Additional compact formulas for vibrational dynamic dipole polarizabilities and hyperpolarizabilities

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Compact expressions, complete through second order in electrical and/or mechanical anharmonicity, are given for the dynamic dipole vibrational polarizability and dynamic first and second vibrational hyperpolarizabilities. Certain contributions not previously formulated are now included. © *1998 American Institute of Physics.* [S0021-9606(98)02324-1]

The past decade has seen an increasing number of calculations of vibrational polarizabilities and hyperpolarizabilities. At this time, some hundred-odd papers have touched on this subject, and it has recently been reviewed in detail by one of us.[1] For some systems and processes these vibrational properties are even more important than the corresponding electronic ones. Together both contributions govern nonlinear optical (NLO) behavior. A large number of the vibrational calculations have been based on one or both of two approximations: (a) the vibrations are assumed to be harmonic, and the electronic properties are assumed to be linear in the normal coordinates—this is the double-harmonic-oscillator approximation;[2] and (b) the optical frequencies are taken to be infinite[2]—this is the enhanced, or infinite frequency approximation.[3,4] These approximations have been analyzed by Bishop and Dalskov.[5] The only rigorous treatment of the dynamic vibrational (hyper)polarizabilities is that given by Bishop and Kirtman[6] in the early nineties. The purpose here is to extend their general formulas so that they are complete through second order of perturbation theory in mechanical and/or electrical anharmonicity. All vibrational effects are included except for zero-point vibrational averaging of the electronic (hyper)polarizability.

We write the vibrational polarizability (α^v) and the first and second vibrational hyperpolarizability (β^v and γ^v) as a sum of terms derived from the sum-over-states expressions for the total (hyper)polarizability, which are given in terms of vibronic energies and dipole moment matrix elements over the vibronic wave functions,[7]

$$\alpha^v(-\omega_\sigma;\omega_1)=[\mu^2], \tag{1}$$

$$\beta^v(-\omega_\sigma;\omega_1,\omega_2)=[\mu\alpha]+[\mu^3], \tag{2}$$

$$\gamma^v(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=[\alpha^2]+[\mu\beta]+[\mu^2\alpha]+[\mu^4]. \tag{3}$$

Here, the optical frequencies ($\omega_1,\omega_2,\omega_3$) define a particular NLO process and $\omega_\sigma=\Sigma_i\omega_i$. The square-bracket terms[6] are sums over vibrational states of a quotient in which the numerator introduces vibrational transition matrix elements of the electronic properties (μ,α,β) and the denominator involves the vibrational and optical frequencies. For example,

$$[\mu\alpha]=\frac{1}{2\hbar}\sum P_{\alpha\beta\gamma}\sum_k{}'(\mu_\alpha)_{0k}(\alpha_{\beta\gamma})_{k0}[(\omega_k+\omega_\sigma)^{-1}+(\omega_k-\omega_\sigma)^{-1}], \tag{4}$$

where $(\mu_\alpha)_{0k}=\langle 0|\mu_\alpha|k\rangle$; $|k\rangle$ is the kth vibrational wave function with energy $\hbar\omega_k$; μ_α is the α component of the dipole moment ($\alpha,\beta,\gamma=$Cartesian coordinates x,y,z); $\Sigma P_{\alpha\beta\gamma}$ indicates a sum over the simultaneous permutations of frequencies and subscripts $(-\omega_\sigma,\alpha)$, (ω_1,β), and (ω_2,γ) (an alternative equivalent notation is $\Sigma P_{-\sigma,1,2}$); and the prime on the second summation denotes exclusion of the vibrational ground state.

The electronic properties are, next, expanded in the normal coordinates ($Q_a,Q_b,\ldots$), e.g.,

$$\mu_\alpha\cong\mu_\alpha^0+\sum_a\left(\frac{\partial\mu}{\partial Q_a}\right)Q_a+\frac{1}{2}\sum_{a,b}\left(\frac{\partial^2\mu}{\partial Q_a\partial Q_b}\right)Q_aQ_b+\frac{1}{6}\sum_{a,b,c}\left(\frac{\partial^3\mu}{\partial Q_a\partial Q_b\partial Q_c}\right)Q_aQ_bQ_c. \tag{5}$$

Here the quadratic term is considered to be first order in electrical anharmonicity and the cubic term is considered to be second order. Thus, it is sufficient for our purposes to truncate the expansion as above after the third derivatives. The vibrational potential, V, is expanded in a similar manner,

$$V\cong V^0+\frac{1}{2}\sum_a\omega_a^2Q_a^2+\frac{1}{6}\sum_{a,b,c}F_{abc}Q_aQ_bQ_c+\frac{1}{24}\sum_{a,b,c,d}F_{abcd}Q_aQ_bQ_cQ_d, \tag{6}$$

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TABLE I. Formulas for the contributions to dynamic vibrational polarizabilities and hyperpolarizabilities.[a]

Term	Formula
$[\mu^2]^{0,0}$	$\frac{1}{2}\Sigma P_{\alpha\beta}\Sigma_a(\partial\mu_\alpha/\partial Q_a)(\partial\mu_\beta/\partial Q_a)\lambda_a^{\pm\sigma}$
$[\mu^2]^{2,0}$	$(\hbar/8)\Sigma P_{\alpha\beta}\Sigma_{a,b}[(\partial^2\mu_\alpha/\partial Q_a\partial Q_b)(\partial^2\mu_\beta/\partial Q_a\partial Q_b)(\omega_a^{-1}+\omega_b^{-1})\lambda_{ab}^{\pm\sigma}+(\partial^3\mu_\alpha/\partial Q_a^2\partial Q_b)(\partial\mu_\beta/\partial Q_b)\omega_a^{-1}\lambda_b^{\pm\sigma}+(\partial\mu_\alpha/\partial Q_b)(\partial^3\mu_\beta/\partial Q_a^2\partial Q_b)\omega_a^{-1}\lambda_b^{\pm\sigma}]$
$[\mu^2]^{1,1}$	$-(\hbar/4)\Sigma P_{\alpha\beta}\Sigma_{a,b,c}[F_{abc}(\partial^2\mu_\alpha/\partial Q_a\partial Q_b)(\partial\mu_\beta/\partial Q_c)\times(\omega_a^{-1}+\omega_b^{-1})\lambda_{ab}^{+\sigma}\lambda_c^{\pm\sigma}+F_{bcc}(\partial^2\mu_\alpha/\partial Q_a\partial Q_b)\times(\partial\mu_\beta/\partial Q_a)\omega_b^{-2}\omega_c^{-1}\lambda_a^{\pm\sigma}]$
$[\mu^2]^{0,2}$	$-(\hbar/8)\Sigma P_{\alpha\beta}\Sigma_{a,b,c}\omega_a^{-1}[F_{aabc}(\partial\mu_\alpha/\partial Q_b)\times(\partial\mu_\beta/\partial Q_c)\lambda_b^{\pm\sigma}\lambda_c^{\pm\sigma}-\Sigma_d\{F_{aab}F_{bcd}(\partial\mu_\alpha/\partial Q_c)\times(\partial\mu_\beta/\partial Q_d)\omega_b^{-2}\lambda_c^{\pm\sigma}\lambda_d^{\pm\sigma}+2F_{abc}F_{abd}(\partial\mu_\alpha/\partial Q_c)\times(\partial\mu_\beta/\partial Q_d)\lambda_{ab}^{\pm\sigma}\lambda_c^{\pm\sigma}\lambda_d^{\pm\sigma}\}]$
$[\mu^3]^{1,0}$	$\frac{1}{2}\Sigma P_{\alpha\beta\gamma}\Sigma_{a,b}(\partial\mu_\alpha/\partial Q_a)(\partial^2\mu_\beta/\partial Q_a\partial Q_b)\times(\partial\mu_\gamma/\partial Q_b)\lambda_a^{\pm\sigma}\lambda_b^{\pm 2}$
$[\mu^3]^{0,1}$	$-\frac{1}{6}\Sigma P_{\alpha\beta\gamma}\Sigma_{a,b,c}F_{abc}(\partial\mu_\alpha/\partial Q_a)(\partial\mu_\beta/\partial Q_b)\times(\partial\mu_\gamma/\partial Q_c)\lambda_a^{\pm\sigma}\lambda_b^{\pm 1}\lambda_c^{\pm 2}$
$[\mu^2\alpha]^{1,0}$	$\frac{1}{4}\Sigma P_{\alpha\beta\gamma\delta}\Sigma_{a,b}[(\partial\mu_\alpha/\partial Q_a)(\partial^2\alpha_{\beta\gamma}/\partial Q_a\partial Q_b)\times(\partial\mu_\delta/\partial Q_b)\lambda_a^{\pm\sigma}\lambda_b^{\pm 3}+2(\partial\mu_\alpha/\partial Q_a)(\partial^2\mu_\beta/\partial Q_a\partial Q_b)\times(\partial\alpha_{\gamma\delta}/\partial Q_b)\lambda_a^{\pm\sigma}\lambda_b^{\pm 23}]$
$[\mu^2\alpha]^{0,1}$	$-\frac{1}{4}\Sigma P_{\alpha\beta\gamma\delta}\Sigma_{a,b,c}F_{abc}(\partial\mu_\alpha/\partial Q_a)(\partial\mu_\beta/\partial Q_b)\times(\partial\alpha_{\gamma\delta}/\partial Q_c)\lambda_a^{\pm\sigma}\lambda_b^{\pm 1}\lambda_c^{\pm 23}$
$[\mu^4]^{2,0}$	$\frac{1}{6}\Sigma P_{\alpha\beta\gamma\delta}\Sigma_{a,b,c}[3(\partial\mu_\alpha/\partial Q_a)(\partial^2\mu_\beta/\partial Q_a\partial Q_b)\times(\partial^2\mu_\gamma/\partial Q_b\partial Q_c)(\partial\mu_\delta/\partial Q_c)\lambda_a^{\pm\sigma}\lambda_b^{\pm 23}\lambda_c^{\pm 3}+(\partial^3\mu_\alpha/\partial Q_a\partial Q_b\partial Q_c)(\partial\mu_\beta/\partial Q_a)(\partial\mu_\gamma/\partial Q_b)\times(\partial\mu_\delta/\partial Q_c)\lambda_a^{\pm 1}\lambda_b^{\pm 2}\lambda_c^{\pm 3}]$
$[\mu^4]^{1,1}$	$-\frac{1}{2}\Sigma P_{\alpha\beta\gamma\delta}\Sigma_{a,b,c,d}F_{abc}(\partial\mu_\alpha/\partial Q_a)(\partial\mu_\beta/\partial Q_b)\times(\partial^2\mu_\gamma/\partial Q_c\partial Q_d)(\partial\mu_\delta/\partial Q_d)\lambda_a^{\pm\sigma}\lambda_b^{\pm 1}\lambda_c^{\pm 23}\lambda_d^{\pm 3}$
$[\mu^4]^{0,2}$	$-\frac{1}{24}\Sigma P_{\alpha\beta\gamma\delta}\Sigma_{a,b,c,d}[F_{abcd}(\partial\mu_\alpha/\partial Q_a)(\partial\mu_\beta/\partial Q_b)\times(\partial\mu_\gamma/\partial Q_c)(\partial\mu_\delta/\partial Q_d)\lambda_a^{\pm\sigma}\lambda_b^{\pm 1}\lambda_c^{\pm 2}\lambda_d^{\pm 3}-3\Sigma_e F_{abc}F_{cde}(\partial\mu_\alpha/\partial Q_a)(\partial\mu_\beta/\partial Q_b)(\partial\mu_\gamma/\partial Q_d)\times(\partial\mu_\delta/\partial Q_e)\lambda_a^{\pm\sigma}\lambda_b^{\pm 1}\lambda_c^{\pm 23}\lambda_d^{\pm 2}\lambda_e^{\pm 3}]$

[a]Abbreviations:

(i) For the $[\mu^2]$ terms, $\omega_\sigma=\omega_1$; for the $[\mu^3]$ and $[\mu^2\alpha]$ terms, $\omega_\sigma=\omega_1+\omega_2$; for the $[\mu^4]$ terms, $\omega_\sigma=\omega_1+\omega_2+\omega_3$.

(ii) $\Sigma P_{\alpha\beta}$ indicates the sum-over-terms generated by the permutation of the pairs of optical frequencies and indices: $(-\omega_\sigma,\alpha)$ and (ω_1,β); $\Sigma P_{\alpha\beta\gamma}$ indicates the permutations of $(-\omega_\sigma,\alpha)$, (ω_1,β), and (ω_2,γ); $\Sigma P_{\alpha\beta\gamma\delta}$ indicates the permutations of $(-\omega_\sigma,\alpha)$, (ω_1,β), (ω_2,γ), and (ω_3,δ).

(iii) $\lambda_x^{\pm i}=(\omega_x^2-\omega_i^2)^{-1}$; $\lambda_{xy}^{\pm i}=[(\omega_x+\omega_y)^2-\omega_i^2]^{-1}$; $\lambda_x^{\pm ij}=[\omega_x^2-(\omega_i+\omega_j)^2]^{-1}$.

but, in this case, the cubic term is taken to be first order in mechanical anharmonicity and the series is terminated after the (second-order) term involving the quartic force constants, F_{abcd}, which are fourth derivatives of V. Treating the electrical and mechanical anharmonicity by double perturbation theory and substituting into Eqs. (1)–(3) leads to

$$\alpha^v(-\omega_\sigma;\omega_1)=[\mu^2]^0+[\mu^2]^{\mathrm{II}}, \tag{7}$$

$$\beta^v(-\omega_\sigma;\omega_1,\omega_2)=[\mu\alpha]^0+[\mu^3]^{\mathrm{I}}+[\mu\alpha]^{\mathrm{II}}, \tag{8}$$

$$\gamma^v(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=[\alpha^2]^0+[\mu\beta]^0+[\mu^2\alpha]^{\mathrm{I}}+[\alpha^2]^{\mathrm{II}}+[\mu\beta]^{\mathrm{II}}+[\mu^4]^{\mathrm{II}}, \tag{9}$$

where we have used the abbreviations $[\ ]^0=[\ ]^{0,0}$, $[\ ]^{\mathrm{I}}=[\ ]^{1,0}+[\ ]^{0,1}$, and $[\ ]^{\mathrm{II}}=[\ ]^{2,0}+[\ ]^{1,1}+[\ ]^{0,2}$. The notation $[\ ]^{n,m}$ indicates the order of electrical anharmonicity (n) and the order of mechanical anharmonicity (m).

As stated in our earlier work,[6] we previously neglected the cubic term in Eq. (5) and all of the $[\ ]^{0,2}$ contributions in $[\ ]^{\mathrm{II}}$. We now include these and, in order that there be a single source of information, we give the complete formulas in Tables I and II.

With the exception of that part of the $[\mu^4]^{0,2}$ term which contains two cubic force constants (F_{abc} and F_{cde}), our results were achieved by arduous algebraic manipulation. The ''F^2'' part of $[\mu^4]^{0,2}$ was found by using a sequential pattern, as discussed in Ref. 1, together with the known *static*

TABLE II. Conversion of formulas for $[\mu^2]$ to those for $[\mu\alpha]$, $[\alpha^2]$, and $[\mu\beta]$.

Initial term	Multiply by	Permutation sum change	Electronic property change and frequency change	Final term
$[\mu^2]^{0,0}$	1	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma}$	$\mu_\beta\rightarrow\alpha_{\beta\gamma}$	$[\mu\alpha]^{0,0}$
$[\mu^2]^{0,0}$	$\frac{1}{4}$	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma\delta}$	$\mu_\alpha\rightarrow\alpha_{\alpha\beta},\mu_\beta\rightarrow\alpha_{\gamma\delta}$ $\lambda_a^{\pm\sigma}\rightarrow\lambda_a^{\pm 23}$	$[\alpha^2]^{0,0}$
$[\mu^2]^{0,0}$	$\frac{1}{3}$	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma\delta}$	$\mu_\beta\rightarrow\beta_{\beta\gamma\delta}$	$[\mu\beta]^{0,0}$
$[\mu^2]^{2,0}$	1	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma}$	$\mu_\beta\rightarrow\alpha_{\beta\gamma}$	$[\mu\alpha]^{2,0}$
$[\mu^2]^{2,0}$	$\frac{1}{4}$	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma\delta}$	$\mu_\alpha\rightarrow\alpha_{\alpha\beta},\mu_\beta\rightarrow\alpha_{\gamma\delta}$ $\lambda_{ab}^{\pm\sigma}\rightarrow\lambda_{ab}^{\pm 23},\lambda_b^{\pm\sigma}\rightarrow\lambda_b^{\pm 23}$	$[\alpha^2]^{2,0}$
$[\mu^2]^{2,0}$	$\frac{1}{3}$	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma\delta}$	$\mu_\beta\rightarrow\beta_{\beta\gamma\delta}$	$[\mu\beta]^{2,0}$
$[\mu^2]^{1,1}$	$\frac{1}{2}$	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma}$	Each term is replaced by two: in the first $\mu_\beta\rightarrow\alpha_{\beta\gamma}$ and in the second $\mu_\alpha\rightarrow\alpha_{\beta\gamma}$ and $\mu_\beta\rightarrow\mu_\alpha$	$[\mu\alpha]^{1,1}$
$[\mu^2]^{1,1}$	$\frac{1}{4}$	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma\delta}$	$\mu_\alpha\rightarrow\alpha_{\alpha\beta},\mu_\beta\rightarrow\alpha_{\gamma\delta}$ $\lambda_{ab}^{\pm\sigma}\rightarrow\lambda_{ab}^{\pm 23},\lambda_a^{\pm\sigma}\rightarrow\lambda_a^{\pm 23},\lambda_c^{\pm\sigma}\rightarrow\lambda_c^{\pm 23}$	$[\alpha^2]^{1,1}$
$[\mu^2]^{1,1}$	$\frac{1}{6}$	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma\delta}$	Each term is replaced by two: in the first $\mu_\beta\rightarrow\beta_{\beta\gamma\delta}$ and in the second $\mu_\alpha\rightarrow\beta_{\beta\gamma\delta}$ and $\mu_\beta\rightarrow\mu_\alpha$	$[\mu\beta]^{1,1}$
$[\mu^2]^{0,2}$	1	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma}$	$\mu_\beta\rightarrow\alpha_{\beta\gamma}$	$[\mu\alpha]^{0,2}$
$[\mu^2]^{0,2}$	$\frac{1}{4}$	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma\delta}$	$\mu_\alpha\rightarrow\alpha_{\alpha\beta},\mu_\beta\rightarrow\alpha_{\gamma\delta}$ $\lambda_{ab}^{\pm\sigma}\rightarrow\lambda_{ab}^{\pm 23},\lambda_b^{\pm\sigma}\rightarrow\lambda_b^{\pm 23},\lambda_c^{\pm\sigma}\rightarrow\lambda_c^{\pm 23}$ $\lambda_\alpha^{\pm\sigma}\rightarrow\lambda_\alpha^{\pm 23}$	$[\alpha^2]^{0,2}$
$[\mu^2]^{0,2}$	$\frac{1}{3}$	$P_{\alpha\beta}\rightarrow P_{\alpha\beta\gamma\delta}$	$\mu_\beta\rightarrow\beta_{\beta\gamma\delta}$	$[\mu\beta]^{0,2}$

expression for $[\mu^4]^{0,2}$. To be more precise, with the abbreviations in the footnote to Table I and changing indices where appropriate, the essential form of $[\mu^4]^{2,0}$ is

$$(\partial\mu_\alpha/\partial Q_a)(\partial^2\mu_\beta/\partial Q_a\partial Q_c)(\partial^2\mu_\gamma/\partial Q_c\partial Q_d)\times(\partial\mu_\delta/\partial Q_d)\lambda_a^{\pm\sigma}\lambda_c^{\pm 23}\lambda_d^{\pm 3},$$

whereas for $[\mu^4]^{1,1}$ it is

$$F_{abc}(\partial\mu_\alpha/\partial Q_a)(\partial\mu_\beta/\partial Q_b)(\partial^2\mu_\gamma/\partial Q_c\partial Q_d)\times(\partial\mu_\delta/\partial Q_d)\lambda_a^{\pm\sigma}\lambda_b^{\pm 1}\lambda_c^{\pm 23}\lambda_d^{\pm 3}.$$

It is apparent that increasing the mechanical anharmonicity and decreasing the electrical anharmonicity simultaneously by one order introduces $\lambda_b^{\pm 1}$; changes the second derivative of μ_β (associated with ω_1) with respect to Q_a and Q_c to a single derivative with respect to Q_b (note the recurrence of b); and introduces the cubic force constant F_{abc}. Repeating this step in a consistent way we have $\partial Q_c\partial Q_d\rightarrow\partial Q_e$ and, then, introducing $\lambda_e^{\pm 2}$ and F_{cde} gives the essential form of $[\mu^4]^{0,2}$ as

$$F_{cde}F_{abc}(\partial\mu_\alpha/\partial Q_a)(\partial\mu_\beta/\partial Q_b)(\partial\mu_\gamma/\partial Q_e)\times(\partial\mu_\delta/\partial Q_d)\lambda_a^{\pm\sigma}\lambda_b^{\pm 1}\lambda_c^{\pm 23}\lambda_d^{\pm 3}\lambda_e^{\pm 2}.$$

With the known numerical factor for the static quantity and with some rearrangement of the indices, the formula for the ''F^2'' part of $[\mu^4]^{0,2}$ given in Table I was obtained.

In deriving the general expressions it has been very helpful to compare with the static limit.[8–10] This led us to discover that the diatomic formulas of Ref. 9 are only approximate because the anharmonic terms in Eq. (5) of that reference were not carried through in deriving Eqs. (11b) and (11c). These terms were included subsequently in the corresponding treatment of polyatomics.[10] However, in the latter case the fact that the field-dependent harmonic force constant matrix contains off-diagonal elements, when expressed in terms of field-free normal coordinates, was ignored. One can determine the effect of these off-diagonal matrix elements on the field-dependent harmonic vibrational frequencies, which are the quantities of interest, by carrying out an appropriate perturbation treatment. Thus, we write

$$\mathbf{T}^\dagger(\mathbf{F})\mathbf{K}(\mathbf{F})\mathbf{T}(\mathbf{F})=\omega^2(\mathbf{F}), \tag{10}$$

where $\mathbf{K}(\mathbf{F})$ is the field-dependent harmonic force constant matrix, $\omega(\mathbf{F})$ is the diagonal matrix of field-dependent harmonic frequencies, and $\mathbf{T}(\mathbf{F})$ is a unitary transformation,

$$\mathbf{T}^\dagger(\mathbf{F})\mathbf{T}(\mathbf{F})=\mathbf{1}. \tag{11}$$

All quantities are, then, expanded as a power series in $\mathbf{F}$ with $\mathbf{K}(0)$ being diagonal and $\mathbf{T}(0)=\mathbf{1}$. After some simplification it can be shown that the resulting formulas agree exactly with those given in Tables I and II when the static limit is taken (see the Appendix for an example). Thus, the equiva-

lence between the perturbation theory[6] and finite field[10] approaches to static vibrational hyperpolarizabilities demonstrated in Ref. 8 is now extended to polyatomic molecules. A similar extension can be made for the infinite frequency limit.

To conclude, we have presented general (dynamic) expressions, complete through second order in perturbation theory, for the vibrational polarizability (α^v), and the first and second vibrational hyperpolarizability (β^v and γ^v). The only additional contributions from the effects of vibration to this order arise from zero-point vibrational averaging.

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APPENDIX

If the vibrational potential is expanded in terms of field-free normal coordinates, **Q**, then the off-diagonal quadratic force constants will no longer vanish when an external field is present. The effect of these force constants on the harmonic vibrational frequencies and, hence, on the linear and nonlinear vibrational polarizabilities, can be evaluated through a perturbation treatment of Eqs. (10) and (11). The purpose of this Appendix is to illustrate how this can be accomplished using the linear polarizability as an example.

Following the procedure of Ref. 10, the field-dependent quadratic force constant matrix for small vibrations about the field-dependent equilibrium geometry, $\mathbf{R}_F$, may be written as

$$K_{ij}(\mathbf{F})=2a_{20}^{ii}\delta_{ij}+\sum_{\alpha}^{x,y,z}\left[2a_{21}^{ij,\alpha}-6\sum_{k=1}^{3N-6}a_{30}^{ijk}q_1^{k,\alpha}\right]F_\alpha+\sum_{\alpha,\beta}^{x,y,z}\left[2a_{22}^{ij,\alpha\beta}-6\sum_{k=1}^{3N-6}a_{30}^{ijk}q_2^{k,\alpha\beta}-6\sum_{k=1}^{3N-6}a_{31}^{ijk,\alpha}q_1^{k,\beta}\right.$$
$$\left.+12\sum_{k,l=1}^{3N-6}a_{40}^{ijkl}q_1^{k,\alpha}q_1^{l,\beta}+6\sum_{k,l=1}^{3N-6}a_{30}^{ijk}a_{21}^{kl,\alpha}q_1^{l,\beta}(a_{20}^{kk})^{-1}-9\sum_{k,l,m=1}^{3N-6}a_{30}^{ijk}a_{30}^{klm}q_1^{l,\alpha}q_1^{m,\beta}(a_{20}^{kk})^{-1}\right]F_\alpha F_\beta+\cdots, \tag{A1}$$

where

$$a_{nm}^{i_1\cdots i_n,j_1\cdots j_m}=\frac{1}{n!m!}\left(\frac{\partial^{(n+m)}V(Q_1,\ldots,Q_{3N-6},F_x,F_y,F_z)}{\partial Q_{i_1}\cdots\partial Q_{i_n}\partial F_{j_1}\cdots\partial F_{j_m}}\right)_{\mathbf{Q}=\mathbf{0},\mathbf{F}=\mathbf{0}}, \tag{A2}$$

$q_1^{\lambda,\alpha}=a_{11}^{\lambda,\alpha}/2a_{20}^{\lambda\lambda}$ and $q_2^{\lambda,\alpha\beta}=a_{12}^{\lambda,\alpha\beta}/2a_{20}^{\lambda\lambda}$.

The term linear in **F** is considered to be first order; the term quadratic in **F** is second order; and so forth. Through second order the harmonic vibrational frequencies from Eq. (13) are given by,

$$\omega_i^2(F)\cong\omega_i^2(0)+\sum_\alpha[\omega_i^2]^\alpha F_\alpha+\sum_{\alpha,\beta}[\omega_i^2]^{\alpha\beta}F_\alpha F_\beta, \tag{A3}$$

with

$$\omega_i^2(0)=K_{ii}(0)=2a_{20}^{ii}, \tag{A4}$$

$$[\omega_i^2]^\alpha=K_{ii}^\alpha=2a_{21}^{ii,\alpha}-6\sum_{k=1}^{3N-6}a_{30}^{iik}q_1^{k,\alpha}, \tag{A5}$$

and

$$[\omega_i^2]^{\alpha\beta}=K_{ii}^{\alpha\beta}+[\mathbf{T}^{\alpha\dagger}\mathbf{K}^\beta]_{ii}+[\mathbf{K}^\alpha\mathbf{T}^\beta]_{ii}+[\mathbf{T}^{\alpha\dagger}\mathbf{K}(0)\mathbf{T}^\beta]_{ii}+2T_{ii}^{\alpha\beta}K_{ii}(0). \tag{A6}$$

In deriving Eqs. (A4)–(A6) we have used the fact that **K** is Hermitian; $\mathbf{K}(0)$ is diagonal; and $\mathbf{T}(\mathbf{F})=\mathbf{1}+\Sigma\mathbf{T}^\alpha F_\alpha+\Sigma T^{\alpha\beta}\mathbf{F}_\alpha F_\beta+\cdots$ is unitary. Thus,

$$T_{ii}^\alpha=0,\quad T_{ij}^\alpha=K_{ij}^\alpha[K_{jj}(0)-K_{ii}(0)]^{-1}\quad(j\neq i) \tag{A7}$$

and

$$T_{ii}^{\alpha\beta}=-\frac{1}{2}\sum_{j\neq i}T_{ji}^\alpha T_{ji}^\beta. \tag{A8}$$

From Eqs. (A6)–(A8) one obtains

$$[\omega_i^2]^{\alpha\beta}=2a_{22}^{ii,\alpha\beta}-6\sum_{j=1}^{3N-6}a_{30}^{iij}q_2^{j,\alpha\beta}-6\sum_{j=1}^{3N-6}a_{31}^{iij,\alpha}q_1^{j,\beta}+12\sum_{j,k=1}^{3N-6}a_{40}^{iijk}q_1^{j,\alpha}q_1^{k,\beta}+6\sum_{j,k=1}^{3N-6}a_{30}^{iij}a_{21}^{jk,\alpha}q_1^{k,\beta}(a_{20}^{jj})^{-1}$$
$$-9\sum_{j,k,l=1}^{3N-6}a_{30}^{iij}a_{30}^{jkl}q_1^{k,\alpha}q_1^{l,\beta}(a_{20}^{jj})^{-1}-4\sum_{j\neq i=1}^{3N-6}a_{21}^{ij,\alpha}a_{21}^{ij,\beta}(A_{20}^{ij})^{-1}+24\sum_{j\neq i,k=1}^{3N-6}a_{21}^{ij,\alpha}a_{30}^{ijk}q_1^{k,\beta}(A_{20}^{ij})^{-1}$$
$$-36\sum_{j\neq i,k,l=1}^{3N-6}a_{30}^{ijk}a_{30}^{ijl}q_1^{k,\alpha}q_1^{k,\beta}(A_{20}^{ij})^{-1}, \tag{A9}$$

where $A_{20}^{ij}=2(\sqrt{a_{20}^i}+\sqrt{a_{20}^j})^2$.

The second-order correction to the static linear polarizability [i.e., $[\mu^2]^{\mathrm{II}}$ in Eq. (7) of the main text with $\omega_\sigma=\omega_1=0$] may be found[8,10] by taking the second derivative of the harmonic vibrational energy,

$$\frac{1}{2}\sum_i\left[\frac{\partial^2\omega_i(\mathbf{F})}{\partial F_\alpha\partial F_\beta}\right]_{\mathbf{F}=\mathbf{0}}=\frac{1}{4}\sum_i^{3N-6}\frac{1}{\omega_i(0)}\left[\left(\frac{\partial^2\omega_i^2(\mathbf{F})}{\partial F_\alpha\partial F_\beta}\right)_{\mathbf{F}=\mathbf{0}}-\frac{1}{2\omega_i^2(0)}\left(\frac{\partial\omega_i^2(\mathbf{F})}{\partial F_\alpha}\right)_{\mathbf{F}=\mathbf{0}}\left(\frac{\partial\omega_i^2(\mathbf{F})}{\partial F_\beta}\right)_{\mathbf{F}=\mathbf{0}}\right], \tag{A10}$$

which (after changing sign) is equal to $\Delta\alpha^{\mathrm{ZPVA}}+[\mu^2]^{\mathrm{II}}$. Using $\omega_i^2(\mathbf{F})$ from Eqs. (A4), (A5), and (A9) in Eq. (A10) and

$$\Delta\alpha_{\alpha\beta}^{\mathrm{ZPVA}}=-\sum_{i=1}^{3N-6}(2a_{20}^{ii})^{-1/2}\left[a_{22}^{ii,\alpha\beta}-3\sum_{j=1}^{3N-6}a_{30}^{iij}q_2^{j,\alpha\beta}\right], \tag{A11}$$

the result is

$$\begin{aligned}[\mu^2]^{\mathrm{II}}=\frac{1}{4}\sum P_{\alpha\beta}\sum_{i=1}^{3N-6}(2a_{20}^{ii})^{-1/2}\Bigg[&6\sum_{j=1}^{3N-6}a_{31}^{iij,\alpha}q_1^{j,\beta}-12\sum_{j,k=1}^{3N-6}a_{40}^{iijk}q_1^{j,\alpha}q_1^{k,\beta}-6\sum_{j,k=1}^{3N-6}a_{30}^{iij}a_{21}^{jk,\alpha}q_1^{k,\beta}(a_{20}^{jj})^{-1}\\&+9\sum_{j,k,l=1}^{3N-6}a_{30}^{iij}a_{30}^{jkl}q_1^{k,\alpha}q_1^{l,\beta}(a_{20}^{jj})^{-1}+4\sum_{j=1}^{3N-6}a_{21}^{ij,\alpha}a_{21}^{ij,\beta}(A_{20}^{ij})^{-1}-24\sum_{j,k=1}^{3N-6}a_{21}^{ij,\alpha}a_{30}^{ijk}q_1^{k,\beta}(A_{20}^{ij})^{-1}\\&+36\sum_{j,k,l=1}^{3N-6}a_{30}^{ijk}a_{30}^{ijl}q_1^{k,\alpha}q_1^{l,\beta}(A_{20}^{ij})^{-1}\Bigg].\end{aligned} \tag{A12}$$

A comparison with the sum $[\mu^2]^{2,0}+[\mu^2]^{1,1}+[\mu^2]^{0,2}$ taken from Table I reveals that the two expressions are identical.

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