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Calculation of the Microscopic and Macroscopic Linear and Nonlinear Optical Properties of Acetonitrile: I. Accurate Molecular Properties in the Gas Phase and Susceptibilities of the Liquid in Onsager's Reaction-Field Model

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As part of a program to investigate the linear and nonlinear susceptibilities of acetonitrile in the condensed phase, we report on the accurate calculation of the molecular electric properties of acetonitrile, taking into account geometry and basis set effects, static and dynamic electronic correlation, vibrational contributions, and frequency dispersion. All correlated single reference state methods as well as the multireference SCF with a Møller−Plesset second-order perturbation correction (MRMP2) yield similar values for the electronic contribution to the polarizability α and the second hyperpolarizability γ. For the first hyperpolarizability, however, differences between the highly correlated methods CCSD(T) and MRMP2 remain. Vibrational contributions to the electric properties are calculated analytically and using two numerical finite difference methods at the Hartree−Fock level and at the correlated second-order Møller−Plesset level using finite field difference methods. Basis set convergence and convergence with the level of anharmonicity are examined. Computed values of the quantity $\mu\beta_{||}(-2\omega; \omega, \omega)/(3kT) + \gamma_{av}(-2\omega; \omega, \omega, 0)$ agree with temperature-dependent experimental values at two different frequencies within 10%. Using the highest correlated methods, liquid-phase susceptibilities are computed in the dipolar Onsager reaction-field approximation. Excellent agreement with experiment for the relative permittivity and the refractive indices is found as well as acceptable agreement for the nonlinear susceptibility.

1. Introduction

The ab initio calculation of molecular hyperpolarizabilities has reached a state of high accuracy due to increasing computing power and recent advances in the development and implementation of sophisticated models for the treatment of electronic correlation, frequency dispersion, vibrational contributions, and relativistic corrections. However, experimental data are usually obtained from measurements on condensed phases, and the computation of condensed-phase susceptibilities is still much less developed. Several self-consistent ab initio methods have been developed in the continuum approach to the molecular environment in a liquid and have been applied to computations of the susceptibilities of solutions and pure liquids.[1−4] However, these models ignore the molecular structure of matter and may miss effects due to long-range intermolecular correlations that do not manifest themselves in the necessary experimental input parameters (i.e., the relative permittivity and/or the refractive indices). Much evidence points to the existence of local structure in polar, aprotic liquids.[5,6] Potential effects of this molecular ordering on linear and nonlinear optical properties of the liquid could be revealed by discrete local-field models explicitly considering the discreteness of the charge distributions of the surrounding molecules, as employed for molecular crystals.[7,8] Similar methods can be applied for pure molecular liquids,[4,9] where the liquid structure is calculated by molecular simulation methods.

Acetonitrile should be a good test case to search for local structure effects on the susceptibilities of the liquid. A wealth of experimental data suggests a strong local order in the liquid with a pair ordering extending to neighbors beyond the first shell of surrounding molecules.[5] Recently, delocalized collective modes of molecular reorientation have been suggested to explain the occurrence of hyper Rayleigh scattering-intensity ratios incompatible with localized modes.[6] Reference values in the form of experimental data for the electric-field-induced second-harmonic generation (EFISH) process of acetonitrile in the gas and liquid phases exist at two different frequencies.[10,11] From the computational side, acetonitrile is a small molecule, so highly correlated methods and large basis sets can be used.

Any successful and convincing prediction of macroscopic susceptibilities must be based on accurate and complete electric properties of the free molecule. Several high-level computations of hyperpolarizabilities of acetonitrile have been published before,[10,12,13] and good agreement of computed first[10] and second[12] electronic hyperpolarizabilities with experimental gas-phase values at one frequency has been claimed (but not for both quantities at the same time). However, no systematic convergence study of these properties with increasing basis sets, including dynamic and static correlation and frequency dependence, has been undertaken. Neither has the effect of vibrational contributions been taken into account in a quantitative manner. In this first part of our investigation, we will report on the accurate computation of the molecular electric properties of acetonitrile, taking into account all of the above-mentioned effects. By comparing with experimental gas-phase results, we will try to establish a converged method/basis set combination that will allow the computation of the molecular properties in the macroscopic phases. An application to liquid acetonitrile in

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a simple reaction-field model, the dipolar Onsager model, will be reported. In the second part, we will compute the linear and nonlinear susceptibilities of liquid and solid acetonitrile in discrete local-field models.

Following the conventions in computational chemistry, the molecular electrical properties will be given in atomic units (au). All other quantities will be given in SI units. The SI unit system will also be followed in the theoretical section. Conversion factors for the electric properties are μ: 1 au = 8.478×10^{-30} C m, α: 1 au = 0.16487×10^{-40} C^2 m^2 J^{-1}, β: 1 au = 0.32066×10^{-52} C^3 m^3 J^{-2}, γ: 1 au = 0.62360×10^{-64} C^4 m^4 J^{-3}.

2. Methods

2.1. Electronic Contributions. The electronic electric properties were calculated by employing the following wave function models: self-consistent field (SCF), second-order Møller−Plesset perturbation theory (MP2), restricted active space self-consistent field (RAS),[22] multireference SCF with Møller−Plesset second-order perturbation (MRMP2),[14,15] and several models in the coupled-cluster (CC) hierarchy: CC with singles and the contribution of doubles arising from the lowest order in perturbation theory, CC2;[17] coupled cluster with singles and doubles (CCSD);[16] and CCSD with a perturbational treatment for connected triples, CCSD(T).[18] Finite field derivative techniques[19] were used to calculate the static properties of the SCF, MP2, MRMP2, and CCSD(T) models using Gaussian 98[20] for SCF, MP2, and CCSD(T) and GAMESS[21] for MRMP2. Static and frequency-dependent properties were calculated analytically with the response theory implementation in the program package Dalton[23] at the SCF level in the random-phase approximation (RPA) and at the RAS,[24] CC2, and CCSD[25,26] levels. CC2 and CCSD are orbital-unrelaxed whereas CCSD(T) includes orbital relaxation effects.[27] A comparison of the hyperpolarizabilities from finite field calculations at the SCF level using different base electric-field values with the analytically derived properties at the RPA level led to the choice of a base field value of 0.003 au for all finite field computations.

In most of the RAS calculations, we employed the same active space as that used by Norman et al.[12] in their study of acetonitrile: the valence orbitals 4−7a_1, 1e constitute the RAS1 space, where the number of electrons is kept between 10 and 12, the complete active space RAS2 consists of 4 electrons distributed without restriction in the four orbitals 2−3e, and RAS3 consists of the orbitals 8−11a_1 and 4e, with the electron occupation restricted between 0 and 2. A clear separation in the MP2 natural orbital occupation numbers calculated with Sadlej's Pol basis set[28] was noted by Norman et al. as the motivation for the choice of these active spaces. We observed comparable separations with the basis set employed by us; all orbitals with occupation numbers larger than 0.01 were included. The active space for the MCSCF wave function used as the reference function in the MRMP2 calculation was the same as that for RAS2. We also performed a static second RAS calculation, where the RAS1 and RAS2 spaces and all numbers of maximum and minimum electrons were unchanged, but the RAS3 space consisted of a total of 16 orbitals instead of 6, including all orbitals with natural MP2 orbital populations larger than 0.003 electrons, where a second clear separation in MP2 natural orbital occupation numbers occurs.

As basis sets, we employed the series of correlation-consistent basis sets *n*-aug-pV*N*Z developed by Dunning and coworkers,[29−34] which allow for the systematic improvement of the basis by increasing *n* and/or *N*. It has been shown that with these basis sets it is possible to obtain frequency-dependent second hyperpolarizabilities of atoms and small molecules in very good agreement with experiment.[27]

TABLE 1: Bond Lengths (Å) and Angles (deg) of Experimental and Optimized Geometries of Acetonitrile

	$r_{\mathrm{N-C}}$	$r_{\mathrm{C-C}}$	$r_{\mathrm{C-H}}$	∠HCC	∠HCH
exptl ref 36	1.1571	1.4584	1.1036	109.45	109.49
SCF/aug-cc-pVDZ	1.1364	1.4690	1.0873	109.55	109.39
SCF/aug-cc-pVTZ	1.1266	1.4641	1.0802	109.66	109.28
MP2/cc-pVDZ	1.184	1.4692	1.1002	110.02	108.92
MP2/cc-pVDZ	1.169	1.4575	1.0866	109.97	108.97
RAS/d-aug-cc-pVDZ	1.1705	1.4876	1.1059	109.83	109.11
CCSD(T)/aug-cc-pVDZ	1.1780	1.4819	1.1024	109.71	109.23

2.2. Geometry. For most calculations, the experimental geometry of Costain,[35] which is based on effective nuclear positions derived from isotopic differences in rotational constants, has been used. This "r_s" geometry is considered to be very close to the geometry based on atomic equilibrium positions.[35] To explore the effect of the geometry on the calculated properties, some calculations were also performed at ab initio optimized geometries. Bond lengths and angles of experimental and some selected optimized geometries are collected in Table 1. The agreement between the different geometries is generally satisfactory, except for the N−C bond length, which becomes 0.03−0.06 Å longer on going from the SCF level to the correlated levels, with the experimental values in between. However, our data suggest that the equilibrium values are approached with an increasing level of correlation and larger basis sets. This is also supported by the calculations of Bak et al.,[36] which show that the experimental C−N bond length of HCN, which is very close to that of acetonitrile, can be accurately reproduced with a cc-pCVQZ basis set at the CCSD(T) level.

2.3. Vibrational Contributions. Accurate calculations of hyperpolarizabilities should take vibrational corrections into account. These may be separated into pure vibrational (PV) and zero-point vibrational average (ZPVA) corrections. PV corrections in the static limit can be quite large, but they are usually strongly quenched at optical frequencies. The dispersion of ZPVA corrections, however, generally resembles more closely the dispersion of the electronic contribution.[37,38]

We calculated PV and ZPVA corrections according to Bishop−Kirtman perturbation theory (BKPT),[29,37] where the perturbation terms are sorted according to the level of mechanical and electrical anharmonicities. The evaluation of the BKPT equations for the vibrational corrections requires a knowledge of the second and higher-order derivatives of the energy with respect to normal coordinates and mixed derivatives of a different order with respect to the field and the normal coordinates. Using the symbolic notation of Bishop and Kirtman concerning the level (n, m) of electrical (n) and mechanical (m) anharmonicities, the first-order term of the ZPVA correction P^{ZPVA} to a property P may be written as

$$P^{\mathrm{ZPVA}} = [P]^{1,0} + [P]^{0,1} = -\frac{\hbar}{4}\sum_a \left[\sum_b \frac{F_{abb}}{\omega_b \omega_a^2} \frac{\partial P^{\mathrm{el}}}{\partial Q_a} - \frac{1}{\omega_a} \frac{\partial^2 P^{\mathrm{el}}}{\partial Q_a^2} \right] \tag{1}$$

where Q_a are the normal coordinates, ω_a are the corresponding vibrational frequencies, and F_{abb} are elements of the matrix of third-order derivatives of the energy with respect to the normal coordinates (cubic anharmonic force constants). P may be any component of μ, α, β, or γ, and P^{el} denotes the electronic contribution to P. Using the same (m, n) notation, PV contributions can be written as[39]

$$\alpha^{\mathrm{PV}}(-\omega;\omega) = [\mu^2]^0 + [\mu^2]^{\mathrm{II}} \tag{2}$$

$$\beta^{\mathrm{PV}}(-\omega;\omega_1,\omega_2) = [\mu\alpha]^0 + [\mu^3]^{\mathrm{I}} + [\mu\alpha]^{\mathrm{II}} \tag{3}$$

$$\gamma^{\mathrm{PV}}(-\omega;\omega_1,\omega_2,\omega_3) = [\alpha^2]^0 + [\mu\beta]^0 + [\mu^2\alpha]^{\mathrm{I}} + [\mu^2\alpha]^{\mathrm{II}} + [\mu\beta]^{\mathrm{II}} + [\mu^4]^{\mathrm{II}} \tag{4}$$

where $[\ ]^0 = [\ ]^{0,0}$, $[\ ]^{\mathrm{I}} = [\ ]^{1,0} + [\ ]^{0,1}$, and $[\ ]^{\mathrm{II}} = [\ ]^{2,0} + [\ ]^{1,1} + [\ ].^{2,0}$ These bracketed terms are functions of derivatives of a different order of the energy with respect to the normal coordinates and fields; for the explicit expressions, see ref 39. Equations 2−4 show that, contrary to the ZPVA contributions, equations for the PV contributions have been derived beyond the first nonvanishing order in perturbation theory, which allows for a check of the initial convergence of the perturbation series for PV contributions. At the lowest level of approximation—the double-harmonic approximation—only the $[\ ]^0$ contributions are retained.

At the static SCF level, some of the derivatives can be calculated analytically with CADPAC, version 5.[40] In a slightly modified "*mnopq*" notation of ref 41, where m, n, o, p, and q refer to the order of derivatives with respect to the normal coordinates of the energy, dipole moment, polarizability, and first and second hyperpolarizabilities, respectively, the highest level of derivative that can be computed with CADPAC5 is 43210. This allows for the computation of all terms for α^{PV} in eq 2 and all $[\ ]^0$ and $[\ ]^{\mathrm{I}}$ and many of the $[\ ]^{\mathrm{II}}$ terms for β^{PV} and γ^{PV}. However, ZPVA corrections to the hyperpolarizabilities cannot be computed at this level.

A more generally applicable method uses numerical derivatives employing geometrical displacements.[41] However, if second derivatives are needed, as in the case of the ZPVA correction, then this method quickly becomes prohibitive for larger molecules and/or at correlated levels. An alternative for the calculation of mixed-field/normal coordinate derivatives is the numerical derivation of the gradient ($F_a = \partial V/\partial Q_a$) or Hessian ($F_{ab} = \partial^2 V/\partial Q_a \partial Q_b$) with respect to the electric field, for example, for the second hyperpolarizability components γ_{ijkl} according to

$$\frac{\partial \gamma_{ijkl}}{\partial Q_a} = \frac{\partial^4 F_a}{\partial E_i\, \partial E_j\, \partial E_k\, \partial E_l} \tag{5}$$

$$\frac{\partial^2 \gamma_{ijkl}}{\partial Q_a\, \partial Q_b} = \frac{\partial^4 F_{ab}}{\partial E_i\, \partial E_j\, \partial E_k\, \partial E_l} \tag{6}$$

We calculated the derivatives at the SCF and MP2 levels with the Gaussian 98 program package. The Hessian at the MP2 level was calculated numerically because the analytical computation with applied fields, although in principle possible, appears to be erroneous in our release of Gaussian 98 (Revision A.9).[42] According to ref 43, this problem has been resolved in Revision A.10. We used a base field value of 0.003 au for the numerical-field derivative calculation. Comparison with derivatives calculated analytically or with the numerical geometry displacement method showed that this value is adequate for a stable numerical derivative. The cubic anharmonic force constants F_{abc} were calculated using the finite geometrical displacement method.[41] At the level thus achieved, 32222, static ZPVA contributions to all electric properties can be computed. A disadvantage of this method is that ZPVA contributions can be calculated only in the static limit. It has been shown in refs 44 and 45, however, and may be corroborated by data in refs 46 and 47 that the ZPVA dispersion may be approximately given by multiplicative scaling factors derived from electronic dispersion functions, although a recent investigation has found that in some cases the electronic dispersion of the polarizability is slightly smaller than the ZPVA dispersion.[38]

All vibrational contribution computations were performed at the geometry optimized with the respective wave function.

2.4. Reaction-Field Model in the Dipolar Onsager Approximation. Macroscopic susceptibilities employing the Onsager reaction-field model were calculated as described in ref 4, following Wortmann and Bishop,[48] including a correction pointed out by Munn et al.[49] The linear susceptibility $\chi^{(1)}(\omega)$ and the EFISH susceptibility $\chi^{(3)}$ in this model are given by

$$\chi^{(1)}(\omega) = \epsilon^{\omega} - 1 = \frac{N}{\epsilon_0}\left[\frac{\mu_z^{\mathrm{eff}}\mu_z^{\mathrm{eff}}}{3f_{zz}^{\mathrm{C0}}kT}\delta_{\omega 0} + \alpha_{\mathrm{av}}^{\mathrm{eff}}(0)\right] \tag{7}$$

$$\chi^{(3)}(-2\omega;\omega,\omega,0) = \frac{N}{6\epsilon_0}\left[\frac{\mu_z^{\mathrm{eff}}\beta_{\|}^{\mathrm{eff}}(-2\omega;\omega,\omega)}{kT} + \gamma_{\mathrm{av}}^{\mathrm{eff}}(-2\omega;\omega,\omega,0)\right] \tag{8}$$

where N is the number density and ϵ^{ω} is the frequency-dependent dielectric constant, equal to the square of the refractive index $n(\omega)$ at an optical frequency ω and equal to the static dielectric constant ϵ at zero frequency. The effective dipole moment is assumed to lie along the molecular z axis, with μ_z^{eff} its component. f_{zz}^{C0} is a cavity field factor to be defined later, $\alpha_{\mathrm{av}}^{\mathrm{eff}}(\omega) = {}^1/_3\Sigma_j\alpha_{jj}^{\mathrm{eff}}(\omega)$ is the mean effective polarizability, the $\delta_{\omega 0}$ factor signifies that the orientational part associated with it disappears at optical frequencies, $\beta_{\|}^{\mathrm{eff}} = {}^1/_5\Sigma_i(\beta_{zii}^{\mathrm{eff}} + 2\beta_{izi}^{\mathrm{eff}})$ is the vector component of the effective first hyperpolarizability in the direction of the dipole moment, and $\gamma_{\mathrm{av}}^{\mathrm{eff}} = {}^1/_{15}\Sigma_j\Sigma_k(2\gamma_{jjkk}^{\mathrm{eff}} + \gamma_{jkkj}^{\mathrm{eff}})$ is the mean effective second hyperpolarizability. The hyperpolarizabilities are defined according to the Taylor expansion of the dipole moment (this is the "T convention" of ref 50) whereas the susceptibilities are defined according to the expansion of the macroscopic polarization without numerical prefactors, corresponding to the "B convention" of ref 50.

If an ellipsoidal cavity with half-axes a_i is chosen to contain the molecule, with the half-axes coinciding with the molecular symmetry axes, then the effective properties are given by[48,49]

$$\mu_z^{\mathrm{eff}} = f_{zz}^{\mathrm{C0}}F_{zz}^{0}\mu_z^{\mathrm{sol}} \tag{9}$$

$$\alpha_{jj}^{\mathrm{eff}}(\omega) = f_{jj}^{\mathrm{C}\omega}F_{jj}^{\omega}\alpha_{jj}^{\mathrm{sol}}(\omega) \tag{10}$$

$$\beta_{jkl}^{\mathrm{eff}}(-2\omega;\omega,\omega) = f_{jj}^{\mathrm{C}2\omega}F_{jj}^{2\omega}f_{kk}^{\mathrm{C}\omega}f_{ll}^{\mathrm{C}\omega}F_{kk}^{\omega}F_{ll}^{\omega}\beta_{jkl}^{\mathrm{sol}}(-2\omega;\omega,\omega) \tag{11}$$

$$\gamma_{jklm}^{\mathrm{eff}}(-2\omega;\omega,\omega,0) = f_{jj}^{\mathrm{C}2\omega}F_{jj}^{2\omega}f_{kk}^{\mathrm{C}\omega}f_{ll}^{\mathrm{C}\omega}F_{kk}^{\omega}F_{ll}^{\omega}f_{mm}^{\mathrm{C0}}F_{mm}^{0}\gamma_{jklm}^{\mathrm{sol}}(-2\omega;\omega,\omega,0) \tag{12}$$

where

$$f_{ij}^{\mathrm{C}\omega} = \frac{\epsilon^{\omega}}{\epsilon^{\omega} - k_i(\epsilon^{\omega} - 1)}\delta_{ij} \tag{13}$$

$$F_{jj}^{\omega} = \frac{1}{1 - f_{jj}^{\mathrm{R}\omega}\alpha_{jj}^{\mathrm{sol}}(\omega)} \quad \text{with} \tag{14}$$

$$f_{ij}^{\mathrm{R}\omega} = \frac{3\kappa_i(1 - \kappa_i)(\epsilon^{\omega} - 1)}{4\pi\epsilon_0 a_1 a_2 a_3[\epsilon^{\omega} - \kappa_i(\epsilon^{\omega} - 1)]}\delta ij \tag{15}$$

The definition of the depolarization factors κ_i is given in ref 48. The superscript "sol" denotes a "solute" property (i.e., the respective molecular property in the presence of the static reaction field E^{R}). The components of this field in the dipole approximation are given by

$$E_i^{\mathrm{R}} = f_{ii}^{\mathrm{R}0} F_{ii}^{\mathrm{R}0} \mu_i^0 \tag{16}$$

where μ^0 is the dipole moment of the isolated molecule. This field and the solute properties can be calculated in a self-consistent manner as described in ref 4.

A crucial point in the Onsager model is the choice of the cavity. As is well known, the choice of the form and magnitude of the enclosing cavity in the Onsager model is not clearly defined and furthermore has a large influence on the calculated properties. Luo et al. describe a method to determine a unique spherical radius for any given wave function by requiring that the static equation for the linear susceptibility in the Onsager description (eq 7) be fulfilled.[51] This method has been used by Norman et al. in their calculation of the nonlinear susceptibilities of liquid acetonitrile in the reaction-field model.[12] Considering lth order spherical multipolar contributions up to $l = 10$, they calculated a cavity radius of 4 Å. This is quite a large value and leads to a rather small value for the dipolar reaction field (about 2 GV/m according to eq 16 and the values given for the RAS model in ref 12). For a compact molecule with a fairly high dipole moment such as acetonitrile, we would expect the dipolar term to be the most dominant contribution to the reaction field; consequently, the susceptibilities calculated by eqs 7−16 are a reasonable approximation for these quantities in the Onsager model. To determine the axes of an ellipsoidal cavity for acetonitrile, which is more appropriate for acetonitrile than a spherical cavity, we used the more standard method of adding bond lengths and van der Waals radii. Following a suggestion in the literature,[52] according to which a mean distance to the surrounding solvent molecules has to be taken into account, an empirical increment of 0.4 Å was added to these axes, leading finally to $(a_1, a_2, a_3) = (2.44, 2.44, 3.25)$ Å. The value of the added increment was suggested to be adequate for dipolar solutes in nonpolar solvents whereas for polar solvents larger increments were proposed.[53] However, we chose this value because, first, the volume of the ellipsoid is very close to the molecular volume derived from the density, which corresponds to Onsager's approximation for the derivation of a spherical cavity radius,[54] and second, it turned out that the linear static and optical susceptibilities of liquid acetonitrile are quite well reproduced with our choice of cavity dimensions in the dipolar approximation. We note that the cavity radii given by Willetts and Rice in ref 13 are different from ours; it is not clear to us how these values were obtained.

3. Results and Discussion

3.1. Gas-Phase Properties. 3.1.1. Electronic Contribution: Influence of Basis Set, Correlation, and Dispersion.

On the left side of Table 2, we show the results of a basis set study of the static properties of acetonitrile at the SCF level. The molecular z axis is oriented along the C−C−N axis, pointing from N to C; one of the C−H bonds lies in the yz plane. All symmetry-unique components are shown, although β_{yyy} does not contribute to $\beta_{\|}^{\mathrm{el}}$ but may be used to calculate the hyper Rayleigh scattering signal.[11] We employed the correlation-consistent basis sets n-aug-cc-pVN Z using single augmentation up to pentuple-ζ ($N = 5$) quality and double ($n = \mathrm{d}$) augmentation up to triple-ζ ($N = \mathrm{T}$) quality basis sets.

The dipole moment and linear polarizability components are already quite converged with the smallest basis set, aug-cc-pVDZ. An exception is $\alpha_{xx}^{\mathrm{el}}$, which is about 2% smaller with aug-cc-pVDZ than with the other basis sets. For the diagonal component of the first hyperpolarizability $\beta_{zzz}^{\mathrm{el}}$, convergence sets in after the singly augmented double-ζ basis set: the value increases about 15% from aug-cc-pVDZ to d-aug-cc-pVDZ and remains at the larger value within a margin of 4% with the other basis sets. The value of $\beta_{xxz}^{\mathrm{el}}$ is more variable with the basis set. At the singly augmented level, the absolute value decreases monotonically in the sequence N = D, T, Q, 5, reaching a converged value at the N = Q basis set. In the sequence of the doubly augmented basis sets, this limiting value is reached at N = T. Because of the opposite sign of the $\beta_{xxz}^{\mathrm{el}}$ and $\beta_{zzz}^{\mathrm{el}}$ components, the value of $\beta_{\|}^{\mathrm{el}}$ is rather small and quite variable with respect to the basis set, ranging from −4 to +4 au.

For the second hyperpolarizability γ^{el}, the convergence is smoother. With the exception of the singly augmented basis sets with N = D and T, all sets yield approximately the same values, with maximum differences of 2−8% for the single components and 5% for the mean quantity $\gamma_{\mathrm{av}}^{\mathrm{el}}$.

A similar convergence pattern to that found at the SCF level is found at the correlated MP2 level, as shown in the middle of Table 2. However, the component $\beta_{xxz}^{\mathrm{el}}$, although still basis set-dependent, is much smaller in absolute magnitude compared with the values at the SCF level whereas $\beta_{zzz}^{\mathrm{el}}$ is nearly 3 times larger. As a consequence, the relative variance of $\beta_{\|}^{\mathrm{el}}$ is quite small (7%) among the three largest basis sets investigated at the MP2 level.

We conclude from the data of the two Tables that the smallest basis set yielding nearly converged values for all electrical properties at the correlated level is d-aug-cc-pVDZ.

Finally, we also compare in Table 2 static data at different levels of correlation—SCF, MP2, CC2, CCSD, CCSD(T), RAS, and MRMP2—obtained with the d-aug-cc-pVDZ basis set. Considering first the single-reference methods, we observe that the CC2 method clearly overshoots polarizabilities and second hyperpolarizabilities compared with the other wave functions. Similar behavior has been found previously (e.g., by Hättig and Jørgensen in ref 27). The first hyperpolarizability components computed at the CC2 level, however, are in line with the general trend. The component $\beta_{xxz}^{\mathrm{el}}$ is small and approximately independent of the MP and CC levels; $\beta_{zzz}^{\mathrm{el}}$, however, decreases by 5 au (14%) from MP2 to CCSD(T) after the sharp increase by a factor of 3 from SCF to MP2. The values at the orbital-unrelaxed CCSD and the orbital-relaxed CCSD(T) levels are generally quite close to each other, as also found in other investigations.[27,55] Only for the $\beta_{zzz}^{\mathrm{el}}$ component do we find a drop of nearly 3 au (8%) caused by connected triples and orbital relaxation effects. The values of the $\gamma_{iijj}^{\mathrm{el}}$ components agree very well among the three correlated levels—MP2, CCSD, and CCSD(T)—with a maximal difference of 5% for the $\gamma_{zzzz}^{\mathrm{el}}$ component.

TABLE 2: Static Electronic Dipole Moments μ_z^{el}, Polarizabilities α_{ii}^{el}, First β_{zii}^{el}, and Second γ_{iijj}^{el} Hyperpolarizabilities of Acetonitrile at Various Levels of Theory with Different Basis Sets *n*-aug-cc-pV*N*Z, Abbreviated *na*NZ[a]

	SCF						MP2					CC2	CCSD	CCSD(T)	RAS	MRMP2
	aDZ	aTZ	aQZ	a5Z	daDZ	daTZ	aDZ	aTZ	aQZ	daDZ	daTZ			daDZ		
μ_z^{el}	1.676	1.674	1.674	1.673	1.673	1.673	1.539	1.545	1.548	1.537	1.544			1.525	1.527	1.532
α_{xx}^{el}	23.50	23.89	23.96	23.96	23.96	23.97	24.04	24.36	24.37	24.48	24.45	25.01	24.52	24.54	23.55	24.58
α_{zz}^{el}	38.42	38.48	38.46	38.46	38.42	38.46	38.84	38.83	38.78	38.88	38.84	40.03	39.13	39.28	36.78	38.69
α_{av}^{el}	28.48	28.75	28.79	28.79	28.78	28.80	28.97	29.18	29.17	29.28	29.25	30.02	29.39	29.45	27.96	29.28
β_{xxz}^{el}	−8.80	−5.39	−3.92	−3.77	−2.90	−3.54	−4.88	−1.35	0.09	1.44	0.73	1.41	1.17	1.23	−0.49	−0.72
β_{yyy}^{el}	−6.12	−6.56	−6.53	−6.49	−6.22	−6.44	−5.13	−5.35	−5.30	−4.96	−5.17	−4.73	−4.98	−5.04	−6.14	−5.07
β_{zzz}^{el}	11.06	12.74	13.24	13.19	12.74	13.27	36.22	37.27	37.76	37.39	37.74	35.72	35.33	32.25	30.04	28.19
$\beta_{\|\|}^{el}$	−3.92	1.18	3.23	3.39	4.14	3.71	15.88	20.74	22.66	24.16	23.52	23.12	22.60	20.83	17.44	16.04
γ_{xxxx}^{el}	1722	20.91	2307	2402	2323	2504	1962	2414	2558	2690	2826	2975	2760	2756	2156	2858
γ_{zzzz}^{el}	3753	3970	3089	3119	4244	4189	5693	5901	6002	6327	6176	7834	6615	6527	4853	6088
γ_{xxyy}^{el}	574	697	768	804	773	834	651	843	847	896	941	992	920	914	719	972
γ_{xxzz}^{el}	826	955	1016	1031	1043	1054	1043	1210	1278	1345	1340	1496	1347	1353	1080	1360
γ_{av}^{el}	2330	2673	2861	2931	2922	3017	3018	3453	3585	3775	3814	4350	3873	3856	2984	3853

[a] All units are au.

TABLE 3: Average Static Electronic Dipole Moments and Hyperpolarizabilities of Acetonitrile Calculated with Different Geometries and Comparison with Selected Literature Values

method	geometry	μ^{el}	α_{av}^{el}	$\beta_{\|\|}^{el}$	γ_{av}^{el}
MP2/daDZ	exptl[a]	1.537	29.28	24.16	3775
MP2/daDZ	MP2/daDZ	1.550	29.74	27.65	3932
MP2/daTZ	exptl[a]	1.544	29.25	23.52	3814
MP2/daTZ	MP2/cc-pVTZ	1.550	29.08	26.47	3806
CCSD(T)/daDZ	CCSD(T)/aDZ	1.538	29.95	21.72	4079
RAS/daDZ	exptl[a]	1.527	27.96	17.44	2984
RAS/daDZ	RAS/daDZ	1.539	28.39	17.00	3046
RAS/Pol[b]	exptl[a]	1.52	27.93	23.29	3269
MP2[7s6p4d1f/6s3p][c]	opt[c]	1.53	27.7	27.8	3870
CCSD(T)[7s6p4d1f/6s3p][c]	opt[c]	1.52	28.9	24.2	4240

[a] Reference 35. [b] Reference 12. [c] Reference 10; a different basis set was used for properties and optimization.

Employing a multiconfigurational reference function yields rather different values for the electrical properties. As noted by Norman et al.,[12] values for the polarizabilities and second hyperpolarizabilities computed at the RAS level are close to the values at the uncorrelated SCF level. However, at the MRMP2 level, using the same reference function as in the complete active space of the RAS calculation, both properties are similar to those calculated in the correlated single-configurational reference-state methods MP2, CCSD and CCSD(T), with the maximal difference of 574 au (9%) for the component γ_{zzzz}^{el}. We conclude, therefore, that both single- and multiconfigurational methods yield similar values for these properties if the level of correlation is sufficiently high.

For the first hyperpolarizability, the situation is more complicated. Here, the two components of β^{el} are considerably smaller at the multiconfigurational MRMP2 level than at the CCSD(T) level, with RAS yielding values in between. To investigate the effect of larger dynamic correlation on the RAS wave function, we additionally computed the properties with a larger RAS3 space spanning 16 orbitals and employing the d-aug-cc-pVDZ basis set. The average properties found were $\alpha_{av}^{el} = 28.49$ au, $\beta_{\|\|}^{el} = 15.56$ au, and $\gamma_{av}^{el} = 3078$ au. Although α and γ are only slightly larger than with the smaller RAS space, $\beta_{\|\|}$ is now *smaller* than at the MRMP2 level. Because of this volatility in the results of the RAS wave function, we consider both the CCSD(T) and MRMP2 results as our "high-end" results for the static electronic contribution to the first hyperpolarizability.

All calculations in Table 2 were performed using the experimental geometry determined by Costain, which is considered to be close to the equilibrium geometry of acetonitrile.[35] To assess the influence of the geometry, we also computed the electric properties at several ab initio optimized geomtries: MP2/d-aug-cc-pVDZ, MP2/cc-pVTZ, RAS/d-aug-cc-pVDZ, and CCSD(T)/aug-cc-pVDZ. As the results for the average quantities collected in Table 3 show, the optimized geometries consistently give larger values for all properties, except for $\beta_{\|\|}^{el}$ with the RAS wave function, where the optimized geometry yields a lower value. Generally, the geometry effect is not very large, not exceeding a few percent, and decreases significantly at the MP2/d-aug-cc-pVTZ//MP2/cc-pVTZ level. As mentioned in section 2, the optimized geometry will probably converge to the experimental equilibrium geometry if larger basis sets with highly correlated methods are applied. We can therefore reasonably expect that the properties calculated with an "ideal" basis set/method combination, defined by giving both an optimized geometry close to the experimental one and converged properties, will be close to the properties calculated at the high

TABLE 4: Frequency-Dependent Electronic Hyperpolarizabilities of Acetonitrile for SHG and EFISH Processes at $\lambda = 514.5$ and 1064 nm at Different Levels of Correlation with Different Basis Sets (daDZ = d-aug-cc-pVDZ, daTZ = d-aug-cc-pVTZ)

	$\lambda = 1064$ nm					$\lambda = 514.5$ nm				
	RPA daDZ	RPA daTZ	CC2 daDZ	CCSD daDZ	RAS daDZ	RPA daDZ	RPA daTZ	CC2 daDZ	CCSD daDZ	RAS daDZ
α_{xx}^{el}	24.09	24.10	25.15	24.66	23.68	24.52	24.54	25.64	25.13	24.11
α_{zz}^{el}	38.71	38.75	40.35	39.43	37.04	39.69	39.73	41.41	40.43	37.94
α_{av}^{el}	28.96	28.98	30.22	29.58	28.13	29.58	29.60	30.90	30.23	28.72
β_{xxz}^{el}	−2.90	−3.59	1.66	1.37	−0.42	−2.64	−3.48	2.94	2.42	−0.02
β_{zxx}^{el}	−2.76	−3.44	2.14	1.76	−0.09	−1.80	−2.66	5.90	4.84	1.92
β_{yyy}^{el}	−6.58	−6.59	−5.02	−5.29	−6.51	−7.98	−8.20	−6.17	−6.53	−8.03
β_{zzz}^{el}	13.60	14.09	37.93	37.79	32.21	16.94	17.40	46.66	47.78	41.25
$\beta_{\|\|}^{el}$	4.74	4.21	24.94	24.47	18.95	7.33	6.59	32.71	32.54	25.50
γ_{xxxx}^{el}	2521	2711	3240	3001	2325	3431	3655	4418	4060	3047
γ_{zzzz}^{el}	4598	4534	8624	7244	5271	6205	6124	12238	10084	7095
γ_{xxyy}^{el}	838	904	1076	997	773	1136	1223	1450	1339	1006
γ_{xxzz}^{el}	1131	1145	1634	1467	1170	1536	1559	2261	2018	1565
γ_{zxzx}^{el}	1141	1156	1658	1486	1182	1600	1629	2437	2151	1645
γ_{zxxz}^{el}	1142	1154	1660	1488	1183	1596	1611	2425	2138	1641
γ_{xzzx}^{el}	1134	1148	1648	1478	1176	1559	1572	2331	2066	1598
γ_{av}^{el}	3173	3273	4772	4232	3236	4328	4449	6691	5855	4332

end of our calculations at the nonoptimized geometry (i.e., CCSD(T)/d-aug-cc-pVDZ and MRMP2/d-aug-cc-pVDZ).

Also shown in Table 3 are some high-level literature values. The values of Norman et al., using the experimental geometry, show that the Pol basis set leads to larger values for $\beta_{\|}^{el}$ and γ_{av}^{el} than do the d-aug-cc-pVDZ and d-aug-cc-pVTZ basis sets whereas the values of Stähelin et al., employing a [7s6p4d1f/6s3p] basis set and an optimized geometry computed at a smaller basis set, are more similar to ours, although still larger.

In Table 4, the frequency-dependent electronic contributions are shown, calculated at the RPA, RAS, CC2, and CCSD levels for second-harmonic generation (SHG) and electric-field-induced second-harmonic generation (EFISH) processes at the two base wavelengths at which experimental gas-phase values are available, $\lambda = 514.5$ and 1064 nm. For $\gamma(-2\omega; \omega, \omega, 0)$, the relation $\gamma_{xxxx} = 2\gamma_{xxyy} + \gamma_{yxxy}$, which is valid for C_{3v} symmetry, has been used to reduce the number of components shown.

The amount of dispersion may be expressed as the ratio $P(\omega)/P(0)$, where P is any component of the hyperpolarizabilities. We chose this kind of representation because we will use these multiplicative scaling factors in the following to incorporate the dispersion effect into those methods for which frequency-dependent values are not available. In Table 5, we have collected the multiplicative scaling factors for selected components computed with four different analytical methods. The dispersion at the RPA/d-aug-cc-pVTZ level is very similar to the dispersion at the RPA/d-aug-cc-pVDZ level and is not shown. For the linear polarizability α and the second hyperpolarizability γ, the dispersion is nearly independent of the computational method used. The same also holds for the component β_{zzz} but definitely not for the nondiagonal components β_{izz} and β_{zzi}, for which the scaling factors vary wildly both with respect to method and frequency. However, the dispersion of the composite quantity $\beta_{\|}$ is very similar at all correlated levels but not at the RPA level, for which a much larger dispersion is obtained than at the correlated levels. This behavior is due to the very small magnitude of the nondiagonal components in comparison to the β_{zzz} component at all correlated levels, which leads to a small influence of the nondiagonal components on the dispersion of $\beta_{\|}$. For the scaling procedure, we will use a component-wise scaling for α and γ components, but the β components will be scaled by the scaling factor of $\beta_{\|}$. The scaling factors computed at the CCSD level, which we consider to be the most accurate and which also happen to lie between those of the RAS and the CC2 methods, will be applied.

TABLE 5: Scaling Factors $P(\lambda)/P(0)$ for Selected Components of the Hyperpolarizabilities of Acetonitrile for $\lambda = 1064$ and 514.5 nm Computed at Different Levels of Theory

	$\lambda = 1064$ nm				$\lambda = 514.5$ nm			
	RPA	CC2	CCSD	RAS	RPA	CC2	CCSD	RAS
α_{xx}^{el}	1.0054	1.0056	1.0054	1.0055	1.02337	1.0252	1.0249	1.0238
α_{zz}^{el}	1.0076	1.0080	1.0074	1.0071	1.03306	1.0345	1.0332	1.0315
β_{xxz}^{el}	1.000	1.177	1.033	0.857	0.910	2.085	2.068	0.041
β_{zxx}^{el}	0.952	1.518	0.971	0.184	0.621	4.184	4.137	−3.939
β_{zzz}^{el}	1.066	1.062	1.068	1.072	1.328	1.306	1.343	1.373
$\beta_{\|\|}^{el}$	1.145	1.079	1.083	1.087	1.754	1.415	1.438	1.462
γ_{xxxx}^{el}	1.089	1.089	1.083	1.078	1.481	1.485	1.471	1.413
γ_{zzzz}^{el}	1.087	1.101	1.092	1.086	1.467	1.562	1.524	1.462
γ_{av}^{el}	1.086	1.097	1.093	1.084	1.481	1.538	1.512	1.452

Norman et al.[12] found a smaller dispersion for $\beta_{\|}(-2\omega; \omega, \omega)$ at the SCF/Pol level at $\lambda = 514.5$ nm (1.39), similar to that at the RAS/Pol level (1.38) and both comparable to those found here at correlated levels. The smaller dispersion at the SCF level in this case is again connected with the very small nondiagonal terms β_{iiz} and β_{zii}. The dispersion of $\gamma_{av}(-2\omega; \omega, \omega, 0)$ is similar to the one found here. The dispersion of $\beta_{\|}$ calculated by Stähelin et al.[10] at the SCF/[7s6p4d1f/6s3p] level is 1.72, which is very similar to ours. However, the dispersion at the MP2 level (1.12) appears to be too small.

3.1.2.Vibrational Contributions. The calculation of vibrational contributions is computationally more expensive than that of the electronic contributions. Studies of convergence behavior with respect to basis set and electronic correlation are therefore

TABLE 6: Comparison of Static Pure Vibrational Corrections Calculated with Different Basis Sets (BS, aDZ = aug-cc-pVDZ, daDZ = d-aug-cc-pVDZ, aTZ = aug-cc-pVTZ), Order of Derivatives (*mnopq*), Correlation Levels, and Derivatives Calculated Analytically (analyt) or Numerically Using Geometric Displacements (displ) or Finite Field (field) Methods

BS	aDZ					daDZ	aTZ	aDZ	
	SCF							MP2	
	analyt			displ	field	displ	field	field	
mnopq	43210	32210	21110[a]	32210	32222	32210	32222	32222	21110[a]
α_{xx}^{PV}	0.39	0.42	0.40	0.45	0.45	0.44	0.45	0.24	0.23
α_{zz}^{PV}	0.35	0.34	0.28	0.35	0.35	0.35	0.34	0.10	0.05
α_{av}^{PV}	0.37	0.40	0.36	0.41	0.41	0.41	0.41	0.20	0.17
β_{xxz}^{PV}	15.21	16.26	18.17	16.84	16.84	15.99	15.70	10.52	10.80
β_{yyy}^{PV}	−4.50	−4.40	−4.05	−4.40	−4.40	−4.22	−4.26	−4.48	−3.90
β_{zzz}^{PV}	26.88	25.88	23.63	26.19	26.18	25.86	25.47	5.38	4.57
$\beta_{\|\|}^{PV}$	34.37	35.04	35.98	35.92	35.92	34.71	34.12	15.85	15.71
γ_{xxxx}^{PV}	496	528	397	535	536	565	546	515	488
γ_{zzzz}^{PV}	1721	1704	1613	1696	1694	1703	1660	1924	1913
γ_{xxyy}^{PV}	165	176	132	178	188	188	192	178	169
γ_{xxzz}^{PV}	513	504	737	475	479	451	442	607	741
γ_{av}^{PV}	1019	1021	1124	1004	1012	1003	981	1148	1238

[a] Double-harmonic approximation.

TABLE 7: Frequency-Dependent Pure Vibrational Corrections for SHG and EFISH at $\lambda = 514.5$ and 1064 nm Calculated at the MP2 Level with the aug-cc-pVDZ Basis Set and *mnopq* = 32222'

λ/nm	1064	514.5		1064	514.5
β_{xxz}^{PV}	0.04	0.01	β_{zxx}^{PV}	0.14	0.03
β_{zzz}^{PV}	0.28	0.06	$\beta_{\|\|}^{PV}$	0.26	0.06
γ_{xxxx}^{PV}	−76	−36	γ_{zzzz}^{PV}	−95	−16
γ_{xxzz}^{PV}	−26	−10	γ_{xyyx}^{PV}	−19	−11
γ_{xxzz}^{PV}	−34	−6	γ_{zzxx}^{PV}	−54	−27
γ_{zxxz}^{PV}	−22	−24	γ_{xzzx}^{PV}	−43	−6
γ_{av}^{PV}	−273	−104			

necessarily more limited for these corrections. Fortunately, for processes at optical frequencies, it often turns out that vibrational contributions are small compared to the electronic contributions so that not completely converged values may be tolerated. In Bishop−Kirtman perturbation theory, the dependence of the vibrational corrections on the level of anharmonicity included in the perturbation series should also be checked.[43,56] As mentioned in section 2, with the methods employed by us, this is possible only for PV contributions.

In Table 6, we have compiled our results for the PV contributions. The data in the first three columns, for which analytically computed derivatives of different order *mnopq* have been used, show that the double-harmonic approximation captures the largest part of the PV contributions; including higher-order derivatives leads only to marginal adjustments. In the case of acetonitrile, the double-perturbation series is therefore convergent. This is also true at the MP2 level, as the last two columns of the Table show. Comparison of the data in the second column (analyt/32210) with those of the fourth and fifth columns, where numerically computed derivatives have been used, either calculated by finite differences with respect to nuclear displacements or with respect to external electric fields, shows that all three approaches yield similar values. Remaining small differences can be explained by inaccuracies of the numerical approach as well as by the use of Cartesian basis functions in the analytical computations instead of the spherical basis functions used in the numerical calculations.

Comparison of the data computed with three different basis sets—aug-cc-pVDZ, d-aug-cc-pVDZ, and aug-ccpVTZ—at the SCF level shows that the PV contributions are nearly independent of the basis set used (i.e., the aug-cc-pVDZ basis set leads to values converged with respect to basis set completeness). Electronic correlation, taken into account at the MP2 level, has quite a large influence on the PV contributions. All components of α^{PV} and β^{PV} are considerably reduced at the MP2 level, up to a factor of 5 in the case of β_{zzz}^{PV}, whereas the components of γ^{PV} are generally slightly enhanced. We note that these trends are in marked contrast to the effect of correlation on the electronic contributions.

We conclude from our data that PV contributions calculated with the aug-cc-pVDZ basis set and an order of energy derivatives that is sufficiently high to allow the simultaneous calculation of ZPVA contributions (i.e., with *mnopq* = 32222 yields converged values with respect to order of anharmonicities and basis set completeness) and that electronic correlation effects are considerable and need to be taken into account.

In Table 7, the nonvanishing frequency-dependent PV contributions at $\lambda = 514.5$ and 1064 nm at the MP2 level with the aug-cc-pVDZ basis set are shown, computed at the *mnopq* = 32222 level and evaluated in the limit of $\omega_\lambda \gg \omega_{vib}$, where ω_λ is the frequency of the optical light and ω_{vib} denotes the vibrational frequencies. As expected, frequency-dependent PV contributions are much smaller than the static contributions. Interestingly, all γ^{PV} contributions for EFISH processes are negative, contrary to ZPVA, static PV, and electronic contributions.

Similar conclusions concerning basis set and correlation dependence as for the PV contributions can be drawn in the case of the ZPVA corrections, as shown by the data collected in Table 8. Again, all of the properties depend very little on the basis set, although there is a slightly larger dependence on additional diffused basis functions for γ^{ZPVA} than for the PV corrections. Similarly, a large correlation effect is found for the ZPVA contributions, resembling more closely the correlation effects on the electronic properties. We note that the vector component along the dipole moment, $\beta_{\|\|}^{ZPVA}$, has an opposite sign to that of the electronic contribution.

TABLE 8: Comparison of Static ZPVA Corrections Calculated with Different Basis Sets (BS), Correlation Levels, and Derivatives Calculated Numerically Using Geometric Displacements (displ) or Finite Field (field) Methods

BS	aDZ		daDZ	aTZ	aDZ
	SCF				MP2
	displ	field	field	field	field
μ_z^{ZPVA}	−0.003	−0.003	−0.003	−0.003	−0.010
$\alpha_{xx}^{\mathrm{ZPVA}}$	0.73	0.73	0.74	0.72	0.68
$\alpha_{zz}^{\mathrm{ZPVA}}$	1.06	1.06	1.07	1.05	1.02
$\alpha_{\mathrm{av}}^{\mathrm{ZPVA}}$	0.84	0.84	0.85	0.83	0.80
$\beta_{xxz}^{\mathrm{ZPVA}}$		−2.06	−2.10	−1.98	−2.00
$\beta_{yxx}^{\mathrm{ZPVA}}$		−0.97	−0.97	−0.92	−0.82
$\beta_{zzz}^{\mathrm{ZPVA}}$		−2.02	−2.15	−2.22	0.11
$\beta_{\|\|}^{\mathrm{ZPVA}}$		−3.68	−3.81	−3.71	−2.33
$\gamma_{xxxx}^{\mathrm{ZPVA}}$		143	165	153	269
$\gamma_{zzzz}^{\mathrm{ZPVA}}$		277	322	294	431
$\gamma_{xxxx}^{\mathrm{ZPVA}}$		48	54	50	121
$\gamma_{xxzz}^{\mathrm{ZPVA}}$		69	82	69	92
$\gamma_{\mathrm{av}}^{\mathrm{ZPVA}}$		187	218	195	316

3.1.3. Comparison with Experiment. In Table 9, we compare the experimental values of the electrical properties $P = \mu, \alpha, \beta, \gamma$ with our calculated total properties at correlated levels, estimated by $P^{\mathrm{method}}(\omega) = [P^{\mathrm{el,method}}(0) + P^{\mathrm{ZPVA,\,MP2}}(0)] \times [P^{\mathrm{el,CCSD}}(\omega)/P^{\mathrm{el,CCSD}}(0)] + P^{\mathrm{PV,\,MP2}}(\omega)$ for those methods where the electronic properties were calculated by finite field methods or otherwise by $P^{\mathrm{method}}(\omega) = P^{\mathrm{el,method}}(\omega) + P^{\mathrm{ZPVA,\,MP2}}(0) \times [P^{\mathrm{el,CCSD}}(\omega)/P^{\mathrm{el,CCSD}}(0)] + P^{\mathrm{PV,\,MP2}}(\omega)$. The polarizability anisotropy and the average polarizability of acetonitrile in the gas phase at $\lambda = 514.5$ nm were measured by Alms et al.[57] The hyperpolarizabilities of acetonitrile in the gas phase have been determined at $\lambda = 514.5$ nm[10] and at $\lambda = 1064$ nm[11] by temperature-dependent EFISH measurements.

The effect of the vibrational contributions on the total quantities is quite small for μ_z, α, and γ_{av}, the largest effect being the positive contribution of 370 au in the case of γ_{av} at $\lambda = 514.5$ nm (about 6−8% depending on the computational method). The vibrational corrections of −2.3 at $\lambda = 1064$ nm and −3.3 at $\lambda = 514.5$ nm for $\beta_{\|\|}$ amount to a more substantial change of 10−20%.

The experimental dipole moment and the polarizabilities, including the polarizability anisotropy, which is generally more difficult to predict, are quite well reproduced by nearly all of the methods, with the exception of CC2 and RAS, for which the deviations are significantly larger than the experimental error limits. The experimental first hyperpolarizability is increasingly better approximated in the sequence of single-configuration reference methods MP2 < CC2 < CCSD < CCSD(T) at both wavelengths. Employing a larger basis set improves the agreement further, as a comparison between MP2/d-aug-cc-pVDZ and MP2/d-aug-cc-pVTZ shows. Adding the difference $\beta_{\|\|}$(MP2/d-aug-cc-pVTZ) − $\beta_{\|\|}$(MP2/d-aug-cc-pVDZ) to $\beta_{\|\|}$(CCSD(T)) leads to approximated best values of 25.8 au at $\lambda = 514.5$ nm and 19.6 au at $\lambda = 1064$ nm. The multiconfiguration reference methods are not conclusive. Although RAS gives a better value for $\beta_{\|\|}$ at $\lambda = 514.5$ nm than CCSD(T), the value at $\lambda = 1064$ nm is far from the experimental value. Furthermore, the higher correlated MRMP2 method leads to even larger disagreement.

For the second hyperpolarizability of the EFISH process, our calculated values show a mixed picture: we find very good agreement with experiment at $\lambda = 1064$ nm with only a 1% deviation for nearly all methods. The exceptions are, as in the case of the linear polarizabilities, CC2 and RAS. For $\lambda = 514.5$ nm, however, the same methods that show good agreeement at the longer wavelength severely overestimate the experimental value, as does CC2. Only RAS leads in this case to an again nearly perfect agreement with experiment, a fact that has been used by Norman et al. to state that γ_{av} of acetonitrile is described properly by the correlated RAS wave function.[12] However, this statement appears doubtful in view of our more complete calculations, which suggest that *all* of the methods applied here, including RAS, overestimate the dispersion of γ_{av} in comparison with experiment.

Considering the similar dispersion computed with RPA, RAS, CC2,and CCSD, it is unlikely that insufficient electronic correlation is the reason for the discrepancy of the dispersion of γ_{av} between theory and experiment. A possible explanation for the disagreement may be found in the experimental procedure to determine $\beta_{\|\|}$ and γ_{av}. These values were determined by a linear regression of temperature-dependent measurements of the gas-phase EFISH susceptibility $\chi^{(3)}$.[10,11] The temperature range accessible for such measurements on acetonitrile is necessarily rather limited (300−500 K), leading to magnified uncertainties for the slope and intercept of the regression lines from which $\beta_{\|\|}$ and γ_{av} are extracted. Instead of comparing $\beta_{\|\|}$ and γ_{av}, one may compare directly the primary experimental quantities $\langle\gamma\rangle = \mu\beta_{\|\|}/(3kT) + \gamma_{\mathrm{av}}$ given in refs 10 and 11 with those computed with the different computational methods, thus sidestepping the regression analysis step. In doing this, the mean percentage differences between experiment and computed values shown in Table 10 result.

For each method, the mean deviations differ between the two wavelengths by only 2−3%, which lies in the error margins given by the standard deviations. This may be an indication that part of the discrepancy found in the dispersion of γ_{av} is due to an erroneous distribution of the total $\langle\gamma\rangle$ values onto the slope and intercept during the regression analysis, which may be caused by small systematic errors such as, for example, small temperature dependencies of $\beta_{\|\|}$ and/or γ_{av}.

In any case, the values show that with high-level correlated methods using large basis sets and including frequency dispersion and vibrational contributions, the experimental $\langle\gamma\rangle$ values of small molecules such as acetonitrile can be computed to an accuracy of about 10%. We note that with this kind of comparison, the two methods CCSD(T) and MRMP2, which furthermore bracket the experimental values, appear to be the most accurate, followed by RAS, CCSD, MP2/d-aug-cc-pVTZ, MP2, and finally CC2. Unfortunately, the differences between RAS and the other methods for γ_{av} are concealed in the composite quantity $\langle\gamma\rangle$.

3.2. Liquid-Phase Properties Predicted with the Onsager Model. Linear and nonlinear EFISH susceptibilities of liquid acetonitrile at $T = 20$ °C with a density of 0.786 g/mL[58] have been calculated using the Onsager model as outlined in section 2, employing CCSD(T) and MRMP2 with the d-aug-cc-pVDZ basis set. The results are shown in Tables 11 and 12. The relative permittivity ϵ and the refractive indices $n(\omega)$ needed for the calculation of the local field factors have been taken from experiment.[10,59]

The reaction field calculated at the CCSD(T) level is 3.65 GV/m (0.0071 au) and was also used for the MRMP2 calculations. For the calculation of the field effect on the electronic contribution, the field has been included in the Hamiltonian whereas the field effect on the vibrational contributions was

TABLE 9: Comparison of Experimental and Calculated Electronic Properties[a]

	μ	α_{anis}[b]	α_{av}	$\beta_{\|\|}$	$\beta_{\|\|}$	γ_{av}	γ_{av}
λ/nm	∞	514.5	514.5	1064	514.5	1064	514.5
exptl[c]	1.542	15.39	30.43	17.9	26.3	4250	4619
error[c]	±0.024 (1.5%)	±0.46 (3%)	±0.61 (2%)	±1.1 (6%)	±0.8 (3%)	±575 (14%)	±370 (8%)
MP2	1.527 (−1%)	15.43 (0.3%)	30.93 (1.6%)	23.9 (34%)	31.5 (20%)	4200 (−1%)	6080 (32%)
MP2/daTZ	1.534 (−0.5%)	15.42 (0.2%)	30.90 (1.5%)	23.2 (30%)	30.6 (16%)	4240 (−0%)	6140 (33%)
CC2		16.13 (4.8%)	31.72 (4.2%)	22.7 (27%)	29.4 (12%)	4840 (14%)	7060 (53%)
CCSD		15.66 (1.8%)	31.05 (2.0%)	22.2 (24%)	29.3 (11%)	4304 (1%)	6230 (35%)
CCSD(T)	1.515 (−1.8%)	15.79 (2.6%)	31.13 (2.3%)	20.3 (13%)	26.7 (2%)	4290 (1%)	6200 (34%)
RAS	1.517 (−1.6%)	14.19 (−8.5%)	29.54 (−3.0%)	16.7 (−7%)	22.2 (−18%)	3310 (−29%)	4700 (2%)
MRMP2	1.522 (−1.3%)	15.14 (−1.7%)	30.94 (1.7%)	15.1 (−19%)	19.8 (−33%)	4280 (1%)	6190 (34%)

[a] Computed properties were calculated with the d-aug-cc-pVDZ basis set if not otherwise indicated. [b] $\alpha_{anis} = \alpha_{zz} - \alpha_{xx}$. [c] μ: ref 67; α: ref 57; β, γ at 514.5 nm: ref 10; 1064 nm, ref 11.

TABLE 10: Mean Deviation of the Calculated Properties $\langle\gamma\rangle(T) = \mu_z\beta_{||}/(3kT) + \gamma_{av}$ from Experimental Values

λ/nm	1064	514.5
MP2	(20 ± 2)%	(23 ± 2)%
MP2/dTZ	(18 ± 2)%	(21 ± 2)%
CC2[a]	(22 ± 2)%	(24 ± 2)%
CCSD[a]	(16 ± 2)%	(19 ± 2)%
CCSD(T)	(7 ± 2)%	(10 ± 2)%
RAS	(−14 ± 1)%	(−11 ± 1)%
MRMP2	(−11 ± 2)%	(−8 ± 1)%

computed according to the series expansion equations. The influence of the field on the vibrational corrections to γ are thus not taken into account, which should not lead to large errors for the computed EFISH susceptibility. The effect of the reaction field on the electric properties follows an established pattern: although the polarizabilities are very little affected, the first hyperpolarizabilies are strongly enhanced, and the dipole moment and second hyperpolarizabilities are moderately changed by the field. We note that the occurrence of the static PV contributions in the total static properties leads to values for the latter that are often larger than the total frequency-dependent properties. We mention that our in-liquid dipole moment is in good agreement with the dipole moment of 1.77 ± 0.04 au estimated by Ohba and Ikawa from integrated far-infrared spectra.[60]

To obtain the dispersion scaling factors including the reaction-field effect, frequency-dependent hyperpolarizabilities were computed with the external field at the CC2 and RPA levels at $\lambda = 532$ and 1064 nm, the two wavelengths for which experimental EFISH data for liquid acetonitrile are available.[10] The dispersion calculated at the two levels is similar: at $\lambda = 1064$ nm, the dispersions of $\beta_{||}^{el}$ and $\gamma_{||}^{el}$ are 9.5 and 9.4%, respectively, at the RPA level and 9.5 and 10.3%, respectively, at the CC2 level. For $\lambda = 532$ nm, the dispersions are 47.8 and 47.6%, respectively, at the RPA level, and 48.3 and 54.5%, respectively, at the CC2 level. The mean of the two computations was used to calculate the scaling factors. We note that the dispersion found here is significantly larger than the one reported in ref 12 using reaction-field response theory for nonequilibrium solvation. Also, we find a normal dispersion for the linear polarizability (0.7% at 1064 nm, 2.7% at 514.5 nm) that is contrary to the anomalous dispersion found by Norman et al. Nevertheless, the experimental static permittivity ϵ and the refractive indices from $\lambda = 1064$ nm down to $\lambda = 266$ nm are very well reproduced by the calculations in the dipolar Onsager model, with maximal deviations of 2.5% for CCSD(T) and 1.9% for MRMP2. Because the relationships between the permittivities and microscopic quantities have been used in ref 12 to determine the cavity radius and the local field factors, a comparison with experimental quantities is not useful in this case.

The local field factors using an ellipsoidal cavity are smaller than those found in ref 12 employing a spherical cavity, which in turn are smaller than those based on the usual Onsager and Lorentz expressions; see ref 12. The choice of an ellipsoidal cavity instead of a spherical one has a considerable effect on the local field factors: for MRMP2, using the radius of a sphere of equal volume to that of the ellipsoid, 2.68 Å, and α_{av}^{sol} yields a static local field factor of 1.92. This radius is close to one of the two used by Willetts and Rice,[13] 2.7 Å. Using instead the long semiaxis, 3.25 Å, as the radius of a enclosing sphere, which is close to the second choice (3.22 Å) employed by Willetts and Rice, together with α_{av}^{sol} yields a static local field factor of 1.69, similar to the one calculated by Norman et al.[12] using CAS/Pol. Employing α_{zz} instead of α_{av}^{sol} leads to even larger values. This shape effect is naturally enhanced in the total local field factor for the EFISH process, which consists of the product of four single local field factors.

Finally, we compare the computed EFISH susceptibilities in the dipolar Onsager model with the experimental values. There are two calibration factors for quartz currently in use,[61,62] differing by about 40%, although the smaller and newer of these values is becoming increasingly more accepted.[63−65] The values in Table 12 show that for both wavelengths and for both methods the computed values are much closer to the lower experimental value, with maximal differences of 20%. The dipolar Onsager reaction-field model therefore also predicts that the lower of the two calibration factors is more accurate.[62] The same conclusion has been drawn by Norman et al., although with less complete molecular data and a different application of the reaction-field model.

4. Conclusions

We have presented a complete study of the hyperpolarizabilities of acetonitrile, including PV and ZPVA vibrational contributions and frequency dispersion. We studied basis set and correlation effects on the static and frequency-dependent electronic and vibrational contributions, employing a series of basis sets designed for a systematic approach of the basis set limit. Results at the highest level of correlation employed—single-reference CCSD(T) and multireference MP2—over- and underestimate, respectively, the experimental EFISH values of the composite quantity $\langle\gamma\rangle = \beta_{||}\mu_z/(3kT) + \gamma_{av}$ at two different wavelengths by about 10%. Larger differences found for the single quantities $\beta_{||}$ and γ_{av} may be partially attributed to difficulties arising from the regression analysis of a limited temperature-dependent set of experimental data. The difference

TABLE 11: Electronic Properties of Liquid Acetonitrile Calculated at the CCSD(T) and MRMP2 Levels Using the d-aug-cc-pVDZ Basis Set with the Onsager Model[a]

	CCSD(T)				MRMP2				RAS/Pol[b]
λ/nm	∞		1064	532	∞		1064	532	514.5
	electronic	total	total	total	electronic	total	total	total	electronic
μ_z^{sol}	1.809	1.806			1.808	1.805		1.66	
α_{xx}^{sol}	24.59	25.59	25.38	25.81	24.61	25.61	25.40	25.83	24.57
α_{zz}^{sol}	39.68	40.90	41.04	41.64	39.05	40.27	40.40	41.00	39.54
α_{av}^{sol}	29.62	30.69	30.60	31.09	29.42	30.50	30.40	30.95	29.56
β_{xxz}^{sol}	11.3	24.8	10.7	14.7	9.0	22.5	8.1	11.3	8.3
β_{zzz}^{sol}	80.6	102.8	91.3	124.2	72.0	94.2	81.9	111.0	86.5
$\beta_{\|\|}^{sol}$	61.9	91.4	67.7	92.1	54.0	83.5	59.0	80.1	63.2
γ_{xxxx}^{sol}	2866	3650	3373	4698	2948	3732	3463	4821	3882
γ_{zzzz}^{sol}	7055	9410	8140	11288	6501	8856	7530	10452	9524
γ_{xxyy}^{sol}	954	1253	1156	1614	1056	1355	1269	1768	1262
γ_{xxzz}^{sol}	1461	2160	1673	2338	1533	2232	1753	2448	2000
γ_{av}^{sol}	3423	5572	4776	6583	3440	5630	4792	6671	5649

[a] Frequency dispersion was computed at CC2 and RPA levels (see text). [b] Reference 12.

TABLE 12: Computed Local Field Factors ($f^{\omega} = f_{zz}^{C\omega} F_{zz}^{R\omega}$, $f^{EFISH} = f^{0}(f^{\omega})^{2} f^{2\omega}$) and Macroscopic Susceptibilities (Relative Permittivity ϵ, Refractive Indices $n(\omega)$, EFISH Susceptibility $\chi^{(3)}/10^{-24}$m ^{2}V^{-2}) of Liquid Acetonitrile and Comparison with Experimental and Literature Values

λ/nm	∞	1064	532	266	1064	532
			f^{ω}			f^{EFISH}
CCSD(T)	1.608	1.209	1.214	1.242	2.863	2.952
MRMP2	1.700	1.210	1.213	1.222	2.855	2.873
RAS/Pol[a]			1.258			3.383
	ϵ		n			$\chi^{(3)b}$
CCSD(T)	36.1	1.345	1.352	1.415	1653	2263
MRMP2	36.3	1.343	1.349	1.385	1477	2019
RAS/Pol[a]						1951
exptl[c]	37.0	1.339	1.347	1.384	1762/2981	1897/3252

[a] Using the experimental dipole moment $\mu_z = 1.542$ au. [b] For comparison with refs 10 and 12: $4\chi^{(3)}_{\text{Stähelin}}/\rho = 6\epsilon_0\chi^{(3)}/N(1.6036 \times 10^{64}$ au)/[(Cm)^4/J^3] = $\chi^{(3)}(7.3795 \times 10^{25}$ au)/[m^2 V^{-2}]. [c] ϵ: ref 60 (intrapolation), $n(\omega)$: ref 10, $\chi^{(3)}$: ref 13: values in this reference differ from those of the original experimental work, ref 10, but appear to be more consistent.

between multireference MP2 and CCSD(T) for γ is nearly completely because of a different prediction of the first hyperpolarizability $\beta_{\|\|}$, which is the result of a delicate balance between a large β_{zzz} value and small positive or negative β_{zzi} and β_{izz} values. This is reminescent of the similarly difficult to predict SHG property of HF,[55,66] although in that case the problem is enhanced by even lower values of the components of β and slower convergence with respect to basis set completeness and correlation treatment.

The main goal of this work was to determine a feasible basis set/method combination that allows for the computation of an accurate set of electric properties for a molecular simulation of the EFISH signal of liquid acetonitrile. We conclude that such a combination can be either d-aug-cc-pVDZ/CCSD(T) or d-aug-cc-pVDZ/MRMP2. Frequency dispersion may be taken into account by CC2 or RPA calculations, except for β, for which RPA yields a dispersion that is too large, at least without an additional external field. Using these two combinations, we also computed the linear and nonlinear (EFISH) susceptibilities of liquid acetonitrile in the dipolar Onsager approximation. With an ellipsoidal cavity determined by standard bond lengths and van der Waals radii, we found very good agreement with experiment for the computed static relative permittivity and the refractive indices over a wide range of optical frequencies and satisfactory agreement for the EFISH susceptibility $\chi^{(3)}(-2\omega; \omega, \omega, 0)$ at two wavelengths, if the lower of the two calibration factors currently in use is employed to extract $\chi^{(3)}$ from the experimental data. This essentially confirms the conclusions drawn previously by Norman et al. on the basis of a different reaction-field model and employing a wave function model combination of RAS/Pol and CAS/Pol.[12] Although they have used a “parameter-free” reaction-field model by using the experimetal linear macroscopic properties to derive the cavity radius and local field factors for the specific wave function under consideration, this leaves only the EFISH susceptibility as an independent test case for the wave function/cavity/reaction field employed. In contrast, our more standard method predicts linear and nonlinear macroscopic properties independently.

The reaction-field model, however, neglects all intermolecular correlations whose existence in liquid acetonitrile is supported by a wealth of experimental data.[5,6] Work currently in progress aims at investigating whether molecular simulation methods are able to provide information about the influence of such intermolecular correlations on the linear and nonlinear susceptibilities of liquid acetonitrile.

References and Notes

(1) Cammi, R.; Mennucci, B.; Tomasi, J. *J. Phys. Chem. B* **2000**, *104*, 4690.

(2) Mikkelsen, K. V.; Jørgensen, P.; Jensen, H. J. Aa. *J. Chem. Phys.* **1994**, *100*, 6597.

(3) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(4) Reis, H.; Papadopoulos, M. G.; Theodorou, D. N. *J. Chem. Phys.* **2001**, *114*, 876.

(5) (a) Evans, G. J. *Adv. Chem. Phys.* **1985**, *63*, 293. (b) Evans, M. J.; Evans G. J. *Adv. Chem. Phys.* **1985**, *63*, 377.

(6) (a) Kaatz, P.; Shelton, D. P. *Phys. Rev. Lett.* **2000**, *82*, 1224. (b) Shelton, D. P. *Chem. Phys. Lett.* **2000**, *325*, 513.

(7) Munn, R. W. *Mol. Phys.* **1988**, *64*, 1.

(8) Reis, H.; Papadopoulos, M. G.; Munn, R. W. *J. Chem. Phys.* **1998**, *109*, 6828.

(9) Janssen, R. H. C.; Bomont, J.-M.; Theodorou, D. N.; Raptis, S.; Papadopoulos, M. G. *J. Chem. Phys.* **1999**, *110*, 6463.

(10) Stähelin, M.; Moylan, C. R.; Burland, D. M.; Willetts, A.; Rice, J. E.; Shelton, D. P.; Donley, E. A. *J. Chem. Phys.* **1993**, *98*, 5595.

(11) Kaatz, P.; Donley, E. A.; Shelton, D. P. *J. Chem. Phys.* **1998**, *108*, 849.

(12) Norman, P.; Luo, Yi; Ågren, H. *J. Chem. Phys.* **1997**, *107*, 9535.

(13) Willetts, A.; Rice, J. E. *J. Chem. Phys.* **1993**, *99*, 426.

(14) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983.

(15) Nakano, H. *Chem. Phys. Lett.* **1993**, *207*, 372.

(16) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(17) Christiansen, O.; Koch, H.; Jørgensen, P. *Chem. Phys. Lett.* **1995**, *244*, 75.

(18) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(19) Cohen, H. D.; Roothaan, C. C. J. *J. Chem. Phys.* **1965**, *43*, S34.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert S. T., Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(22) Olsen, J.; Jørgensen, P. *J. Chem. Phys.* **1985**, *82*, 3235.

(23) Helgaker, T.; Jensen, H. J. Aa.; Joergensen, P.; Olsen, J.; Ruud, K.; Aagren, H.; Auer, A. A.; Bak, K. L.; Bakken, V.; Christiansen, O.; Coriani, S.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernandez, B.; Haettig, C.; Hald, K.; Halkier, A.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Pedersen, T. B.; Ruden, T. A.; Sanchez, A.; Saue, T.; Sauer, S. P. A.; Schimmelpfennig, B.; Sylvester-Hvid, K. O.; Taylor, P. R.; Vahtras, O. *Dalton*, release 1.2, 2001 (a molecular electronic structure program).

(24) Jonsson, D.; Jørgensen, P.; Ågren, H. *J. Chem. Phys.* **1996**, *105*, 6401 and references therein.

(25) Hättig, C.; Christiansen, O.; Jørgensen, P. *Chem. Phys. Lett.* **1997**, *269*, 428.

(26) Hättig, C.; Christiansen, O.; Jørgensen, P. *Chem. Phys. Lett.* **1998**, *282*, 139.

(27) Hättig, C.; Jørgensen, P. *J. Chem. Phys.* **1998**, *109*, 2762.

(28) Sadlej, A. J. *Collect. Czech. Chem. Commun.* **1995**, *53* 1988.

(29) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1994**, *100*, 2975.

(30) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(31) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(32) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1994**, *98*, 1538.

(33) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1995**, *103*, 4572.

(34) Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 2/12/03, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.

(35) Costain, C. C. *J. Chem. Phys.* **1958**, *29*, 864.

(36) Bak, K. L.; Gauss, J.; Helgaker, T.; Stanton, J. F. *J. Chem. Phys.* **2001**, *114*, 6548.

(37) Bishop, D. M. *Adv. Chem. Phys.* **1998**, *104*, 1.

(38) Quinet, O.; Champagne, B.; Kirtman, B. *J. Comput. Chem.* **2001**, *22*, 1920.

(39) Bishop, D. M.; Luis, J. M.; Kirtman, B. *J. Chem. Phys.* **1998**, *108*, 10013.

(40) Amos, R. D.; Alberts, I. L.; Andrews, J. S.; Colwell, S. M.; Handy, N. C.; Jayatilaka, D.; Knowles, P. J.; Kobayashi, R.; Laming, G. L.; Lee, A. M.; Maslen, P. E.; Murray, C. W.; Palmieri, P.; Rice, J. E.; Simandiras, E. M.; Stone, A. J.; Su, M. D. *CADPAC5.0, The Cambridge Analytic Derivatives Package*; Cambridge, U.K., 1992.

(41) Ingamells, V. E.; Papadopoulos, M. G.; Raptis, S. G. *Chem. Phys. Lett.* **1999**, *233*, 484.

(42) Luis, J. M.; Champagne, B.; Kirtman, B. *Int. J. Quantum Chem.* **2000**, *80*, 471.

(43) Torrent-Sucarrat, M.; Solà, M.; Duran, M.; Luis, J. M.; Kirtman, B. *J. Chem. Phys.* **2002**, *116*, 5363.

(44) Bishop, D. M.; Sauer, S. P. A. *J. Chem. Phys.* **1997**, *107*, 8502.

(45) Kirtman, B.; Luis, J. M.; Bishop, D. M. *J. Chem. Phys.* **1998**, *108*, 10008.

(46) Luo, Y.; Ågren, H.; Vatras, O. *J. Chem. Phys.* **1993**, *98*, 7159.

(47) Spirko, V.; Luo, Y.; Ågren, H.; Jørgensen, P. *J. Chem. Phys.* **1993**, *99*, 9815.

(48) Wortmann, R.; Bishop, D. M. *J. Chem. Phys.* **1998**, *108*, 1001.

(49) Munn, R. W.; Luo, Y.; Macák, P.; Ågren, H. *J. Chem. Phys.* **2001**, *114*, 3105.

(50) Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, *97*, 7590.

(51) Luo, Y.; Ågren, H.; Mikkelsen, K. V. *Chem. Phys. Lett.* **1997**, *275*, 145.

(52) Liptay, W.; Walz, G.; Baumann, W.; Schlosser, H.-J.; Deckers, H.; Detzer, N. *Z. Naturforsch., A: Phys. Sci.* **1971**, *26*, 2020.

(53) Liptay, W.; Becker, J.; Wehning, D.; Lang, W. *Z. Naturforsch., A: Phys. Sci.* **1982**, *37*, 1396.

(54) Boettcher, C. J. F.; Bordewijk, P. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1978; Vol. 1.

(55) Larsen, H.; Olsen, J.; Hättig, C.; Jørgensen, P.; Christiansen, O.; Gauss, J. *J. Chem. Phys.* **1999**, *111*, 1917.

(56) Eckart, U.; Sadlej, A. J. *Mol. Phys.* **2001**, *99*, 735.

(57) Alms, G. R.; Burnham, A. K.; Flygare, W. H. *J. Chem. Phys.* **1975**, *63*, 3321.

(58) *CRC Handbook of Chemistry and Physics*, 62nd edition; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1981.

(59) Würflinger, A. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 653.

(60) Ohba, T.; Ikawa, S. *Mol. Phys.* **1991**, *75*, 985.

(61) Kurtz, S. K.; Jerphagnon, J.; Choy, M. M. In *Landolt-Börnstein*, New Series, Group III; Hellwege K.-H., Hellwege, A. M., Eds., Springer: Berlin, 1979; Vol. 11.

(62) Eckkardt, R.; Masuda, H.; Fan, Y.; Byer, R. *IEEE J. Quantum Electron.* **1990**, *26*, 922.

(63) Roberts, D. A. *IEEE J. Quantum Electron.* **1992**, *QE-28*, 2057.

(64) Bosshard, C.; Gubler, U.; Kaatz, P.; Mazerant, W.; Meier, U. *Phys. Rev.* **2000**, *61*, 10688.

(65) Gubler, U.; Bosshard, C. *Phys. Rev.* **2000**, *61*, 10702.

(66) Gauss, J.; Christiansen, O.; Stanton, J. F. *Chem. Phys. Lett.* **1998**, *296*, 117.

(67) Ghosh, S. N.; Trambarulo, R.; Gordy, W. *Phys. Rev.* **1952**, *87*, 172. Ghosh, S. N.; Trambarulo, R.; Gordy, W. *J. Chem. Phys.* **1953**, *21*, 368.