

A comparison of calculated and experimental hyperpolarizabilities for acetonitrile in gas and liquid phases

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The nonlinear susceptibility of acetonitrile has been measured in both the gas and liquid phases by dc electric field-induced second harmonic generation (dc-SHG or EFISH). The EFISH signal for this molecule is dominated by the first hyperpolarizability β . It is shown that local field factors do not adequately describe the effect of the solvent environment. Thus it is not possible to extract "gas phase" values of hyperpolarizabilities from measurements made in solution. First and second hyperpolarizabilities, β and γ , have been calculated for acetonitrile using *ab initio* techniques. These calculations are compared to the gas phase experimental measurements. Excellent agreement is obtained when electron correlation effects are included.

I. INTRODUCTION

The effective electric field felt by a molecule in a solvent when an external field is applied is known to be strongly dependent upon the particular solvent. This phenomenon, which results in the solvatochromic effect, has been used to obtain an estimate of excited state dipole moments,¹ to define the polarity of the solvent itself,² and as a means of estimating molecular hyperpolarizabilities.^{3,4} It has also been shown that solvent interactions can affect the magnitude of the hyperpolarizability of a solute molecule.^{5,6} Traditionally, the solvent effect is modelled by a set of "local field factors." These depend upon macroscopic properties of the solvent, such as the dielectric constant and refractive index. Even when these local field factors are taken into account, however, recent dc electric field-induced second harmonic generation (EFISH or dc-SHG) measurements have shown that the first molecular hyperpolarizability β of para-nitroaniline (PNA) varies by a factor of more than 2 as a function of solvent polarity.⁷

In order to investigate the origins of this solvent effect, a molecule was identified which has a significant first molecular hyperpolarizability β that can be measured using both gas and solution EFISH techniques. Acetonitrile has a high enough vapor pressure to allow gas phase measurements. The first electronic absorption maximum is well into the vacuum ultraviolet, so resonance effects are not expected to be significant. Its large dipole moment for a molecule of its size (4.5 D) makes solution phase EFISH measurements feasible. Acetonitrile is also of a size appropriate for high-quality *ab initio* calculations. The aim of this work was twofold: to compare gas and liquid phase experimental measurements in order to establish the applicability of local field factors to the determination of the molecular hyperpolarizability β for acetonitrile; and to establish whether *ab initio* methods can give accurate results

for the gas phase hyperpolarizabilities β and γ for a molecule of this size.

II. CONVENTIONS AND STANDARDS

When making comparisons between measurements and calculations using different techniques, hyperpolarizabilities must be defined in a consistent way. Knowledge of the definitions used in any particular experiment enables one to compare measurements from different laboratories. Consistency is particularly important when results obtained using different experimental techniques are being compared. When consistent conventions are used, there is reasonable agreement from laboratory to laboratory.⁸ It is not as straightforward, however, to compare hyperpolarizability values measured in the gas phase with solution phase EFISH results, or to compare either of these results with calculations.⁹

The third order nonlinear susceptibility, $\chi^{(3)}(-2\omega; \omega, \omega, 0)$, a macroscopic property, is the quantity directly measured in an EFISH experiment. It is related to the microscopic effective second hyperpolarizability $\langle \gamma^T(-2\omega; \omega, \omega, 0) \rangle$ by

$$\chi^{(3)}(-2\omega; \omega, \omega, 0) = \frac{\rho}{4} f_{2\omega} f_{\omega}^2 f_0 \langle \gamma^T(-2\omega; \omega, \omega, 0) \rangle. \quad (1)$$

Here the f_0 , f_{ω} , and $f_{2\omega}$ are local field factors, ρ is the number of molecules/volume, and $\langle \gamma^T \rangle$ is a quantity orientationally averaged over the thermal distribution of dipolar molecules in a static electric field,

$$\langle \gamma^T(-2\omega; \omega, \omega, 0) \rangle = \bar{\gamma}^T(-2\omega; \omega, \omega, 0) + \frac{\mu_0 \beta_z^T(-2\omega; \omega, \omega)}{5kT}, \quad (2)$$

where β_z^T denotes the component of the third order tensor β_{ijk}^T in the direction of the dipole moment, $\beta_z^T = \frac{1}{3} \sum_{\xi} \{ \beta_{z\xi\xi}^T + \beta_{\xi z\xi}^T + \beta_{\xi\xi z}^T \}$ ($\xi = x, y, z$) and $\bar{\gamma}^T$ is the scalar component of the fourth order tensor γ_{ijkl}^T , $\bar{\gamma}^T = 1/15 \sum_{\xi\eta} \{ \gamma_{\xi\xi\eta\eta}^T + \gamma_{\xi\eta\eta\xi}^T + \gamma_{\xi\eta\xi\eta}^T \}$. (The subscripts ijk represent

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the axes of the molecule and the superscript T refers to the particular convention used to define the hyperpolarizabilities, see Ref. 9.)

Local field factors attempt to describe the environment of the molecule under consideration in terms of the refractive index n_ω at frequency ω and the dielectric constant ϵ of the surrounding medium. In the presence of a static (or dc) electric field, the local field factor is frequently assumed to be given by the Onsager/Lorentz expression,¹⁰

$$f_0 = \frac{\epsilon(n_\omega^2 + 2)}{n_\omega^2 + 2\epsilon} \quad (3)$$

At optical frequencies, the local field may be described by the Lorentz local field,¹⁰

$$f_\omega = \frac{n_\omega^2 + 2}{3} \quad (4)$$

For an isolated molecule *in vacuo* these local field factors reduce to unity. Equations (1) and (2) are consistent with a Taylor series definition of the effective electric field-dependent dipole moment in the presence of a time-dependent field, $F = F_0 + F_\omega \cos \omega t$,

$$\begin{aligned} \mu_{\text{Ind}} = & \mu_0 + \alpha_0^T F_0 + \alpha^T(-\omega; \omega) F_\omega \cos \omega t + \frac{1}{2} \beta_0^T F_0^2 + \beta^T(-\omega; \omega, 0) F_0 F_\omega \cos \omega t + \frac{1}{4} \beta^T(0; \omega, -\omega) F_\omega^2 \\ & + \frac{1}{4} \beta^T(-2\omega; \omega, \omega) F_\omega^2 \cos 2\omega t + \frac{1}{8} \gamma_0^T F_0^3 + \frac{1}{2} \gamma^T(-\omega; \omega, 0, 0) F_0^2 F_\omega \cos \omega t + \frac{1}{4} \gamma^T(0; \omega, -\omega, 0) F_0 F_\omega^2 \\ & + \frac{1}{4} \gamma^T(-2\omega; \omega, \omega, 0) F_0 F_\omega^2 \cos 2\omega t + 1/24 \gamma^T(-3\omega; \omega, \omega, \omega) F_\omega^3 \cos 3\omega t + \frac{1}{8} \gamma^T(-\omega; \omega, \omega, -\omega) F_\omega^3 \cos \omega t + \dots, \end{aligned} \quad (5)$$

hence the superscript T . In the limit $\omega \rightarrow 0$, properties of the same order tend to the same limiting value, namely the static value. For example, in the case of the different second order hyperpolarizabilities, this means

$$\gamma(-2\omega; \omega, \omega, 0)_{\text{EFISH}} = \gamma(-3\omega; \omega, \omega, \omega)_{\text{THG}} = \gamma(-\omega; 0, 0, \omega)_{\text{dc-KERR}} \quad (6)$$

as $\omega \rightarrow 0$. Here THG refers to third harmonic generation.

An alternative definition of the hyperpolarizabilities has been used by Miller and Ward¹¹ based on a simple perturbation series expansion of the effective dipole moment in terms of the electric field

$$\begin{aligned} \mu_{\text{Ind}} = & \mu_0 + \alpha_0^B F_0 + \alpha^B(-\omega; \omega) F_\omega \cos \omega t + \beta_0^B F_0^2 + 2\beta^B(-\omega; \omega, 0) F_0 F_\omega \cos \omega t + \frac{1}{2} \beta^B(0; \omega, -\omega) F_\omega^2 \\ & + \frac{1}{2} \beta^B(-2\omega; \omega, \omega) F_\omega^2 \cos 2\omega t + \gamma_0^B F_0^3 + 3\gamma^B(-\omega; \omega, 0, 0) F_0^2 F_\omega \cos \omega t + \frac{3}{2} \gamma^B(0; \omega, -\omega, 0) F_0 F_\omega^2 \\ & + \frac{3}{2} \gamma^B(-2\omega; \omega, \omega, 0) F_0 F_\omega^2 \cos 2\omega t + \frac{1}{4} \gamma^B(-3\omega; \omega, \omega, \omega) F_\omega^3 \cos 3\omega t + \frac{3}{4} \gamma^B(-\omega; \omega, \omega, -\omega) F_\omega^3 \cos \omega t + \dots \end{aligned} \quad (7)$$

This results in the following expression for the thermally averaged value of γ

$$\langle \gamma^B(-2\omega; \omega, \omega, 0) \rangle = \frac{\mu \beta_z^B(-2\omega; \omega, \omega)}{15kT} + \bar{\gamma}^B(-2\omega; \omega, \omega, 0). \quad (8)$$

Many experimentalists making EFISH measurements in solution^{8,12,13} have used a hybrid expression (B^*) that includes $\gamma^B(-2\omega; \omega, \omega, 0)$ (since $\gamma^B = \gamma^{B^*}$) but defines $\beta^{B^*}(-2\omega; \omega, \omega)$ to be $3\beta^B(-2\omega; \omega, \omega)$, i.e.,

$$\begin{aligned} \langle \gamma^{B^*}(-2\omega; -\omega, \omega, 0) \rangle = & \frac{\mu \beta_z^{B^*}(-2\omega; \omega, \omega)}{5kT} \\ & + \bar{\gamma}^{B^*}(-2\omega; \omega, \omega, 0). \end{aligned} \quad (9)$$

Note that in this convention, the limiting value of $\beta^{B^*}(-2\omega; \omega, \omega)$ as $\omega \rightarrow 0$ is $3 \times \beta_0^B$, not β_0^B .

In this paper the hyperpolarizabilities are defined consistently using the Taylor series definition and thus are given by Eqs. (1), (2), and (5). Note that β^T and γ^T are larger than β^B and γ^B by factors of 2 and 6, respectively. In

the remainder of the paper the superscript T will be dropped for notational simplicity.

Both gas and liquid third order susceptibilities are relative measurements, i.e., they are measured with respect to a standard. For the gas phase EFISH measurements, the primary standard is a calculation of the second hyperpolarizability of helium.¹⁴ For solution EFISH measurements, the standard is the second harmonic coefficient d_{11} of quartz. The most frequently used value for this quantity is 1.2×10^{-9} esu (0.49 pm/V) measured at 1064 nm.¹⁵ This reference value is itself obtained by ultimate reference to the d_{31} coefficient of LiIO₃, measured by parametric fluorescence.¹⁶ The solution EFISH calibration is questionable since recent second harmonic generation experiments by Eckardt *et al.*¹⁷ give a much smaller result for d_{31} of LiIO₃, -4.1 pm/V $\pm 10\%$ instead of -7.1 pm/V $\pm 8\%$. If this recently measured value for LiIO₃ is accepted, then the quartz and the solution values must also be reduced by 42%. In the words of Eckardt *et al.*, "It is remarkable that after more than 25 years of study in nonlinear optics, there should exist such uncertainty in the scale of the nonlinear parameters." In this paper, except where explicitly indicated, the larger value of d_{11} for quartz will be used.

III. EXPERIMENTAL RESULTS

A. Gas phase measurements

Gas phase EFISH measurements were performed with periodic phase matching as previously described.¹⁸⁻²⁰ In these experiments an argon-ion laser beam ($\lambda = 514.5$ nm) was focused through a cylindrical cell containing a periodic electrode array (41 electrode pairs, period 5.08 mm).^{19,21} Periodic phase matching and maximum signal occur when the coherence length of the gas in the cell is made to match the period of the electrode array. This condition is achieved simply by adjusting the gas pressure. The ratio of the thermally averaged hyperpolarizabilities of a sample gas A and a reference gas B is given by

$$\frac{\langle \gamma \rangle_A}{\langle \gamma \rangle_B} = \left[\frac{S_A^{(2\omega)}}{S_B^{(2\omega)}} \right]^{1/2} \left[\frac{\rho_A n'_A V_A}{\rho_B n'_B V_B} \right]^{-1}, \quad (10)$$

where $S^{2\omega}$ is the peak signal and ρ is the gas number density under phase matching conditions. The factor $n' = (n_0^4 n_\omega^3 n_{2\omega})^{1/6}$, with n_ω the refractive index at frequency ω , includes the combined effects of the Lorentz local field factors $f_0 f_\omega^2 f_{2\omega}$ and the refractive index dependence of the laser beam focusing; the compact form given for n' is an approximation valid when $n - 1 \ll 1$.¹⁹ V is the applied voltage.

Measurements were made with samples consisting of a mixture of 25 or 50 Torr of acetonitrile and about 1000 Torr of N_2 buffer gas. Reference measurements using pure N_2 gas were performed before and after each sample measurement. There are several differences from the previously reported experimental apparatus and techniques.²⁰ The cell was enclosed in an oven in order to make measurements over a range of gas temperatures up to 200 °C. To prevent outgassing, absorption or reaction of the sample with the cell interior, a stainless steel cell was constructed with metal-to-metal seals and with the windows contacted to optically polished end flanges (i.e., no O rings). A magnetically coupled piston, moving in an outrigger cylinder connected to the main sample cell, was employed to ensure rapid and complete mixing during gas sample preparation. An electrode array with a long period was employed so that phase matching would occur at a lower gas density. Sample densities were calculated from the measured pressures and temperatures using the virial equation of state²²

$$P = \rho RT(1 + B\rho), \quad (11)$$

where the second virial coefficient for a mixture (m) of acetonitrile and nitrogen is given by

$$B_m = B_A X_A^2 + 2B_{NA} X_A X_N + B_N X_N^2. \quad (12)$$

Since no data were available for the N_2 - CH_3CN interaction second virial coefficient, B_{NA} , it was estimated as $2B_{NA} = (B_N + B_A) \pm (B_N - B_A)$, where N and A refer to nitrogen and acetonitrile. The quantity after the \pm sign is a pessimistic estimate of the error. Self-consistent values of ρ_m , B_m and the mole fractions X were calculated iteratively from the pressure data.

The results of the hyperpolarizability ratio measurements are presented in Table I and in Fig. 1. Typically, five

TABLE I. Results of gas phase measurements of the hyperpolarizability ratio for acetonitrile and nitrogen at $\lambda = 514.5$ nm. The error bars reflect both systematic and statistical uncertainties. The ratio of phase-match densities for the pure gases was determined to be $\rho_{N_2}/\rho_{CH_3CN} = 3.75 \pm 0.06$.

| T (°C) | $\langle \gamma \rangle_{CH_3CN} / \langle \gamma \rangle_{N_2}$ |
|----------|--|
| 26.6 | 15.55 ± 0.15 |
| 56.4 | 14.54 ± 0.15 |
| 112.0 | 12.70 ± 0.30 |
| 192.0 | 11.41 ± 0.15 |

complete measurements were made at each temperature, giving statistical uncertainties of about $\pm 1\%$. Uncertainties in the virial coefficients contribute a systematic error of at most $\pm 0.7\%$. Local field corrections are very small, 0.05%, and nearly cancel in the ratio. There are indications that the gas temperature may have been overestimated by as much as 2 °C at the highest cell temperature, but this will have a negligible effect on the measured ratios, since the temperature is the same for sample and reference gases. The hyperpolarizability ratios plotted in Fig. 1 show the linear variation with $1/T$, which is predicted by Eq. (2). The first and second hyperpolarizabilities of acetonitrile are obtained from the slope and intercept of the weighted-least-squares fit of a straight line to $\langle \gamma \rangle_{CH_3CN} / \langle \gamma \rangle_{N_2}$ vs $1/T$. The hyperpolarizabilities of acetonitrile are extracted from the hyperpolarizability ratios using the previously measured result for γ_{N_2} .¹⁹ The error bars on the final results include the effect of possible systematic errors in the temperature measurements.

Table II lists the values obtained for the gas phase hyperpolarizabilities of acetonitrile, β and γ . Also included in the table are values of the dipole moment and the linear

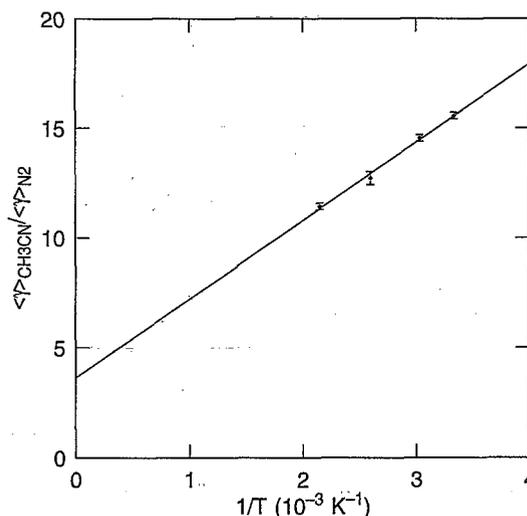


FIG. 1. Experimental measurements of the ratio of hyperpolarizabilities for acetonitrile and nitrogen, at $\lambda = 514.5$ nm, are plotted as a function of temperature. The slope and intercept of the straight line fit to the data, 3521 ± 111 K and 3.81 ± 0.32 are used to obtain the gas phase nonlinear optical property values given for acetonitrile in Table I.

TABLE II. The linear and nonlinear optical properties of acetonitrile and nitrogen in gas and liquid phases.

| Property | State | Value (a.u.) | Value (SI) | Value (esu) | Uncertainty |
|---------------------|--------|--------------|-------------------------|-------------------------|-------------|
| $\gamma_{N_2}^a$ | Gas | 1210 | 75.46×10^{-63} | 6.095×10^{-37} | $\pm 1\%$ |
| $\mu_{CH_3CN}^b$ | Gas | 1.542 | 1.307×10^{-29} | 3.919×10^{-18} | $\pm 1\%$ |
| β_{CH_3CN} | Gas | 43.8 | 1.404×10^{-51} | 3.784×10^{-31} | $\pm 3\%$ |
| γ_{CH_3CN} | Gas | 4619 | 2.880×10^{-61} | 2.327×10^{-36} | $\pm 8\%$ |
| $\mu_{CH_3CN}^c$ | Liquid | 1.77 | 1.5×10^{-29} | 4.5×10^{-18} | $\pm 2\%$ |
| $\alpha_{CH_3CN}^d$ | Liquid | 30.2 | 4.98×10^{-40} | 4.48×10^{-24} | |

Units of μ are $e a_0$ (a.u.), Cm (SI), and Fr cm (esu).
 Units of α are $e^2 a_0^2 E_h^{-1}$ (a.u.), $C^2 m^2 J^{-1}$ (SI), and $Fr^2 cm^2 erg^{-1}$ (esu).
 Units of β are $e^3 a_0^3 E_h^{-2}$ (a.u.), $C^3 m^3 J^{-2}$ (SI), and $Fr^3 cm^3 erg^{-2}$ (esu).
 Units of γ are $e^4 a_0^4 E_h^{-3}$ (a.u.), $C^4 m^4 J^{-3}$ (SI), and $Fr^4 cm^4 erg^{-3}$ (esu).
 All properties measured at $\lambda=514.5$ nm except α_{CH_3CN} at 589.3 nm.

^aReference 19.^bReference 44.^cReference 42.^dReference 46, in CCl₄.

polarizability. Values are presented in atomic, SI, and esu units. Atomic units will be used in the remainder of the paper, unless otherwise indicated.

B. Liquid phase measurements

The optical nonlinearity of acetonitrile in the neat liquid phase was measured using a previously described EFISH apparatus.^{3,8} Measurements on acetonitrile dissolved in nonpolar solvents were also attempted, but the resulting second harmonic signals attributable to the solute were too weak to be accurately evaluated. The beam from a Nd:YAG laser ($\lambda=1064$ nm) was focused into a cell containing acetonitrile (Aldrich Gold Label). The intensity of the emerging second harmonic signal was compared to the second harmonic signal from a quartz reference crystal. In order to compare the solution results to the gas phase measurements at 514.5 nm, EFISH measurements were made, not only at 1064 nm, but also at 532 nm. The 532 nm fundamental radiation was obtained by doubling the frequency of the Nd:YAG laser.

The bulk properties used for the evaluation of $\langle \gamma \rangle$ in these EFISH experiments are collected in Table III. The values used for the density (0.786 g/cm³) and dielectric constant (37.5) of neat acetonitrile are from Ref. 23. Measured values of $\chi^{(3)}$ ($-2\omega; \omega, \omega, 0$) for the Suprasil fused silica windows and d_{11} of quartz at 532 nm have not been

reported. These values were obtained by extrapolating from values measured at 1064 nm by using Miller's rule.²⁴ Miller's rule is the following relationship between properties of a crystalline system

$$d_{ijk} = \delta_{ijk} \chi_{ii}^{(1)}(\omega_1) \chi_{jj}^{(1)}(\omega_2) \chi_{kk}^{(1)}(\omega_3), \quad (13)$$

where d_{ijk} is the second-order susceptibility and $\chi_{ii}^{(1)}(\omega_1)$ is the linear susceptibility in the crystallographic principal axis system. It is found that δ_{ijk} generally varies less with frequency, material and nonlinear phenomenon (e.g., SHG, electro-optic effect, ...) than does d_{ijk} . Therefore, knowledge of the linear susceptibilities at 1064 nm and the value of d_{ijk} allows the value of δ_{ijk} to be calculated. Using this value with the linear susceptibilities at 532 nm gives the value of d_{ijk} at 532 nm. In assuming that δ_{ijk} is essentially constant with respect to frequency some error is introduced. An idea of its magnitude can be gained by examining the results of Lotem, Koren, and Yacoby who observed a variation of <15% in GaAs over the range 690–1000 nm.²⁵

The values of $\langle \gamma \rangle$ obtained for neat acetonitrile at both 532 and 1064 nm are listed in Table IV, along with the gas phase value for comparison. It is not possible to obtain the individual components of $\langle \gamma \rangle$, i.e., $\bar{\gamma}$ and β_z , since measurements in solution cannot be made over a broad enough temperature range. Also shown in Table IV is the quantity

TABLE III. Parameters used in analysis of liquid EFISH data.

| | Index of refraction | | | $\chi^{(3)} (10^{-14}$ esu) | | $d_{11} (10^{-9}$ esu) | |
|--------------------|---------------------|--------------------|--------------------|-----------------------------|--------|------------------------|--------|
| | 1064 nm | 532 nm | 266 nm | 1064 nm | 532 nm | 1064 nm | 532 nm |
| Glass ^a | 1.450 ^b | 1.461 ^b | 1.500 ^b | 3.1 ^c | 3.6 | ... | ... |
| Quartz | 1.534 ^d | 1.547 ^d | 1.592 ^d | ... | ... | 1.2 ^e | 1.4 |
| Acetonitrile | 1.339 ^f | 1.347 ^g | 1.384 ^f | ... | ... | ... | ... |

^aSuprasil fused silica.^bOptics Guide 4, Melles Griot, p. 3–5 (1988).^cF. Kajzar and J. Messier, Phys. Rev. A 36, 2210 (1988).^dM. J. Weber, *Handbook of Laser Science and Technology* (CRC, Boca Raton, 1986).^eReferences 15 and 16.^fValues of n calculated from experimental values of coherence length.^gLandolt-Börnstein, *Zahlenwerte und Funktionen* (Springer, Berlin, 1955).

TABLE IV. Experimental values of the total third order hyperpolarizability in gas and liquid phases.^a

| Gas | | Liquid | | |
|------------------------|------------------------|--------------------|------------------------|--------------------|
| $\langle\gamma\rangle$ | $\langle\gamma\rangle$ | $4\chi^{(3)}/\rho$ | $\langle\gamma\rangle$ | $4\chi^{(3)}/\rho$ |
| 514.5 nm | 532 nm | | 1064 nm | |
| 1.89 | 6.6(4.4) | 26(17) | 5.8(3.8) | 22(15) |

^aAll hyperpolarizabilities in units of 10^4 a.u. Values in brackets relative to value of $d_{31}(\text{LiIO}_3)$ from Ref. 17, otherwise values are relative to $d_{31}(\text{LiIO}_3)$ from Ref. 16. Measurements made at 300 K.

$4\chi^{(3)}/\rho$, which, referring to Eq. (1), can be viewed as a value of $\langle\gamma\rangle$ without any correction for local field effects.

IV. AB INITIO CALCULATIONS

A. Method

Electron correlation was treated by second-order Moller–Plesset perturbation theory (MP2), and single and double excitation coupled-cluster theory with a perturbational estimate of connected triple excitations²⁶ denoted CCSD(T). Static moments and polarizabilities were calculated using analytic energy derivatives for the self-consistent field (SCF) method through β and for MP2 through α ; the higher derivatives (SCF γ , MP2 β , and γ) were obtained by finite difference differentiation of the lower order polarizabilities. The CCSD(T) values were all obtained by finite difference differentiation of the energy using a range of field strengths from 0.001 to 0.006 a.u. $\alpha(-\omega;\omega)$ and $\beta(-2\omega;\omega,\omega)$ were calculated analytically at the SCF level of theory; $\gamma(-2\omega;\omega,\omega,0)$ was obtained from finite difference calculations on $\beta(-2\omega;\omega,\omega)$. $\alpha(-\omega;\omega)$ was obtained analytically at the MP2 level of theory. $\beta(-2\omega;\omega,\omega)$ was obtained from a single finite difference procedure on a “pseudoenergy” second derivative as outlined previously.²⁷

In the coupled-cluster calculations, the $1s$ orbitals on carbon and nitrogen were kept doubly occupied in all configurations. In the analytic MP2 derivative calculations the core electrons were included in the correlation procedure. Comparison of the MP2 results obtained with and without core–valence correlation show insignificant (less than 1%) differences for γ since no functions suitable for core–valence correlation are included in this basis. It should be noted, however, that inclusion of suitable correlating functions in the basis for Ne (Ref. 28) had very little effect on the value of γ .

The primitive basis sets used consisted of van Duijneveldt's²⁹ $13s8p$ sets for carbon and nitrogen, and the corresponding $8s$ set for hydrogen augmented with $6d(\text{C,N})/6p(\text{H})$ polarization functions. The polarization function orbital exponents were chosen as even-tempered sequences of the form $\alpha = 2.5^{-n}\alpha_0$; $n = 0, \dots, k$ with $\alpha_0 = 7.12$ for the C d function, 9.88 for the N d function, and 9.88 for the H p function. These primitive sets were contracted to $[4s3p2d/3s2p]$ using atomic natural orbitals³⁰ (ANOs). The outermost primitives on each atom were uncontracted to give $[4+1s3+1p2+1d/3+1s2+1p]$. Additional diffuse s , p , and d functions were then added by extrapolating from the

TABLE V. The nonzero SCF Cartesian components of μ , α , β , and γ for HCN (in a.u.). Basis I is $[4+1s3+1p2+1d]+(2s2p1d1f)$ on the carbon and nitrogen, $[3+1s2+1p]+(2s)$ on the hydrogen. Basis II is $[4+1s3+1p2+1d1+1f]+(2s2p1d1f)$ on the carbon and nitrogen, $[3+1s2+1p1+1d]+(2s1p1d)$ on the hydrogen.

| Property | Basis I | Basis II | Expt. ^a |
|-----------------|---------|----------|--------------------|
| μ_z | 1.2963 | 1.2950 | 1.17 |
| α_{xx} | 13.776 | 13.884 | |
| α_{zz} | 22.401 | 22.494 | |
| $\bar{\alpha}$ | 16.651 | 16.754 | 17.5 16.6 |
| β_{xxx} | 3.09 | 2.89 | |
| β_{zzz} | 5.42 | 5.63 | |
| β_z | 11.60 | 11.41 | |
| γ_{xxxx} | 2080 | 2061 | |
| γ_{xxzz} | 647 | 629 | |
| γ_{zzzz} | 1642 | 1641 | |
| $\bar{\gamma}$ | 1835 | 1816 | |

^aThe dipole moment and linear polarizability are from *Handbook of Chemistry and Physics*, 71st ed. (CRC, Boca Raton, 1990).

outermost function in an even-tempered sequence $\xi = 2.5^{-n}\xi_0$. These diffuse functions are denoted $+(2s2p1d/2s)$. A diffuse f function, $\alpha_f(\text{N}) = 0.12$, $\alpha_f(\text{C}) = 0.088$ was added to the nitrogen and carbon sets to give a final basis of $[4+1s3+1p2+1d/3+1s2+1p]+(2s2p1d1f/2s)$. Only the pure spherical harmonic components of the d and f functions were included in the basis. Selection of this basis set was made after testing the importance of higher angular momentum functions on the hyperpolarizabilities of HCN. In this smaller test case it was possible to include more basis functions than for CH_3CN , and hence to check the convergence of the non-linear optical properties with basis set. Results for the hyperpolarizabilities of HCN determined with the above basis set are compared to those obtained using the $[4+1s3+1p2+1d1+1f/3+1s2+1p1+1d]+(2s2p1d1f/2s1p1d)$ basis set in Table V. For γ , the difference between the two sets of results is smaller than 3%. For β the difference between the components determined with the two basis sets is only 0.2 a.u., although this is a somewhat larger percentage since the absolute value of β_z is small. Nevertheless, these results indicate that the $[4+1s3+1p2+1d/3+1s2+1p]+(2s2p1d1f/2s)$ basis set should give reasonable values for the hyperpolarizabilities of CH_3CN . All calculations were performed at the MP2 optimized geometry obtained using a triple-zeta plus double polarization basis set. This basis set was derived from Dunning's³¹ $[5s4p]$ contraction of Huzinaga's³² $(10s6p)$ primitive set for carbon and nitrogen, and the corresponding $[3s]$ contraction of the $(5s)$ primitive set for hydrogen. The polarization functions were $\alpha_d(\text{C}) = 1.5$, 0.35, $\alpha_d(\text{N}) = 1.5$, 0.35, and $\alpha_p(\text{H}) = 1.4$, 0.25, as suggested by van Duijneveldt.²⁹ The geometrically optimized parameters are $r_{\text{CN}} = 1.166$ Å, $r_{\text{CH}} = 1.083$ Å, $r_{\text{CC}} = 1.459$ Å, $\angle\text{HCC} = 108.9^\circ$, $\angle\text{HCH} = 110.1^\circ$. These compare very well to the experimental geometry: $r_{\text{CN}} = 1.157$ Å, $r_{\text{CH}} = 1.112$ Å, $r_{\text{CC}} = 1.458$ Å, $\angle\text{HCH} = 109.27^\circ$ measured by microwave spectroscopy.³³

The calculations were performed using the MOLECULE,³⁴ CADPAC,³⁵ and TITAN³⁶ programs.

TABLE VI. The calculated and observed NLO properties (a.u.) of acetonitrile in the gas phase.

| Property | Static | | | 514.5 nm | | | Expt. ^a |
|--|--------|-------|---------|----------|-------------------------|-------------------------|--------------------|
| | SCF | MP2 | CCSD(T) | SCF | MP2 | Best Est. | |
| μ | 1.69 | 1.53 | 1.52 | | | 1.52 | 1.542 ^b |
| α_{xx} | 23.43 | 23.92 | 23.99 | 23.98 | 24.44 | 24.5 | 26.0 ^c |
| α_{zz} | 37.96 | 38.27 | 38.69 | 39.22 | 39.63 | 40.1 | 38.7 ^c |
| $\bar{\alpha}$ | 28.3 | 28.7 | 28.9 | 29.1 | 29.5 | 29.7 | 30.2 ^c |
| β_{xxx} | -5.64 | -4.55 | -4.66 | -6.97 | | | |
| β_{xxz} | -1.97 | 3.10 | 2.80 | -1.03 | 3.07 | | |
| β_{zxx} | -1.97 | 3.10 | 2.80 | -0.18 | 3.93 | | |
| β_{zzz} | 14.10 | 40.15 | 34.72 | 18.69 | 44.89 | | |
| β_z | 10.2 | 46.4 | 40.3 | 17.5 | 51.9 | 45.8(45.1) ^c | 43.8 |
| γ_{xxxx} | 2532 | 2900 | 3310 | 3736 | | | |
| γ_{xxxz} | 57 | 59 | ... | 105 | | | |
| γ_{xxyy} | 844 | 967 | 1100 | 1240 | | | |
| γ_{xxzz} | 1048 | 1360 | 1440 | 1541 | | | |
| γ_{zzzz} | 4114 | 6160 | 6630 | 6018 | | | |
| $\bar{\gamma}$ | 3012 | 3870 | 4240 | 4427 | 5290(5690) ^d | 5660(6230) ^c | 4619 |
| $\mu\beta/5kT/10^3$ ^f | 3.65 | 15.0 | 13.0 | 6.27 | 16.8 | 14.8(14.6) | 14.3 |
| $\langle\gamma\rangle/10^3$ ^f | 6.67 | 18.9 | 17.2 | 10.7 | 22.1(22.5) | 20.4(20.8) | 18.9 |

^aExperimental values at 514.5 nm.^bReference 44.^cReference 46.^dThe MP2 frequency dependent values of $\bar{\gamma}$ are estimated by either adding the difference of the SCF frequency dependent and static values or by using a percentage correction to the MP2 static value (see the text for details). (The percentage correction is given in parentheses.)^eThe best estimate frequency dependent results are determined from CCSD(T) static values in conjunction with an additive MP2 frequency dependent correction for β and additive SCF frequency dependent corrections for γ . (The percentage correction is given in parentheses.)^fEvaluated at 298 K.

B. Results

The theoretical static and frequency dependent results at $\lambda=514.5$ nm are displayed in Table VI together with experimentally measured quantities. It is useful to examine the static results in order to understand the effects of electron correlation on the hyperpolarizabilities. It should be noted that the CCSD(T) method has previously been demonstrated to be reliable in the determination of hyperpolarizabilities even when the contribution from electron correlation is significant.³⁷ It is clear that the SCF value of 10.2 a.u. for β_z severely underestimates the value of β_z determined at the CCSD(T) level of theory (40.3 a.u.), and that this increase is dominated by the difference in the β_{zzz} component. This difference is even greater than that observed for ammonia, where electron correlation increases β_z by around a factor of 2.²⁷ For CH₃CN, second-order perturbation theory (MP2) somewhat overestimates β_{zzz} and therefore overestimates β_z by 6 a.u. compared to the CCSD(T) value, but nevertheless gives a reasonable description of the large change due to electron correlation. The 40% increase in γ with electron correlation is considerably smaller than for β_z , and MP2 is again quite reliable, underestimating the total CCSD(T) value by only 9%. The results for CH₃CN support the general conclusion that the hyperpolarizabilities of small molecules can be extremely sensitive to electron correlation, whereas the linear polarizability α is much less sensitive—for CH₃CN, α increases by only 2% from SCF to CCSD(T).

In order to compare theory with experiment, we must determine the quantity $\langle\gamma\rangle$ corresponding to the experi-

mentally measured second hyperpolarizability at $\lambda=514.5$ nm as defined by Eq. (2). Comparison thus requires knowledge of $\beta(-2\omega;\omega,\omega)$, $\gamma(-2\omega;\omega,\omega,0)$ and the dipole moment, μ . The frequency-dependent contribution to $\beta(-2\omega;\omega,\omega)$ was determined at both the SCF and MP2 levels of theory. Given the inadequacy of the SCF method for determining the static value of β as described above, the total SCF frequency-dependent value should be viewed as unreliable. In cases such as ammonia²⁷ and neon³⁸ where the SCF static value also underestimates the correlated static value, use of a percentage SCF frequency dependent correction factor in conjunction with a correlated static value, e.g., $\beta(-2\omega;\omega,\omega)^{(MP2)} = \beta(-2\omega;\omega,\omega)^{SCF} / \beta_0^{SCF} \times \beta_0^{MP2}$ has been more reliable. (The subscript 0 here refers to the static value.) However, in the case of acetonitrile the scaling method using the SCF frequency dependent correction is clearly inappropriate. This appears to be the first case where use of "SCF scaling" gives results which substantially overestimate the calculated correlated frequency dependent hyperpolarizability. These results caution against the use of frequency dependent corrections from lower levels of theory when the static values of these and higher levels of theory differ significantly. It is interesting to note that for acetonitrile, use of an additive SCF correction for frequency dependence, namely, $[\beta(-2\omega;\omega,\omega)^{SCF} - \beta_0^{SCF}] + \beta_0^{MP2}$ is in good agreement with the full MP2 $\beta(-2\omega;\omega,\omega)$ value. (53.7 a.u. vs 51.9 a.u.)

The MP2 static value for β_z is in reasonable agreement with the CCSD(T) value and thus use of either a scaled or additive MP2 correction to the coupled cluster value gives

similar results. The best-estimate (column 7 of Table VI) of $\beta(-2\omega; \omega, \omega)$ is determined by adding the MP2 frequency dependent correction of 5.4 a.u. to the CCSD(T) static value giving 45.8 a.u., i.e.,

$$\beta_z^{\text{BestEst.}}(-2\omega; \omega, \omega) = \beta_0^{\text{CCSD(T)}} + [\beta_z(-2\omega; \omega, \omega)^{\text{MP2}} - \beta_0^{\text{MP2}}]. \quad (14)$$

The best estimate of $\beta(-2\omega; \omega, \omega)$ obtained using the scaled MP2 correction (45.1 a.u.) is included in parentheses in Table VI.

$\gamma(-2\omega; \omega, \omega, 0)$ was determined only at the SCF level of theory. Thus we have estimated the frequency dependent contribution to the correlated static values using this SCF correction both additively and as a percentage correction, although, given the results for β discussed above, one might expect the additive correction to be more reliable. This gives an adjusted CCSD(T) value of $\gamma(-2\omega; \omega, \omega, 0)^{\text{[CCSD(T)]}}$ of 5660 a.u. (additive correction) or 6230 a.u. (percentage correction) at $\lambda = 514.5$ nm. The difference between these two values (570 a.u.) is only 10% of the value for $\bar{\gamma}(-2\omega; \omega, \omega, 0)$. Furthermore, this difference is even less significant when considering $\langle \gamma \rangle$ since the orientational (or “ $\mu\beta_z$ ”) term dominates $\langle \gamma \rangle$. The best-estimate results are summarized in Table VI and are discussed in context with the experimental results in the following section.

V. DISCUSSION

The experimental gas and liquid phase measurements have been reported in Table IV. The liquid phase results are reported both as the macroscopic susceptibility per molecule, i.e., $4\chi^{(3)}(-2\omega; \omega, \omega, 0)/\rho$ and the microscopic effective second hyperpolarizability, $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$ (solution) defined by Eqs. (1) and (2). The latter values are derived from the former through the use of the appropriate local field factors [Eqs. (3) and (4)]. These results show that there is a factor of 13 increase from the microscopic gas phase hyperpolarizability $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$ (gas) to the “molecular” susceptibility value $4\chi^{(3)}(-2\omega; \omega, \omega, 0)/\rho$ measured in solution. This factor drops to 8 if the smaller quartz reference value is used. This large increase is only partially accounted for by the local field factors, since the value of the combined local field factors for acetonitrile, namely, $f_0 f_\omega^2 f_{2\omega}$, is 3.90 at 532 nm. The discrepancy between solution and gas phase results is large; $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$ (solution) is larger than $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$ (gas) by a factor of 3.5 (or 13.8/3.9). Even using the more recent quartz standard,¹⁷ this factor is significant (2.3), although smaller.

Doubling the frequency of the incoming radiation from 1064 to 532 nm has only a small effect (around 12%) on the measured hyperpolarizability $\langle \gamma \rangle$. This is as expected, since in this frequency range the hyperpolarizability is far from resonance. The $\pi \rightarrow \pi^*$ absorption transition for acetonitrile in the gas phase is at $\lambda < 180$ nm,³⁹ and at $\lambda < 220$ nm (Ref. 40) in neat solution. The extrapolation of the quartz reference d_{11} value from 1064 to 532 nm using Eq. (13) increased d_{11} by 14%. Frequency dispersion is much

TABLE VII. $\langle \gamma \rangle$ for CHCl_3 , C_6H_6 , and CCl_4 in gas and liquid phases.

| Molecule | Environment | Wavelength (nm) | $\langle \gamma \rangle$ (a.u. $\times 10^4$) |
|-----------------|-------------|-----------------|--|
| CHCl_3 | Gas | 694 | 1.33 ^a |
| | Liquid | 1064 | 4.1(2.5) ^b |
| Benzene | Gas | 670 | 2.46 ^c |
| | Gas | 1064 | 1.68 ^d |
| | Liquid | 1064 | 4.3(2.6) ^b |
| CCl_4 | Gas | 694 | 1.63 ^a |
| | Liquid | 1064 | 3.9(2.3) ^b |

^aC. K. Miller and J. F. Ward, Phys. Rev. A **16**, 1179 (1977).

^bReference 8. Values in parentheses use the d_{11} value for quartz from Ref. 17.

^cReference 20.

^dValue at 670 nm extrapolated to 1064 nm using $\langle \gamma \rangle = A(1 + B\omega^2)$, where A and B are taken from Ref. 20.

too small to account for the large difference between $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$ (gas) and $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$ (solution).

The large difference between $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$ (gas) and $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$ (solution) for acetonitrile indicates that the assumptions implicit in the derivation of the local field factors are not applicable to the determination of the molecular hyperpolarizability β from solution measurements. The solvent effect on $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$ (gas) as estimated by these local field factors is too small. Possible reasons for the inadequacy of the local field factors include the neglect of any structural properties of the liquid.^{41,42} Local interactions between molecules are not included and the dielectric constant ϵ in the vicinity of the solute is assumed to have the bulk value. There are also a number of assumptions implicit in the derivation of the local field factors themselves,¹⁰ regarding the polarity of the solvent, the frequency of observation, and the shape of the cavity in which the molecule is embedded. Finally, the molecule in solution is in some senses a different molecule from that in the gas phase. Its molecular geometry may be different and its electronic energy levels are shifted. It is interesting to note that the dipole moment for CH_3CN is much less sensitive to solvent effects. Its value in neat solution is 1.77 a.u.,⁴² not too different from its value measured in a variety of nonpolar solvents,⁴³ although slightly larger than the value of 1.54 a.u. measured in the gas phase.⁴⁴

Another way to measure the effectiveness of the local field factors is to compare the molecular hyperpolarizability of a system obtained in a number of different solvents. Such measurements are available for para-nitroaniline.⁷ The results for $\langle \gamma(-2\omega; \omega, \omega, 0) \rangle$ of PNA (which is strongly dominated by the orientational term) show a marked dependence on solvent, a further indication that the local field factors are not adequately describing the solvent effect.

It is interesting to examine other systems for which both gas and liquid phase measurements of the hyperpolarizability are available. Table VII compares gas and liquid phase values of $\langle \gamma \rangle$ for chloroform, benzene and carbon tetrachloride. Chloroform has a significantly smaller dipole moment (1.01 compared to 3.92 D, both in the gas phase) and dielectric constant (4.81 compared to 37.5)

than acetonitrile. Interestingly though, the local field factor for chloroform (4.3 at 532 nm) is actually larger than that for acetonitrile, reflecting the dependence of this factor on the refractive index as well as on the dielectric constant of the medium. There is a substantial difference between gas and solution phase values of $\langle\gamma\rangle$, as Table VII shows. Use of the more recent (but not necessarily more accurate) quartz reference value brings the results into much closer agreement. In this case, it is interesting to note that not only is the dipole moment of chloroform smaller than that of acetonitrile, but the calculated first hyperpolarizability is also considerably smaller (2.0 a.u. vs 43.8 a.u.).⁴⁵ Thus unlike acetonitrile, $\langle\gamma(-2\omega;\omega,\omega,0)\rangle$ of chloroform is dominated by $\bar{\gamma}(-2\omega;\omega,\omega,0)$ and not by the orientational term involving $\beta(-2\omega;\omega,\omega)$. Similar differences are seen for benzene and carbon tetrachloride in Table VII. In the case of benzene it is more useful to compare Shelton's extrapolation of $\langle\gamma\rangle$ to 1064 nm, the frequency of the liquid phase experimental measurement, since the benzene values at 670 nm are increased by resonance contributions. Clearly, the orientational term is identically zero in these symmetric molecules.

The calculated values of the hyperpolarizabilities should be compared with experimental values measured in the gas phase, since no environmental effects are included in the calculations and local field factors have a very small effect on $\langle\gamma\rangle$ in the gas phase. The comparison is particularly important given the results summarized in Tables IV and VII, indicating a large difference between gas and solution values for β_z and $\langle\gamma\rangle$ when conventional local field correction factors are used. The directly measured quantity $\langle\gamma\rangle$ (gas) is reported in Table VI. The best-estimate theoretical value of 20.4×10^3 a.u. for acetonitrile is in good agreement with the experimental measurement of 18.9×10^3 . The SCF value of 10.7×10^3 , however, significantly underestimates the experimental value, emphasizing once again the importance of including electron correlation in the determination of hyperpolarizabilities. As discussed earlier, measurements of the temperature dependence of the second hyperpolarizability allowed experimental determination of the individual terms in Eq. (2). Comparison of the best-estimate and experimental values for these two terms shows that both terms are slightly overestimated theoretically. The calculated value of the linear polarizability agrees well with the experimental one, even though the experimental value was obtained in a CCl_4 solution,⁴⁶ which would seem to indicate only a small environmental effect on $\bar{\alpha}$.

These calculations for CH_3CN corroborate the fact that, provided electron correlation effects are taken into account, and provided the one-particle basis set is adequate (i.e., it includes appropriate diffuse functions), it is possible to calculate hyperpolarizabilities β and γ of small molecules to within 10%–20% of experiment. The remaining error for CH_3CN may be reduced through improvements to the one-particle basis set, improvements in the electron correlation treatment (e.g., inclusion of higher excitations), and incorporation of the vibrational dependence of the hyperpolarizability. None of these effects are expected

to be large; the one-particle basis set was chosen to reproduce limiting values for the hyperpolarizabilities of HCN and the CCSD(T) method has reliably determined hyperpolarizabilities for other small systems (e.g., Refs. 37 and 47). Although the vibrational contribution can be significant for static values, calculations to date^{48,49} show that the effect on the hyperpolarizabilities relevant for second harmonic generation is small. The effect of zero-point vibration on the hyperpolarizability is more difficult to quantify, and direct calculation for this six atom system with the large basis set needed for hyperpolarizabilities is currently prohibitive. The change in β at different geometries may give some estimate of the size of this effect. The above calculations have been carried out at the MP2 optimized geometry which is close to the experimental structure⁵⁰ (within 0.01 Å and 0.8°). Additional calculations at the SCF optimized geometry, which has a considerably shorter C–N bond distance (0.03 Å shorter than experiment; a known deficiency of the SCF method for multiple bonds) shows that β_0^{MP2} decreases by 16% relative to the value at the MP2 optimized geometry. Such a change in β would result in an overall decrease of 13% to $\langle\gamma(-2\omega;\omega,\omega,0)\rangle$ giving a result which is still in good agreement with experiment.

VI. CONCLUSIONS

The local field factor expressions given in Eqs. (2) and (3) were derived using a simple liquid model. Detailed aspects of the solvent environment, e.g., local molecular interactions, which may be important for some systems, are not specifically included. Consequently, the experimental gas and solution phase hyperpolarizabilities may differ. This is indeed the case for acetonitrile as shown in Table IV. The local field factors may not be used satisfactorily in this case to predict the gas phase hyperpolarizability from solution phase measurements alone. These results, together with those for para-nitroaniline demonstrate that, at least for the first hyperpolarizability $\beta(-2\omega;\omega,\omega)$, use of local field factors does not factor out the entire solvent dependence of the solution phase measurement. The magnitude of this effect is clearly affected by the choice of quartz reference, but for both para-nitroaniline and acetonitrile the effect is significant no matter which reference is used. The dipole moment and linear polarizability seem to be affected much less by the environment.

Good agreement can be achieved between gas phase experimental and theoretical results provided that high levels of theory, in particular including electron correlation, are used. Consequently, there is a sound theoretical platform on which to build the model necessary to calculate solution phase hyperpolarizabilities. The significant difference between the gas and solution phase experimental values highlights the importance of developing such a model. Certainly, attempting to estimate the solution value by using $[\langle\gamma(-2\omega;\omega,\omega,0)\rangle_{\text{gas}} f_{\omega}^2 f_{2\omega}]$ yields unreliable results in this case.

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