Electronic Physics Auxiliary Publication for "The polarization anisotropy of vibrational quantum beats in resonant pump-probe experiments: diagrammatic calculations for square symmetric molecules"

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This auxiliary publication describes the equations and method used in calculation of the asymmetric vibrational quantum beat anisotropy by numerical diagonalization of the linear Jahn-Teller coupling Hamiltonian matrix.

The symmetry properties of the effective spectroscopic Hamiltonian for Jahn-Teller coupling within doubly degenerate $E$ symmetry states of four-fold symmetric molecules have been carefully discussed by Hougen.[1] The Hamiltonians for three electronic states ($g, e, f$) influence the pump-probe polarization anisotropy of vibrational quantum beats:

\[
\hat{H}_g = \hat{H}^o \quad \text{(EPAPS.1)}
\]

\[
\hat{H}_e = \hbar \omega_{eg} + \hat{H}^o + \hat{H}_{ev} \quad \text{(EPAPS.2)}
\]

\[
\hat{H}_f = \hbar \left( \omega_{eg} + \omega_{fe} \right) + \hat{H}^o \quad \text{(EPAPS.3)}
\]

$\hat{H}_g, \hat{H}_e, \hat{H}_f$ are the vibronic Hamiltonians for ground ($A_{1g}$ symmetry), singly excited ($E_u$ symmetry), and doubly excited electronic states ($A_{1g}, A_{2g}, B_{1g},$ and $B_{2g}$ symmetry are considered), respectively. $\omega_{eg}$ and $\omega_{fe}$ are the vertical energy gaps from the ground state to the $E_u$ state, and from the $E_u$ state to the doubly excited state, respectively. The ground state Hamiltonian is

\[
\hat{H}^o = \hat{H}_{e\text{c}} + \hat{H}_{\text{vib}}, \text{ where } \hat{H}_{e\text{c}} \text{ is the Hamiltonian of the electrons when the nuclei are fixed in the symmetrical } D_{4h} \text{ configuration. } \hat{H}_{e\text{c}} \text{ has electronic eigenstates } |g\rangle, |x\rangle, |y\rangle, \text{ and } |f\rangle, \text{ where}
\]
\(|x\rangle\) and \(|y\rangle\) are a basis for the doubly degenerate singly excited state. \(\hat{H}_{\text{vib}}\) is the harmonic oscillator vibrational Hamiltonian of the ground state given by

\[
\hat{H}_{\text{vib}} = \frac{1}{2} \hbar \omega_1 (\hat{q}_1^2 + \hat{p}_1^2) + \frac{1}{2} \hbar \omega_2 (\hat{q}_2^2 + \hat{p}_2^2),
\]

(EPAPS.4)

where \(\hat{q}_n\) and \(\hat{p}_n\) are position and momentum operators in dimensionless normal coordinates, \(\omega_n\) is vibrational frequency, and subscripts (1) and (2) refer to asymmetric normal mode coordinates of \(b_{1g}\) and \(b_{2g}\) symmetry, respectively. In the doubly degenerate excited state, the lowest order electronic–vibrational coupling in \(\hat{H}_{\text{ev}}\) is a linear Jahn-Teller coupling,

\[
\hat{H}_{\text{ev}} = \hat{V}_1 \hat{q}_1 + \hat{V}_2 \hat{q}_2,
\]

(EPAPS.5)

where \(\hat{V}_1 = \hbar \omega_d x \left( |x\rangle\langle x| - |y\rangle\langle y| \right)\) and \(\hat{V}_2 = \hbar \omega_d y \left( |x\rangle\langle y| + |y\rangle\langle x| \right)\) are diagonal and off-diagonal electronic operators, respectively. Because vibrational modes 1 and 2 differ in symmetry, the diagonal energy splitting (due to mode 1) and off-diagonal coupling (due to mode 2) are generally not equal in fourfold symmetric molecules (in contrast to the Jahn-Teller effect in other point groups).[2] These differences in vibronic coupling matrix elements reflect the symmetry difference between \(b_{1g}\) and \(b_{2g}\) vibrational coordinates in the chosen coordinate system. In this coordinate system, \(\hat{V}_1\) effectively alters the vibrational levels within \(|x\rangle\) and \(|y\rangle\), leaving the original electronic character intact in the resulting eigenstates.[1] In contrast, \(\hat{V}_2\) couples vibronic states on \(|x\rangle\) states to vibronic states on \(|y\rangle\), mixing the electronic character. This electronic mixing is independent of vibrational level if \(\hat{V}_1 = 0\), but generates non-separable vibronic eigenstates otherwise. The vibronic eigenstates of the above Hamiltonian always remain doubly degenerate.[1] Hamiltonians with \(\hat{V}_1 = 0\) or \(\hat{V}_2 = 0\) are "accidental Born-Oppenheimer cases" yielding doubly-degenerate, vibrational-electronic product eigenstates;[1]
the general Hamiltonian with $\hat{V}_1 \neq 0$ and $\hat{V}_2 \neq 0$ gives rise to doubly-degenerate, non-separable, vibronic eigenstates, a "dynamic Jahn-Teller effect".[2]

Representative adiabatic electronic potential energy surfaces of this Hamiltonian for the doubly degenerate excited state are shown in Fig. 1 of ref. [3], which color codes the potential surfaces to show the adiabatic electronic states at each geometry. The most important analytic results for the adiabatic potential surfaces are: 1) along each coordinate, the equilibrium displacements of the two electronic states are $\pm d_n$, equal and opposite; 2) along each coordinate, the Jahn-Teller stabilization energy is $(D\omega)_n = (1/2)\hbar \omega_n d_n^2$ for both states.[3-6] Considering the two degenerate states one at a time, the above results are the same as those for the displacement and Marcus stabilization energy of a totally symmetric vibration and have the same interpretation: relative to the vertical excitation energy, the adiabatic potential energy minima along $q_n$ are stabilized by $(D\omega)_n$ at distances $\pm d_n$ from the vertical excitation geometry. (Note that a 1D minimum can be a saddle point in 2D; for two modes, the mode with the smaller stabilization energy will have saddle points at $\pm d_n$).[2] $\hbar \omega_n d_n$ is also commonly referred to as $V_{JT}$, which emphasizes its electrostatic potential energy coupling origin in the Herzberg-Teller picture of vibronic interactions.[7]

For treatment of vibronic coupling in the $E_u$ state, it is convenient to use a direct product basis of diabatic electronic basis states having polarized emission along $x$ and $y$ with undisplaced harmonic oscillator basis states for $b_{1g}$ and $b_{2g}$ symmetry vibrations in $D_{4h}$ symmetry. Thus, the $E_u$ symmetry diabatic electronic basis states and the molecular coordinate system are defined so that

$$\langle x | \hat{\mu} | g \rangle = \mu_{xg} \hat{x} \quad \text{and} \quad \langle y | \hat{\mu} | g \rangle = \mu_{yg} \hat{y}, \quad \text{with} \quad \mu_{xg} = \mu_{yg}$$

(EPAPS.6)
where $|\mu_{sg}| = |\mu_{yg}|$ by symmetry and the full equality depends on the arbitrary choice of phases.

The standard point group tables specify electronic transition dipole moment directions, but not signs, based on the change in symmetry during a transition.[2] The signs are not specified because they depend on the arbitrary choice of phases for the two eigenfunctions involved. For cyclic sets of 4 transition dipole moments, the arbitrary phases cancel, and the sign is physically significant.[8, 9] For cyclic sets involving two states with a symmetry-required degeneracy, the symmetry properties of the two-photon tensor determine relative transition moment directions and the physically significant overall sign.[9, 10] Based on the symmetry of the two-photon tensor and the phases used in Eq. (EPAPS.6), doubly excited states of symmetry $A_{1g}$ must have the purely electronic transition dipole moments

$$\langle x | \hat{\mu} | f \rangle = \mu_{sf} \hat{x} \quad \text{and} \quad \langle y | \hat{\mu} | f \rangle = \mu_{sf} \hat{y} \quad \text{with} \quad \mu_{sf} = \mu_{sf}; \quad (\text{EPAPS.7})$$

doubly excited states of $A_{2g}$ symmetry have

$$\langle x | \hat{\mu} | f \rangle = \mu_{sf} \hat{y} \quad \text{and} \quad \langle y | \hat{\mu} | f \rangle = \mu_{sf} \hat{x} \quad \text{with} \quad \mu_{sf} = -\mu_{sf}; \quad (\text{EPAPS.8})$$

doubly excited states of $B_{1g}$ symmetry have

$$\langle x | \hat{\mu} | f \rangle = \mu_{sf} \hat{x} \quad \text{and} \quad \langle y | \hat{\mu} | f \rangle = \mu_{sf} \hat{y} \quad \text{with} \quad \mu_{sf} = -\mu_{sf}; \quad (\text{EPAPS.9})$$

and doubly excited states of $B_{2g}$ symmetry have

$$\langle x | \hat{\mu} | f \rangle = \mu_{sf} \hat{y} \quad \text{and} \quad \langle y | \hat{\mu} | f \rangle = \mu_{sf} \hat{x} \quad \text{with} \quad \mu_{sf} = \mu_{sf}. \quad (\text{EPAPS.10})$$

In the diabatic basis used here, all of the purely electronic transition dipole moments given by Eqs. (EPAPS.6) to (EPAPS.10) are real.

The vibrational basis states are eigenfunctions of $\hat{H}_{vib}$, each specified as a product of undisplaced, harmonic oscillator wavefunctions along $b_{1g}$ and $b_{2g}$ coordinates

$$|v_{k,l}\rangle = |v_1 = k\rangle|v_2 = l\rangle. \quad \text{The vibrational energy is} \quad E_{kl} = \left[\hbar \omega_1 (k + (1/2)) + \hbar \omega_2 (l + (1/2))\right], \quad \text{with}$$
vibrational partition function $Q_{vb} = [2\sinh(\beta \hbar \omega_1/2)]^{-1}[2\sinh(\beta \hbar \omega_2/2)]^{-1}$, where $\beta$ is the inverse temperature. The phases of the vibrational basis states are chosen so that

$$\langle v_n | \hat{q}_n | v_n + 1 \rangle = [(v_n + 1)/2]^{1/2} \text{ (see Appendix E of ref. [11]).}$$

Using $| j \rangle$ to denote the diabatic electronic basis state, the vibronic basis states $| j, k, l \rangle$ are eigenfunctions of $\hat{H}_{\text{elec}} + \hat{H}_{\text{vib}}$. In this direct product basis, all matrix elements for the non-degenerate states $g$ and $f$ are diagonal, so the basis set used for numerical diagonalization of the vibronic Hamiltonian for the singly excited state ($e$) is

$$j = x, y; \quad k = 0, N_1 - 1; \quad l = 0, N_2 - 1. \quad (\text{EPAPS.11})$$

$\hat{H}_e$ is represented by a $2N_1N_2 \times 2N_1N_2$ matrix where $N_1(N_2)$ is the number of harmonic oscillator basis states included for the $b_{1g}$ ($b_{2g}$) coordinate in each of the two degenerate electronic states. The off-diagonal elements of the Hamiltonian are

$$\langle j, k, l | \hat{H}_{\text{ev}} | j', k', l' \rangle = \langle j | \hat{V}_1 | j' \rangle \langle v_1 = k | \hat{q}_1 | v_1 = k' \rangle \langle v_2 = l | v_2 = l' \rangle + \langle j | \hat{V}_2 | j' \rangle \langle v_1 = k | v_1 = k' \rangle \langle v_2 = l | \hat{q}_2 | v_2 = l' \rangle \quad (\text{EPAPS.12})$$

The vibrational integrals involving $\hat{q}_1$ ($\hat{q}_2$) are only non-zero for $k' = k \pm 1$ ($l = l' \pm 1$) with

$$\langle v_n = k | \hat{q}_n | v_n = k - 1 \rangle = [k/2]^{1/2}, \quad \text{while} \quad \langle v_1 = k | v_1 = k' \rangle = \delta_{kk'} \quad \text{and} \quad \langle v_2 = l | v_2 = l' \rangle = \delta_{ll'}.$$ 

Diagonalization of the Hamiltonian in this basis (using IMSL routine DEVCSF) produces a set of $2N_1N_2$ energy eigenvalues $E_m$ and energy eigenvectors $| m \rangle$, each represented as a sum of contributions from individual basis states as $| m \rangle = \sum_{j, k, l} c_{mjk} | j, k, l \rangle$. All coefficients $c_{mjk}$ are real.

The dipole matrix element between a vibronic state on the $E_u$ degenerate states and a vibrational state on the totally symmetric ground state is a vibronic transition dipole vector
Because vibrations on all electronic states are described by un-displaced harmonic oscillator basis states, the overlap integral \( \langle l'|l \rangle \langle k'|k \rangle \) is only non-zero when \( l = l', k = k' \) (when it equals one). Letting \( h = g \) or \( f \), Eq. (EPAPS.13) generalizes to

\[
\bar{\mu}_{hk'lv',m} = \left( c_{mklg} \mu_{xv} + c_{nklf} \mu_{yv} \right) \delta_{kk'} \delta_{ll'}.
\]  

In other words, the transition dipole vector for a vibronic transition from a given vibrational state \((k'l')\) on the ground \((g)\) or doubly excited \((f)\) state to a given vibronic eigenstate \(m\) of the singly excited state can be determined directly from the purely electronic transition dipole matrix elements and the matrix of \( E_u \) vibronic eigenstate coefficients obtained by diagonalization of the \( E_u \) state vibronic Hamiltonian. Below, it will be convenient to rewrite Eq. (EPAPS.14)a as

\[
\bar{\mu}_{om} = \mu_{ox} \hat{x} + \mu_{oy} \hat{y}.
\]  

where \(|o\rangle = |g\rangle |k'\rangle |l'\rangle \) or \(|o\rangle = |f\rangle |k'\rangle |l'\rangle \). All of the vibronic transition dipole vectors are real.

Using the vibronic transition dipole matrix element vectors in Eq. (EPAPS.14)b, it is possible to calculate the amplitude of the quantum pathways that contribute to parallel and perpendicular pump-probe signals. In the impulsive limit, parallel and perpendicular pump-probe signals are proportional to sums over quantum pathways \( R_{abcd} \), where \( a-d \) represent the 4 states involved in one diagrammatic contribution to the third order nonlinear optical polarization excited by the pump and probe electric fields. When the probe pulse follows the pump, there are three kinds of signal pathways: Ground State Bleaching (GSB diagrams D3 and D4 in ref. [12]),
Excited State Emission (ESE diagrams D_1 and D_2 in ref. [12]), and Excited State Absorption (ESA diagrams D_5 and D_6 in ref. [12]). For delta function pulses, each diagram is evaluated at the time intervals \( t_1 = 0, t_2 = T, \) and \( t_3 = 0, \) where \( T \) is the pump-probe delay. The signal field is phase-shifted from the source polarization (Eq. (24) of ref. [12]) so that when the complex conjugate diagrams are added, one obtains a cosinusoidal modulation from the Green function during \( t_2 = T. \) Physically, this modulation arises from vibrational and/or vibronic quantum beats within the electronic states \( g \) (GSB) or \( e \) (ESE and ESA). Writing the signal contributions in a form that parallels Eq. (6.60) of ref. [13] as closely as possible yields:

\[
S_{\text{GSB}} = \sum_{a,b,c} P(a) \left( (\vec{\mu}_{ad} \cdot \vec{R})(\vec{\mu}_{dc} \cdot \vec{R})(\vec{\mu}_{cb} \cdot \vec{U}) \right) \cos \left( \omega_{ca} T \right) \tag{EPAPS.15}
\]

\[
S_{\text{ESE}} = \sum_{a,d} P(a) \left( (\vec{\mu}_{bd} \cdot \vec{R})(\vec{\mu}_{dc} \cdot \vec{R})(\vec{\mu}_{ca} \cdot \vec{U}) \right) \cos \left( \omega_{cb} T \right) \tag{EPAPS.16}
\]

\[
S_{\text{ESA}} = \sum_{a,d} \sum_{b,c} P(a) \left( (\vec{\mu}_{bd} \cdot \vec{R})(\vec{\mu}_{dc} \cdot \vec{R})(\vec{\mu}_{ca} \cdot \vec{U}) \right) \cos \left( \omega_{cb} T \right) \tag{EPAPS.17}
\]

\( \vec{\mu}_{dc}, \vec{\mu}_{da}, \vec{\mu}_{cb}, \) and \( \vec{\mu}_{ab} \) are the transition dipole vectors from Eq. (EPAPS.14)b which contribute to the signal pathway through states \( a, b, c \) and \( d. \) The starting state is always \( a, \) a vibrational level on the ground electronic state with \( E_a = E_{kl} \) and thermal equilibrium population

\[
P(a) = \exp(-\beta E_a) / Q_{\text{vib}}, \quad \text{where } \beta \text{ is the inverse temperature for } (1/k_B \beta) = 295K. \quad \text{The brackets indicate an orientational average (see below), while the sum over states } a \text{ with Boltzmann probability } P(a) \text{ incorporates the thermal vibrational average. In Eq. (EPAPS.15), the superscripts over the sums indicate that vibronic states } a \text{ and } c \text{ are on the ground electronic state, } g, \text{ while vibronic states } b \text{ and } d \text{ are on the singly excited state, } e. \quad \text{For each term in Eq. (EPAPS.15), } \omega_{ca} = (E_e - E_a) / \hbar \text{ is the frequency of a purely vibrational coherent superposition.}
state on the ground electronic state during the pump-probe delay, $T$. In Eqs. (EPAPS.16) and (EPAPS.17), the vibronic state $a$ is on the ground electronic state, $g$, the vibronic states $b$ and $c$ are on electronic state $e$, and $\omega_{cb} = (E_e - E_g) / \hbar$ is the frequency of a vibronic superposition state on the doubly degenerate singly excited electronic state. $\vec{U}$ and $\vec{R}$ are unit vectors for the optical electric field of the pump and probe pulses in the lab frame. In contrast, the transition dipole matrix elements are defined in terms of unit vectors $\hat{x}$ and $\hat{y}$ in the molecular frame. To evaluate the orientational averages, this change of frame must be taken into account. The method used in the code is described for a single term in Eq. (EPAPS.15) in the next paragraph.

In the parallel transient ($S_\|$), both pump and probe fields are polarized along $\hat{Z}$ ($\vec{R}_{UU} = ZZZZ$). For the perpendicular transient ($S_\perp$), the pump is polarized along $\hat{Z}$ while the probe is polarized along $\hat{Y}$ ($\vec{R}_{UU} = YYZZ$). As discussed in refs. [9, 14, 15], the integral over four field/dipole projections is either zero or equivalent to one of five orientational integrals. After expanding the field dipole product, terms with a common dipole field pattern are grouped together and multiplied by a common orientational integral in the code. By the isotropy of space, many integral averages are equal, for example $\langle (\hat{Z} \cdot \hat{x})^4 \rangle = \langle (\hat{Z} \cdot \hat{y})^4 \rangle$. Further, any orientational integral in which $\hat{x}$, $\hat{y}$, $\hat{Z}$ or $\hat{Y}$ appears an odd number of times vanishes. Therefore

$$\left\langle (\vec{\mu}_{ad} \cdot \vec{R})(\vec{\mu}_{dc} \cdot \vec{R})(\vec{\mu}_{cb} \cdot \vec{U})(\vec{\mu}_{ba} \cdot \vec{U}) \right\rangle_{||}$$

$$= (\mu_{dc}^x \mu_{ad}^x \mu_{cb}^x \mu_{ba}^x + \mu_{dc}^y \mu_{ad}^y \mu_{cb}^y \mu_{ba}^y) \times \left\langle (\hat{Z} \cdot \hat{x})^4 \right\rangle$$

$$+ (\mu_{dc}^x \mu_{ad}^y \mu_{cb}^y \mu_{ba}^x + \mu_{dc}^y \mu_{ad}^x \mu_{cb}^x \mu_{ba}^y) \times \left\langle (\hat{Z} \cdot \hat{x})^2 (\hat{Z} \cdot \hat{y})^2 \right\rangle$$

$$+ (\mu_{dc}^x \mu_{ad}^y \mu_{cb}^x \mu_{ba}^y + \mu_{dc}^x \mu_{ad}^x \mu_{cb}^y \mu_{ba}^y + \mu_{dc}^y \mu_{ad}^x \mu_{cb}^x \mu_{ba}^y + \mu_{dc}^y \mu_{ad}^y \mu_{cb}^x \mu_{ba}^y) \times \left\langle (\hat{Z} \cdot \hat{x})^2 (\hat{Z} \cdot \hat{y})^2 \right\rangle$$

(EPAPS.18)
The forms of the averages above are readily adaptable to the ESE and ESA signals.

Finally, the sum over pathways in Eqs. (EPAPS.15) to (EPAPS.17) is carried out with a series of four loops. The total parallel and perpendicular transients are calculated from a sum of GSB, ESE, and ESA.

\[
S_\parallel = S_{\parallel}^{GSB} + S_{\parallel}^{ESE} - S_{\parallel}^{ESA} \quad \text{ (EPAPS.20)}
\]

\[
S_\perp = S_{\perp}^{GSB} + S_{\perp}^{ESE} - S_{\perp}^{ESA} \quad \text{ (EPAPS.21)}
\]

ESA makes a negative contribution to the signal because it reduces the probe intensity instead of increasing it, as is the case for ESE and GSB. The time dependent anisotropy, \( r(T) \), is calculated from these amplitudes

\[
r(T) = (S_\parallel (T) - S_\perp (T)) / (S_\parallel (T) + 2S_\perp (T)). \quad \text{ (EPAPS.22)}
\]

The Fortran code for these calculations is reproduced in Appendices A2 and A3 of ref. [16].

Calculations were run to check the convergence of the code for a single pair of \( b_{1g} / b_{2g} \) modes. For the calculations described in the paper, parallel and perpendicular signals are converged to within 4 significant digits when 15 vibrational eigenstates are included for each coordinate. In testing convergence, it was found that thermally excited vibrational levels on the ground electronic state play an important role in the calculated anisotropy decay. This requires diagonalization of a fairly large matrix (450x450) even though the strong transitions all obey
\[ \Delta v = 0, \pm 1 \] selection rules. Most of the computational time is spent in the sum over cosinusoidal terms.

The converged calculations were checked by comparison to analytic results for the initial electronic anisotropies, the time-dependent anisotropies from Brownian oscillator models, and the vibrational anisotropies of \( b_{2g} \) modes. Purely vibrational quantum beats cancel in the impulsive limit, in agreement with ref. [4] and the discussion in the main paper. This cancellation can be eliminated by dropping transitions from the sum, as suggested by diagrammatic calculations. This restricted summation approach was used to calculate the vibrational anisotropy of purely vibrational quantum beats.

References


