock (HF), and coupled Hartree-Fock (CHF)—and a single other experimental value are included for comparison. The sign of $\mu\chi_{\parallel}^{(2)}$ is unambiguously determined by the experiment and is independent of the sense chosen for the molecular $z$ axis. We further *ascribe* to $\chi_{\parallel}^{(2)}$ the sign *measured* for $\mu\chi_{\parallel}^{(2)}$ which implies that the sense of the molecular $z$ axis has been chosen to be along the permanent dipole moment. In order to present a calculated $\chi_{\parallel}^{(2)}$ with sign appropriate to this convention it is necessary to know, in addition, the direction of the permanent dipole moment (and therefore of the $z$ axis) with respect to the molecular structure. The dipole moment lies along the molecular symmetry axis in each case (see Table V for $CH_3OH$) in the sense indicated in the first column.[a]

| | | | | Theory | | | Other |
|---|---|---|---|---|---|---|---|
| | $\mu$[a] | $R^{(2)}$ | $\chi_{\parallel}^{(2)}$ | SE | HF | CHF | expt. |
| $C^-O^+$ | 0.112 ±0.005 | ··· | +129±14 | −43.5[b]<br>(+95)[d] | +879[c]<br>+420[c]<br>+387[c]<br>−438[e] | | |
| $N^-O^+$ | 0.158 72±0.000 02 | ··· | +147±17 | +47.7[b] | | | |
| $H_2{}^+S^-$ | 0.974 ±0.005 | ··· | −43± 9 | | | | |
| $N^-H_3{}^+$ | 1.474 ±0.009 | 2.82±0.08 | −209± 5 | 56.4[b] | | −44.4[f]<br>−65.1[f]<br>−19.0[f]<br>−15.6[h]<br>−40.8[h] | −3500[g] |
| $H_2{}^+O^-$ | 1.86 ±0.02 | 3.12±0.38 | −94± 4 | 120[b] | +90.6[e] | −52.5[f]<br>−79.2[f]<br>−21.9[f]<br>−51.6[h]<br>−48.0[h] | |
| $(CH_3)_2{}^+O^-$ | 1.307 ±0.010 | 3.02±0.10 | −287± 5 | | | | |
| $(CH_3)^+O^-H^+$ | 1.71 ±0.02 | 2.92±0.18 | −150± 9 | | | | |

[a] Electric dipole moments in Debye units from Landolt-Bernstein, Zahlenwerte und Funktionen, Neue Serie, Vols. II/4 and II/6 (Springer-Verlag, Berlin) and Ref. 18. The sense of the NO moment is suggested by F. P. Billingsley II, J. Chem. Phys. 63, 2267 (1975); 62, 864 (1975).

[b] N. S. Hush and M. L. Williams, Theoret. Chim. Acta (Berlin) 25, 346 (1972). Signs for $NH_3$ and $H_2O$ are ambiguous.

[c] Reference 19.

[d] $\chi_{zzz}^{(2)}(0;0,0)$ from Ref. 16.

[e] S. P. Liebmann and J. W. Moskowitz, J. Chem. Phys. 54, 3622 (1971).

[f] Reference 20. *Note added in proof.* Recent reconsideration of the sign of these entries yields the negative signs now shown here—P. Lazzeretti (private communication). Overall consistency is substantially improved by this change.

[g] Refractivity virial data from A. R. Blythe, J. D. Lambert, P. J. Petter, and H. Spoel, Proc. R. Soc. (Lond.) A 255, 427 (1960).

[h] Reference 21.

Fock (HF), or coupled Hartree-Fock (CHF). We make no attempt to ascertain the relative merits of these methods, but merely note that wide discrepancies in magnitude, and even differences in sign, occur among the results of different authors using various techniques of calculation. In $H_2O$, for example, the theoretical results for $10^{33}\chi_{\parallel}^{(2)}$ range from −79 to + 90 esu, and in CO they include −44 and + 880 esu. In addition, results by the same author vary considerably depending on the number and nature of basis functions used.[19-21] Whereas our experimental data have uncertainties of 21% in the worst case and 3%–12% in the rest, no set of magnitudes calculated by any one group of authors comes consistently within a factor of 3 of the experimental results and only for $H_2O$ do individual calculated values come closer than a factor of 2. We conclude that the calculations are not yet adequate.

## IV. DISCUSSION

Several molecules or groups of molecules which warrant further discussion are now considered in turn.

### A. $NH_3$

The permanent electric dipole moment for ammonia appearing in Table IV is that of the static pyramidal configuration. The ground state of $NH_3$ is inversion split[22] by the energy $\epsilon$ corresponding to the frequency of tunneling of the N atom through the center of the triangle formed by the three H nuclei. However, it can be shown that for

$$\epsilon^2/(kT)^2 \ll 1 \tag{14}$$

ammonia behaves like a gas of ordinary polar molecules for the purposes of these experiments. In the range of temperatures used here, the value of $\epsilon^2/(kT)^2$ is less than $2\times10^{-5}$, so the inequality (14) is well satisfied. The fact that $\chi^e$ for ammonia is a linear function of $T^{-1}$ is evidence of its ordinary behavior.

For ammonia the deviations of $R^e$, $R^{(3)}$, and $R^{(2)}$ from 3 are among the largest and most significant for any molecule in this group (see Tables II–IV). The ratio $R^{(3)}/R^{(2)} = 1.13 \pm 0.02$ is more directly derivable from the measurements, has a smaller fractional uncertainty and emphasizes that $R^{(3)}$ or $R^{(2)}$ or both deviate significantly from 3. This deviation is related to dispersion and demonstrates the presence of dispersion in the corresponding hyperpolarizability.

### B. $H_2O$

The other experimental value of $\chi^{(2)}$ for $H_2O$ listed in Table IV is due to measurements by Levine and Bethea[23] of $\chi_\parallel^e$ in liquid water and in water-methanol and water-dioxane solutions by the method of dcSHG in the liquid phase. Because the contributions of intermolecular interactions to the dielectric properties of strongly associating liquids are not well understood, Levine and Bethea were not able to extract precise isolated-molecule values of $\chi_\parallel^{(2)}$ and $\chi_\parallel^{(3)}$ for water from their data. By postulating a simple phenomenological model of the interactions, however, they arrive at the following expression for $\chi_S^{(2)}$, the second-order polarizability per molecule of water in solutions:

$$\chi_S^{(2)} = (\chi_\parallel^{(2)} + \chi_{\text{hb}}^{(2)}) + \chi_{\text{dip}}^{(2)}(1-g). \tag{15}$$

The terms in Eq. (15) are defined as follows: $\chi_\parallel^{(2)}$ is the value for an isolated molecule (corresponding to our gas-phase value); $\chi_{\text{hb}}^{(2)}$ is the second-order nonlinearity due to intermolecular hydrogen bonding among water and solvent molecules; $\chi_{\text{dip}}^{(2)}$ is the effective second-order polarizability induced in the molecule by the action on the molecular $\chi^{(3)}$ of the average electric field from the permanent dipole moments of the surrounding molecules; and $g$ is the Kirkwood-Frölich correlation parameter,[24] having to do with short-range molecular alignment. These authors derive values of $\chi_S^{(2)}$ from their data using an estimate for the gas-phase value of $\chi_\parallel^{(3)}$ consistent with our measured value. They calculate values of $g$ for liquid mixtures on the basis of data on the static dielectric constants of such mixtures. Their derived values of $\chi_S^{(2)}$ range from about $\frac{1}{2}$ to $\frac{1}{8}$ of our $\chi_\parallel^{(2)}$ value, and they find that in this range, $\chi_S^{(2)}$ varies approximately as $(1-g)$. This behavior, along with Eq. (15), implies that for a water molecule in these solutions

$$\chi_\parallel^{(2)} + \chi_{\text{hb}} = 0 \tag{16}$$

to within the broad uncertainty limits of the data and the model. Such a cancellation would be interesting, since it would suggest that hydrogen bonding might cause H and O atoms to be arranged with a higher degree of short-range symmetry than that of the water molecule. For example, an O atom might be surrounded by four H atoms in $T_d$ symmetry, while an H atom could be situated between two O atoms in $C_{\infty v}$ symmetry. The value of $\chi_\parallel^{(2)}$, as defined by Eq. (5), is identically zero for both of these symmetries.[2]

### C. $H_2O$, $(CH_3)_2O$, and $CH_3OH$

*Ab initio* calculations of molecular electric tensor properties are notoriously difficult, as evidenced by the wide discrepancies among the results of various molecular orbital calculations for second- and third-order polarizabilities cited earlier. As a result, semiempirical correlation schemes are often employed in an attempt to relate the dipole electric tensor properties (dipole moment $\vec{\mu}$, linear polarizability $\vec{\alpha}$, hyperpolarizabilities $\vec{\chi}^{(2)}$, $\vec{\chi}^{(3)}, \ldots$) among molecules of similar structure. The most popular of these schemes is the bond-additivity approximation,[25] in which the $i$th bond or structural group of a molecule is ascribed the tensor properties $\vec{\chi}_i^{(n)}$, $n = 0, 1, \ldots$, with $\vec{\chi}_i^{(0)}$ being the electric dipole moment, $\vec{\chi}_i^{(1)}$ the linear polarizability, and so on. The corresponding tensors for the molecule are then given by the sums of the respective bond tensors:

$$\vec{\chi}^{(n)\prime} = \sum_i \vec{\chi}_i^{(n)}. \tag{17}$$

The bond tensors are assumed to be noninteracting and transferable from molecule to molecule. Application of the BAA has provided good results for the isotropic part of the linear polarizability[26] and for $\chi^{(3)}$ of a set of halogenated methanes.[6] However, BAA yields a poor fit to $\vec{\mu}$ (Ref. 27) and to $\chi_\parallel^{(2)}$ (Refs. 1,6) for the halogenated methanes. The set of molecules $H_2O$, $(CH_3)_2O$, and $CH_3OH$ is a group of structurally similar molecules which may be analyzed using the bond-additivity approach.

TABLE V. Experimental and BAA values of electric tensor properties in esu for $CH_3OH$. The dipole moment of $CH_3OH$ lies in the plane of the molecule at an angle $\theta$ to the OH bond in the sense $(CH_3)^+O^-H^+$.

| Parameter | Experimental value | BAA estimate |
|---|---|---|
| $10^{18}\mu$ | $1.71 \pm 0.01$ [a] | 1.55 [b] |
| $\theta$ | 52° [c] | 43° |
| $10^{24}\alpha$ | 3.36 [d] | 3.27 [e] |
| $10^{33}\chi_{\parallel}^{(2)}$ | $-150 \pm 9$ | −176 [f] |
| $10^{39}\chi_{\parallel}^{(3)}$ | $385 \pm 11$ | 361 |

[a] Reference 18.

[b] Based on dipole moment data from Ref. 18 and bond angles from Ref. 28 for $H_2O$ and $(CH_3)_2O$.

[c] Reference 29. No uncertainty was listed.

[d] Reference 30.

[e] Based on $\alpha$ data from: G. D. Zeiss and W. J. Meath, Mol. Phys. 30, 161 (1975) ($H_2O$); and linear index of refraction data in Ref. 30 [$(CH_3)_2O$], uncertainty of 3–10%.

[f] Computed using experimentally determined direction of dipole moment from Ref. 29.

These molecules may be thought of as an oxygen atom plus two structural groups, either of which may be (H atom plus O–H bond) or ($CH_3$ group plus C–O bond). From the measured electric tensor properties of water and dimethyl ether, one may use bond additivity, experimentally determined bond angles,[28] and symmetry to derive bond or group values of tensor properties for O–H and O–$CH_3$. Then, making use of the experimental H–C–O bond angle[28] and electric dipole moment direction[29] in $CH_3OH$, one can employ bond additivity to estimate $\mu$, $\alpha$, $\chi_{\parallel}^{(2)}$, and $\chi_{\parallel}^{(3)}$ (the tensor observables[27]) for this molecule. Table V lists these estimates along with the experimental values of the parameters. The values of $\alpha$ and $\chi^{(3)}$ are in good agreement with experiment, which is not surprising based on, for example, the results from the halogenated methanes.[27] However, the BAA estimates for $\mu$ and $\chi_{\parallel}^{(2)}$ also agree remarkably well with experiment, perhaps owing, at least in part, to the simple geometry of the molecules.

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