

Efficient treatment of the effect of vibrations on Electrical, Magnetic, and Spectroscopic Properties

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Abstract

Vibrational motions can play an important role in determining electrical, magnetic, and spectroscopic properties through so-called nuclear relaxation, zero-point vibrational averaging, or a combination of the two. Recent advances in the analysis and computational treatment of these phenomena include the finite field/nuclear relaxation technique and field-induced coordinates. These methodologies, which were originally developed for non-resonant electric dipole (hyper)polarizabilities, are reviewed and extended to magnetic properties as well as properties involving simultaneous electric and magnetic fields. In addition, spectroscopic applications such as two-photon absorption, circular dichroism, and infrared/Raman vibrational intensities are considered. With the finite field/nuclear relaxation technique and field-induced coordinates computations are now feasible for much larger molecules than before.

I. Introduction

The effect of vibrations on electric dipole polarizabilities and hyperpolarizabilities has been under detailed study for some time now as discussed in several recent reviews. [1-4] As a result of such investigations it has been established that the vibrational contribution to these properties can be of major significance, especially in the case of large conjugated organic molecules which are of interest for nonlinear optical (NLO) applications [3]. In the course of this work there have been, and continue to be, important theoretical advances in the understanding and treatment of the vibronic coupling that leads to the vibrational contribution. The purpose of this article is to present some of these advances and, in addition, to show how they can be extended to: (1) magnetic properties as well as properties involving a combination of magnetic and electric response; (2) spectroscopic, or resonant, processes; and (3) infrared and Raman intensities. Thus, about half of the text will constitute a review of our own work, but there will be substantial new material as well. Since the developments discussed here are quite recent we have chosen to focus on the computational methodology rather than on numerical results.

Two closely intertwined, though somewhat different, methods for determining vibrational effects will be described in Sec. II. One of these is based on a perturbation theory (PT) treatment of the fields [5-7] and the other involves a finite field/nuclear relaxation (FF/NR) approach [8,9]. Despite the name the latter may be applied either in a numerical or an analytical mode. However, in its most common form, at least one of the fields must be static whereas the PT method is purely analytical and can be used with fields of arbitrary frequency. The treatments developed thus far have focused on the non-resonant regime where the frequencies of the applied fields are assumed to lie well below the first electronic transition. A canonical approximation is, then, applied which treats the action of the fields on the electronic and vibrational motions sequentially, rather than simultaneously [10]. Finally, the vibrational terms that emerge are

determined by considering mechanical and electrical anharmonicity as a perturbation of a double harmonic initial approximation.

There is a general FF/NR scheme that is applicable at arbitrary frequencies [11], but the most convenient form (as noted above) is limited to properties involving at least one static field. In addition, for the remaining optical fields, we assume the infinite optical frequency approximation (i.e. $(\omega_i/\omega)^2 \ll 1$ where ω is a field frequency and ω_i a vibrational frequency). These mild limitations may be balanced against computational efficiency and the fact that the FF/NR method leads to a division of the total vibrational contribution that is both physically and quantitatively meaningful. Each of the terms in this division can be systematically related to a set of terms in the perturbation treatment of the mechanical and electrical anharmonicity. All of these aspects are explored in Sec. II where we describe how the FF/NR and PT formalisms can be adapted to accommodate properties involving a combination of electric and magnetic fields. NMR/ESR properties are also discussed and the extension to optical absorption is treated in a preliminary way.

The FF/NR procedure affords substantial computational advantages over a straightforward application of PT in treating nuclear relaxation effects in large molecules, especially – but not only – when anharmonicity is important. A second major advance which leads to further computational efficiencies, with regard to zero-point vibrational averaging (ZPVA) as well as nuclear relaxation, concerns the choice of vibrational coordinates. In the past, the evaluation of vibrational contributions has always been carried out in terms of normal modes. Recently, it has been discovered that, for any given property, all relevant information is completely contained in a much smaller set of so-called field-induced coordinates (FICs) [12]. A rigorous definition of these FICs is presented in Sec. III along with an analysis of their characteristics. The properties considered here include static/dynamic dipole polarizabilities and hyperpolarizabilities; NMR/ESR parameters; the Cotton-Mouton constant; and infrared and

Raman vibrational intensities as well as their optical rotation counterparts. It turns out that the number of FICs necessary to determine each property remains the same regardless of the size of the molecule. As a result calculations are feasible for much larger molecules than could previously be handled. In Sec. IV we discuss general computational considerations and, finally, Sec. V contains the conclusions and some of our plans for further development.

II. General Perturbation Treatment and Finite Field/Nuclear Relaxation Approach

In this paper we limit ourselves, for sake of convenience, to properties associated with electric and magnetic dipoles. There are, of course, many interesting multipolar properties that, we note, can be treated by a similar formalism. In fact, electric quadrupoles and magnetic dipoles are often considered together since they have many aspects in common [13]. Our starting point, then, is the perturbation equations for the electric dipole polarization properties of a molecule in a set of spatially uniform oscillating electric fields [14] generalized to include vibronic states:

$$\alpha_{\alpha\beta}(-\omega_\sigma; \omega_1) = \hbar^{-1} \sum_{k,K} \left(\frac{\langle 0,0|\hat{\mu}_\alpha|K,k\rangle\langle k,K|\hat{\mu}_\beta|0,0\rangle}{(\omega_{kK} - i\Gamma_{kK} - \omega_\sigma)} + \frac{\langle 0,0|\hat{\mu}_\alpha|K,k\rangle\langle k,K|\hat{\mu}_\beta|0,0\rangle}{(\omega_{kK} + i\Gamma_{kK} + \omega_1)} \right) \quad (1)$$

$$\beta_{\alpha\beta\gamma}(-\omega_\sigma; \omega_1, \omega_2) = \hbar^{-2} \sum_{k,K} P_{1,2} \sum_{l,L} \left(\frac{\langle 0,0|\hat{\mu}_\alpha|K,k\rangle\langle k,K|\hat{\mu}_\beta|L,l\rangle\langle l,L|\hat{\mu}_\gamma|0,0\rangle}{(\omega_{kK} - i\Gamma_{kK} - \omega_\sigma)(\omega_{lL} - i\Gamma_{lL} - \omega_2)} \right. \\ \left. + \frac{\langle 0,0|\hat{\mu}_\gamma|K,k\rangle\langle k,K|\hat{\mu}_\beta|L,l\rangle\langle l,L|\hat{\mu}_\alpha|0,0\rangle}{(\omega_{kK} + i\Gamma_{kK} + \omega_2)(\omega_{lL} + i\Gamma_{lL} + \omega_\sigma)} + \frac{\langle 0,0|\hat{\mu}_\gamma|K,k\rangle\langle k,K|\hat{\mu}_\alpha|L,l\rangle\langle l,L|\hat{\mu}_\beta|0,0\rangle}{(\omega_{kK} + i\Gamma_{kK} + \omega_2)(\omega_{lL} - i\Gamma_{lL} - \omega_1)} \right) \quad (2)$$

$$\begin{aligned}
\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = & \hbar^{-3} \sum P_{1,2,3} \left(\sum'_{k,K} \sum'_{l,L} \sum'_{m,M} \right. \\
& \left(\frac{\langle 0,0|\hat{\mu}_\alpha|K,k\rangle \langle k,K|\hat{\mu}_\beta|L,l\rangle \langle l,L|\hat{\mu}_\gamma|M,m\rangle \langle m,M|\hat{\mu}_\delta|0,0\rangle}{(\omega_{kK} - i\Gamma_{kK} - \omega_\sigma)(\omega_{lL} - i\Gamma_{lL} - \omega_2 - \omega_3)(\omega_{mM} - i\Gamma_{mM} - \omega_3)} \right. \\
& + \frac{\langle 0,0|\hat{\mu}_\beta|K,k\rangle \langle k,K|\hat{\mu}_\alpha|L,l\rangle \langle l,L|\hat{\mu}_\gamma|M,m\rangle \langle m,M|\hat{\mu}_\delta|0,0\rangle}{(\omega_{kK} + i\Gamma_{kK} + \omega_1)(\omega_{lL} - i\Gamma_{lL} - \omega_2 - \omega_3)(\omega_{mM} - i\Gamma_{mM} - \omega_3)} \\
& + \frac{\langle 0,0|\hat{\mu}_\beta|K,k\rangle \langle k,K|\hat{\mu}_\gamma|L,l\rangle \langle l,L|\hat{\mu}_\alpha|M,m\rangle \langle m,M|\hat{\mu}_\delta|0,0\rangle}{(\omega_{kK} + i\Gamma_{kK} + \omega_1)(\omega_{lL} + i\Gamma_{lL} + \omega_1 + \omega_2)(\omega_{mM} - i\Gamma_{mM} - \omega_3)} \\
& \left. + \frac{\langle 0,0|\hat{\mu}_\beta|K,k\rangle \langle k,K|\hat{\mu}_\gamma|L,l\rangle \langle l,L|\hat{\mu}_\delta|M,m\rangle \langle m,M|\hat{\mu}_\alpha|0,0\rangle}{(\omega_{kK} + i\Gamma_{kK} + \omega_1)(\omega_{lL} + i\Gamma_{lL} + \omega_1 + \omega_2)(\omega_{mM} + i\Gamma_{mM} + \omega_\sigma)} \right) \\
& - \sum'_{k,K} \sum'_{l,L} \left(\frac{\langle 0,0|\hat{\mu}_\alpha|K,k\rangle \langle k,K|\hat{\mu}_\beta|0,0\rangle \langle 0,0|\hat{\mu}_\gamma|L,l\rangle \langle l,L|\hat{\mu}_\delta|0,0\rangle}{(\omega_{kK} - i\Gamma_{kK} - \omega_\sigma)(\omega_{kK} - i\Gamma_{kK} - \omega_1)(\omega_{lL} - i\Gamma_{lL} - \omega_3)} \right. \\
& + \frac{\langle 0,0|\hat{\mu}_\alpha|K,k\rangle \langle k,K|\hat{\mu}_\beta|0,0\rangle \langle 0,0|\hat{\mu}_\gamma|L,l\rangle \langle l,L|\hat{\mu}_\delta|0,0\rangle}{(\omega_{kK} - i\Gamma_{kK} - \omega_1)(\omega_{lL} + i\Gamma_{lL} + \omega_2)(\omega_{lL} - i\Gamma_{lL} - \omega_3)} \\
& + \frac{\langle 0,0|\hat{\mu}_\beta|K,k\rangle \langle k,K|\hat{\mu}_\alpha|0,0\rangle \langle 0,0|\hat{\mu}_\gamma|L,l\rangle \langle l,L|\hat{\mu}_\delta|0,0\rangle}{(\omega_{kK} + i\Gamma_{kK} + \omega_1)(\omega_{kK} + i\Gamma_{kK} + \omega_\sigma)(\omega_{lL} + i\Gamma_{lL} + \omega_2)} \\
& \left. + \frac{\langle 0,0|\hat{\mu}_\beta|K,k\rangle \langle k,K|\hat{\mu}_\alpha|0,0\rangle \langle 0,0|\hat{\mu}_\gamma|L,l\rangle \langle l,L|\hat{\mu}_\delta|0,0\rangle}{(\omega_{kK} + i\Gamma_{kK} + \omega_1)(\omega_{lL} + i\Gamma_{lL} + \omega_2)(\omega_{lL} - i\Gamma_{lL} - \omega_3)} \right) \Big) \quad (3)
\end{aligned}$$

In Eqs. (1)-(3) $\psi_K \varphi_k = |K, k\rangle$ is a vibronic wavefunction where K and k refer to the electronic and vibrational states respectively; $\hbar\omega_{kK}$ is the energy of the state $|K, k\rangle$ relative to the ground state; Γ_{kK} is the damping factor associated with the transition from $|0,0\rangle$ to $|K, k\rangle$; $\overline{\hat{\mu}_\zeta} = \hat{\mu}_\zeta - \langle 0,0|\hat{\mu}_\zeta|0,0\rangle$ with ζ being a cartesian direction; the sum over permutations indicated by $\sum P_{1,2,3}$, for example, refers to the pairs (ω_1/μ_β) , (ω_2/μ_γ) and (ω_3/μ_δ) ; $\omega_\sigma = \sum\omega_i$; and the prime on the sum over vibronic states means that $|0,0\rangle$ is omitted.

In the non-resonant regime the damping factor can be neglected and Eqs. (1)-(3) simplify to: [5]

$$\alpha_{\alpha\beta}(-\omega_\sigma; \omega_1) = \hbar^{-1} \sum P_{-\sigma,1} \sum_{k,K} \frac{\langle 0,0 | \hat{\mu}_\alpha | K, k \rangle \langle k, K | \hat{\mu}_\beta | 0,0 \rangle}{(\omega_{kK} - \omega_\sigma)} \quad (4)$$

$$\beta_{\alpha\beta\gamma}(-\omega_\sigma; \omega_1, \omega_2) = \hbar^{-2} \sum P_{-\sigma,1,2} \sum_{k,K} \sum_{l,L} \frac{\langle 0,0 | \hat{\mu}_\alpha | K, k \rangle \langle k, K | \hat{\mu}_\beta | L, l \rangle \langle l, L | \hat{\mu}_\gamma | 0,0 \rangle}{(\omega_{kK} - \omega_\sigma)(\omega_{lL} - \omega_2)} \quad (5)$$

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \hbar^{-3} \sum P_{-\sigma,1,2,3} \left[\begin{aligned} & \sum_{k,K} \sum_{l,L} \sum_{m,M} \frac{\langle 0,0 | \hat{\mu}_\alpha | K, k \rangle \langle k, K | \hat{\mu}_\beta | L, l \rangle \langle l, L | \hat{\mu}_\gamma | M, m \rangle \langle m, M | \hat{\mu}_\delta | 0,0 \rangle}{(\omega_{kK} - \omega_\sigma)(\omega_{lL} - \omega_2 - \omega_3)(\omega_{mM} - \omega_3)} \\ & - \sum_{k,K} \sum_{l,L} \frac{\langle 0,0 | \hat{\mu}_\alpha | K, k \rangle \langle k, K | \hat{\mu}_\beta | 0,0 \rangle \langle 0,0 | \hat{\mu}_\gamma | L, l \rangle \langle l, L | \hat{\mu}_\delta | 0,0 \rangle}{(\omega_{kK} - \omega_\sigma)(\omega_{lL} - \omega_3)(\omega_{lL} + \omega_2)} \end{aligned} \right] \quad (6)$$

Note that in the permutations $P_{-\sigma,1}$, etc. the pair involving ω_σ is $(-\omega_\sigma/\mu_\alpha)$. The quantities usually referred to as the vibrational (hyper)polarizabilities correspond to the set of terms in Eqs. (4)-(6) in which at least one of the intermediate electronic states is the ground state. Then, in evaluating the contribution that arises from excited electronic states, we assume that vibrational energy differences are negligible compared to electronic energy differences so that ω_{kK} is independent of k . Both a theoretical and computational justification of this assumption has been given [10]. Using these approximations one can write the vibrational (hyper)polarizabilities in the general form:

$$\alpha_{\alpha\beta}^v(-\omega_\sigma; \omega_1) = [\mu^2] \quad (7)$$

$$\beta_{\alpha\beta\gamma}^v(-\omega_\sigma; \omega_1, \omega_2) = [\mu\alpha] + [\mu^3] \quad (8)$$

$$\gamma_{\alpha\beta\gamma\delta}^v(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = [\alpha^2] + [\mu\beta] + [\mu^2\alpha] + [\mu^4] \quad (9)$$

where the ‘‘square bracket’’ $[\mu\alpha]$, for example, is given by –

$$[\mu\alpha] = \frac{1}{2} \hbar^{-1} \sum P_{-\sigma,1,2} \sum_k' (\mu_\alpha)_{0k} (\alpha_{\beta\gamma})_{k0} [(\omega_k + \omega_\sigma)^{-1} + (\omega_k - \omega_\sigma)^{-1}] \quad (10)$$

Expressions for the other square bracket quantities are presented in Table II of Ref. [5]. These are readily extended [15] to include magnetic dipole polarization properties as well. The vibrational matrix elements of the electronic properties μ_ζ , $\alpha_{\zeta\eta}$, etc. and the vibrational frequencies, ω_k , can be obtained by expanding the properties and the vibrational potential as a power series in the normal coordinates, Q_i . In the double harmonic approximation only linear terms are considered in the property expansion and only quadratic terms in the vibrational potential. Starting with this approximation one can obtain the corrections due to electrical and mechanical anharmonicity by means of double perturbation theory, which yields a series of the general form:

$$\begin{aligned} [\mu\alpha] &= [\mu\alpha]^{0,0} + [\mu\alpha]^{2,0} + [\mu\alpha]^{1,1} + [\mu\alpha]^{0,2} + \dots \\ &= [\mu\alpha]^0 + [\mu\alpha]^{\text{II}} + \dots \end{aligned} \quad (11)$$

in the case of $[\mu\alpha]$. In the first line of Eq. (11) the first superscript refers to the order in electrical anharmonicity and the second to the order in mechanical anharmonicity; the Roman superscripts in the second line give the total order. Note that only terms of even total order appear in the expression for $[\mu\alpha]$. The same is true for other square bracket expressions in which the electronic properties occur to an even (total) power. (For $[\mu^4]$ the term zeroth-order in anharmonicity also vanishes.) In contrast $[\mu^3]$ and $[\mu^2\alpha]$ contain only terms of odd (total) order in anharmonicity.

Analytical expressions for all the square bracket quantities through order II have been derived [7] as a function of the anharmonic mechanical and electrical parameters as well as the optical and harmonic vibrational frequencies. The case where at least one field is static, and the harmonic vibrational frequencies are assumed to be negligible compared with the optical frequencies for all other fields, can be singled out for special attention. This assumption regarding the optical frequencies is known as the infinite optical frequency approximation [8].

The special case just described applies not only to static (hyper)polarizabilities but, at ordinary experimental frequencies, it is a good approximation [16,17] for the hyperpolarizabilities that govern several important nonlinear optical (NLO) processes including the electro-optic Pockels effect (EOPE) $\beta(-\omega;\omega,0)$, the electro-optic Kerr effect (EOKE) $\gamma(-\omega;\omega,0,0)$, the degenerate four-wave mixing (DFWM), $\gamma(-\omega;\omega,-\omega,\omega)$ and dc-second harmonic generation (dc-SHG) $\gamma(-2\omega;\omega,\omega,0)$.

In the infinite optical frequency approximation we may use a finite field/nuclear relaxation (FF/NR) procedure to evaluate the PT sum-over-modes formulas for the low-order square bracket terms [8]. The major step in the FF/NR method is determining the nuclear relaxation, *i.e.* the change in optimum molecular geometry $\mathbf{R}_F - \mathbf{R}_0$, induced by a finite static applied field. This must be done with due care to satisfy the Eckart conditions so that the molecule does not re-orient with respect to the field during optimization [9]. Then, the difference between a molecular electronic property evaluated in the presence of the field and at the field-dependent equilibrium geometry, *i.e.* $\Delta P^e = P^e[\mathbf{F}, \mathbf{R}_F] - P^e[0, \mathbf{R}_0]$, may be written as a power series in the field. The coefficients in this expansion yield nuclear relaxation static and infinite optical frequency (hyper)polarizabilities depending upon the property that is being expanded:

$$\Delta\mu_\alpha^e = a_{\alpha\beta}^{1,e} F_\beta + \frac{b_{\alpha\beta\gamma}^{1,e}}{2} F_\beta F_\gamma + \frac{g_{\alpha\beta\gamma\delta}^{1,e}}{6} F_\beta F_\gamma F_\delta + \dots \quad (12)$$

$$\Delta\alpha_{\alpha\beta}^e = b_{\alpha\beta\gamma}^{2,e} F_\gamma + \frac{g_{\alpha\beta\gamma\delta}^{2,e}}{2} F_\gamma F_\delta + \dots \quad (13)$$

$$\Delta\beta_{\alpha\beta\gamma}^e = g_{\alpha\beta\gamma\delta}^{3,e} F_\delta + \dots \quad (14)$$

where

$$a_{\alpha\beta}^{1,e} = \alpha_{\alpha\beta}^e(0;0) + \alpha_{\alpha\beta}^{nr}(0;0) \quad (15)$$

$$b_{\alpha\beta\gamma}^{1,e} = \beta_{\alpha\beta\gamma}^e(0;0,0) + \beta_{\alpha\beta\gamma}^{nr}(0;0,0) \quad (16)$$

$$g_{\alpha\beta\gamma\delta}^{1,e} = \gamma_{\alpha\beta\gamma\delta}^e(0;0,0,0) + \gamma_{\alpha\beta\gamma\delta}^{nr}(0;0,0,0) \quad (17)$$

$$b_{\alpha\beta\gamma}^{2,e} = \beta_{\alpha\beta\gamma}^e(0;0,0) + \beta_{\alpha\beta\gamma}^{nr}(-\omega;\omega,0)_{\omega \rightarrow \infty} \quad (18)$$

$$g_{\alpha\beta\gamma\delta}^{2,e} = \gamma_{\alpha\beta\gamma\delta}^e(0;0,0,0) + \gamma_{\alpha\beta\gamma\delta}^{nr}(-\omega;\omega,0,0)_{\omega \rightarrow \infty} \quad (19)$$

$$g_{\alpha\beta\gamma\delta}^{3,e} = \gamma_{\alpha\beta\gamma\delta}^e(0;0,0,0) + \gamma_{\alpha\beta\gamma\delta}^{nr}(-2\omega;\omega,\omega,0)_{\omega \rightarrow \infty} \quad (20)$$

In Eqs. (18)-(20) the subscript $\omega \rightarrow \infty$ refers to the infinite optical frequency limit. By comparing the analytical expressions for the nuclear relaxation quantities (symbolized by the superscript nr) with the corresponding perturbation formulas [18] it is easy to verify that the coefficient of the linear field term gives the zeroth-order (*i.e.* double harmonic) approximation and the coefficient of the quadratic field term gives the hyperpolarizability through order I. The coefficient of the cubic field term - like the linear and quadratic field terms - contains the lowest-order square bracket contribution of each type [cf. Eq. (9)].

If P^e is taken to be the electronic energy, E^e , then the (hyper)polarizabilities obtained are exactly the same as those derived from $\mu_\alpha^e = -\partial E^e / \partial F_\alpha$. The FF/NR method cannot be applied to degenerate four-wave mixing (DFWM), $\gamma(-\omega;\omega,-\omega,\omega)$ - or, equivalently, the intensity-dependent refractive index. However, in the infinite optical frequency approximation only the $[\alpha^2]$ survives. Since nuclear relaxation includes just the lowest order term of each square bracket type [see Eqs. (21)-(27) below] the double harmonic approximation is sufficient to provide the complete nuclear relaxation effect for DFWM. Finally, the infinite optical frequency nuclear relaxation hyperpolarizabilities can be written as simple linear combinations of the *static* square bracket quantities (designated by the subscript $\omega = 0$):

$$\alpha_{\alpha\beta}^{nr}(0;0) = [\mu^2]_{\omega=0}^0 \quad (21)$$

$$\beta_{\alpha\beta\gamma}^{nr}(0;0,0) = [\mu\alpha]_{\omega=0}^0 + [\mu^3]_{\omega=0}^I \quad (22)$$

$$\gamma_{\alpha\beta\gamma\delta}^{nr}(0;0,0,0) = [\alpha^2]_{\omega=0}^0 + [\mu\beta]_{\omega=0}^0 + [\mu^2\alpha]_{\omega=0}^I + [\mu^4]_{\omega=0}^{II} \quad (23)$$

$$\beta_{\alpha\alpha\alpha}^{nr}(-\omega;\omega,0)_{\omega \rightarrow \infty} = \frac{1}{3}[\mu\alpha]_{\omega=0}^0 \quad (24)$$

$$\gamma_{\alpha\alpha\alpha\alpha}^{nr}(-\omega;\omega,0,0)_{\omega \rightarrow \infty} = \frac{1}{3}[\alpha^2]_{\omega=0}^0 + \frac{1}{2}[\mu\beta]_{\omega=0}^0 + \frac{1}{6}[\mu^2\alpha]_{\omega=0}^I \quad (25)$$

$$\gamma_{\alpha\alpha\alpha\alpha}^{nr}(-2\omega;\omega,\omega,0)_{\omega \rightarrow \infty} = \frac{1}{4}[\mu\beta]_{\omega=0}^0 \quad (26)$$

$$\gamma_{\alpha\alpha\alpha\alpha}^{nr}(-\omega;\omega,-\omega,\omega)_{\omega \rightarrow \infty} = \frac{2}{3}[\alpha^2]_{\omega=0}^0 \quad (27)$$

Note that Eqs. (24)-(27) pertain specifically to the diagonal elements. The same relations also hold for the average property values.

It is possible to extend the FF/NR approach so as to calculate hyperpolarizabilities at an arbitrary frequency [11]. In order to do so one must add the corresponding nuclear relaxation property to the lhs of Eqs. (13) and (14) and compute both terms at the desired frequency. This calculation of the nuclear relaxation property requires evaluation of the appropriate PT expression.

The vibrational (hyper)polarizabilities as defined above do not include the ZPVA corrections. These corrections may also be evaluated as a double perturbation series in mechanical and electrical anharmonicity. For the ZPVA only terms of odd (total) order are non-vanishing:

$$P^{zpv} = [P]^I + [P]^{III} + \dots \quad (28)$$

Ordinarily, only the first-order term –

$$P^{zpv} = [P]^{0,1} + [P]^{1,0} = -\frac{\hbar}{4} \sum_i^{3N-6} \left(\sum_j^{3N-6} \frac{F_{ij}}{\omega_j} \right) \frac{\partial P / \partial Q_i}{\omega_i^2} + \frac{\hbar}{4} \sum_i^{3N-6} \frac{\partial^2 P / \partial Q_i^2}{\omega_i} \quad (29)$$

is considered. Here F_{ij} is a cubic vibrational force constant and $\omega_i = \sqrt{F_{ii}}$ is a harmonic vibrational frequency. Given the vibrational potential $V(\mathbf{Q})$, then F_{ii} may be evaluated as $\partial^2 V / \partial Q_i^2$. In Eq. (29) this derivative is determined at \mathbf{R}_0 (or, equivalently, $\mathbf{Q} = 0$) but, in general, it may be considered a function of \mathbf{Q} . Thus, if the zero-point energy is defined by:

$$E^{zp}(\mathbf{Q}) = \hbar/2 \sum_i^{3N-6} [F_{ii}(\mathbf{Q})]^{1/2} = \hbar/2 \sum_i^{3N-6} \omega_i(\mathbf{Q}) \quad (30)$$

then the two terms that make up the first-order ZPVA can be written –

$$[P]^{0,1} = - \sum_i^{3N-6} \left(\frac{\partial E^{zp}}{\partial Q_i} \right) \frac{\partial P^e / \partial Q_i}{\omega_i^2} \quad (31)$$

and

$$[P]^{1,0} = - \frac{\hbar}{4} \sum_i^{3N-6} \left(\frac{1}{\omega_i} \frac{\partial^n F_{ii}}{\partial F^n} \right) = - \frac{\partial^n E^{zp}}{\partial F^n} \quad (32)$$

where $n = 1$ for μ^e ; $n = 2$ for α^e ; $n = 3$ for β^e ; and $n = 4$ for γ^e .

There are higher-order vibrational (hyper)polarizability terms that are not included in the FF/NR treatment as described thus far. That is because we have considered the effect of nuclear relaxation on the pure electronic properties but not on the ZPVA. The remaining (infinite frequency approximation) terms may be obtained simply by replacing P^e in Eqs. (12)-(14) with P^{zpv} . This leads to [19]:

$$\Delta \mu_{\alpha}^{zpv} = a_{\alpha\beta}^{1,zpv} F_{\beta} + \frac{b_{\alpha\beta\gamma}^{1,zpv}}{2} F_{\beta} F_{\gamma} + \frac{g_{\alpha\beta\gamma\delta}^{1,zpv}}{6} F_{\beta} F_{\gamma} F_{\delta} + \dots \quad (33)$$

$$\Delta \alpha_{\alpha\beta}^{zpv} = b_{\alpha\beta\gamma}^{2,zpv} F_{\gamma} + \frac{g_{\alpha\beta\gamma\delta}^{2,zpv}}{2} F_{\gamma} F_{\delta} + \dots \quad (34)$$

$$\Delta \beta_{\alpha\beta\gamma}^{zpv} = g_{\alpha\beta\gamma\delta}^{3,zpv} F_{\delta} + \dots \quad (35)$$

in which

$$a_{\alpha\beta}^{1,zpva} = \alpha_{\alpha\beta}^{zpva}(0;0) + \alpha_{\alpha\beta}^{c-zpva}(0;0) \quad (36)$$

$$b_{\alpha\beta\gamma}^{1,zpva} = \beta_{\alpha\beta\gamma}^{zpva}(0;0,0) + \beta_{\alpha\beta\gamma}^{c-zpva}(0;0,0) \quad (37)$$

$$g_{\alpha\beta\gamma\delta}^{1,zpva} = \gamma_{\alpha\beta\gamma\delta}^{zpva}(0;0,0,0) + \gamma_{\alpha\beta\gamma\delta}^{c-zpva}(0;0,0,0) \quad (38)$$

$$b_{\alpha\beta\gamma}^{2,zpva} = \beta_{\alpha\beta\gamma}^{zpva}(0;0,0) + \beta_{\alpha\beta\gamma}^{c-zpva}(-\omega;\omega,0)_{\omega \rightarrow \infty} \quad (39)$$

$$g_{\alpha\beta\gamma\delta}^{2,zpva} = \gamma_{\alpha\beta\gamma\delta}^{zpva}(0;0,0,0) + \gamma_{\alpha\beta\gamma\delta}^{c-zpva}(-\omega;\omega,0,0)_{\omega \rightarrow \infty} \quad (40)$$

$$g_{\alpha\beta\gamma\delta}^{3,zpva} = \gamma_{\alpha\beta\gamma\delta}^{zpva}(0;0,0,0) + \gamma_{\alpha\beta\gamma\delta}^{c-zpva}(-2\omega;\omega,\omega,0)_{\omega \rightarrow \infty} \quad (41)$$

Here $a_{\alpha\beta}^{1,zpva}$ is the exact analogue of $a_{\alpha\beta}^{1,e}$, etc., and the superscript $c-zpva$ refers to the fact that $a_{\alpha\beta}^{1,zpva}$, $b_{\alpha\beta\gamma}^{1,zpva}$, and $g_{\alpha\beta\gamma\delta}^{1,zpva}$ are determined by the shape, or *curvature*, of the field-dependent vibrational potential (evaluated at \mathbf{R}_F). (Specifically, the notation $c-zpva$ refers to the fact that the $zpva$ term plus the $c-zpva$ term add up to the total curvature effect [20].) If the first-order P^{zpva} is used in Eqs. (33)-(35), then the C-ZPVA properties (in the infinite frequency approximation) may be expressed in terms of square brackets as [20]:

$$\alpha_{\alpha\beta}^{c-zpva}(0;0) = [\mu^2]_{\omega=0}^{\text{II}} \quad (42)$$

$$\beta_{\alpha\beta\gamma}^{c-zpva}(0;0,0) = [\mu\alpha]_{\omega=0}^{\text{II}} + [\mu^3]_{\omega=0}^{\text{III}} \quad (43)$$

$$\gamma_{\alpha\beta\gamma\delta}^{c-zpva}(0;0,0,0) = [\alpha^2]_{\omega=0}^{\text{II}} + [\mu\beta]_{\omega=0}^{\text{II}} + [\mu^2\alpha]_{\omega=0}^{\text{III}} + [\mu^4]_{\omega=0}^{\text{IV}} \quad (44)$$

$$\beta_{\alpha\alpha\alpha}^{c-zpva}(-\omega;\omega,0)_{\omega \rightarrow \infty} = \frac{1}{3}[\mu\alpha]_{\omega=0}^{\text{II}} \quad (45)$$

$$\gamma_{\alpha\alpha\alpha\alpha}^{c-zpva}(-\omega;\omega,0,0)_{\omega \rightarrow \infty} = \frac{1}{3}[\alpha^2]_{\omega=0}^{\text{II}} + \frac{1}{2}[\mu\beta]_{\omega=0}^{\text{II}} + \frac{1}{6}[\mu^2\alpha]_{\omega=0}^{\text{III}} \quad (46)$$

$$\gamma_{\alpha\alpha\alpha\alpha}^{c-zpva}(-2\omega;\omega,\omega,0)_{\omega \rightarrow \infty} = \frac{1}{4}[\mu\beta]_{\omega=0}^{\text{II}} \quad (47)$$

$$\gamma_{\alpha\alpha\alpha\alpha}^{c-zpva}(-\omega;\omega,-\omega,\omega)_{\omega \rightarrow \infty} = \frac{2}{3}[\alpha^2]_{\omega=0}^{\text{II}} \quad (48)$$

Again, as in the case of ordinary nuclear relaxation, Eqs. (45)-(48) hold for the average value of the properties as well as the diagonal elements. Higher-order $P^{zpv\alpha}$ terms will yield square bracket corrections of higher-order. The form of the latter should be obvious from Eqs. (42)-(48). Finally, the *complete* set of electronic and vibrational contributions to the property P may be divided into the following two sequences –

$$\begin{aligned}
 \text{(A)} \quad & P^e, [P^{zpv\alpha}]^I, [P^{zpv\alpha}]^{III}, \dots \\
 \text{(B)} \quad & P^{nr}, P^{c-zpv\alpha}(I), P^{c-zpv\alpha}(III), \dots
 \end{aligned}
 \tag{49}$$

in which $P^{c-zpv\alpha}(I)$, for example, represents the C-ZPVA term derived from $[P^{zpv\alpha}]^I$ using the FF/NR procedure. In monitoring the convergence of the perturbation series in electrical and mechanical anharmonicity it turns out to be preferable to examine these two sequences separately since P^{nr} is, in many instances, larger than P^e and we expect that the same will prove true of $P^{c-zpv\alpha}(I)$ versus $[P^{zpv\alpha}]^I$. Except, perhaps, for some instances where "floppy" motions are involved one expects rapid convergence for sequence (A). On the other hand, for sequence (B), the convergence has been checked only for one large molecule. [20]

All of the above pertains to the non-resonant regime. The intensity of a resonant process is proportional to the imaginary part of Eqs. (1)-(3), which will be non-negligible only when the difference between an optical frequency and the transition energy to an excited state is small. In order to derive the appropriate formulas for near-resonant conditions it is very important to use correct signs for the damping factors [21].

The intensity of linear absorption is proportional to the imaginary part of Eq. (1). Assuming that under near-resonant conditions the second term on the rhs of this equation is negligible compared to the first one, and that only one electronic excited state $|K\rangle$ is close to the optical frequency, the imaginary part of Eq. (1) can be simplified to:

$$\text{Im} \alpha_{\alpha\beta}(-\omega; \omega) = \hbar^{-1} \sum_k \left(\frac{\langle 0,0|\hat{\mu}_\alpha|K,k\rangle \langle k,K|\hat{\mu}_\beta|0,0\rangle \Gamma_{kK}}{(\omega_{kK} - \omega)^2 + \Gamma_{kK}^2} \right) \quad (50)$$

For a resonant process such as linear absorption it is clear from Eq. (50) that the vibrational energy differences cannot be neglected, as they are in the non-resonant regime, because the difference between the pure electronic contribution to ω_{kK} and ω is close to zero. Thus, the vibrational contribution from both the numerator and the denominator must be considered.

Two-photon absorption (TPA) is given by the imaginary part of Eq. (3) with $\omega = \omega_1 = -\omega_2 = \omega_3$. It is harmful for optical switching processes, leading to strong alteration of the signal and damage to the samples due to severe heating. On the other hand, TPA may be useful in two-photon fluorescence microscopy [22], optical limiting [23,24], three dimensional optical memory [25] and two-photon-induced biological caging [26]. The potentially important role of vibrations, however, has yet to be investigated [27]. Using the same general procedure as for linear absorption, and assuming that 2ω coincides exactly with the electronic transition frequency ω_L , in Eq. (3) we have ($\omega = \omega_{0L}/2$):

$$\begin{aligned} \text{Im} \gamma_{\alpha\beta\gamma\delta} \left(-\frac{\omega_{0L}}{2}, \frac{\omega_{0L}}{2}, -\frac{\omega_{0L}}{2}, \frac{\omega_{0L}}{2} \right) &= \text{Im} \hbar^{-3} \sum_{K,k} P_{\beta\delta} \sum_{M,m} \sum_l \frac{\omega_{lL} - \omega_{0L} + i\Gamma_{lL}}{(\omega_{lL} - \omega_{0L})^2 + \Gamma_{lL}^2} \\ &\left[\frac{\langle 0,0|\hat{\mu}_\gamma|K,k\rangle \langle k,K|\hat{\mu}_\alpha|L,l\rangle \left(\omega_{kK} - \frac{\omega_{0L}}{2} - i\Gamma_{kK} \right)}{\left(\omega_{kK} - \frac{\omega_{0L}}{2} \right)^2 + \Gamma_{kK}^2} \times \frac{\langle l,L|\hat{\mu}_\beta|M,m\rangle \langle m,M|\hat{\mu}_\delta|0,0\rangle \left(\omega_{mM} - \frac{\omega_{0L}}{2} + i\Gamma_{mM} \right)}{\left(\omega_{mM} - \frac{\omega_{0L}}{2} \right)^2 + \Gamma_{mM}^2} \right. \\ &\left. + \frac{\langle 0,0|\hat{\mu}_\alpha|K,k\rangle \langle k,K|\hat{\mu}_\gamma|L,l\rangle \left(\omega_{kK} - \frac{\omega_{0L}}{2} + i\Gamma_{kK} \right)}{\left(\omega_{kK} - \frac{\omega_{0L}}{2} \right)^2 + \Gamma_{kK}^2} \times \frac{\langle l,L|\hat{\mu}_\beta|M,m\rangle \langle m,M|\hat{\mu}_\delta|0,0\rangle \left(\omega_{mM} - \frac{\omega_{0L}}{2} + i\Gamma_{mM} \right)}{\left(\omega_{mM} - \frac{\omega_{0L}}{2} \right)^2 + \Gamma_{mM}^2} \right] \quad (51) \end{aligned}$$

If the sum over states $|k,K\rangle$ is treated in the same manner as we have done previously for the non-resonant regime, then –

$$\text{Im}\gamma_{\alpha\beta\gamma\delta}\left(-\frac{\omega_L}{2}, \frac{\omega_L}{2}, -\frac{\omega_L}{2}, \frac{\omega_L}{2}\right) = \frac{1}{4}\hbar^{-1}\sum P_{\beta\delta}\sum P_{\alpha\gamma} \left[\frac{1}{\Gamma_{0L}}(\alpha_{\gamma\alpha}^{0L})_{00}(\alpha_{\beta\delta}^{L0})_{00} + \sum_l \left(\frac{\Gamma_{lL}}{(\omega_{lL} - \omega_{0L})^2 + \Gamma_{lL}^2} (\alpha_{\gamma\alpha}^{0L})_{0l} (\alpha_{\beta\delta}^{L0})_{l0} \right) \right] \quad (52)$$

where

$$\hat{\alpha}_{\gamma\alpha}^{0L} = 2\hbar^{-1}\sum_K \frac{\langle 0|\hat{\mu}_\gamma|K\rangle\langle K|\hat{\mu}_\alpha|L\rangle}{\omega_K - \omega_L/2} \quad (53)$$

Of the two terms in square brackets on the rhs of Eq. (52) the first is due to zero-point vibrations. The second is the analogue of the non-resonant nuclear relaxation contribution to DFWM given by Eq. (27) - both arise from the set of terms containing pure vibrational energy denominators and both consist solely of an α^2 “square bracket”. However, for TPA it is the *transition* polarizability defined by equation (53) that occurs, rather than the ground state polarizability, and there are also damping factors involved.

Eq. (52) may be evaluated by expanding in orders of electrical and mechanical anharmonicity. The validity of taking $\omega_k \ll \omega_K - \omega_L/2$ and neglecting the damping factors Γ_{kK} (as we have done) should be examined. In fact, a more rigorous formulation including these vibrational contributions is currently under investigation [27].

Let us turn now to properties involving magnetic dipoles. There are three distinct contributions to the molecular magnetic dipole operator arising from the angular momentum associated with electronic orbital motion, electron spin, and nuclear spin. These three types of magnetic moment can interact with an external magnetic field and with each other leading to a variety of terms in the effective Hamiltonian. In one sense the treatment of vibrational motions is simpler than for electric dipole properties because one is normally interested only in those terms that arise through the second-order of perturbation theory.

It turns out that the properties measured in nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectroscopy do not contain a nuclear relaxation contribution, at

least in orbitally non-degenerate states, as we now show. In NMR spectroscopy the key parameters are nuclear shielding and nuclear spin-spin coupling. The spin-spin coupling constant is the sum of a direct (first-order PT) contribution plus an indirect (second-order PT) contribution, which arises primarily through the Fermi contact interaction between nuclear and electron spins. This contact interaction connects electronic states of different spin multiplicity. Since the vibrational nuclear relaxation effect requires the intermediate electronic state to be the ground state there is no such effect associated with the contact interaction. The nuclear spins can also be coupled indirectly by the interaction between nuclear spin and electronic orbital angular momentum ($\mathbf{L} \bullet \mathbf{I}$). This, too will be unaffected by vibrational nuclear relaxation, in this case because of the quenching of orbital angular momentum. For nuclear shielding the second-order PT contribution is due to a cross-term involving, on the one hand, the nuclear spin/electronic orbital angular momentum interaction and, on the other, the Zeeman interaction between the external field and the electronic angular momentum. Once more the quenching of orbital angular momentum precludes a vibrational nuclear relaxation effect. Nonetheless, all the NMR properties mentioned here will be influenced by vibration through the ZPVA correction as we discuss later.

In ESR spectroscopy the key parameters are the magnetic hyperfine coupling (a first-order effect), the electronic \mathbf{g} -tensor (first and second-order) and the electron spin-spin coupling. The second-order contribution to the \mathbf{g} -tensor arises from the cross-term between the spin-orbit interaction and the $\mathbf{L} \bullet \mathbf{B}$ Zeeman interaction between the external field (\mathbf{B}) and the electronic orbital angular momentum. As in the case of the analogous NMR property, *i.e.* nuclear shielding, there will be a ZPVA correction but no effect due to vibrational nuclear relaxation because of orbital quenching. The same result holds for the electron spin-spin coupling, which is due to the quadratic $\mathbf{L} \bullet \mathbf{S}$ interaction (*cf.* indirect nuclear spin-spin coupling),

and for the same reason. In paramagnetic transition metal complexes with weak crystal fields the Jahn-Teller effect may play a substantial role in lifting the orbital degeneracy. For such cases there can be a nuclear relaxation effect associated with the Jahn-Teller distortion modes. However, we leave that possibility, as well as the study of rare earth complexes, for future work.

The nuclear (electron) spin-spin coupling and magnetic hyperfine coupling are both zeroth-order in the external magnetic field whereas the nuclear shielding and electronic \mathbf{g} -tensor terms are first-order. Finally, we come to terms that are second-order (in the field), *i.e.* the magnetizability or magnetic susceptibility, χ . For diamagnetic or paramagnetic molecules in orbitally non-degenerate states the second-order term in the spin Hamiltonian [28] arises from the quadratic ($\mathbf{L}\cdot\mathbf{B}$) interaction which, again, means that the effect of vibrations will be felt only through the ZPVA.

In addition to pure magnetic properties we may also consider properties that depend simultaneously on electric, \mathbf{F} , and magnetic fields. The relevant cross-terms in the general energy expression are given, through second-order in \mathbf{B} and fourth-order in total, by [29] –

$$\begin{aligned}
V(\mathbf{F}, \mathbf{B}) = & -\delta_{\alpha,\beta} F_\alpha B_\beta - \frac{1}{2} \varepsilon_{\alpha\beta,\gamma} F_\alpha F_\beta B_\gamma - \frac{1}{2} \xi_{\alpha,\beta\gamma} F_\alpha B_\beta B_\gamma - \frac{1}{6} \sigma_{\alpha\beta\gamma,\delta} F_\alpha F_\beta F_\gamma B_\delta \\
& - \frac{1}{4} \eta_{\alpha\beta,\gamma\delta} F_\alpha F_\beta B_\gamma B_\delta - \dots
\end{aligned} \tag{54}$$

Since each of the fields may have both static and frequency-dependent components Eq. (54) is, in fact, a short-hand that is useful for cataloguing purposes. The bilinear term, for example, is associated with (natural) optical activity when both fields are frequency-dependent. On the other hand, magnetic field-induced optical activity - or the Faraday effect – corresponds to the $F_\alpha F_\beta B_\gamma$ term where the electric fields are frequency-dependent but the magnetic field is static. This contrasts with the magnetic dipole-induced second-order susceptibility [30], in which case the magnetic field is also frequency-dependent. Finally, we mention the Cotton-Mouton effect (CME) – or linear birefringence. This process is second-order in the frequency-dependent

electric field and second-order in the static magnetic field. The molar Cotton-Mouton constant (${}_mC$) is proportional to the anisotropy of the refractive index when the static magnetic field is applied perpendicular to the direction of propagation of the light beam [31,32]. This constant is given by [33]:

$${}_mC = \frac{2\pi N_A}{27} (\Delta\eta + Q(T)) \quad (55)$$

where

$$\Delta\eta = \frac{1}{15} \sum_{\alpha,\beta}^{x,y,z} (3\eta_{\alpha\beta,\alpha\beta} - \eta_{\alpha\alpha,\beta\beta}) \quad (56)$$

$$Q(T) = \frac{1}{15kT} \sum_{\alpha,\beta}^{x,y,z} (3\alpha_{\alpha\beta} \chi_{\alpha\beta} - \alpha_{\alpha\alpha} \chi_{\beta\beta}) \quad (57)$$

$$\chi_{\alpha\beta} = - \left(\frac{\partial^2 V(\mathbf{B})}{\partial B_\alpha \partial B_\beta} \right)_{B=0} \quad (58)$$

and N_A , k and T are Avogadro's number, Boltzman's constant and the temperature, respectively.

One can easily envision experiments that involve the two remaining terms of Eq. (54), such as electric field-induced magnetizability (order FB^2), although such possibilities have not been exploited to our knowledge. Those terms that are linear in \mathbf{B} are not subject to a vibrational nuclear relaxation effect because of orbital quenching (for orbitally non-degenerate molecules and ignoring nuclear spin) but that is not true for the quadratic terms. In fact, by generalizing the BHK treatment [8,18] to magnetic fields it is easy to show that the nuclear relaxation contribution to η in Eq. (56) is given by –

$$\Delta\alpha_{\alpha\beta}^e = e_{\alpha\beta,\gamma}^{2,e} B_\gamma + \frac{h_{\alpha\beta,\gamma\delta}^{2,e}}{2} B_\gamma B_\delta + \dots \quad (59)$$

where

$$h_{\alpha\beta,\gamma\delta}^{2,e} = \eta_{\alpha\beta,\gamma\delta}^e(0;0,0,0) + \eta_{\alpha\beta,\gamma\delta}^{nr}(-\omega;\omega,0,0)_{\omega \rightarrow \infty} \quad (60)$$

In Eq. (60) we have explicitly indicated the frequency-dependence of $\eta_{\alpha\beta,\gamma\delta}^{nr}(-\omega;\omega,0,0)_{\omega\rightarrow\infty}$ which was suppressed in Eq. (56). By comparing with the analytical perturbation formula $\eta_{\alpha\beta,\gamma\delta}^{nr}(-\omega;\omega,0,0)_{\omega\rightarrow\infty}$ can be written as:

$$\eta_{\alpha\alpha,\alpha\alpha}^{nr}(-\omega;\omega,0,0)_{\omega\rightarrow\infty} = [\alpha\chi]_{\omega=0}^0 \quad (61)$$

This relation is simpler than the formula for the hyperpolarizability $\gamma_{\alpha\beta\gamma\delta}^{nr}(-\omega;\omega,0,0)_{\omega\rightarrow\infty}$ because the analogues of the second and third terms on the rhs of Eq. (25) vanish due to the orbital quenching. Eq. (61) has also been derived by Ruud, *et al.* [15]

Near a resonance even the linear \mathbf{B} terms in Eq. (54) may exhibit strong vibronic effects akin to nuclear relaxation because one is dealing with a transition between different electronic states and, thus, the orbital angular momentum is not quenched. For example, circular dichroism (bilinear term in Eq. (54)) is analogous to linear absorption with the major difference being that $\langle k,K | \boldsymbol{\mu}_\beta | 0,0 \rangle$ in Eq. (50) is replaced by $\langle k,K | \mathbf{m}_\beta | 0,0 \rangle$ where \mathbf{m} is the magnetic dipole operator. As in the case of linear absorption there is a vibrational contribution that arises from the dependence of the transition electric dipole moment on the normal coordinates and another from the vibrational energy included in ω_{kK} . For circular dichroism one must also take into account the fact that the transition magnetic dipole is a function of normal coordinates. An analogous situation occurs in the case of magnetic circular dichroism.

The first implementation of the general FF/NR procedure, which requires rigorous enforcement of the field-free Eckart conditions, was presented only quite recently. However, additional applications have begun to appear. They include a treatment of the static linear polarizability of infinite polymers [34] as well as second hyperpolarizability calculations for eight different homologous series of conjugated oligomers, each containing up to twelve heavy atoms along the backbone [35]. In the latter study, carried out at the RHF/6-31G level, the

magnitude of the static vibrational second hyperpolarizability due to the Raman term (i.e. $[\alpha^2]_{\omega=0}^0$) varied between 0.64 and 6.80 times the static γ^e . As a result there is typically a large nuclear relaxation contribution to the DFWM and EOKE processes. On the other hand, the magnitude of the nuclear relaxation dc-SHG was smaller than 20% of the static γ^e for polysilane and much less in all other cases. This is due to the fact that the hyperRaman term (i.e. $[\mu\beta]_{\omega=0}^0$) is quite small for undoped π -conjugated oligomers and, in addition, is multiplied by a factor of 1/4 in the infinite frequency approximation [cf. Eq. (26)]. For the molecules investigated thus far it appears that anharmonicity is relatively unimportant for planar π -conjugated oligomers whereas it is quite significant for polysilanes [35] and even more so for push-pull π -conjugated molecules [12].

The work described above was carried out prior to the introduction of field-induced coordinates. These coordinates provide important simplifications and new insights that will be discussed in the following section.

III. Field-Induced Coordinates (FICs)

Thus far we have used ordinary normal coordinates, either explicitly or implicitly, to describe the vibrational motions. It turns out, however, that it is more efficient to employ what we have called field-induced coordinates (FICs). Such coordinates were first defined in the context of the FF/NR method. In fact, they were obtained from the shift in the equilibrium geometry caused by a static external field, which is the primary step in an FF/NR calculation. In order to relate this numerical procedure to an analytical formulation we begin by writing the molecular potential energy in the presence of the field in terms of the $3N-6$ normal coordinates:

$$V(\mathbf{Q}, \mathbf{F}) = \sum_{n=0}^{3N-6} \sum_{i_1=1}^{3N-6} \dots \sum_{i_n=1}^{3N-6} \sum_{m=0}^{x,y,z} \sum_{\alpha_1=1}^{x,y,z} \dots \sum_{\alpha_m=1}^{x,y,z} a_{nm}^{i_1 \dots i_n, \alpha_1 \dots \alpha_m} Q_{i_1} \dots Q_{i_n} F_{\alpha_1} \dots F_{\alpha_m} \quad (62)$$

where

$$a_{nm}^{i,j,\dots,\alpha,\beta,\dots} = \frac{1}{n! m!} \left(\frac{\partial^{(n+m)} V(Q_1, \dots, Q_{3N-6}, F_x, F_y, F_z)}{\partial Q_i \partial Q_j \dots \partial F_\alpha \partial F_\beta \dots} \right)_{Q=0, F=0} \quad (63)$$

In Eq. (62)-(63) n is the order of differentiation with respect to normal coordinates, while m is the order of differentiation with respect to the field. Derivatives with $m > 0, n > 1$ are electrical anharmonicity parameters; derivatives with $m = 0, n > 2$ determine the mechanical anharmonicity. For $F = 0$ the terms in Eq. (62) that are linear in Q , i.e. $a_{10^i} Q_i$ must vanish by virtue of the field-free equilibrium condition. However for $F \neq 0$ there will be non-vanishing terms such as $a_{11}^{i,\alpha} Q_i F_\alpha$ that will cause the equilibrium geometry to relax from R_0 to R_F . The new equilibrium geometry may be calculated by means of a conventional finite field geometry optimization provided that, in practice, the field-free Eckart conditions are rigorously enforced so that the orientation of the molecule with respect to the field does not change [9]. This is the key step in the numerical application of the FF/NR method. Alternatively, the same treatment can be carried out analytically by applying the condition:

$$\left(\frac{\partial V}{\partial Q_i} \right)_{Q^F} = 0 \quad \forall i \quad (64)$$

to the expression in Eq. (62). Here Q^F is the value of the field-free normal coordinate displacement vector at $R = R^F$. The solution of the nonlinear set of equations (64) may be found as a power series in the field by iteratively taking into account successive higher-order anharmonicity terms [18,36]. This yields –

$$Q_i^F = - \sum_{\alpha} q_1^{i,\alpha} F_\alpha - \sum_{\alpha,\beta} q_2^{i,\alpha\beta} \left[q_2^{i,\alpha\beta} - \sum_{j=1}^{3N-6} \frac{a_{21}^{ij,\alpha}}{a_{20}^{ii}} q_1^{j,\beta} + \sum_{j,k=1}^{3N-6} \frac{3 a_{30}^{ijk}}{2 a_{20}^{ii}} q_1^{j,\alpha} q_1^{k,\beta} \right] F_\alpha F_\beta + \dots \quad (65)$$

where

$$q_1^{i,\alpha} = \frac{a_{11}^{i,\alpha}}{2 a_{20}^{ii}} \quad (66)$$

$$q_2^{i,\alpha\beta} = \frac{a_{12}^{i,\alpha\beta}}{2a_{20}^{ii}} \quad (67)$$

It is straightforward to obtain expressions for the (field-dependent) properties μ^f , α^f , and β^f at the field-dependent equilibrium geometry by evaluating:

$$\begin{aligned} \mu_\alpha(R_F, F) = & \mu_\alpha(R_0, 0) + \sum_\beta^{x,y,z} \left[\frac{\partial \mu_\alpha}{\partial F_\beta} + \sum_{i=1}^{3N-6} \frac{\partial \mu_\alpha}{\partial Q_i} \frac{\partial Q_i^F}{\partial F_\beta} \right] F_\beta + \frac{1}{2} \sum_{\beta,\gamma}^{x,y,z} \left[\frac{\partial^2 \mu_\alpha}{\partial F_\beta \partial F_\gamma} \right. \\ & + \sum_{i=1}^{3N-6} \left(\frac{\partial \mu_\alpha}{\partial Q_i} \frac{\partial^2 Q_i^F}{\partial F_\beta \partial F_\gamma} + 2 \frac{\partial^2 \mu_\alpha}{\partial Q_i \partial F_\beta} \frac{\partial Q_i^F}{\partial F_\gamma} \right) + \sum_{i,j=1}^{3N-6} \frac{\partial^2 \mu_\alpha}{\partial Q_i \partial Q_j} \frac{\partial Q_i^F}{\partial F_\beta} \frac{\partial Q_j^F}{\partial F_\gamma} \left. \right] F_\beta F_\gamma \\ & + \frac{1}{6} \sum_{\beta,\gamma,\delta}^{x,y,z} \left[\frac{\partial^3 \mu_\alpha}{\partial F_\beta \partial F_\gamma \partial F_\delta} + \sum_{i=1}^{3N-6} \left(\frac{\partial \mu_\alpha}{\partial Q_i} \frac{\partial^3 Q_i^F}{\partial F_\beta \partial F_\gamma \partial F_\delta} + 3 \frac{\partial^2 \mu_\alpha}{\partial Q_i \partial F_\beta} \frac{\partial^2 Q_i^F}{\partial F_\gamma \partial F_\delta} \right. \right. \\ & + \left. \left. 3 \frac{\partial^3 \mu_\alpha}{\partial Q_i \partial F_\beta \partial F_\gamma} \frac{\partial Q_i^F}{\partial F_\delta} \right) + 3 \sum_{i,j=1}^{3N-6} \left(\frac{\partial^2 \mu_\alpha}{\partial Q_i \partial Q_j} \frac{\partial Q_i^F}{\partial F_\beta} \frac{\partial^2 Q_j^F}{\partial F_\gamma \partial F_\delta} + \frac{\partial^3 \mu_\alpha}{\partial Q_i \partial Q_j \partial F_\beta} \frac{\partial Q_i^F}{\partial F_\gamma} \frac{\partial Q_j^F}{\partial F_\delta} \right) \right. \\ & \left. + \sum_{i,j,k=1}^{3N-6} \frac{\partial^3 \mu_\alpha}{\partial Q_i \partial Q_j \partial Q_k} \frac{\partial Q_i^F}{\partial F_\beta} \frac{\partial Q_j^F}{\partial F_\gamma} \frac{\partial Q_k^F}{\partial F_\delta} \right] F_\beta F_\gamma F_\delta + \dots \end{aligned} \quad (68)$$

$$\begin{aligned} \alpha_{\alpha\beta}(R_F, F) = & \alpha_{\alpha\beta}(R_0, 0) + \sum_\gamma^{x,y,z} \left[\frac{\partial \alpha_{\alpha\beta}}{\partial F_\gamma} + \sum_{i=1}^{3N-6} \frac{\partial \alpha_{\alpha\beta}}{\partial Q_i} \frac{\partial Q_i^F}{\partial F_\gamma} \right] F_\gamma + \frac{1}{2} \sum_{\gamma,\delta}^{x,y,z} \left[\frac{\partial^2 \alpha_{\alpha\beta}}{\partial F_\gamma \partial F_\delta} \right. \\ & + \sum_{i=1}^{3N-6} \left(\frac{\partial \alpha_{\alpha\beta}}{\partial Q_i} \frac{\partial^2 Q_i^F}{\partial F_\gamma \partial F_\delta} + 2 \frac{\partial^2 \alpha_{\alpha\beta}}{\partial Q_i \partial F_\gamma} \frac{\partial Q_i^F}{\partial F_\delta} \right) + \sum_{i,j=1}^{3N-6} \frac{\partial^2 \alpha_{\alpha\beta}}{\partial Q_i \partial Q_j} \frac{\partial Q_i^F}{\partial F_\gamma} \frac{\partial Q_j^F}{\partial F_\delta} \left. \right] F_\gamma F_\delta + \dots \end{aligned} \quad (69)$$

$$\beta_{\alpha\beta\gamma}(R_F, F) = \beta_{\alpha\beta\gamma}(R_0, 0) + \sum_\delta^{x,y,z} \left[\frac{\partial \beta_{\alpha\beta\gamma}}{\partial F_\delta} + \sum_{i=1}^{3N-6} \frac{\partial \beta_{\alpha\beta\gamma}}{\partial Q_i} \frac{\partial Q_i^F}{\partial F_\delta} \right] F_\delta + \dots \quad (70)$$

and thereby obtain analytical formulas for the quantities that appear on the rhs of Eqs. (12)-(14), which yield the square brackets in Eqs. (21)-(26). The square bracket formulas obtained by the analytical FF/NR approach must, of course, be identical to those given by time-dependent PT in the infinite frequency approximation. Using either method the result may be written as a sum over 3N-6 normal modes. The simplest case is the static nuclear relaxation polarizability [cf. Eqs. (12),(15),(21)] given by:

$$\alpha_{\alpha\beta}^{nr}(0;0) = \sum_{i=1}^{3N-6} \frac{\partial \mu_\alpha}{\partial Q_i} \frac{\partial Q_i^F}{\partial F_\beta} = \frac{1}{2} \sum_{i=1}^{3N-6} P_{\alpha\beta} a_{i1}^{i,\alpha} q_1^{i,\beta} \quad (71)$$

From now on, for the sake of simplicity, we will often provide just the diagonal tensor elements. The extension to off-diagonal elements will be obvious. It turns out that the sum in Eq. (71) can be reduced to a single term by transforming to an alternative set of coordinates which may be defined in the following manner [12]. Let

$$\phi_i = \sum_{j=1}^{3N-6} M_{ij} Q_j \quad (72)$$

where \mathbf{M} is an orthogonal transformation matrix. At \mathbf{R}_F the value of ϕ_i is –

$$\phi_i^F = \sum_{j=1}^{3N-6} M_{ij} Q_j^F \left(\frac{\partial \phi_i^F}{\partial F_\alpha} = \sum_{j=1}^{3N-6} M_{ij} \frac{\partial Q_j^F}{\partial F_\alpha} \right) \quad (73)$$

If we take –

$$M_{1j} = \frac{\partial Q_j^F}{\partial F_\alpha} = -q_1^{j,\alpha} \quad (74)$$

then, since

$$\frac{\partial \mu_\alpha}{\partial Q_j} = \sum_{i=1}^{3N-6} \frac{\partial \mu_\alpha}{\partial \phi_i} \frac{\partial \phi_i}{\partial Q_j} = \sum_{i=1}^{3N-6} \frac{\partial \mu_\alpha}{\partial \phi_i} M_{ij} \quad (75)$$

it follows from the orthogonality of \mathbf{M} that

$$\alpha_{\alpha\alpha}^{nr}(0;0) = \sum_{j=1}^{3N-6} \frac{\partial \mu_\alpha}{\partial Q_j} \frac{\partial Q_j^F}{\partial F_\alpha} = \sum_{i,j=1}^{3N-6} \frac{\partial \mu_\alpha}{\partial \phi_i} M_{ij} M_{1j} = \frac{\partial \mu_\alpha}{\partial \phi_1} \sum_{j=1}^{3N-6} M_{1j}^2 = \frac{\partial \mu_\alpha}{\partial \phi_1} \frac{\partial \phi_1^F}{\partial F_\alpha} \quad (76)$$

Hence, all the information required to calculate $\alpha_{\alpha\alpha}^{nr}(0;0)$ is contained in the single coordinate ϕ_1 .

If one is interested in the complete α tensor instead of only one component, then three FICs are necessary. At this point it's interesting to remark that, on one hand, the derivation doesn't require the orthogonalization of the three FICs, and on the other hand, it is not necessary to specify the remaining ϕ_i except for the orthogonality property. The contribution of Q_i to ϕ_1 is determined by

the change in Q_i induced by the field, which explains why we call ϕ_l a field-induced coordinate (FIC). Exactly the same procedure can be employed with Eqs. (13) and (14) to obtain:

$$\beta_{\alpha\alpha\alpha}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty} = \frac{\partial \alpha_{\alpha\alpha}}{\partial \phi_1} \frac{\partial \phi_1^F}{\partial F_\alpha} \quad (77)$$

and

$$\gamma_{\alpha\alpha\alpha\alpha}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty} = \frac{\partial \beta_{\alpha\alpha\alpha}}{\partial \phi_1} \frac{\partial \phi_1^F}{\partial F_\alpha} \quad (78)$$

In addition to the above there are higher-order (in the field and/or anharmonicity) FICs, and also various closely related coordinates, that provide a similar simplification for other properties.

An example of a closely related set of coordinates is the *intensity-carrying modes* introduced by Torii and co-workers [37] in their recent treatment of infrared intensities. They showed that three vibrational degrees of freedom carry the entire IR intensity. Likewise, as shown in Table II of Ref. [12], the three FICs of Eq. (74) are sufficient to obtain all the components of $\alpha_{\alpha\beta}^{nr}(0;0)$. In fact, the *intensity-carrying modes* are the same as these FICs but with the denominator in $q_1^{j,\alpha}$ set equal to unity rather than the harmonic force constant, *i.e.*

$$M_{1j} = -a_{11}^{j,x} \quad (79)$$

$$M_{2j} = -a_{11}^{j,y} \quad (80)$$

$$M_{3j} = -a_{11}^{j,z} \quad (81)$$

There are two alternative expressions for the total infrared intensity that can be derived starting with the three coordinates defined by Eqs. (79)-(81). Following the approach of Torii, *et al.* [37] one may carry out an initial orthogonalization to the set $\{\phi_1', \phi_2', \phi_3'\}$ which yields:

$$I \propto \sum_{i=1}^{3N-6} \sum_{\alpha}^{x,y,z} \left(\frac{\partial \mu_{\alpha}}{\partial Q_i} \right)^2 = \sum_{i=1}^3 \sum_{\alpha}^{x,y,z} \left(\frac{\partial \mu_{\alpha}}{\partial \phi_i} \right)^2 \quad (82)$$

If the original non-orthogonal coordinates are used instead then, as in Eq. (75)

$$\sum_i (\partial \mu_x / \partial Q_i)^2 = (\partial \mu_x / \partial \phi_1)^2$$

where it is understood that the partial derivative with respect to ϕ_l is evaluated while holding constant a set of $3N-5$ coordinates orthogonal to ϕ_l . With that understanding the expression for I can be written as the sum of just 3 terms -

$$I \propto \sum_{i=1}^{3N-6} \sum_{\alpha}^{x,y,z} \left(\frac{\partial \mu_{\alpha}}{\partial Q_i} \right)^2 = \left(\frac{\partial \mu_x}{\partial \phi_1} \right)^2 + \left(\frac{\partial \mu_y}{\partial \phi_2} \right)^2 + \left(\frac{\partial \mu_z}{\partial \phi_3} \right)^2 \quad (83)$$

Moving on to second-order in the field it can be seen from Eq. (65) that $\partial^2 Q_j^F / \partial F_{\alpha}^2$ contains both harmonic and anharmonic contributions. Thus, two different second-order FICs can be defined by setting $M_{2j} = \left(\partial^2 Q_j^F / \partial F_{\alpha}^2 \right)_{har} = -q_2^{j,\alpha\alpha}$ or by using the entire expression in square brackets of Eq. (65), i.e. $M_{2j} = \partial^2 Q_j^F / \partial F_{\alpha}^2$. The former choice yields the harmonic second-order FIC while the latter choice yields the complete second-order coordinate. Although it might initially be thought that the complete coordinate would be necessary to determine both $\beta_{\alpha\alpha\alpha}^{nr}(0;0,0)$ and $\gamma_{\alpha\alpha\alpha\alpha}^{nr}(-\omega;\omega,0,0)_{\omega \rightarrow \infty}$ that turns out not to be so. Utilizing the same overall procedure that was employed above in connection with Eq. (12), and some additional manipulations, one can write $\beta_{\alpha\alpha\alpha}^{nr}(0;0,0)$ solely in terms of the first-order ϕ_l [cf. Eq. (68)]:

$$\beta_{\alpha\alpha\alpha}^{nr}(0;0,0) = 3 \frac{\partial \alpha_{\alpha\alpha}}{\partial \phi_1} \frac{\partial \phi_1^F}{\partial F_{\alpha}} + 3 \frac{\partial^2 \mu_{\alpha}}{\partial \phi_1^2} \left(\frac{\partial \phi_1^F}{\partial F_{\alpha}} \right)^2 - \frac{\partial^3 V}{\partial \phi_1^3} \left(\frac{\partial \phi_1^F}{\partial F_{\alpha}} \right)^3 \quad (84)$$

On the other hand, the expression for $\gamma_{\alpha\alpha\alpha\alpha}^{nr}(-\omega;\omega,0,0)_{\omega \rightarrow \infty}$ obtained from Eq. (13) requires the first-order ϕ_i and *either* the harmonic second-order FIC *or* the complete second-order FIC. As we

will see later, the latter can be particularly useful for computational purposes and the former for interpretation. The expression for the Kerr effect in terms of the FICs is given by:

$$\begin{aligned}
\gamma_{\alpha\alpha\alpha\alpha}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty} = & -\sum_{i=1}^2 \left(2 \frac{\partial \beta_{\alpha\alpha\alpha}}{\partial \phi_i} \frac{\partial \phi_i^F}{\partial F_\alpha} + \frac{\partial \alpha_{\alpha\alpha}}{\partial \phi_i} \left(\frac{\partial^2 \phi_i^F}{\partial F_\alpha^2} \right)_{har} \right) \\
& + \sum_{i,j=1}^2 \left(\frac{\partial^2 \alpha_{\alpha\alpha}}{\partial \phi_i \partial \phi_j} \frac{\partial \phi_i^F}{\partial F_\alpha} \frac{\partial \phi_j^F}{\partial F_\alpha} + 2 \frac{\partial^2 \mu_\alpha}{\partial \phi_i \partial \phi_j} \frac{\partial \phi_i^F}{\partial F_\alpha} \left(\frac{\partial^2 \phi_j^F}{\partial F_\alpha^2} \right)_{har} \right) \\
& + \sum_{i,j,k=1}^2 \frac{\partial^3 V}{\partial \phi_i \partial \phi_j \partial \phi_k} \frac{\partial \phi_i^F}{\partial F_\alpha} \frac{\partial \phi_j^F}{\partial F_\alpha} \left(\frac{\partial^2 \phi_k^F}{\partial F_\alpha^2} \right)_{har}
\end{aligned} \tag{85}$$

or

$$\gamma_{\alpha\alpha\alpha\alpha}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty} = -\sum_{i=1}^2 \left(2 \frac{\partial \beta_{\alpha\alpha\alpha}}{\partial \phi_i} \frac{\partial \phi_i^F}{\partial F_\alpha} + \frac{\partial \alpha_{\alpha\alpha}}{\partial \phi_i} \frac{\partial^2 \phi_i^F}{\partial F_\alpha^2} \right) + \sum_{i,j=1}^2 \frac{\partial^2 \alpha_{\alpha\alpha}}{\partial \phi_i \partial \phi_j} \frac{\partial \phi_i^F}{\partial F_\alpha} \frac{\partial \phi_j^F}{\partial F_\alpha} \tag{86}$$

Eq. (86) can be derived from Eq. (85) by recombining the terms that contain $(\partial^2 \phi_j^F / \partial F_\alpha^2)_{har}$. In either relation we can use the harmonic or the complete second-order FIC and exactly the same value for the second hyperpolarizability will be obtained [12]. Note that we do not insist here on ϕ_1 being orthogonal to ϕ_2 but only that both of these coordinates are orthogonal to all others.

At this point it is convenient to consider $\gamma_{\alpha\alpha\alpha\alpha}^{nr}(-\omega; \omega, -\omega, \omega)_{\omega \rightarrow \infty}$, although the latter does not emerge directly from the FF/NR treatment. However, we have seen that PT gives a simple square bracket expression for this quantity, *i.e.* $2/3[\alpha^2]_{\omega=0}^0$. Comparing to $[\mu^2]_{\omega=0}^0$ one might surmise that both quantities could be written in the same form if the first-order FIC in Eq. (76) is replaced by the harmonic second-order FIC and, indeed, that turns out to be the case –

$$\gamma_{\alpha\alpha\alpha\alpha}^{nr}(-\omega; \omega, -\omega, \omega)_{\omega \rightarrow \infty} = -2 \frac{\partial \alpha_{\alpha\alpha}}{\partial \phi_1} \left(\frac{\partial^2 \phi_1^F}{\partial F_\alpha^2} \right)_{har} \tag{87}$$

Coordinates simply related to the harmonic second-order FICs can be used to extend the treatment of Torii, *et al.* to Raman scattering intensities. Both the isotropic and anisotropic Raman intensities [38] depend on the first derivative of the polarizability tensor with respect to

normal coordinates. Thus, we may employ for this purpose the set of modified harmonic second-order coordinates determined by –

$$M_{ij} = -a_{12}^{j,\alpha\beta} \quad 1 \leq i \leq 6 \quad (88)$$

where $i = 1, 2, \dots, 6$ correspond to the six unique $\alpha\beta$ pairs and the harmonic force constant has been set equal to unity (just like in the treatment of infrared intensities). As in the case of the IR intensity, alternative formulas can be developed depending upon whether the individual coordinates are orthogonalized or not. Using the set of three orthogonalized coordinates derived from $M_{1j} = -a_{12}^{j,xx}$, $M_{2j} = -a_{12}^{j,yy}$ and $M_{3j} = -a_{12}^{j,zz}$ the isotropic intensity expression is –

$$I_A \propto \sum_{i=1}^{3N-6} \sum_{\alpha,\beta}^{x,y,z} \left(\frac{\partial \alpha_{\alpha\alpha}}{\partial Q_i} \frac{\partial \alpha_{\beta\beta}}{\partial Q_i} \right) = \sum_{i=1}^3 \sum_{\alpha,\beta}^{x,y,z} \left(\frac{\partial \alpha_{\alpha\alpha}}{\partial \phi_i} \frac{\partial \alpha_{\beta\beta}}{\partial \phi_i} \right) \quad (89)$$

For the anisotropic Raman intensity all six orthogonalized coordinates must be utilized:

$$I_B \propto \sum_{i=1}^{3N-6} \sum_{\alpha,\beta}^{x,y,z} \left(3 \frac{\partial \alpha_{\alpha\beta}}{\partial Q_i} \frac{\partial \alpha_{\alpha\beta}}{\partial Q_i} - \frac{\partial \alpha_{\alpha\alpha}}{\partial Q_i} \frac{\partial \alpha_{\beta\beta}}{\partial Q_i} \right) = \sum_{i=1}^6 \sum_{\alpha,\beta}^{x,y,z} \left(3 \frac{\partial \alpha_{\alpha\beta}}{\partial \phi_i} \frac{\partial \alpha_{\alpha\beta}}{\partial \phi_i} - \frac{\partial \alpha_{\alpha\alpha}}{\partial \phi_i} \frac{\partial \alpha_{\beta\beta}}{\partial \phi_i} \right) \quad (90)$$

If one is interested in only the isotropic Raman intensity, then a single second-order harmonic coordinate will suffice. This follows from the fact that the isotropic term can be written as:

$$I_A = 9 \sum_{i=1}^{3N-6} \left(\frac{\partial \bar{\alpha}}{\partial Q_i} \right)^2 = \left(\frac{\partial \bar{\alpha}}{\partial \phi_1} \right)^2 \quad (91)$$

where

$$\bar{\alpha} = \frac{1}{3} \sum_{\alpha}^{x,y,z} \alpha_{\alpha\alpha} \quad (92)$$

and ϕ_i , in this case, is defined by:

$$M_{1j} = \frac{\partial \bar{\alpha}}{\partial Q_j} \quad (93)$$

It should be noted that this same treatment applies to the $(\partial\alpha_{\alpha\alpha}/\partial Q_i)(\partial\alpha_{\beta\beta}/\partial Q_i)$ term in the anisotropic formula of Eq. (90). The remaining $(\partial\alpha_{\alpha\beta}/\partial Q_i)(\partial\alpha_{\alpha\beta}/\partial Q_i)$ term can be evaluated using the coordinates in Eq. (88) without orthogonalization:

$$\sum_{i=1}^{3N-6} \sum_{\alpha,\beta}^{x,y,z} \left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_i} \frac{\partial\alpha_{\alpha\beta}}{\partial Q_i} \right) = \left(\frac{\partial\alpha_{xx}}{\partial\phi_1} \right)^2 + 2 \left(\frac{\partial\alpha_{yx}}{\partial\phi_2} \right)^2 + \left(\frac{\partial\alpha_{yy}}{\partial\phi_3} \right)^2 + 2 \left(\frac{\partial\alpha_{zx}}{\partial\phi_4} \right)^2 + 2 \left(\frac{\partial\alpha_{zy}}{\partial\phi_5} \right)^2 + \left(\frac{\partial\alpha_{zz}}{\partial\phi_6} \right)^2 \quad (94)$$

The combination of Eqs. (91) and (94) constitute an alternative to Eqs. (89) and (90). Torii *et al.* used infrared intensity-carrying modes to simplify the study of the IR spectra of radical cations of polycyclic aromatic hydrocarbons. The Raman intensity-carrying modes defined here can be applied in an analogous fashion to Raman spectra.

Beyond ordinary infrared and Raman spectra the same formalism can be extended to hyperRaman spectra as well as infrared and Raman vibrational optical activity (VOA). For infrared VOA the dipole strength $(\partial\mu_{\alpha l}/\partial Q_i)^2$ in Eq. (82) is replaced by the rotational strength [39] $\text{Im} (\partial\mu_{\alpha l}/\partial Q_i)(\partial m_{\alpha l}/\partial Q_i)$. Although the magnetic dipole derivative is very small, and was previously neglected in calculating the nuclear relaxation contribution to magnetic properties, this factor must be considered here since the entire effect would vanish if it were zero. The derivative $(\partial m_{\alpha l}/\partial Q_i)$ is the sum of an electronic term, which is non-zero due to breakdown of the Born-Oppenheimer approximation, and a nuclear term [40]. Regardless of the origin of $(\partial m_{\alpha l}/\partial Q_i)$, we can write the intensity in terms of non-orthogonalized coordinates, as –

$$I \propto \text{Im} \sum_{i=1}^{3N-6} \sum_{\alpha}^{x,y,z} \left(\frac{\partial\mu_{\alpha}}{\partial Q_i} \frac{\partial m_{\alpha}}{\partial Q_i} \right) = \text{Im} \left[\left(\frac{\partial\mu_x}{\partial\phi_1} \frac{\partial m_x}{\partial\phi_1} \right) + \left(\frac{\partial\mu_y}{\partial\phi_2} \frac{\partial m_y}{\partial\phi_2} \right) + \left(\frac{\partial\mu_z}{\partial\phi_3} \frac{\partial m_z}{\partial\phi_3} \right) \right] \quad (95)$$

The coordinates $\{\phi_1, \phi_2, \phi_3\}$ may be based either on the electric dipole derivatives [cf. Eqs. (79)-(81)] or the magnetic dipole derivatives, *i.e.*

$$M_{1j} = \frac{\partial m_x}{\partial Q_j} \quad (96)$$

$$M_{2j} = \frac{\partial m_y}{\partial Q_j} \quad (97)$$

$$M_{3j} = \frac{\partial m_z}{\partial Q_j} \quad (98)$$

If electric dipole derivatives are chosen, then the intensity carrying modes are identical to those used for ordinary infrared spectroscopy. Of course, the infrared VOA (rotational) intensity will be exactly the same in either event. Once again, an alternative expression can be developed in terms of orthogonal coordinates although, in the interest of brevity, we do not present it here. The Raman VOA intensities may be treated in a similar fashion. In this case one of the linear polarizability derivatives in each term of Eq. (89)-(90) is replaced by a derivative of the corresponding component of the quantity $\delta_{\alpha\beta}$ in Eq. (54) [41]. (There is also a second contribution to the Raman VOA due to the quadrupole moment which may be treated in the same fashion as $\delta_{\alpha\beta}$.) In analogy with the analysis of infrared VOA given above one can choose the same six coordinates to carry both the ordinary Raman intensity and the Raman VOA intensity. However, if coordinates based on the derivatives of $\delta_{\alpha\beta}$ are used to express the Raman VOA intensity, then, the number necessary increases to nine since $\delta_{\alpha\beta} \neq \delta_{\beta\alpha}$.

Of all the electric dipole nuclear relaxation properties only the static second hyperpolarizability *requires* the complete second-order FIC. After some manipulation, the procedure that leads to Eq. (12) yields –

$$\begin{aligned} \gamma_{aaaa}^{nr}(0;0,0,0) = & - \sum_{i=1}^2 12 \left(\frac{1}{3} \frac{\partial \beta_{aaa}}{\partial \phi_i} \frac{\partial \phi_i^F}{\partial F_\alpha} + \frac{1}{4} \frac{\partial \alpha_{aa}}{\partial \phi_i} \frac{\partial^2 \phi_i^F}{\partial F_\alpha^2} \right) \\ & + \sum_{i,j=1}^2 6 \left(\frac{\partial^2 \alpha_{aa}}{\partial \phi_i \partial \phi_j} \frac{\partial \phi_i^F}{\partial F_\alpha} \frac{\partial \phi_j^F}{\partial F_\alpha} + \frac{\partial^2 \mu_\alpha}{\partial \phi_i \partial \phi_j} \frac{\partial \phi_i^F}{\partial F_\alpha} \frac{\partial^2 \phi_j^F}{\partial F_\alpha^2} \right) \\ & - \sum_{i,j,k=1}^2 4 \left(\frac{\partial^3 \mu_\alpha}{\partial \phi_i \partial \phi_j \partial \phi_k} \frac{\partial \phi_i^F}{\partial F_\alpha} \frac{\partial \phi_j^F}{\partial F_\alpha} \frac{\partial \phi_k^F}{\partial F_\alpha} - \frac{3}{4} \frac{\partial^3 V}{\partial \phi_i \partial \phi_j \partial \phi_k} \frac{\partial \phi_i^F}{\partial F_\alpha} \frac{\partial \phi_j^F}{\partial F_\alpha} \frac{\partial^2 \phi_k^F}{\partial F_\alpha^2} \right) \\ & - \sum_{i,j,k,l=1}^2 \left(\frac{\partial^4 V}{\partial \phi_i \partial \phi_j \partial \phi_k \partial \phi_l} \frac{\partial \phi_i^F}{\partial F_\alpha} \frac{\partial \phi_j^F}{\partial F_\alpha} \frac{\partial \phi_k^F}{\partial F_\alpha} \frac{\partial \phi_l^F}{\partial F_\alpha} \right) \end{aligned} \quad (99)$$

The two (non-orthogonal) FICs ϕ_l and ϕ_2 (defined by $M_{1j} = \partial Q_j^F / \partial F_\alpha$ and $M_{2j} = \partial^2 Q_j^F / \partial F_\alpha^2$) are sufficient to determine $\gamma_{aaaa}^{nr}(0;0,0,0)$ regardless of the size of the molecule.

The formalism we have presented is readily extended to include electric/magnetic field interactions represented by the cross-terms in Eq. (54). Because of the quenching of orbital angular momentum, nuclear relaxation effects will occur only for those properties that are quadratic in the magnetic field - *i.e.* the coefficients $\xi_{\alpha,\beta\gamma}$ and $\eta_{\alpha\beta,\gamma\delta}$. In order to deduce the NR contribution to these properties we begin with the complete expression for the molecular potential energy:

$$V(\mathbf{Q}, \mathbf{F}, \mathbf{B}) = \sum_{n=0}^{3N-6} \sum_{i_1=1}^{3N-6} \dots \sum_{i_n=1}^{3N-6} \sum_{m=0}^{x,y,z} \sum_{\alpha_1=1}^{x,y,z} \dots \sum_{\alpha_m=1}^{x,y,z} \sum_{l=0}^{x,y,z} \sum_{\beta_1=1}^{x,y,z} \dots \sum_{\beta_l=1}^{x,y,z} a_{nml}^{i_1 \dots i_n, \alpha_1 \dots \alpha_m \beta_1 \dots \beta_l} Q_{i_1} \dots Q_{i_n} F_{\alpha_1} \dots F_{\alpha_m} B_{\beta_1} \dots B_{\beta_l} \quad (100)$$

in which

$$a_{nml}^{i_1 \dots i_n, \alpha_1 \dots \alpha_m \beta_1 \dots \beta_l} = \frac{1}{n! m! l!} \left(\frac{\partial^{(n+m+l)} V(Q_1, \dots, Q_{3N-6}, F_x, F_y, F_z, B_x, B_y, B_z)}{\partial Q_{i_1} \dots \partial Q_{i_n} \partial F_{\alpha_1} \dots \partial F_{\alpha_m} \partial B_{\beta_1} \dots \partial B_{\beta_l}} \right)_{Q=0, F=0, B=0} \quad (101)$$

Then the field-free normal coordinate displacement vector, $Q_i^{F,B}$, at the field-dependent equilibrium geometry $R^{F,B}$ may be found in exactly the same manner as Q_i^F was determined earlier. Taking into account orbital quenching ($q_{0l}^{i,\alpha} = 0$; no terms linear in B) one obtains:

$$Q_i^{F,B} = - \sum_{\alpha}^{x,y,z} q_{10}^{i,\alpha} F_{\alpha} - \sum_{\alpha,\beta}^{x,y,z} \left[q_{20}^{i,\alpha\beta} - \sum_{j=1}^{3N-6} \frac{a_{210}^{ij,\alpha}}{a_{200}^{ii}} q_{10}^{j,\beta} + \sum_{j,k=1}^{3N-6} \frac{3 a_{300}^{ijk}}{2 a_{200}^{ii}} q_{10}^{j,\alpha} q_{10}^{k,\beta} \right] F_{\alpha} F_{\beta} - \sum_{a,b}^{x,y,z} q_{02}^{i,\alpha\beta} B_{\alpha} B_{\beta} - \dots \quad (102)$$

where

$$q_{10}^{i,\alpha} = \frac{a_{110}^{i,\alpha}}{2 a_{200}^{ii}} \quad (103)$$

$$q_{20}^{i,\alpha\beta} = \frac{a_{120}^{i,\alpha\beta}}{2 a_{200}^{ii}} \quad (104)$$

$$q_{02}^{i,\alpha\beta} = \frac{a_{102}^{i,\alpha\beta}}{2a_{200}^{ii}} \quad (105)$$

The nuclear relaxation contribution to $\eta_{\alpha\beta,\gamma\delta}$ - which is associated with the Cotton-Mouton effect – can be obtained from the expansion of electric polarizability at the magnetic field-dependent equilibrium geometry given by:

$$\alpha_{\alpha\beta}(R_B, B) = \alpha_{\alpha\beta}(R_0, 0) + \sum_{\gamma} \frac{\partial \alpha_{\alpha\beta}}{\partial B_{\gamma}} B_{\gamma} + \frac{1}{2} \sum_{\gamma, \delta} \left[\frac{\partial^2 \alpha_{\alpha\beta}}{\partial B_{\gamma} \partial B_{\delta}} + \sum_{i=1}^{3N-6} \frac{\partial \alpha_{\alpha\beta}}{\partial Q_i} \frac{\partial^2 Q_i^F}{\partial B_{\gamma} \partial B_{\delta}} \right] B_{\gamma} B_{\delta} + \dots \quad (106)$$

From the above equation it is straightforward to obtain (*cf.* Eqs. (13), (19)) the following sum-over-normal modes expression for the quantity that appears on the rhs of Eq. (61) –

$$\eta_{\alpha\beta,\gamma\delta}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty} = \sum_{i=1}^{3N-6} \frac{\partial \alpha_{\alpha\beta}}{\partial Q_i} \frac{\partial^2 Q_i^{F,B}}{\partial B_{\gamma} \partial B_{\delta}} = 4 \sum_{i=1}^{3N-6} a_{120}^{i,\alpha\beta} q_{02}^{i,\gamma\delta} \quad (107)$$

The above equation can be simplified by defining a second-order FIC, *i.e.*

$M_{1j} = \partial^2 Q_j^{F,B} / \partial B_{\gamma} \partial B_{\delta} = -2q_{02}^{j,\gamma\delta}$, which leads to:

$$\eta_{\alpha\beta,\gamma\delta}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty} = \frac{\partial \alpha_{\alpha\beta}}{\partial \phi_1} \frac{\partial^2 \phi_1^{F,B}}{\partial B_{\gamma} \partial B_{\delta}} \quad (108)$$

As seen above there is an analogue of ordinary nuclear relaxation for resonant processes involving transition, rather than ground state, properties. This suggests the possibility of obtaining analogues of the FICS that have been defined here for non-resonant properties - a possibility which remains to be explored.

The FICs employed for nuclear relaxation can also be used to beneficial effect in calculating ZPVA's. Returning to Eq. (31) one can readily see that, for electric dipole properties, the desired definition is [20]:

$$M_{1j} = \left(\frac{\partial^n Q_j^F}{\partial F_{\alpha_1} \dots \partial F_{\alpha_n}} \right)_{har} = -n! q_n^{j,\alpha_1 \dots \alpha_n} \quad (109)$$

where $n = 1$ refers to μ^ℓ , $n = 2$ refers to α^ℓ , *etc.* and the superscript $\alpha_1 \dots \alpha_n$ denotes the particular component. It follows immediately that -

$$[P]^{0,1} = -\frac{\partial E^{zp}}{\partial \phi_1} \left(\frac{\partial^n \phi_1^F}{\partial F_{\alpha_1} \dots \partial F_{\alpha_n}} \right)_{har} \quad (110)$$

Calculation of $[P]^{0,1}$ from Eq. (110) requires the evaluation of just one mechanical anharmonicity parameter, *i.e.* $\left(\partial^n \phi_1^F / \partial F_{\alpha_1} \dots \partial F_{\alpha_n} \right)_{har}$, as opposed to $3N-6$ in Eq. (31). The remaining contribution to the first-order ZPVA, namely $[P]^{1,0}$, can be determined from Eq. (32). Since there are no derivatives of E^{zp} with respect to vibrational coordinates this relation is already in its simplest form. Even though compact expressions for the two terms that enter into the ZPVA have been obtained using E^{zp} it is important to recognize that one must still compute the complete Hessian because $\sum_i \omega_i = \sum_i \sqrt{F_{ii}} \neq \sqrt{\sum_i F_{ii}}$

The FIC treatment can also be applied to the ZPVA contributions to magnetic properties. For pure magnetic (hyper)magnetizabilities the mechanical first-order correction term is given by:

$$[P]^{0,1} = -\frac{\partial E^{zp}}{\partial \phi_1} \left(\frac{\partial^n \phi_1^B}{\partial B_{\alpha_1} \dots \partial B_{\alpha_n}} \right)_{har} \quad (111)$$

in which n is the order of the (hyper)magnetizability and

$$M_{1j} = \left(\frac{\partial^n Q_j^{F,B}}{\partial B_{\alpha_1} \dots \partial B_{\alpha_n}} \right)_{har} = -n! q_{0n}^{j,\alpha_1 \dots \alpha_n} \quad (112)$$

Furthermore, for cross-terms involving both electric and magnetic fields:

$$[P]^{0,1} = -\frac{\partial E^{zp}}{\partial \phi_1} \left(\frac{\partial^{n+m} \phi_1^{F,B}}{\partial F_{\alpha_1} \dots \partial F_{\alpha_n} \partial B_{\beta_1} \dots \partial B_{\beta_m}} \right)_{har} \quad (113)$$

where ϕ_l defined by:

$$M_{1j} = \left(\frac{\partial^{n+m} Q_j^{F,B}}{\partial F_{\alpha_1} \dots \partial F_{\alpha_n} \partial B_{\beta_1} \dots \partial B_{\beta_m}} \right)_{har} = n!m!q_{nm}^{j,\alpha_1 \dots \alpha_n, \beta_1 \dots \beta_m} \quad (114)$$

The parameters involved in NMR/ESR occur as the coefficients of the nuclear and/or electron spin (or, equivalently, the magnetic moment associated with that spin) as well as the applied magnetic field (in most but not all cases). One can formally take derivatives with respect to the magnetic moments in the same way that derivatives are taken with respect to the magnetic field and, then, FICs can be utilized in a straightforward manner [42]. For instance the nuclear shielding tensor of a nucleus K with a nuclear spin magnetic moment I_K might be expressed as [43]:

$$\sigma_{K,\alpha\alpha} = 1 + \left(\frac{\partial^2 V(\mathbf{B}, \mathbf{I})}{\partial B_\alpha \partial I_{K,\alpha}} \right)_{B=0, I=0} \quad (115)$$

Thus, the first-order ZPVA contribution due to mechanical anharmonicity is given by:

$$[P]^{0,1} = - \frac{\partial \mathcal{E}^{zp}}{\partial \phi_1} \left(\frac{\partial^2 \phi_1^{B,I}}{\partial B_\alpha \partial I_{K,\alpha}} \right)_{har} \quad (116)$$

where the FIC ϕ_l is defined by:

$$M_{1j} = \left(\frac{\partial^2 Q_j^{B,I}}{\partial B_\alpha \partial I_{K,\alpha}} \right)_{har} \quad (117)$$

Similarly, the nuclear spin-spin coupling tensor can be defined as a second derivative of the potential energy with respect to the magnetic moments of the two coupled nuclei [44] –

$$J_{KL,\alpha\alpha} = \frac{\hbar}{2\pi} \gamma_K \gamma_L \left(\frac{\partial^2 V(\mathbf{I})}{\partial I_{K,\alpha} \partial I_{L,\alpha}} \right)_{I=0} \quad (118)$$

where γ_K is the dimensionless gyromagnetic ratio of the nucleus K . At this point, it can be readily seen that the mechanical ZPVA term for nuclear spin-spin coupling depends on the single FIC defined by:

$$M_{1j} = \left(\frac{\partial^2 Q_j^I}{\partial I_{K,\alpha} \partial I_{L,\alpha}} \right)_{har} \quad (119)$$

The electronic g-tensor is completely parallel to nuclear shielding except that the electron spin magnetic moment replaces the nuclear spin magnetic moment. Similarly, the magnetic hyperfine interaction is analogous to nuclear spin-spin coupling except that one of the nuclear spin magnetic moments is replaced by an electron spin magnetic moment. Thus, the ZPVA contribution to ESR properties arising from mechanical anharmonicity is also given in terms of a single FIC for each tensor component.

The discovery of FICs is very recent. Nonetheless, Hartree-Fock (split valence) calculations have already been carried out on electric dipole properties for a representative set of push-pull compounds, as well as hexasilane and hexatriene, with interesting results [12]. (At the same time it has been demonstrated [19] that MP2 calculations including the C-ZPVA contribution are also feasible.) Not only are the nuclear relaxation hyperpolarizabilities often as large as the corresponding static electronic properties in these calculations, but for the Kerr effect and for the first and second static hyperpolarizabilities the anharmonic terms often make a very important contribution to the total value. On the other hand, the initial convergence within the two perturbation sequences shown in Eq. (49) was determined to be rapid, although this evaluation was done for only one molecule [NH₂-(CH=CH)₃-NO₂] and for just the static ZPVA correction. [20] There is evidence from a methane calculation [44] that the ZPVA correction may become more significant at optical frequencies. Of course, other large molecules and other properties remain to be considered.

By analogy with ordinary nuclear relaxation, we expect that the effect of nuclear relaxation on the ZPVA correction to any electronic property (i.e. the C-ZPVA term) will often be comparable to, or substantially larger than, the ZPVA term itself. Indeed, for NH₂-(CH=CH)₃-NO₂, $\gamma^{c-zpva}(0; 0, 0, 0)$ is of the same size as the *electronic* $\gamma(0; 0, 0, 0)$ [46].

Finally, from the standpoint of interpretation, it is important to mention that FICs can also be utilized to distinguish anharmonic from harmonic contributions to nuclear relaxation and, in addition, to separate mechanical from electrical anharmonicity [12]. For the static β and for the EOKE this result can be obtained directly from Eqs. (84) and (85) respectively because each individual term can be associated with a particular term in the PT expression. In the case of the static γ an additional calculation must be made where the harmonic second-order FIC is substituted for the complete FIC in Eq. (99). We note further that the division between harmonic and anharmonic contributions to the nuclear relaxation properties cannot be made when the FF/NR method is applied using ordinary normal coordinates rather than FICs.

IV. General computational considerations

It has now been shown how the effect of vibrations on a variety of electrical, magnetic and spectroscopic properties can be described entirely in terms of field-induced coordinates, or FICs. The key point is that the number of FICs involved remains the same regardless of the size of the molecule. As a result, the computer time required to calculate the anharmonicity parameters needed for determining vibrational effects in large molecules is considerably reduced in comparison with using normal coordinates for the same problem.

From a computational perspective our treatment is carried out in two distinct steps. The first step is to find the FICs. In general, for the harmonic FICs one must obtain the quadratic vibrational force constant matrix, (*i.e.* the Hessian) and first derivatives of the electronic property with respect to normal coordinates. These quantities may or may not be available analytically depending upon the computational method and the property. If analytical higher-order property derivatives are not available one may obtain them numerically from lower-order derivatives using finite fields. The complete FICs, including both harmonic and anharmonic terms, are most

conveniently calculated by finite field geometry optimization. This avoids explicit computation of any anharmonicity parameters; not even the Hessian is required. Since only low-order (in the field) FICs are needed, a few small fields are sufficient for this purpose. For the first-order (in the field) FIC there is no anharmonic contribution, which means that either the analytical or numerical method can be employed. In cases where there is a choice, *e.g.* $\gamma_{\alpha\beta\gamma\delta}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}$, geometry optimization may be preferable for computational purposes.

The second step in our treatment is to evaluate the nuclear relaxation, ZPVA, and C-ZPVA terms. For this purpose it is convenient to transform the Hessian to the reduced FIC basis and diagonalize, if necessary, to find the associated vibrational frequencies and orthogonalized FICs. Then, P^{nr} and $P^{zpv\alpha}$ are given by the usual formulas in terms of normal coordinates except that the normal coordinates are replaced by FICs. Closed form expressions for the resulting nuclear relaxation contribution to electric dipole properties have been presented elsewhere [12] and the corresponding expression for $\eta_{\alpha\beta,\gamma\delta}$ is given by Eq. (108).

The $[P]^{0,1}$ contribution to $P^{zpv\alpha}$ is given in terms of FICs by Eqs. (110), (111), (113) and (116) while the $[P]^{1,0}$ term remains exactly as shown on the rhs of Eq. (32) (or the obvious analogue of this equation for the other properties discussed in this paper) since the latter does not *explicitly* contain derivatives with respect to normal coordinates or vibrational frequencies. Finally, in order to obtain the C-ZPVA contribution it is necessary evaluate the ZPVA term at several field-dependent equilibrium geometries. With the exception of $\gamma_{\alpha\beta\gamma\delta}^{c-zpv\alpha}(0; 0, 0, 0)$ a few small fields will, again, suffice. A larger field or two may be required for the latter property since it is third-order in the field.

V. Conclusions and future work

Vibrational motions play a role that ranges from negligible to major in various molecular properties associated with field-induced (or internal) electric and/or magnetic dipoles. These dipoles may be oscillating at frequencies that are either on resonance for a vibronic transition or far away from resonance. The vibrational effects can be ascribed to nuclear relaxation (NR), zero-point vibrational averaging (ZPVA), or a combination of the two (C-ZPVA). A comprehensive theoretical/computational treatment recently developed specifically for non-resonant electric dipole properties has been reviewed here and extended to cover all of these properties. We refer to our treatment as the finite field/nuclear relaxation (FF/NR) method although, in fact, it can be applied in an analytical mode and it owes much to the earlier (PT) method.

Computations on large molecules, taking into account harmonic and anharmonic contributions, are facilitated by the introduction of field-induced coordinates (FICs). All information required to carry out the computations can be obtained in terms of these coordinates, the number of which is the regardless of molecular size. Extending the work of Torii, *et al.* we have also shown that a set of closely related coordinates can be used to provide a compact description of infrared and Raman intensities with or without optical activity. Initial calculations of electric dipole hyperpolarizabilities, reported elsewhere, confirm the efficiency of the FF/NR approach as well as the importance of both harmonic and anharmonic vibrational contributions in a number of instances.

Although significant progress has been made much remains to be done. It can be anticipated that there will be an increasing number of applications to diverse properties. More needs to be learned about how the relative magnitude of the vibrational contribution varies for different electronic properties depending upon the chemical system. One can also imagine that the treatment presented here may eventually prove useful in understanding the role of vibrations

in dynamical processes such as electron transfer. Our formalism can certainly provide an interpretive framework for vibrational spectroscopies as already shown in the case of infrared spectroscopy by Torii, *et al.* [37]

Further methodological advances also are desired, especially for the treatment of frequency-dependence and of resonant phenomena. These subjects are currently under investigation. On the computational side the possibility of combining semiempirical force constants with *ab initio* properties has shown some initial promise that calls for further exploration.

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