

Off-Resonant Electronic and Vibrational Molecular Polarizabilities. Time-Dependent Collective-Oscillator Expansion

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The nonlinear optical response of molecules is calculated using classical equations of motion for the electronic density matrix coupled to nuclear coordinates. The equations apply to an arbitrary (gauge-invariant) parametrization of the electronic density matrix. The electronic problem is treated at the time-dependent Hartree–Fock level, but the extension to time-dependent density functional theory is straightforward. An expansion in the inverse nuclear masses provides a low-cost calculation of polarizabilities at intermediate frequencies (high compared to nuclear vibrations and low compared to electronic transitions). This regime is particularly relevant for optical materials applications. Closed expressions are derived for the electronic and nuclear contributions to the lowest two polarizabilities α and β .

I. Introduction

Linear and nonlinear molecular polarizabilities depend on the combined electronic and nuclear response to optical fields. Calculations are considerably simplified when the characteristic frequency ω_L of the driving fields is low compared to both electronic (Ω_e) and vibrational (Ω_N) frequencies: $\omega_L \ll \Omega_e, \Omega_N$. In this limit both electrons and nuclei are fast, and have enough time to respond to the instantaneous value of the driving field. Static polarizabilities computed using a constant, time-independent field ($\omega_L = 0$) provide a good approximation in this case. In the static limit we simply optimize the ground-state geometry in the presence of the field, and the polarizabilities are computed as partial derivatives of the molecular ground-state energy with respect to the applied dc field. Extensive effort was devoted to computing both electronic and nuclear response using this finite field approach.^{1–4} These computations unambiguously establish the important role of both types of contributions to the purely static polarizabilities.^{5–7} In the opposite limit of very high frequencies, $\omega_L \gg \Omega_e, \Omega_N$ (which corresponds to X-ray rather than optical measurements), neither the electronic nor the nuclear degrees of freedom have enough time to fully respond, and the polarizabilities can be computed perturbatively in Ω_e/ω_L and Ω_N/ω_L using a short-time expansion. For intermediate, resonant field frequencies, the complete dynamical response should be calculated. This is a much more complicated task since it involves the excited states as well as the ground state of the system.

In this paper we consider a third limiting case, namely, the intermediate frequency regime (IFR), $\Omega_N \ll \omega_L \ll \Omega_e$. In this case the driving field can be considered as static with respect to electronic motions but fast with respect to the nuclear degrees of freedom. This regime is most relevant for optical materials applications where resonances are avoided to minimize dissipative losses. In conjugated polymers, e.g., Ω_e varies in the range 2–4 eV, the highest vibrational frequencies are $\Omega_N \approx 0.25$ eV, and the characteristic frequency of the driving field $\omega_L \approx 0.7$ eV. Developing a low-cost algorithm for computing the response in this regime, which avoids dealing with nuclear dynamics explicitly, constitutes the primary goal of this paper. Our scheme starts with the collective electronic

oscillators (CEO) approach,⁸ which computes the electronic contributions to the dynamical response with numerical effort comparable to the finite field method for the static response. The technique is based on closed classical equations of motion for the electronic density matrix $\rho(t)$ derived using the time-dependent Hartree–Fock (TDHF) procedure and solved using the density matrix spectral moment algorithm. Assuming $N = N_e + N_h$ orbitals as a single electron basis set (N_h occupied and N_e unoccupied), ρ has $N_\rho = N_e \cdot N_h$ independent parameters which may be viewed as collective electronic oscillators.

We extend the CEO in two ways. First we include classical nuclear dynamics by implementing the time-dependent variational principle. This step is formally straightforward, and merely involves adding classical equations of motion for K nuclear coordinates. Calculations of optical polarizabilities require finding the joint $N_T = N_\rho + K$ coupled electron nuclear oscillators, which leads to an enormous increase of numerical effort. Second, we recast the equations in an invariant form,⁹ which allows for an arbitrary parametrization of single Slater determinants through the electronic density matrix. This is done by adopting a system of local coordinates in phase space. We are thus not limited to the Thouless representation¹⁰ and can use parametrizations more suitable for particular applications, e.g., computing polarizabilities. In addition, the invariant form allows an arbitrary basis set to be used in the single-electron orbital space. Basis set transformations are treated as gauge transformations, which provides a deeper insight into the nature of the nonadiabatic coupling. We further address the dependence of the single-electron space on molecular geometry, and distinguish between two cases: in the first the single-electron space changes with molecular geometry, whereas in the second case only the basis set elements depend on geometry.

A perturbative expansion of polarizabilities in Ω_N/ω_L , which can be conveniently formulated as an expansion of the response in the inverse nuclear mass M^{-1} , is developed. This is accomplished by expanding the dynamical equations in M^{-1} to obtain a closed system of equations for the dynamical variables in each order. The explicit calculation of vibrational modes is avoided, and only the electronic degrees of freedom are treated explicitly. Solving the resulting equations perturbatively in the driving field yields closed expressions for IFR polarizabilities.

In section II we introduce the Hamiltonian and derive the collective electronic–nuclear oscillator equations. The equations are given in an invariant form, i.e., independent of any particular parametrization of the electronic density matrix. These equations are applied in section III to construct a perturbation theory in the inverse nuclear mass M^{-1} , which accounts for vibrational contributions. In section IV we derive closed expressions for the first- and second-order polarizabilities obtained by expanding the solution in powers of the driving field.

The relative magnitude of electronic and vibrational contributions to the off-resonant optical response is of special interest for conjugated molecules where π -electron delocalization strongly enhances the former, and the latter is strong due to their nonrigid geometry.^{1,2,11} For a simple model of a push–pull polyene, which includes two electronic states (neutral and zwitteronic) and a single vibrational mode (the C–C stretch), the two contributions to the static polarizabilities turn out to be exactly the same.¹² In section V we apply our expansion to this model and estimate the relative magnitude of both contributions in the IFR. Our results are finally summarized and discussed in section VI. For clarity, details of the derivations are given in the Appendices.

II. Gauge-Invariant Oscillator Representation of Coupled Electronic and Nuclear Dynamics

The quantum molecular Hamiltonian, for the coupled electronic and nuclear dynamics, is

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_{\text{int}} \quad (2.1)$$

Here

$$\hat{H}_0 \equiv \sum_{\mu} \frac{P_{\mu}^2}{2M_{\mu}} + u(\mathbf{r}) \quad (2.2)$$

is the nuclear Hamiltonian with $P_{\mu}(r_{\mu})$ being the nuclear momentum (coordinate) operators. The electronic Hamiltonian is

$$\hat{H}_1 \equiv \sum_{ij} t_{ij}(\mathbf{r}) c_i^+ c_j + \frac{1}{2} \sum_{ijrs} V_{ij,rs}(\mathbf{r}) c_i^+ c_j^+ c_r c_s \quad (2.3)$$

where c_j (c_j^+) are the electron annihilation (creation) operators and $|v_j(\mathbf{r})\rangle$ represent a basis set in the single-electron space, which depends on the nuclear configuration \mathbf{r} . \hat{H}_{int} describes the interaction with an external electric field $\mathcal{E}(\tau)$

$$\hat{H}_{\text{int}} = - \sum_{ij} \mu_{ij}(\mathbf{r}) c_i^+ c_j \mathcal{E}(\tau) \quad (2.4)$$

The coupling of electronic and nuclear motions enters through the \mathbf{r} dependence of the transfer $t(\mathbf{r})$ and dipole $\mu(\mathbf{r})$ single-electron operators, and the Coulomb two-electron operator $V(\mathbf{r})$. The parametric \mathbf{r} dependence of the orbitals gives rise to an additional source of coupling: the nonadiabatic coupling which can be described in terms of the matrix vector field $A_{ij,\mu}(\mathbf{r})$ defined by

$$A_{ij,\mu}(\mathbf{r}) \equiv -\langle v_i(\mathbf{r}) | \partial_{\mu} v_j(\mathbf{r}) \rangle \quad (2.5)$$

We recall that the electronic basis set size is N and the number of nuclear coordinates is K . A is a real antisymmetric $N \times N$ matrix in electronic space where the i and j indices denote the basis orbitals. Each element of A is a K -component vector in the K -dimensional nuclear space, and μ denotes its components.

A transformation to a new set of orbitals

$$v_j'(\mathbf{r}) = \sum_j Y_{ji}(\mathbf{r}) v_j(\mathbf{r}) \quad (2.6)$$

generates the following gauge transformation of the vector field A_{μ} ¹³

$$A_{\mu}'(\mathbf{r}) = Y^{-1}(\mathbf{r}) \partial_{\mu} Y(\mathbf{r}) + Y^{-1}(\mathbf{r}) A_{\mu}(\mathbf{r}) Y(\mathbf{r}) \quad (2.7)$$

The nonadiabatic coupling, therefore, may be incorporated formally through a gauge field or a nonabelian vector field. In the following we further make use of the intensity tensor corresponding to $A_{\mu}(\mathbf{r})$, which is defined as¹³

$$F_{\mu\nu}(\mathbf{r}) = \partial_{\mu} A_{\nu}(\mathbf{r}) - \partial_{\nu} A_{\mu}(\mathbf{r}) - [A_{\mu}(\mathbf{r}), A_{\nu}(\mathbf{r})] \quad (2.8)$$

F is transformed under gauge transformations in the following way:

$$F_{\mu\nu}'(\mathbf{r}) = Y^{-1}(\mathbf{r}) F_{\mu\nu}(\mathbf{r}) Y(\mathbf{r}) \quad (2.9)$$

One should distinguish between two cases. In the first, the single-electron space does not depend on molecular geometry, even though the basis set itself, namely, the orbitals $v_j(\mathbf{r})$, are \mathbf{r} -dependent. This is, e.g., the case when the electronic basis is complete. The vector potential is then represented by a pure gauge:

$$A_{\mu}(\mathbf{r}) = Y^{-1}(\mathbf{r}) \partial_{\mu} Y(\mathbf{r}) \quad (2.10)$$

and the intensity tensor vanishes, $F_{\mu\nu}(\mathbf{r}) = 0$. The field A_{μ} can now be eliminated by a gauge transformation, $Y(\mathbf{r})$. This corresponds to the crude-adiabatic basis set¹⁴ where the orbitals become independent of \mathbf{r} , and the \mathbf{r} dependence of t , V , and μ constitutes the only source of electron–nuclear coupling. In the second case, the single-electron space itself varies with \mathbf{r} , and it is no longer possible to choose \mathbf{r} -independent orbitals. The vector potential may not be represented in the form of eq 2.10 and $F_{\mu\nu}(\mathbf{r}) \neq 0$. It should be emphasized that only if $F_{\mu\nu}(\mathbf{r}) = 0$ can the nonadiabatic coupling be eliminated by a proper choice of a basis set.

In the following we assume that the electronic state is represented by a single Slater determinant at all times, and treat nuclear motions classically. Applying the time-dependent variational approach to the quantum Hamiltonian (eqs 2.1–2.3) leads to the closed system of equations for the electronic–nuclear oscillators.⁹

$$\frac{d\rho}{d\tau} = \sum_{\nu} [A_{\nu}, \rho] \dot{r}_{\nu} - i[t(\mathbf{r}) + 2V(\mathbf{r})\rho, \rho] + i\mathcal{E}(\tau)[\mu(\mathbf{r}), \rho] \quad (2.11)$$

$$\frac{dr_{\alpha}}{d\tau} = M_{\alpha}^{-1} P_{\alpha} \quad (2.12)$$

$$\frac{dP_{\alpha}}{d\tau} = - \sum_{\nu} M_{\nu}^{-1} P_{\nu} \text{Tr}\{\rho F_{\alpha\nu}(\mathbf{r})\} - \partial_{\alpha} u(\mathbf{r}) - \text{Tr}\{\nabla_{\alpha} t(\mathbf{r})\rho\} - \text{Tr}\{\rho \nabla_{\alpha} V(\mathbf{r})\rho\} + \partial_{\alpha} \mu_N(\mathbf{r}) \mathcal{E}(\tau) + \text{Tr}\{\rho \nabla_{\alpha} \mu(\mathbf{r})\} \mathcal{E}(\tau) \quad (2.13)$$

Here ρ stands for the single-electron density matrix, with elements $\rho_{ij} \equiv \langle c_i^+ c_j \rangle$, which parametrizes the electron state represented by a single Slater determinant. $P_{\alpha}(\mathbf{r}_{\alpha})$ represent the nuclear momenta (coordinates) whereas A is the matrix vector field defined in eq 3.4. $\mu_N(\mathbf{r})$ is the dipole moment corresponding to the nuclear charges.

In eq 2.13 we have used long derivatives ∇_α of operators [such as $t(\mathbf{r})$ and $\mu(\mathbf{r})$] acting in the single-electron space. These are defined by

$$\nabla_\alpha t(\mathbf{r}) \equiv \partial_\alpha t(\mathbf{r}) - [A_\alpha(\mathbf{r}), t(\mathbf{r})] \quad (2.14)$$

For superoperators $V(\mathbf{r})$ the operation of long derivatives is defined similarly:

$$\nabla_\alpha V(\mathbf{r}) \equiv \partial_\alpha V(\mathbf{r}) - [\hat{A}_\alpha(\mathbf{r}), V(\mathbf{r})] \quad (2.15)$$

The second term in eq 2.15 is a Liouville space commutator of the superoperator $V(\mathbf{r})$ and the superoperator $\hat{A}_\alpha(\mathbf{r})$ defined by its action on an arbitrary density matrix ρ :

$$\hat{A}_\alpha(\mathbf{r})\rho \equiv [A_\alpha(\mathbf{r}), \rho] \quad (2.16)$$

These equations of the motion have a simple interpretation: The first term on the right-hand side (rhs) of eq 2.11 describes the electronic motion along the vector potential and determines how the single-electron density matrix $\rho_{ij}(\mathbf{r})$ which acts in the single-electron space at point \mathbf{r} moves to point $\mathbf{r} + d\mathbf{r}$. The remaining terms in this equation constitute the TDHF equations. It is possible to use time-dependent density functional theory (TDDFT) instead.¹⁵ The conceptual and operational similarities of TDHF and TDDFT are made clear by formulating the latter using the density matrix.¹⁶

The first term on the rhs of the equation for the nuclear momenta (eq 2.13) represents the Lorentz force. This term vanishes for systems with time-reversal symmetry. The remaining terms on the rhs of eq 2.13 can be viewed as the differential of the Hartree–Fock energy, where the differentiation is performed using the long derivatives (eqs 2.14 and 2.15) which involve the vector potential. The operators $t(\mathbf{r})$ and $\mu(\mathbf{r})$ and the superoperators $V(\mathbf{r})$ are expressed in terms of the dyadic $t_{ij}(\mathbf{r})$ and $\mu_{ij}(\mathbf{r})$ and the tetradic $V_{ij,rs}(\mathbf{r})$ matrix elements, respectively.¹⁷

Equations 2.11, 2.12, and 2.13 together with the expression for polarization

$$\mathcal{P} = \mu_N(\mathbf{r}) + \text{Tr}\{\rho\mu(\mathbf{r})\} \quad (2.17)$$

constitute a closed system of equations for the optical response. These equations allow a complete freedom in parametrizing the density matrix in phase space (which is not specified yet). Adopting the language of differential geometry, the equations are given in a gauge-invariant form.⁹ The END equations of ref 18 were derived using the Thouless parametrization of Slater determinants. In the next section we adopt a different parametrization which we found to be more convenient for the present applications.

When these equations are solved to first-order in the external field, they require an $N_T \times N_T$ diagonalization, which results in $N_T = N_\rho + K$ joint electronic–nuclear normal modes. The solution to higher orders in the field can be expressed using these modes. This procedure yields the entire frequency dependence of the polarizabilities. The $N_T \times N_T$ diagonalization can be avoided in the two limiting cases described in the introduction: (i) In the static limit where the field is independent of time, we can incorporate it in eq 2.11 by simply replacing t with $t + \mu\mathcal{E}$. Solving the stationary part of eq 2.11, $d\rho/d\tau = 0$, will result in the ground state perturbed by the field. Analytic or numerical derivatives then give the polarizabilities. In this limit we only work in the electronic space and view the nuclei as parameters, and the polarizabilities are independent of the nuclear mass M . (ii) In the opposite, high-frequency limit, the response can be expanded in a Taylor series in time (short-

time expansion). Fourier transform of the series yields the high-frequency expansion of the optical susceptibilities (in powers of $1/\omega_L$). The IFR is more delicate and requires a new type of expansion, which will be developed in the next section.

III. Optical Response in the Intermediate-Frequency Regime

In the static limit the optical frequency is low compared to both electronic and vibrational frequencies. All degrees of freedom have enough time to respond to the external field, and the nuclear and electronic contributions to the polarizabilities should be treated along the same footing. In the IFR the electronic response is very similar to the static limit since the optical frequency is low compared to the electronic frequencies. The situation with the vibrational degrees of freedom is very different: Since the nuclei are driven at a higher frequency compared to the vibrational frequency, the amplitude of the driven oscillations is small, and the contribution of nuclear motions to the IFR polarizabilities can be treated as a perturbation to the electronic contribution.

An adequate perturbative approach for the nuclear IFR response can be developed by expanding the dynamical variables ρ , \mathbf{P} , and \mathbf{r} of eqs 2.11–2.13 in powers of the inverse typical nuclear mass M^{-1} ¹⁹

$$\begin{aligned} \rho(\tau) &= \rho^{(0)}(\tau) + \rho^{(1)}(\tau) + \dots \\ P_\mu(\tau) &= P_\mu^{(0)}(\tau) + P_\mu^{(1)}(\tau) + \dots \\ r_\mu(\tau) &= r_\mu^{(0)}(\tau) + r_\mu^{(1)}(\tau) + \dots \end{aligned} \quad (3.1)$$

Note that the superscripts denote powers of M^{-1} and not of the field. At this point we fully retain the field to all orders: An expansion in the field will be made only in the next section.

Our goal is to solve eqs 2.11–2.13 to first order in M^{-1} . In zero order, eq 2.12 immediately yields $r_\mu^{(0)}(\tau) \equiv 0$ ($\mathbf{r} = 0$ is the equilibrium geometry). Setting $\mathbf{r} = 0$ in eq 2.11, the first term on the rhs vanishes and eq 2.11 adopts the form of the TDHF equation for $\rho^{(0)}(\tau)$, which gives the electronic dynamics when the nuclei are held fixed in their equilibrium positions:

$$\frac{d\rho^{(0)}}{d\tau} = -i[t + 2V\rho^{(0)}, \rho^{(0)}] + i\mathcal{E}(\tau)[\mu, \rho^{(0)}] \quad (3.2)$$

Here we used the notation $t \equiv t(0)$, $V \equiv V(0)$, and $\mu \equiv \mu(0)$. The equation for $P_\mu^{(0)}(\tau)$ is obtained by omitting the first term in eq 2.13 and setting $\mathbf{r} = 0$ in the remaining terms, which implies replacing ρ with $\rho^{(0)}$. Substituting the equation for $P_\mu^{(0)}$ into eq 2.12 yields the equation for $r_\alpha^{(1)}(\tau)$:

$$M_\alpha \frac{d^2 r_\alpha^{(1)}}{d\tau^2} = -u_\alpha - \text{Tr}(t_\alpha \rho^{(0)}) - \text{Tr}(\rho^{(0)} V_\alpha \rho^{(0)}) + \mu_{N,\alpha} \mathcal{E}(\tau) + \text{Tr}(\mu_\alpha \rho^{(0)}) \mathcal{E}(\tau) \quad (3.3)$$

where we have used the notation $t_\mu \equiv \nabla_\mu t|_{\mathbf{r}=0}$, $V_\mu \equiv \nabla_\mu V|_{\mathbf{r}=0}$, etc.

To obtain the equation for $\rho^{(1)}(\tau)$ in a gauge-invariant form, we write

$$\rho^{(1)} = \sum_\mu r_\mu^{(1)} A_\mu(0) \rho^{(0)} + \xi \quad (3.4)$$

Gauge invariance of the following equations is guaranteed by the first term on the rhs of eq 3.4. The equation for the new

variables ξ is obtained by expanding eq 2.11 to first order, which after some straightforward transformations yields

$$\frac{d\xi}{d\tau} = -i[t + 2V\rho^{(0)}, \xi] - i2[V\xi, \rho^{(0)}] + i\mathcal{L}(\tau)[\mu, \xi] - i\sum_{\alpha} [t_{\alpha} + 2V_{\alpha}\rho^{(0)}, \rho^{(0)}]r_{\alpha}^{(1)} + i\mathcal{L}(\tau)\sum_{\alpha} [\mu_{\alpha}, \rho^{(0)}]r_{\alpha}^{(1)} \quad (3.5)$$

The polarization finally assumes the form

$$\rho = \rho^{(0)} + \rho^{(1)} \quad (3.6)$$

where

$$\rho^{(0)} = \mu_N + \text{Tr}(\mu\rho^{(0)}) \quad (3.7)$$

and

$$\rho^{(1)} = \sum_{\alpha} \mu_{N,\alpha} r_{\alpha}^{(1)} + \text{Tr}(\mu\xi) + \sum_{\alpha} \text{Tr}(\mu_{\alpha}\rho^{(0)}) r_{\alpha}^{(1)} \quad (3.8)$$

equations 3.2, 3.3, and 3.5 together with eqs 3.6–3.8 describe the optical response to first order in M^{-1} . This approximate solution to eqs 2.11–2.13 is useful provided the nuclear corrections to the electronic contributions are not large, which is the case in the IFR. The iterative solution (eqs 3.2, 3.3, and 3.5) in the driving field involves the electronic modes alone, which requires considerably lower time and memory numerical effort compared with computing the entire set of N_T coupled electronic–nuclear modes when the full set of equations is solved.

IV. First- and Second-Order Optical Polarizabilities at Intermediate Frequencies

Optical polarizabilities are defined through an expansion of the induced polarization ρ in powers of the driving field \mathcal{E} :

$$\rho(\omega_s) = R^{(1)}(\omega_s) \mathcal{E}(\omega_s) + \int \int_{-\infty}^{\infty} \frac{d\omega_1 d\omega_2}{(2\pi)^2} \times 2\pi\delta(\omega_1 + \omega_2 - \omega_s) R^{(2)}(-\omega_s; \omega_1, \omega_2) \mathcal{E}(\omega_1) \mathcal{E}(\omega_2) + \dots \quad (4.1)$$

Here $\rho(\omega_s)$ and $\mathcal{E}(\omega)$ are the Fourier transforms of the polarization and driving field, respectively. The response functions $R^{(n)}$ are obtained by solving eqs 3.2, 3.3, and 3.5 perturbatively in the driving field and making use of eqs 3.6–3.8.

We now turn to the parametrization of the density matrix. To avoid redundant electronic variables, we introduce the relevant particle–hole components η and ζ (eqs A1 and A7). Expanding in the eigenmodes of the linearized TDHF equation (see eqs A10) results in a system of equations for a set of parameters z_{α} , w_{α} , and r_{α} (eqs A11–A13). Solving these equations perturbatively in \mathcal{E} yields the response functions. However, the number of terms in these expressions grows rapidly with the order of response. The total number of contributions in the IFR is 4 for $R^{(1)}$ and 20 for $R^{(2)}$ (compared with 1 and 3, respectively, for the purely electronic contributions¹⁷). In the expressions given below we combine these terms to obtain final compact expressions resembling the purely electronic contribution.¹⁷

The linear response can be represented as a sum of two contributions: $R^{(1)} = R_1^{(1)} + R_2^{(1)}$. The first

$$R_1^{(1)}(\omega) = -\sum_{\alpha\beta} \hat{\mu}_{\alpha}^{(s)}(\omega) \hat{G}_{\alpha\beta}(\omega) \hat{\mu}_{\beta}(\omega) \quad (4.2)$$

is reminiscent of $R^{(1)}$ in the purely electronic case,¹⁷ except that

we use the renormalized Green function

$$\hat{G}_{\alpha\beta}(\omega) \equiv \frac{\delta_{\alpha\beta}}{\omega - \Omega_{\alpha} + i\Gamma} + \frac{1}{\omega^2} \sum_{\gamma} M_{\gamma}^{-1} W_{\alpha,\gamma} \bar{W}_{\gamma,\beta} \frac{1}{\omega - \Omega_{\alpha} + i\Gamma} \frac{1}{\omega - \Omega_{\beta} + i\Gamma} \quad (4.3)$$

and the renormalized frequency-dependent dipoles

$$\hat{\mu}_{\alpha}(\omega) \equiv \mu_{\alpha} + \frac{1}{\omega^2} \sum_{\beta} M_{\beta}^{-1} W_{\alpha,\beta} \mu_{\beta}^{(N)} \quad (4.4)$$

$$\hat{\mu}_{\alpha}^{(s)}(\omega) \equiv \mu_{\alpha}^{(s)} + \frac{1}{\omega^2} \sum_{\beta} M_{\beta}^{-1} \bar{W}_{\beta,\alpha} \mu_{\beta}^{(N)} \quad (4.5)$$

Ω_{α} are the frequencies that correspond to the eigenmodes ξ_{α} of the linearized TDHF equation

$$L\xi_{\alpha} = \Omega_{\alpha}\xi_{\alpha} \quad (4.6)$$

L being the linearized TDHF operator¹⁷ defined by eq A3. The expressions for W in terms of the modes ξ_{α} are given in Appendix A. For any mode ξ_{α} there is a mode $\xi_{-\alpha} \equiv \xi_{\alpha}^+$ with the frequency $\Omega_{-\alpha} = -\Omega_{\alpha}$.¹⁷ To demonstrate a close resemblance with classical oscillators, the linear combinations P_{α} and Q_{α} of the eigenmodes ξ_{α} and $\xi_{-\alpha}$ have been introduced in ref 17. These are oscillator momenta and coordinates, respectively. Below we work with the eigenmodes ξ_{α} . The first term on the rhs of eqs 4.3–4.5 represents the electronic contribution corrected by nuclear motions (the second term). $R_2^{(1)}$ is a new contribution, induced by nuclear motions, which may not be obtained by simply renormalizing the quantities in eq 4.2:

$$R_2^{(1)}(\omega) = -\frac{1}{\omega^2} \sum_{\alpha} M_{\alpha}^{-1} \mu_{\alpha}^{(N)} \mu_{\alpha}^{(N)} \quad (4.7)$$

The second-order response can be calculated similarly. Closed expressions for $R^{(2)}$ are given in Appendix C.

The optical polarizabilities are obtained from the response functions $R^{(j)}$ by performing permutations over the j incoming frequencies. The linear polarizability α is given by

$$\alpha(\omega) = R^{(1)}(\omega) \quad (4.8)$$

whereas the second-order polarizability β is

$$\beta(-\omega_s; \omega_1, \omega_2) = R^{(2)}(-\omega_s; \omega_1, \omega_2) + R^{(2)}(-\omega_s; \omega_2, \omega_1) \quad (4.9)$$

V. Second-Order IFR Polarizabilities for a Two-Level System Coupled to a Single Vibrational Mode

In this section we calculate $\alpha(\omega)$ and $\beta(-2\omega; \omega, \omega)$ for a two-level model coupled to a single vibrational mode introduced in ref 12. In the static $\omega = 0$ limit the vibrational contribution to β for this model has the same magnitude as the electronic contribution.⁷

The Hamiltonian is introduced using a diabatic basis set which includes a neutral valence bond $|\psi_{VB}\rangle$ and zwitterionic charge transfer $|\psi_{CT}\rangle$ states, linearly coupled to a single harmonic vibrational mode:

$$\hat{H} = E_{\text{VB}}(r)|\psi_{\text{VB}}\rangle\langle\psi_{\text{VB}}| + E_{\text{CT}}(r)|\psi_{\text{CT}}\rangle\langle\psi_{\text{CT}}| + J(|\psi_{\text{VB}}\rangle\langle\psi_{\text{CT}}| + |\psi_{\text{CT}}\rangle\langle\psi_{\text{VB}}|) + \frac{\hat{P}^2}{2M} - \mathcal{E}(t)\mathcal{P} \quad (5.1)$$

We assume that the permanent dipole in the zwitterionic state is the only nonzero element of the dipole operator in the diabatic basis set

$$\mathcal{P} = \mu_{\text{CT}}|\psi_{\text{CT}}\rangle\langle\psi_{\text{CT}}| \quad (5.2)$$

The fourth term in eq 5.1 represents the kinetic energy of the vibrational mode, with reduced mass M . Equation 5.2 shows that since the states $|\psi_{\text{VB}}\rangle$ and $|\psi_{\text{CT}}\rangle$ do not depend on the nuclear coordinate q , the nonadiabatic coupling terms represented by the gauge field A vanish in this basis set: $A \equiv 0$. $E_{\text{VB}}(r)$ and $E_{\text{CT}}(r)$ are given by

$$E_{\text{VB}}(r) = \frac{1}{2}k(r + Q)^2 \\ E_{\text{CT}}(r) = \frac{1}{2}k(r - Q)^2 + E_0 \quad (5.3)$$

where $2Q$ represents the displacement between the diabatic surfaces.

Comparison of eqs 2.1–2.3 and 2.17 with eqs 5.1–5.3 yields for the parameters of eqs 2.11–2.13 in the diabatic basis set

$$t(r) = \begin{pmatrix} E_{\text{VB}}(r) & J \\ J & E_{\text{CT}}(r) \end{pmatrix}, \quad \mu(r) = \begin{pmatrix} 0 & 0 \\ 0 & \mu_{\text{CT}} \end{pmatrix} \quad (5.4)$$

The coulomb operator $V(r) \equiv 0$, which is always the case of a two-level system, and $\mu_{\text{N}}(r) \equiv 0$. The calculation is simplified considerably by noting that since in the diabatic basis set μ is independent of \mathbf{r} and $A \equiv 0$, we have $\nabla\mu \equiv 0$. This implies that only the contributions $R_1^{(2)}$, $R_2^{(2)}$, and $R_3^{(2)}$ (eqs C1, C2, and C3) are nonzero. The nuclear-induced corrections to $\hat{\mu}^{(s)}$, $\hat{\mu}$, \hat{B} , and \hat{S} vanish; i.e., $\hat{\mu}_{\alpha}^{(s)} = \mu_{\alpha}^{(s)}$, $\hat{\mu}_{\alpha} = \mu_{\alpha}$, $\hat{B}_{\alpha,\beta} = \mu_{\alpha,\beta}$, and $\hat{S}_{\alpha,\beta} = S_{\alpha,\beta}$. $\hat{V}_{\gamma,\alpha\beta}$ is given by the last two terms in eq C4.

The calculations are most conveniently performed in the crude-adiabatic basis set where $\bar{\rho}$ is diagonal and we have

$$\bar{\rho} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \quad \xi_1 = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \xi_{-1} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad (5.5)$$

where $\xi_{\pm 1}$ are the two modes with frequencies $\pm\Omega$ that represent a single electronic oscillator. We further introduce the matrix elements of μ and h_r in the crude adiabatic basis set:

$$\mu = \begin{pmatrix} \mu_{\text{e}} & \mu_{\text{ge}} \\ \mu_{\text{ge}} & \mu_{\text{g}} \end{pmatrix}, \quad h_r = \begin{pmatrix} \kappa_{\text{e}} & \kappa_{\text{ge}} \\ \kappa_{\text{ge}} & \kappa_{\text{g}} \end{pmatrix} \quad (5.6)$$

Expressions for these matrix elements as well as for Ω in terms of the parameters of the original model, and the IFR polarizabilities, are given in Appendix D.

For the linear response we have

$$\alpha(\omega) = \alpha_{\text{E}}(\omega) + \alpha_{\text{V}}(\omega) \quad (5.7)$$

where the purely electronic contribution α_{E} is given by

$$\alpha_{\text{E}}(\omega) = \alpha_0 I_0(\omega) \quad (5.8)$$

α_0 is the electronic contribution to the static polarizability

$$\alpha_0 = 2 \frac{(\mu_{\text{eg}})^2}{\Omega} \quad (5.9)$$

and we have introduced the auxiliary quantity

$$I_0(\omega) \equiv \frac{\Omega^2}{\Omega^2 - \omega^2} \quad (5.10)$$

The vibrationally induced contribution α_{V} is

$$\alpha_{\text{V}}(\omega) = 2 \frac{(\kappa_{\text{eg}})^2}{M\omega^2\Omega} \alpha_{\text{E}}(\omega) I_0(\omega) \quad (5.11)$$

where $\kappa_{\text{eg}} = kQ/(\mathcal{E}^2(r) + 1)^{1/2}$ and $\mathcal{E}(r) = [\mathcal{E}_{\text{CT}}(r) - \mathcal{E}_{\text{VB}}(r)]/2J$.

The second-order polarizability is similarly given by

$$\beta(-2\omega; \omega, \omega) = \beta_{\text{E}}(-2\omega; \omega, \omega) + \beta_{\text{V}}(-2\omega; \omega, \omega) \quad (5.12)$$

with the electronic contribution

$$\beta_{\text{E}}(-2\omega; \omega, \omega) = \frac{\beta_0}{3} [I_0(\omega) + I_1(\omega)] \quad (5.13)$$

$$\beta_0 = 6 \frac{(\mu_{\text{eg}})^2 (\mu_{\text{e}} - \mu_{\text{g}})}{\Omega^2} \quad (5.14)$$

$$I_1(\omega) \equiv \frac{\Omega^2}{\Omega^2 - 4\omega^2} \frac{4\omega}{\Omega - \omega} \quad (5.15)$$

and the vibrationally-induced contribution

$$\beta_{\text{V}}(-2\omega; \omega, \omega) = - \frac{(\kappa_{\text{eg}})^2}{M\omega^2\Omega} \beta_{\text{E}}(-2\omega; \omega, \omega) [4I_0(\omega) + \frac{1}{2}I_0(2\omega)] \quad (5.16)$$

Numerical calculations of the electronic (eq 5.12) and the vibrational (eq 5.17) polarizabilities in the IFR regime for this model show that in the IFR ($0.2 \text{ eV} < \omega < 1 \text{ eV}$) the purely electronic contribution dominates and vibrational corrections only slightly reduce the total polarizability by 5–10%.²⁰ Higher, ~30%, vibrational contributions were reported for more realistic models.⁵

VI. Discussion

In this paper we have developed a procedure for computing the vibrational contributions to molecular polarizabilities in the IFR that avoids the explicit calculation of vibrational modes. The procedure is based on the time-dependent variational principle for the dynamics of a molecule driven by an optical field, where the many-electron state is taken to be a single Slater determinant at all times, whereas the vibrational motions are treated classically.^{9,18} The resulting dynamical equations are represented in an invariant form (eqs 2.11–2.13) that requires no specific set of local coordinates in the single Slater determinants space as well as a basis set in the space of single-electron orbitals. This is accomplished by treating the nonadiabatic coupling terms as a gauge field and the transformations of the basis set as gauge transformations. The equations of motion are then naturally interpreted by implementing the geometrical picture of the gauge field as the shift in the electronic space induced by a shift of the nuclear positions. This gives a complete flexibility in choosing the basis sets and local coordinates for particular applications. Computation of the dynamical optical response using this approach requires finding the N_{T} coupled electronic–vibrational eigenmodes of the

corresponding linearized equation. Using the oscillator language, this means that the electronic and vibrational motions are coupled even on the level of the linear response, and each of the oscillators that diagonalize the linearized problem has both electronic and vibrational components. Computing the joint N_T modes (oscillators) can be avoided in the IFR ($\Omega_N \ll \omega_L \ll \Omega_e$) by making use of the different roles played by the vibrational Ω_N and electronic Ω_e frequencies. In the present paper this is achieved by deriving closed equations of motion for the electronic density matrix $\rho^{(0)}$ of a driven system with fixed nuclear positions, the nuclear coordinates $r^{(1)}$, and the deviation $\rho^{(1)}$ of the electronic density matrix from $\rho^{(0)}$ induced by nuclear motions. The perturbative expansion in the inverse nuclear mass M^{-1} is also given in a gauge-invariant form (eqs 3.2–3.5), which allows use of the freedom in the choice of the basis sets and local coordinates when the IFR equations are solved. In particular it results in compact expressions for the vibrational contributions to optical polarizabilities in terms of the TDHF modes. This approach, which is justified in the IFR, requires finding explicitly only the electronic modes, considerably reducing the numerical effort.

The picture that emerges from this study shows that the IFR is very different from the static limit.⁷ The two-level model coupled to a vibrational mode provides a qualitatively transparent picture of the underlying physics. In the static limit both electronic and vibrational contributions are positive and have comparable magnitudes, which enhances the total polarizability. In the IFR the purely electronic contribution $\beta_E(\omega)$ dominates the second-order response and is larger than $\beta_E(0)$ since the IFR frequency is closer to those of the electronic resonances. On the other hand, the vibrational contribution $\beta_V(\omega)$ becomes negative and is smaller than $\beta_E(\omega)$, so that it reduces the total polarizability.

The different roles of the vibrational contribution to the optical polarizabilities in the static limit versus IFR originate from the relative positions of the driving frequency ω_L and the vibrational frequency Ω_N . In the IFR the driving frequency becomes higher than the vibrational frequency, and therefore the corresponding contribution changes sign with respect to the static case. Since the sign of the electronic contribution remains unchanged, the two contributions have opposite signs in the IFR.

The IFR expansion can be alternatively obtained in the following way. Since the variational principle recasts the dynamics in a classical form, one can obtain a classical Hamiltonian and expand it in the vicinity of the stationary point in powers of z , r , and P , where P are the nuclear momenta and r are the deviations of nuclear positions from the equilibrium geometry. The z variables characterize the deviation of the electronic density matrix from $\bar{\rho}$. They can be defined as the expansion coefficients of the particle–hole component of $\rho - \bar{\rho}$ in the eigenmodes of the linearized TDHF equation, as is done here, or z can represent the Thouless parameters as is done in ref 18. We can then partition the classical Hamiltonian $H = H_0 + H_{\text{int}}$, where H_0 contains bilinear terms in the variables z , r , and P but excludes any coupling between electronic and vibrational variables. H_1 contains the anharmonic terms and the bilinear terms that couple the electronic and vibrational variables (i.e., zr and z^*r). Following ref 17, we can obtain closed expressions for the optical polarizabilities in terms of the parameters of H_1 and the Green functions $G_e(\omega)$ and $G_N(\omega)$ of the uncoupled linearized electronic and nuclear motions described by the Hamiltonian H_0 . The electronic Green function is expressed in terms of the eigenmodes ξ_α of the linearized TDHF equation,¹⁷ and does not require the vibrational eigen-

modes. The latter are in principle needed to compute $G_N(\omega)$. However, in the IFR where $\omega \gg \Omega_N$, $G_N(\omega)$ can be evaluated using an expansion in powers of ω^{-2} . The expansion coefficients can be obtained using the sum rules for the vibrational motions, which do not require finding the vibrational eigenmodes. Substituting $G_N(\omega)$ expanded to order ω^{-2} into the general expression polarizabilities described above yields expressions for the IFR polarizabilities which are identical to those presented in section IV and Appendix C.

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Appendix A: Nuclear Contributions to Optical Polarizabilities

In section III we have derived a system of coupled equations (eqs 3.2, 3.3, and 3.5), which describes the correction to the optical response induced by the nuclear motions in the IFR. In this Appendix we obtain closed expressions for optical polarizabilities by solving these equations iteratively in the driving field.

Equation 3.2 constitutes the TDHF equation for the electronic degree of freedom alone. By representing the density matrix $\rho^{(0)}$ in the form

$$\rho^{(0)} = \bar{\rho} + \eta + T(\eta) \quad (\text{A1})$$

where $\bar{\rho}$ is the solution of the HF equation and η is the particle–hole component of the deviation of ρ from $\bar{\rho}$. The TDHF equation (3.2) reads¹⁷

$$i \frac{d\eta}{dt} = L(\eta) - \mathcal{E}(\tau)[\mu, \bar{\rho}] + 2[V^{(0)}(\eta + T(\eta)), \eta] + 2[V^{(1)}(T(\eta)), \bar{\rho}] + 2[V^{(1)}(\eta + T(\eta)), T(\eta)] - \mathcal{E}(\tau)[\mu^{(0)}, \eta] - \mathcal{E}(\tau)[\mu^{(1)}, T(\eta)] \quad (\text{A2})$$

Here L is the linearized TDHF equation operator

$$L(\eta) \equiv [t + 2V(\bar{\rho}), \eta] - 2[\bar{\rho}, V(\eta)] \quad (\text{A3})$$

where $V^{(j)}$ and $\mu^{(j)}$ for $j = 0$ and 1 stand for the intraband and particle–hole components, respectively. Using the notation of eq A1, the equation for r_α (3.3) adopts the form

$$M \frac{d^2 r_\alpha}{dt^2} = -\text{Tr}\{h_\alpha(\eta + T(\eta))\} - \text{Tr}\{(\eta + T(\eta))V_\alpha(\eta + T(\eta))\} + \mu_{N,\alpha}\mathcal{E}(\tau) + \text{Tr}\{\mu_\alpha(\bar{\rho} + \eta + T(\eta))\} \mathcal{E}(\tau) \quad (\text{A4})$$

where

$$h_\alpha \equiv t_\alpha + 2V_\alpha(\bar{\rho}) \quad (\text{A5})$$

ξ must satisfy the constraint

$$[\rho, [\rho, \xi]] = \xi \quad (\text{A6})$$

To avoid redundant variables, we represent it in the form

$$\xi = \zeta + \bar{T}(\eta, \zeta) \quad (\text{A7})$$

where ζ is the particle–hole component of ξ with respect to $\bar{\rho}$. (Note that eq A6 implies that ξ has only particle–hole

components with respect to ρ . $\bar{T}(\eta, \zeta)$ is linear in ζ and can be found by combining eqs A6 and A1, which yields

$$\bar{T}(\eta, \zeta) = \frac{\partial T(\eta)}{\partial \eta} \zeta \quad (\text{A8})$$

Substitution of eq A7 into eq 3.5 gives the equation of motion for ζ :

$$\begin{aligned} i \frac{d\zeta}{d\tau} = & L(\zeta) + 2[V^{(0)}(\eta + T(\eta)), \zeta] + \\ & 2[V^{(1)}(\eta + T(\eta)), \bar{T}(\eta, \zeta)] + 2[V^{(0)}(\zeta + \bar{T}(\eta, \zeta)), \eta] + \\ & 2[V^{(1)}(\zeta + \bar{T}(\eta, \zeta)), T(\eta)] + \sum_{\alpha} [h_{\alpha}, \bar{\rho}] r_{\alpha} + \sum_{\alpha} [h_{\alpha}^{(0)}, \eta] r_{\alpha} + \\ & \sum_{\alpha} [h_{\alpha}^{(1)}, T(\eta)] r_{\alpha} + 2 \sum_{\alpha} [V_{\alpha}(\eta + T(\eta)), \bar{\rho}] r_{\alpha} + \\ & 2 \sum_{\alpha} [V_{\alpha}(\eta + T(\eta)), \eta] r_{\alpha} + 2 \sum_{\alpha} [V_{\alpha}^{(1)}(\eta + T(\eta)), T(\eta)] r_{\alpha} - \\ & \mathcal{E}(\tau) \sum_{\alpha} [\mu_{\alpha}, \bar{\rho}] r_{\alpha} - \mathcal{E}(\tau) [\mu^{(0)}, \zeta] - \mathcal{E}(\tau) [\mu^{(1)}, \bar{T}(\eta, \zeta)] - \\ & \mathcal{E}(\tau) \sum_{\alpha} [\mu_{\alpha}^{(0)}, \eta] r_{\alpha} - \mathcal{E}(\tau) \sum_{\alpha} [\mu_{\alpha}^{(1)}, T(\eta)] r_{\alpha} \quad (\text{A9}) \end{aligned}$$

Expanding η and ζ in the eigenmodes of the linearized TDHF equation

$$\eta = \sum_{\alpha} z_{\alpha} \xi_{\alpha}; \quad \zeta = \sum_{\alpha} w_{\alpha} \xi_{\alpha} \quad (\text{A10})$$

and neglecting the terms leading to higher than the third-order contributions in the driving field, we obtain the following closed system of equations for z_{α} , w_{α} , and r_{α} :

$$\begin{aligned} i \frac{\partial z_{\alpha}}{\partial \tau} = & \Omega_{\alpha} z_{\alpha} + \sum_{\beta\gamma} V_{\alpha,\beta\gamma} z_{\beta} z_{\gamma} + \sum_{\beta\gamma\delta} V_{\alpha,\beta\gamma\delta} z_{\beta} z_{\gamma} z_{\delta} - \mathcal{E}(\tau) \mu_{\alpha} - \\ & \mathcal{E}(\tau) \sum_{\beta} \mu_{\alpha,\beta} z_{\beta} - \mathcal{E}(\tau) \sum_{\beta\gamma} \mu_{\alpha,\beta\gamma} z_{\beta} z_{\gamma} \quad (\text{A11}) \end{aligned}$$

$$\begin{aligned} i \frac{\partial w_{\alpha}}{\partial \tau} = & \Omega_{\alpha} w_{\alpha} + \sum_{\beta\gamma} U_{\alpha,\beta\gamma} w_{\beta} z_{\gamma} + \sum_{\beta\gamma\delta} U_{\alpha,\beta\gamma\delta} w_{\beta} z_{\gamma} z_{\delta} + \\ & \sum_{\beta} W_{\alpha,\beta} r_{\beta} + \sum_{\beta\gamma} W_{\alpha,\beta\gamma} r_{\beta} z_{\gamma} + \sum_{\beta\gamma\delta} W_{\alpha,\beta\gamma\delta} r_{\beta} z_{\gamma} z_{\delta} \\ & - \mathcal{E}(\tau) \sum_{\beta} \bar{\mu}_{\alpha,\beta} w_{\beta} - \mathcal{E}(\tau) \sum_{\beta\gamma} \bar{\mu}_{\alpha,\beta\gamma} w_{\beta} z_{\gamma} - \mathcal{E}(\tau) \sum_{\beta\gamma} \bar{\mu}_{\alpha,\beta\gamma}^{(1)} r_{\beta} z_{\gamma} - \\ & \mathcal{E}(\tau) \sum_{\beta} \mu_{\alpha,\beta}^{(1)} r_{\beta} \quad (\text{A12}) \end{aligned}$$

$$\begin{aligned} M \frac{d^2 r_{\alpha}}{d\tau^2} = & - \sum_{\beta} \bar{W}_{\alpha,\beta} z_{\beta} - \sum_{\beta\gamma} \bar{W}_{\alpha,\beta\gamma} z_{\beta} z_{\gamma} + \mathcal{E}(\tau) \mu_{\alpha}^{(N)} - \\ & \sum_{\beta\gamma\delta} \bar{W}_{\alpha,\beta\gamma\delta} z_{\beta} z_{\gamma} z_{\delta} + \mathcal{E}(\tau) \sum_{\beta} \mu_{\alpha,\beta}^{(N)} z_{\beta} + \mathcal{E}(\tau) \sum_{\beta\gamma} \mu_{\alpha,\beta\gamma}^{(N)} z_{\beta} z_{\gamma} \quad (\text{A13}) \end{aligned}$$

The parameters V and μ which enter eq A11 and the parameters U , W , $\bar{\mu}$, and $\mu^{(N)}$ which enter eqs A12 and A13 are given in Appendix B.

We also have

$$\rho^{(0)} = \sum_{\alpha} \mu_{\alpha}^{(s)} z_{\alpha} + \sum_{\alpha\beta} S_{\alpha\beta} z_{\alpha} z_{\beta} \quad (\text{A14})$$

$$\begin{aligned} \rho^{(1)} = & \sum_{\alpha} \mu_{\alpha}^{(s)} w_{\alpha} + \sum_{\alpha} \mu_{\alpha}^{(N)} r_{\alpha} + \sum_{\alpha\beta} \bar{S}_{\alpha\beta} z_{\alpha} r_{\beta} + \\ & \sum_{\alpha\beta} S_{\alpha\beta} (z_{\alpha} w_{\beta} + z_{\beta} w_{\alpha}) \quad (\text{A15}) \end{aligned}$$

The optical response functions are derived by substituting eqs A1 and A7 into eqs 3.7 and 3.8 and making use of eq A10. The parameters of eqs A14 and A15 are also given in Appendix B. z_{α} , w_{α} , and v_{α} are obtained by solving eqs A11–A13 order by order in the driving field $\mathcal{E}(\tau)$.

Appendix B: Parameters of Equations A11–A15

The parameters of the equations of motion for the oscillators z_{α} , w_{α} , and r_{α} presented in Appendix A can be obtained by projecting eqs A2 and A9 onto the modes ξ_{α} of the linearized TDHF equation, and using eq A4 followed by substitution of the expansions of eq A10 into these equations. This yields eq A11 with

$$\mu_{\alpha} = \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [\mu, \bar{\rho}])$$

$$\mu_{\alpha,\beta} = \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [\mu, \xi_{\beta}])$$

$$\mu_{\alpha,\beta\gamma} = \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [\mu, \frac{1}{2} [[\xi_{\beta}, \bar{\rho}], \xi_{\gamma}]])$$

$$V_{\alpha,\beta\gamma} = 2 \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [V(\xi_{\beta}), \xi_{\gamma}]) +$$

$$\text{Tr}([\bar{\rho}, \xi_{-\alpha}] [V([\xi_{\beta}, \bar{\rho}], \xi_{\gamma}), \bar{\rho}])$$

$$V_{\alpha,\beta\gamma\delta} = \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [V([\xi_{\beta}, \bar{\rho}], \xi_{\gamma}), \xi_{\delta}]) +$$

$$\text{Tr}([\bar{\rho}, \xi_{-\alpha}] [V(\xi_{\beta}), [[\xi_{\beta}, \bar{\rho}], \xi_{\gamma}]) \quad (\text{B1})$$

The parameters of eq A12 are listed below:

$$U_{\alpha,\beta\gamma} = V_{\alpha,\beta\gamma} + V_{\alpha,\gamma\beta}$$

$$U_{\alpha,\beta\gamma\delta} = V_{\alpha,\beta\gamma\delta} + V_{\alpha,\delta\gamma\beta} + V_{\alpha,\gamma\delta\beta}$$

$$\bar{\mu}_{\alpha,\beta} = \mu_{\alpha,\beta}, \quad \bar{\mu}_{\alpha,\beta\gamma} = \mu_{\alpha,\beta\gamma} + \mu_{\alpha,\gamma\beta} \quad (\text{B2})$$

$$W_{\alpha,\beta} = \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [h_{\beta}, \bar{\rho}])$$

$$W_{\alpha,\beta\gamma} = \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [h_{\beta}, \xi_{\gamma}]) + 2 \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [V_{\beta}(\xi_{\gamma}), \bar{\rho}])$$

$$W_{\alpha,\beta\gamma\delta} = \frac{1}{2} \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [h_{\beta}, [[\xi_{\gamma}, \bar{\rho}], \xi_{\delta}]]) +$$

$$\text{Tr}([\bar{\rho}, \xi_{-\alpha}] [V_{\beta}([\xi_{\gamma}, \bar{\rho}], \xi_{\delta}), \bar{\rho}]) +$$

$$2 \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [V_{\beta}(\xi_{\gamma}), \xi_{\delta}]) \quad (\text{B3})$$

$$\bar{\mu}_{\alpha,\beta}^{(1)} = \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [\mu_{\beta}, \bar{\rho}])$$

$$\bar{\mu}_{\alpha,\beta\gamma}^{(1)} = \text{Tr}([\bar{\rho}, \xi_{-\alpha}] [\mu_{\beta}, \xi_{\gamma}])$$

The parameters of eq A13 are given by

$$\bar{W}_{\alpha,\beta} = \text{Tr}(h_{\alpha} \xi_{\beta})$$

$$\bar{W}_{\alpha,\beta\gamma} = \frac{1}{2} \text{Tr}([h_{\alpha} [[\xi_{\beta}, \bar{\rho}], \xi_{\gamma}]] + \text{Tr}(\xi_{\beta} V_{\alpha}(\xi_{\gamma}))$$

$$\bar{W}_{\alpha,\beta\gamma\delta} = \frac{1}{2} \text{Tr}([[[\xi_{\beta}, \bar{\rho}], \xi_{\gamma}] V_{\alpha}(\xi_{\gamma})]) +$$

$$\frac{1}{2} \text{Tr}(\xi_{\beta} V_{\alpha}([[\xi_{\gamma}, \bar{\rho}], \xi_{\delta}])) \quad (\text{B4})$$

$$\mu_{\alpha}^{(N)} = \mu_{N,\alpha} + \text{Tr}(\mu_{\alpha} \bar{\rho})$$

$$\mu_{\alpha,\beta}^{(N)} = \text{Tr}(\mu_{\alpha} \xi_{\beta})$$

$$\mu_{\alpha,\beta\gamma}^{(N)} = \frac{1}{2} \text{Tr}(\mu_{\alpha} [[\xi_{\beta}, \bar{\rho}], \xi_{\gamma}])$$

Finally, the parameters of eqs A14 and A15 are

$$\begin{aligned}\mu_{\alpha}^{(s)} &\equiv \mu_{-\alpha}, & S_{\alpha\beta} &\equiv 1/2\mu_{-\alpha\beta} \\ \bar{S}_{\alpha\beta} &\equiv \mu_{\beta,\alpha}^{(N)}\end{aligned}\quad (\text{B5})$$

Equations B1 and B3 are valid for $\alpha < 0$. The corresponding expressions for $\alpha > 0$ are obtained by changing the sign of the rhs of eqs B1 and B3.

Appendix C: Second-Order Polarizability

The second-order response function can be represented as a sum of five contributions: $R^{(2)} = \sum_{m=1}^5 R_m^{(2)}$. The first three have the same form as the purely electronic contributions,¹⁷ renormalized by nuclear dynamics

$$R_1^{(2)}(-\omega_s; \omega_1, \omega_2) = \sum \hat{\mu}_{\delta}^{(s)}(\omega_s) \hat{G}_{\delta\gamma}(\omega_s) \hat{V}_{\gamma,\alpha\beta}(-\omega_s; \omega_1, \omega_2) \times \hat{G}_{\alpha\alpha}(\omega_1) \hat{G}_{\beta\beta}(\omega_2) \hat{\mu}_{\alpha}(\omega_1) \hat{\mu}_{\beta}(\omega_2) \quad (\text{C1})$$

$$R_2^{(2)}(-\omega_s; \omega_1, \omega_2) = \sum \hat{\mu}_{\delta}^{(s)}(\omega_s) \hat{G}_{\delta\gamma}(\omega_s) \hat{B}_{\gamma,\beta}(-\omega_s; \omega_1, \omega_2) \times \hat{G}_{\beta\alpha}(\omega_1) \hat{\mu}_{\alpha}(\omega_1) \quad (\text{C2})$$

$$R_3^{(2)}(-\omega_s; \omega_1, \omega_2) = \sum \hat{S}_{\beta\delta}(-\omega_s; \omega_1, \omega_2) \hat{\mu}_{\alpha}(\omega_1) \hat{\mu}_{\gamma}(\omega_2) \times \hat{G}_{\beta\alpha}(\omega_1) \hat{G}_{\delta\gamma}(\omega_2) \quad (\text{C3})$$

where $\hat{\mu}$, $\hat{\mu}^{(s)}$, and \hat{G} are given by eqs 4.3–4.5. The remaining renormalized quantities in eqs C1–C3 are

$$\begin{aligned}\hat{V}_{\gamma,\alpha\beta}(-\omega_s; \omega_1, \omega_2) &\equiv V_{\gamma,\alpha\beta} + \frac{1}{\omega_1^2} \sum_{\delta} M_{\delta}^{-1} \bar{W}_{\gamma,\delta\beta} \bar{W}_{\delta,\alpha} + \\ &\frac{1}{\omega_s^2} \sum_{\delta} M_{\delta}^{-1} W_{\gamma,\delta} \bar{W}_{\delta,\alpha\beta} \quad (\text{C4})\end{aligned}$$

$$\begin{aligned}\hat{B}_{\alpha\beta}(-\omega_s; \omega_1, \omega_2) &\equiv \mu_{\alpha\beta} + \frac{1}{\omega_1^2} \sum_{\gamma} M_{\gamma}^{-1} \bar{\mu}_{\alpha,\gamma}^{(1)} \bar{W}_{\gamma,\beta} + \\ &\frac{1}{\omega_2^2} \sum_{\gamma} M_{\gamma}^{-1} W_{\alpha,\gamma\beta} \mu_{\gamma}^{(N)} + \frac{1}{\omega_s^2} \sum_{\gamma} M_{\gamma}^{-1} W_{\alpha,\gamma} \mu_{\gamma,\beta}^{(N)} \quad (\text{C5})\end{aligned}$$

$$\hat{S}_{\alpha\beta}(-\omega_s; \omega_1, \omega_2) \equiv S_{\alpha\beta} + \frac{1}{\omega_1^2} \sum_{\gamma} M_{\gamma}^{-1} \bar{S}_{\alpha\gamma} \bar{W}_{\gamma,\beta} \quad (\text{C6})$$

The remaining terms $R_4^{(2)}$ and $R_5^{(2)}$ are induced by vibrational motions and have no purely electronic counterparts:

$$R_4^{(2)}(-\omega_s; \omega_1, \omega_2) = \sum_{\alpha\beta} \hat{T}_{\alpha}^{(s)}(-\omega_s; \omega_1, \omega_2) \hat{G}_{\alpha\beta}(\omega_1) \hat{\mu}_{\beta}(\omega_2) \quad (\text{C7})$$

$$R_5^{(2)}(-\omega_s; \omega_1, \omega_2) = \sum_{\alpha\beta} \hat{\mu}_{\alpha}^{(s)}(\omega_s) \hat{G}_{\alpha\beta}(\omega_s) \hat{T}_{\beta}(-\omega_s; \omega_1, \omega_2) \quad (\text{C8})$$

with

$$\begin{aligned}\hat{T}_{\alpha}^{(s)}(-\omega_s; \omega_1, \omega_2) &\equiv \frac{1}{\omega_1^2} \sum_{\gamma} M_{\gamma}^{-1} \bar{S}_{\alpha\gamma} \mu_{\gamma}^{(N)} + \\ &\frac{1}{\omega_s^2} \sum_{\gamma} M_{\gamma}^{-1} \mu_{\gamma}^{(N)} \mu_{\gamma,\alpha}^{(N)} \quad (\text{C9})\end{aligned}$$

$$\hat{T}_{\alpha}(-\omega_s; \omega_1, \omega_2) \equiv \frac{1}{\omega_1^2} \sum_{\gamma} M_{\gamma}^{-1} \mu_{\alpha,\gamma}^{(N)} \mu_{\gamma}^{(N)} \quad (\text{C10})$$

Appendix D: Calculation of β for the Two-level Model. Diabatic and Adiabatic Basis Sets

In this Appendix we derive the expressions for the matrix elements of μ and h_r in the adiabatic basis set (eq 5.6) and sketch the derivation of eqs 5.13 and 5.16.

For the present model in the adiabatic basis, $t(r)$ is diagonal, whereas in the crude adiabatic basis, $t(r_0)$ is diagonal, where r_0 represents the equilibrium geometry. The adiabatic basis set is

$$\begin{aligned}|\psi_g(r)\rangle &= a(r)|\psi_{\text{VB}}\rangle + b(r)|\psi_{\text{CT}}\rangle \\ |\psi_e(r)\rangle &= -b(r)|\psi_{\text{VB}}\rangle + a(r)|\psi_{\text{CT}}\rangle\end{aligned}\quad (\text{D1})$$

Combining eqs D1 and 5.1 yields

$$\begin{aligned}a(r) &= \frac{1}{\sqrt{2}} \left(1 + \frac{\mathcal{E}(r)}{(\mathcal{L}^2(r) + 1)^{1/2}} \right)^{1/2} \\ b(r) &= -\frac{1}{\sqrt{2}} \left(1 - \frac{\mathcal{E}(r)}{(\mathcal{L}^2(r) + 1)^{1/2}} \right)^{1/2}\end{aligned}\quad (\text{D2})$$

The Hartree–Fock energy $E_g(r)$ is given by the eigenvalue of $t(r)$, which corresponds to the ground state $|\psi_g(r)\rangle$

$$E_g(r) = \frac{E_{\text{VB}}(r) + E_{\text{CT}}(r)}{2} - J(\mathcal{L}^2(r) + 1)^{1/2} \quad (\text{D3})$$

whereas the frequency of the electronic oscillator $\Omega(r)$ is given by $E_e(r) - E_g(r) = \Omega(r) = 2J(\mathcal{L}^2(r) + 1)^{1/2}$, and we have used the notation $\mathcal{E}(r) = [E_{\text{CT}}(r) - E_{\text{VB}}(r)]/2J$. The equilibrium geometry r_0 is obtained by minimizing $E_g(r)$ (eq D3).

In the diabatic basis set, μ is given by eq 5.4. It also follows from eqs 5.4 and 5.3 that in this basis set

$$h_r(r) = \frac{\partial t(r)}{\partial r} = k \begin{pmatrix} r + Q & 0 \\ 0 & r - Q \end{pmatrix} \quad (\text{D4})$$

Switching to the adiabatic basis set using eq D1, we immediately obtain

$$\begin{aligned}\kappa_e(r) - \kappa_g(r) &= 2[b^2(r) - a^2(r)]kQ, \\ \kappa_{\text{eg}}(r) &= -2a(r)b(r)kQ \\ \mu_e(r) - \mu_g(r) &= [a^2(r) - b^2(r)]\mu_{\text{CT}}, \\ \mu_{\text{eg}}(r) &= a(r)b(r)\mu_{\text{CT}}\end{aligned}\quad (\text{D5})$$

Equations 5.13 and 5.16 are obtained starting with the expressions for the second-order polarizability (eqs 4.9 and C1–C3) and using eqs 5.5, 5.6, and D5. In deriving eq 5.16, we made use of the fact that for our model $(\kappa_e - \kappa_g)\kappa_{\text{eg}}^{-1} = (\mu_e - \mu_g)\mu_{\text{eg}}^{-1}$.

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