Theory of Vibrational Circular Dichroism and Infrared Absorption: Extension to Molecules with Low-Lying Excited Electronic States

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A vibronic theory of unpolarized infrared absorption and vibrational circular dichroism (VCD) is presented that is valid in the limit of vibrational resonance with low-lying electronic states (LLESs). The theory is developed within the complete adiabatic vibronic coupling formalism that describes both the correlation of electron density to nuclear positions and the correlation of electron current density to nuclear velocities. It is found that additional terms contribute to the electric-dipole and magnetic-dipole transition moments that become zero in the limit where all excited electronic states in the molecule are much higher in energy relative to fundamental vibrational transitions. Two correction terms appear that are extensions of the lowest-order non-Born−Oppenheimer expansion term when vibronic detail is included in the energy denominators. One term is a resonance term with respect to the energy difference between the electronic and vibrational transitions, and the other is a nonresonance term. Under the assumption that vibrational sublevels in LLES are not significantly changed from those in the ground electronic state, the two correction terms can be reduced to a simple frequency-dependent factor that becomes unity in the limit that electronic-state transitions are much higher than vibrational transition energies. The theory is applied to the case of transitions to LLESs that are electric-dipole forbidden and magnetic-dipole allowed, and the relation of these expressions to recent experimental results of VCD enhanced by such LLESs is discussed.

I. Introduction

The theory of unpolarized infrared (IR) absorption and vibrational circular dichroism (VCD) is well-established.[1−6] The theory has been developed within the framework of several traditional assumptions. The most fundamental of these is that the manifold of excited electronic states in the molecule is much higher in energy than the manifold of fundamental vibrational transitions. In particular, there is an absence of low-lying electronic excited states (LLESs) that may be close to or within the manifold of vibrational transitions. Relaxing this assumption requires a modification of the theory of unpolarized IR and VCD intensities.

The vibronic coupling theory (VCT) of VCD intensities, including demonstration of the formal equivalence of the position and velocity forms of IR absorption, was first published in 1983.[4] Subsequently, the theory of the velocity form of IR intensity and VCD was formulated in terms of adiabatic dependence on nuclear velocities, as well as the traditional nuclear positions.[7] It was shown that the lowest-order correction to the Born−Oppenheimer (BO) approximation provides a correlation between vibrationally induced electron *current density* in an electronic state and the *velocities* of the nuclei. This is the dynamic analogue of the correlation between electron probability density and nuclear positions that is found within the BO approximation. This level of theory is called the complete adiabatic (CA) approximation because the complex electronic wave function, which depends parametrically on both the nuclear positions and the momenta, can be factored from the vibrational wave function. More recently, this theory has been extended to the electron transition current density that can be visualized for transitions between any pair of states in molecules[8] and in particular for pure electronic transitions[9] and pure vibrational transitions.[10] In the case of vibrational transitions, the electron transition current density, a vector field, is the electron motion complement to the nuclear displacement vectors associated with the molecular vibrational motion of a particular normal mode.

Starting from the VCT theory of VCD, it has been shown that the formal sum over states associated with the expression for the electronic contribution to the magnetic-dipole transition moment can be avoided by introduction of a magnetic field perturbation (MFP).[5,6] This is most recently calculated using coupled Hartree−Fock perturbation theory. Similarly, VCD can be formulated in terms of a nuclear velocity perturbation (NVP)[3] where origin independence is guaranteed by use of an electronic wave function with nuclear velocity gauges on atomic orbitals. Analogously, the MFP theory can be formulated using magnetic-field gauge-invariant atomic orbitals, and it is this form of the theory that is currently available in the VCD intensity subroutine of Gaussian 98 and Gaussian 03.[11] The NVP formulation of VCD has not yet been programmed.

IR intensities are proportional the absolute square of the electric-dipole transition moment. The position form of this transition moment can be expressed fully within the BO approximation, and the lowest-order BO correction term vanishes. Conversely, the velocity form of this transition moment is described equivalently with the lowest-order BO correction term and the BO approximation contribution vanishes. Computationally, the velocity formulation of the IR intensity is found to be less accurate than the position form, and the two only become identical in the limit of the exact electronic wave function. The magnetic-dipole transition moment is expressed in direct analogy to the velocity form of the electric-dipole transition moment and, hence, is fully described to the first order

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by the non-BO correction term. In this paper, it is shown that as the energy of the electronic states in a molecule approach those of the vibrational states, the separation between these two intensity mechanisms is lost and new non-BO contributions appear for all three of these formulations of transition moments.

Motivation for pursuing this theoretical development has arisen over the years from experimental studies involving enhanced or unusually large VCD intensities associated with molecules possessing transition metals or rare earth metals. In the first full paper published on VCD, the VCD spectra of two rare earth complexes with (+)-camphorato-type ligands are presented, one of praseodymium and the other europium.[12] The two otherwise identical complexes have nearly identical IR spectra and similar but significantly different VCD spectra owing possibly to the presence of magnetic-dipole *f*−*f* transitions in the IR region of the spectrum. There is a hint of a small bisignate electronic circular dichroism (CD) band, with no associated absorption band, in the Eu(III) complex.

A more dramatic example is the observation several years later of the IR and VCD spectra of Zn(II), Co(II), and Ni(II) complexes of (+)-sparteine in the CH stretching.[13] Here, all three complexes exhibit nearly the same IR absorption spectrum whereas the VCD of all three complexes are significantly different from one another. The Zn(II) complex possesses a typical VCD spectrum, whereas the Co(II) and Ni(II) VCD spectra are different from that of Zn(II) and one another and are enhanced by nearly an order of magnitude. The VCD spectra of Co(II) and Ni(II) are superimposed on broad backgrounds of IR electronic CD of completely different character for the two complexes. The fact that the IR spectrum is virtually the same for all three complexes implies that the *d*−*d* transitions are still strongly electric-dipole forbidden and magnetic-dipole allowed and, therefore, make an insignificant contribution to an electric-dipole transition moment. We have repeated these measurements recently with Fourier transform VCD instrumentation and have extended the measurements into the mid-IR region where there is no discernible underlying electronic CD intensity.[14] Here again, the IR spectra are nearly identical and the VCD spectra are different for all three complexes. The Zn(II) complex is not enhanced and the Co(II) and Ni(II) VCD spectra are enhanced differently by approximately one order of magnitude over that of the Zn(II) complex.

Other examples of transition metal complexes with enhanced VCD are confined mainly to small ligands, such as azide and cyanide, in metalloproteins, such as myoglobin and hemoglobin. VCD associated with the lone stretching vibrations of these ligands gives rise to enhanced VCD with a ratio of VCD to IR intensity of approximately of 10^{-3}. These vibrational modes gain VCD intensity from their chiral environment and borrow intensity from low-lying *d*−*d* transitions in the low-spin Fe(II) center of these heme proteins.[15,16] More examples of transition metal enhanced VCD have been obtained recently from measurements in our laboratory, and these will be reported in future publications.

The remainder of this paper is organized as follows. First, a theoretical background section is presented to establish basic definitions and nomenclature for vibronic coupling formalism under the usual assumption of an absence of LLESs. In section III, the expressions for the transition moments needed for IR and VCD intensities are also defined and presented using standard VCT. Both the position and velocity forms of the electric-dipole transition moment are included because identical correction terms for LLESs are derived for these two formulations of IR intensities. In Section IV, the lowest-order correction terms to the wave functions and transition moments for LLESs are presented, and in the following section a reasonable approximation is introduced that simplifies the expression of these correction terms relative to the standard vibronic coupling formulation of IR and VCD intensities. Further sections of the paper deal with the consequences of these LLES-correction terms, including approaches to their calculation and experimental isolation.

II. Theoretical Background

IR intensities are expressed theoretically as the dipole strength, *D*. For a transition of the molecule between the 0 and the 1 levels of the *a*th vibrational mode in the ground electronic state g, one can write[2]

$$D_{\mathrm{g1,g0}}{}^{a} = |\langle \Psi_{\mathrm{g1}}{}^{a} | \mu_{\beta} | \Psi_{\mathrm{g0}}{}^{a} \rangle|^{2} \tag{1}$$

The dipole strength is the absolute square of the electric-dipole transition moment, always a positive quantity. The subscript β refers to a molecule-based Cartesian coordinate system where repeated occurrence of a Greek subscript, as present here, implies summation over all three Cartesian directions. The β component of the electric-dipole moment operator in the position form is given by

$$\mu_{\beta} = \mu_{\beta}{}^{\mathrm{E}} + \mu_{\beta}{}^{\mathrm{N}} = -\sum_{j} e r_{j\beta} + \sum_{J} Z_{J} e R_{J\beta} \tag{2}$$

where the sums are over the products of the charges and positions of the electrons and nuclei of the molecule.

IR intensities can also be expressed in the dipole velocity formalism, where the dipole strength is defined as[2]

$$D_{\mathrm{g1,g0}}{}^{a} = \omega_{a}{}^{-2} |\langle \Psi_{\mathrm{g1}}{}^{a} | \dot{\mu}_{\beta} | \Psi_{\mathrm{g0}}{}^{a} \rangle|^{2} \tag{3}$$

where ω_a is the angular vibrational frequency of normal mode *a* and the electric-dipole velocity operator is defined as

$$\dot{\mu}_{\beta} = \dot{\mu}_{\beta}{}^{\mathrm{E}} + \dot{\mu}_{\beta}{}^{\mathrm{N}} = -\sum_{j} e \dot{r}_{j\beta} + \sum_{J} Z_{J} e \dot{R}_{J\beta} = -\sum_{j} \frac{e}{m} p_{j\beta} + \sum_{J} \frac{Z_{J} e}{M_{J}} P_{J\beta} \tag{4}$$

where the velocity dipole operator is obtained from the product of the charge and the velocity of the electrons and the nuclei in the molecule and where the velocity can also be obtained from the ratio of the momentum to the mass of each particle.

The intensity of a VCD band is defined as the rotational strength

$$R_{\mathrm{g1,g0}}{}^{a} = \mathrm{Im}[\langle \Psi_{\mathrm{g0}}{}^{a} | \mu_{\beta} | \Psi_{\mathrm{g1}}{}^{a} \rangle \langle \Psi_{\mathrm{g1}}{}^{a} | m_{\beta} | \Psi_{\mathrm{g0}}{}^{a} \rangle] \tag{5}$$

where the magnetic-dipole moment operator is expressed in the notation of eqs 2 and 4 as

$$m_{\beta} = m_{\beta}{}^{\mathrm{E}} + m_{\beta}{}^{\mathrm{N}} = -\sum_{j} \frac{e}{2mc} \epsilon_{\beta\gamma\delta} r_{j\gamma} p_{j\delta} + \sum_{J} \frac{Z_{J} e}{2M_{J} c} \epsilon_{\beta\gamma\delta} R_{J\gamma} P_{J\delta} \tag{6}$$

and $\epsilon_{\beta\gamma\delta}$ is the alternating tensor that is +1 for even permutations of *xyz* and −1 for odd permutations. The rotational strength is the scalar product of two different transition moments, the electric-dipole and the magnetic-dipole transition moments. As such, the rotational strength can assume both positive and negative, as well as 0, values. Alternatively, the rotational strength can be defined using the velocity form of the electric-dipole transition moment as

$$R_{g1,g0}{}^{a} = \omega_{a}{}^{-1}\,\mathrm{Re}[\langle\Psi_{g0}{}^{a}|\dot{\mu}_{\beta}|\Psi_{g1}{}^{a}\rangle\langle\Psi_{g1}{}^{a}|m_{\beta}|\Psi_{g0}{}^{a}\rangle] \quad (7)$$

While this form of the rotational strength possesses the advantage of immediate origin independence, it is not often used, in preference to eq 5, because of the higher computational accuracy of calculation of the electric-dipole transition moment and, hence, IR intensities, in the position, rather than the velocity, dipole form. However, we provide this formalism as an alternative for reasons to be made clear in the following.

To develop further the electric-dipole and magnetic-dipole transition moments defined above, the molecular wave function is first factored into electronic and vibrational parts, and the nuclear dependence of the ensuing electronic wave function is expanded to first order in the nuclear variables. The molecular Hamiltonian at the level of the BO approximation can be written as a sum of separate electronic and nuclear parts

$$H_{\mathrm{BO}} = H_{\mathrm{E}} + H_{\mathrm{N}} \quad (8)$$

The Schrödinger equation then becomes

$$H_{\mathrm{BO}}\Psi_{\mathrm{ev}}(\mathbf{r},\mathbf{R}) = E_{\mathrm{ev}}\Psi_{\mathrm{ev}}(\mathbf{r},\mathbf{R}) = E_{\mathrm{ev}}\psi_{\mathrm{e}}(\mathbf{r},\mathbf{R})\,\phi_{\mathrm{ev}}(\mathbf{R}) \quad (9)$$

with the usual dependence of the electronic and nuclear wave functions on the electron and nuclear coordinates. This level of approximation is called the adiabatic approximation because the electronic wave function is separated from the nuclear wave function and depends parametrically on the positions of the nuclei. It is possible to express the adiabatic dependence of the electronic wave function on nuclear position in terms of first-order time-independent perturbation theory, called the Herzberg–Teller expansion, as

$$\psi_{\mathrm{e}}(\mathbf{r},\mathbf{R}) = \psi_{\mathrm{e}}{}^{0}(\mathbf{r}) + \sum_{\mathrm{s}\neq\mathrm{e}}\sum_{A}\frac{\langle\psi_{\mathrm{s}}{}^{0}|(\partial H_{\mathrm{E}}/\partial R_{A,\alpha})_{0}|\psi_{\mathrm{e}}{}^{0}\rangle R_{A,\alpha}}{E_{\mathrm{s}}{}^{0} - E_{\mathrm{e}}{}^{0}}\psi_{\mathrm{s}}{}^{0}(\mathbf{r}) \quad (10)$$

where the superscripts or subscripts 0 refer to the equilibrium nuclear position of the electronic *e* state of the molecule and repeated Greek subscripts are summed over *xyz* as mentioned above. This equation can also be expressed as

$$\psi_{\mathrm{e}}(\mathbf{r},\mathbf{R}) = \psi_{\mathrm{e}}{}^{0}(\mathbf{r}) + \sum_{\mathrm{s}\neq\mathrm{e}}\sum_{A}\langle\psi_{\mathrm{s}}{}^{0}|(\partial\psi_{\mathrm{e}}/\partial R_{A,\alpha})_{0}\rangle R_{A,\alpha}\psi_{\mathrm{s}}{}^{0}(\mathbf{r}) \quad (11)$$

and can be further reduced, if desired, by summing over the excited state electronic manifold to closure leaving only a Taylor expansion of the first-order dependence of the electronic wave function on nuclear positions, namely,

$$\psi_{\mathrm{e}}(\mathbf{r},\mathbf{R}) = \psi_{\mathrm{e}}{}^{0}(\mathbf{r}) + \sum_{A}[\partial\psi_{\mathrm{e}}(\mathbf{r})/\partial R_{A,\alpha}]_{0}R_{A,\alpha} \quad (12)$$

To extend the formalism to the lowest order beyond the BO adiabatic approximation, we include nuclear kinetic energy coupling between the electronic and nuclear motion as a perturbation term to the BO adiabatic Hamiltonian as

$$H + H_{\mathrm{E}} + H_{\mathrm{N}} + (T_{\mathrm{N}})_{\mathrm{perturb}} = H_{\mathrm{E}} + H_{\mathrm{N}} - \sum_{A}\frac{\hbar^{2}}{M_{A}}\left(\frac{\partial}{\partial R_{A,\alpha}}\right)_{\mathrm{elec}}\left(\frac{\partial}{\partial R_{A,\alpha}}\right)_{\mathrm{nucl}} \quad (13)$$

where the subscripts on the operators refer to the wave function on which the operator will be applied. From standard quantum mechanical perturbation theory, the perturbed vibronic wave function is now given by

$$\Psi_{\mathrm{ev}}(\mathbf{r},\mathbf{R}) = \psi_{\mathrm{e}}(\mathbf{r},\mathbf{R})\,\phi_{\mathrm{ev}}(\mathbf{R}) + \sum_{\mathrm{su}\neq\mathrm{ev}}\sum_{A}\left(\frac{\hbar^{2}}{M_{A}}\right)\frac{\langle\psi_{\mathrm{s}}|\partial/\partial R_{A,\alpha}|\psi_{\mathrm{e}}\rangle\langle\phi_{\mathrm{su}}|\partial/\partial R_{A,\alpha}|\phi_{\mathrm{ev}}\rangle}{E_{\mathrm{su}} - E_{\mathrm{ev}}}\psi_{\mathrm{s}}(\mathbf{r},\mathbf{R})\,\phi_{\mathrm{su}}(\mathbf{R}) \quad (14)$$

Here, the wave function is no longer factorable into the product of electronic and nuclear wave functions due principally to coupling of vibrational levels between different electronic states. However, separation can be reestablished by first writing the nuclear kinetic perturbation term as

$$(T_{\mathrm{N}})_{\mathrm{perturb}} = -i\hbar\sum_{A}\left(\frac{\partial}{\partial R_{A,\alpha}}\right)_{\mathrm{elec}}\dot{R}_{A,\alpha} \quad (15)$$

where the classical form of the nuclear velocity is used for that part of the wave function that is associated with the nuclear motion and the quantum mechanical form of the nuclear momentum operator, the coupling operator, is left for the electronic wave function

$$\Psi_{\mathrm{ev}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}}) = \psi_{\mathrm{e}}(\mathbf{r},\mathbf{R})\,\phi_{\mathrm{ev}}(\mathbf{R}) + i\hbar\sum_{\mathrm{su}\neq\mathrm{ev}}\sum_{A}\frac{\langle\psi_{\mathrm{s}}|\partial/\partial R_{A,\alpha}|\psi_{\mathrm{e}}\rangle\langle\phi_{\mathrm{su}}|\phi_{\mathrm{ev}}\rangle\dot{R}_{A,\alpha}}{E_{\mathrm{su}} - E_{\mathrm{ev}}}\psi_{\mathrm{s}}(\mathbf{r},\mathbf{R})\,\phi_{\mathrm{su}}(\mathbf{R}) \quad (16)$$

The wave function is now complex and able to support the existence of vibrationally induced electron current density by specifying nonzero values for the nuclear velocity, in analogy to magnetically induced electronic current density in the presence of finite magnetic fields.

Next, the vibronic detail from the energy denominator is removed, which permits summing over the excited vibronic states to closure and evaluation of wave functions and energies at the equilibrium nuclear configuration of state e. This yields a wave function factored into electronic and nuclear parts carrying parametric dependence on both the nuclear positions and nuclear velocities.

$$\Psi_{\mathrm{ev}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}}) = \left[\psi_{\mathrm{e}}(\mathbf{r},\mathbf{R}) + i\hbar\sum_{\mathrm{s}\neq\mathrm{e}}\sum_{A}\frac{\langle\psi_{\mathrm{s}}{}^{0}|(\partial\psi_{\mathrm{e}}/\partial\dot{R}_{A,\alpha})_{0}\rangle}{E_{\mathrm{s}}{}^{0} - E_{\mathrm{e}}{}^{0}}\psi_{\mathrm{s}}{}^{0}(\mathbf{r})\dot{R}_{A,\alpha}\right]\phi_{\mathrm{ev}}(\mathbf{R}) \quad (17)$$

The real part of the electronic wave function expresses the usual BO adiabatic dependence on nuclear position, while the imaginary part expresses the first-order non-BO dependence of the electronic wave function on nuclear velocity. By expanding the BO electronic wave function to first order in the nuclear position, the lowest-order dependences of the electronic wave function on both nuclear position and nuclear velocity can be expressed as[7]

$$\Psi_{\mathrm{ev}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}}) = \left\{\psi_{\mathrm{e}}{}^{0}(\mathbf{r}) + \sum_{\mathrm{s}\neq\mathrm{e}}\sum_{A}\left[\langle\psi_{\mathrm{s}}{}^{0}|(\partial\psi_{\mathrm{e}}/\partial R_{A,\alpha})_0\rangle R_{A,\alpha} + i\hbar\frac{\langle\psi_{\mathrm{s}}{}^{0}|(\partial\psi_{\mathrm{e}}/\partial R_{A,\alpha})_0\rangle}{E_{\mathrm{s}}{}^{0}-E_{\mathrm{e}}{}^{0}}\dot{R}_{A,\alpha}\right]\psi_{\mathrm{s}}{}^{0}(\mathbf{r})\right\}\phi_{\mathrm{ev}}(\mathbf{R}) \quad (18)$$

$$\Psi_{\mathrm{ev}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}}) = \left\{\psi_{\mathrm{e}}{}^{0}(\mathbf{r}) + \sum_{\mathrm{s}\neq\mathrm{e}}\sum_{A}\langle\psi_{\mathrm{s}}{}^{0}|(\partial\psi_{\mathrm{e}}/\partial R_{A,\alpha})_0\rangle\psi_{\mathrm{s}}{}^{0}(\mathbf{r}) \times \left[R_{A,\alpha} + \frac{i\hbar\dot{R}_{A,\alpha}}{E_{\mathrm{s}}{}^{0}-E_{\mathrm{e}}{}^{0}}\right]\right\}\phi_{\mathrm{ev}}(\mathbf{R}) \quad (19)$$

As has been previously stated, this wave function is factored into an electronic part, depending parametrically on nuclear positions and velocities, and contains both BO and non-BO terms. Because it is factored and has parametric nuclear dependence, it is still an adiabatic wave function, and to distinguish it from the normal definition of an adiabatic wave function it has been referred to as the CA wave function.[1-3,7]

III. Transition Moments, Polar Tensors, and Axial Tensors

The dipole strength and rotational strength, defined above for unpolarized IR absorption and VCD intensities, respectively, are defined in terms of electric- and magnetic-dipole transition moments. The electric-dipole transition moment can be written conveniently as sums over atomic contributions, which can in turn be written as products of atomic polar tensors (ATPs) $P_{\alpha\beta}{}^{A}$ multiplied by **s** vectors and nuclear vibrational transition moments. Assuming a fundamental vibrational transition from level 0 to level 1 of the normal mode a in the ground electronic state, one can write the electric-dipole transition moments as

$$\langle\Psi_{\mathrm{g0}}{}^{a}|\mu_\beta|\Psi_{\mathrm{g1}}{}^{a}\rangle = \langle\Psi_{\mathrm{g0}}{}^{a}|\mu_\beta{}^{\mathrm{E}}|\Psi_{\mathrm{g1}}{}^{a}\rangle + \langle\Psi_{\mathrm{g0}}{}^{a}|\mu_\beta{}^{\mathrm{N}}|\Psi_{\mathrm{g1}}{}^{a}\rangle = \sum_A P_{r,\alpha\beta}{}^{A}s_{A\alpha,a}\langle\phi_{\mathrm{g1}}{}^{a}|Q_a|\phi_{\mathrm{g0}}{}^{a}\rangle \quad (20)$$

$$\langle\Psi_{\mathrm{g0}}{}^{a}|\dot{\mu}_\beta|\Psi_{\mathrm{g1}}{}^{a}\rangle = \langle\Psi_{\mathrm{g0}}{}^{a}|\dot{\mu}_\beta{}^{\mathrm{E}}|\Psi_{\mathrm{g1}}{}^{a}\rangle + \langle\Psi_{\mathrm{g0}}{}^{a}|\dot{\mu}_\beta{}^{\mathrm{N}}|\Psi_{\mathrm{g1}}{}^{a}\rangle = \sum_A P_{r,\alpha\beta}{}^{A}s_{A\alpha,a}\,\langle\phi_{\mathrm{g1}}{}^{a}|P_a|\phi_{\mathrm{g0}}{}^{a}\rangle \quad (21)$$

where the **s** vectors are defined either in terms of nuclear position or velocity and convert the nuclear function dependence from Cartesian ($R_{A\alpha}$, $\dot{R}_{A\alpha}$) to normal (Q_a, $P_a = \dot{Q}_a$) coordinates

$$s_{A\alpha,a} = \left(\frac{\partial R_{A\alpha}}{\partial Q_a}\right)_{Q=0} = \left(\frac{\partial \dot{R}_{A\alpha}}{\partial \dot{Q}_a}\right)_{\dot{Q}=0} = \left(\frac{\partial \dot{R}_{A\alpha}}{\partial P_a}\right)_{P=0} \quad (22)$$

The ATP represents the derivative of the electric-dipole transition moment of the entire molecule with respect to the Cartesian displacement or velocity vector of the Ath atom. The ATP can also be divided into electron and nuclear contributions by writing

$$P_{r,\alpha\beta}{}^{A} = E_{r,\alpha\beta}{}^{A} + N_{\alpha\beta}{}^{A} \quad \text{or} \quad P_{v,\alpha\beta}{}^{A} = E_{v,\alpha\beta}{}^{A} + N_{\alpha\beta}{}^{A} \quad (23)$$

The corresponding parts of the electric-dipole transition moment in the position formalism are given by

$$\langle\Psi_{\mathrm{g0}}{}^{a}|\mu_\beta{}^{\mathrm{E}}|\Psi_{\mathrm{g1}}{}^{a}\rangle = \sum_A E_{r,\alpha\beta}{}^{A}s_{A\alpha,a}\langle\phi_{\mathrm{g1}}{}^{a}|Q_a|\phi_{\mathrm{g0}}{}^{a}\rangle \quad (24)$$

$$\langle\Psi_{\mathrm{g0}}{}^{a}|\mu_\beta{}^{\mathrm{N}}|\Psi_{\mathrm{g1}}{}^{a}\rangle = \sum_A N_{\alpha\beta}{}^{A}s_{A\alpha,a}\langle\phi_{\mathrm{g1}}{}^{a}|Q_a|\phi_{\mathrm{g0}}{}^{a}\rangle \quad (25)$$

with an analogous expression of for the velocity-dipole formalism. From eq 2, one can write

$$N_{\alpha\beta}{}^{A} = \left(\frac{\partial\mu_\beta{}^{\mathrm{N}}}{\partial R_{A\alpha}}\right)_{R=0} = Z_A e\delta_{\alpha\beta} \quad (26)$$

The corresponding expressions for magnetic-dipole transition moments start with the definition of the atomic axial tensor (AAT) given by

$$\langle\Psi_{\mathrm{g0}}{}^{a}|m_\beta|\Psi_{\mathrm{g1}}{}^{a}\rangle = \langle\Psi_{\mathrm{g0}}{}^{a}|m_\beta{}^{\mathrm{E}}|\Psi_{\mathrm{g1}}{}^{a}\rangle + \langle\Psi_{\mathrm{g0}}{}^{a}|m_\beta{}^{\mathrm{N}}|\Psi_{\mathrm{g1}}{}^{a}\rangle = \sum_A M_{\alpha\beta}{}^{A}s_{A\alpha,a}\langle\phi_{\mathrm{g1}}{}^{a}|P_a|\phi_{\mathrm{g0}}{}^{a}\rangle \quad (27)$$

where the electronic and nuclear parts of the AAT are defined as

$$M_{\alpha\beta}{}^{A} = I_{\alpha\beta}{}^{A} + J_{\alpha\beta}{}^{A} \quad (28)$$

and where

$$\langle\Psi_{\mathrm{g0}}{}^{a}|m_\beta{}^{\mathrm{E}}|\Psi_{\mathrm{g1}}{}^{a}\rangle = \sum_A I_{\alpha\beta}{}^{A}s_{A\alpha,a}\langle\phi_{\mathrm{g1}}{}^{a}|P_a|\phi_{\mathrm{g0}}{}^{a}\rangle \quad (29)$$

$$\langle\Psi_{\mathrm{g0}}{}^{a}|m_\beta{}^{\mathrm{N}}|\Psi_{\mathrm{g1}}{}^{a}\rangle = \sum_A J_{\alpha\beta}{}^{A}s_{A\alpha,a}\langle\phi_{\mathrm{g1}}{}^{a}|P_a|\phi_{\mathrm{g0}}{}^{a}\rangle \quad (30)$$

and where the nuclear AAT is given explicitly by

$$J_{\alpha\beta}{}^{A} = \left(\frac{\partial m_\beta{}^{\mathrm{N}}}{\partial \dot{R}_{A\alpha}}\right)_{R=0} = \frac{Z_A e}{2c}\epsilon_{\alpha\beta\gamma}R_{A\gamma}{}^{0} \quad (31)$$

as determined by eq 6. Finally, the relation between position and momentum transition matrix elements for normal coordinates in the harmonic approximation can be used.

$$\langle\phi_{\mathrm{g1}}{}^{a}|P_a|\phi_{\mathrm{g0}}{}^{a}\rangle = \langle\phi_{\mathrm{g1}}{}^{a}|\dot{Q}_a|\phi_{\mathrm{g0}}{}^{a}\rangle = i\omega_{\alpha\beta}\langle\phi_{\mathrm{g1}}{}^{a}|Q_a|\phi_{\mathrm{g0}}{}^{a}\rangle \quad (32)$$

The electronic parts of these transition moments can be developed further; however, the nuclear parts are already fully expressed in terms of simple algebraic expressions in the harmonic approximation. For the electric-dipole transition moment, substitution of eq 11 or 19 into eq 20 yields

$$\langle\Psi_{\mathrm{g1}}{}^{a}|\mu_\beta{}^{\mathrm{E}}|\Psi_{\mathrm{g0}}{}^{a}\rangle = 2\sum_{\mathrm{e}\neq\mathrm{g}}\sum_A\langle\psi_{\mathrm{g}}{}^{0}|\mu_\beta{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{e}}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle s_{A\alpha,a}\langle\phi_{\mathrm{g1}}{}^{a}|Q_a|\phi_{\mathrm{g0}}{}^{a}\rangle \quad (33)$$

and the following expression for the electronic part of the ATP,

$$E_{r\alpha,\beta}{}^{A} = 2\sum_{\mathrm{e}\neq\mathrm{g}}\langle\psi_{\mathrm{g}}{}^{0}|\mu_\beta{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{g}}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle \quad (34)$$

The factor of 2 arises from substitution into the electronic wave function in the transition moment and the fact the wave functions are real and Hermitian, allowing interchange of the wave functions in the matrix elements. As has been shown previously, the imaginary part of the wave function in eq 18 or 19 makes no contribution to IR intensities using the position form of the electric-dipole moment operator.

On the other hand, the velocity form of the electric-dipole transition moment derives none of its intensity from the real

(BO) part of eq 18 or 19 and is expressed entirely by the imaginary (non-BO) part of these equations. The transition moment is given by

$$\langle \Psi_{g1}{}^{a} | \dot{\mu}_{\beta}{}^{E} | \Psi_{g0}{}^{a} \rangle = 2i\hbar \sum_{e\neq g} \sum_{A} \frac{\langle \psi_{g}{}^{0} | \dot{\mu}_{\beta}{}^{E} | \psi_{e}{}^{0} \rangle \langle \psi_{e}{}^{0} | (\partial \psi_{g} / \partial R_{A,\alpha})_{0} \rangle s_{A\alpha,a} \langle \phi_{g1}{}^{a} | P_{a} | \phi_{g0}{}^{a} \rangle}{E_{e}{}^{0} - E_{g}{}^{0}} \tag{35}$$

and the corresponding expression for the electronic part of the ATP is

$$E_{v,\alpha\beta}{}^{A} = 2i\hbar \sum_{e\neq g} \sum_{A} \frac{\langle \psi_{g}{}^{0} | \dot{\mu}_{\beta}{}^{E} | \psi_{e}{}^{0} \rangle \langle \psi_{e}{}^{0} | (\partial \psi_{g} / \partial \mathrm{R}_{A,\alpha})_{0} \rangle}{E_{e}{}^{0} - E_{g}{}^{0}} \tag{36}$$

Equations 36 and 34 are formally equivalent as shown by use of the hypervirial relation,

$$\langle \psi_{e}{}^{0} | \dot{\mu}_{\beta}{}^{E} | \psi_{g}{}^{0} \rangle = i \frac{(E_{e}{}^{0} - E_{g}{}^{0})}{\hbar} \langle \psi_{e}{}^{0} | \mu_{\beta}{}^{E} | \psi_{g}{}^{0} \rangle \tag{37}$$

a condition satisfied only by exact electronic wave functions.

The electronic contribution to the magnetic-dipole transition moment can be written in an analogous fashion by substitution of eq 19 into eq 29.

$$\langle \Psi_{g1}{}^{a} | m_{\beta}{}^{E} | \Psi_{g0}{}^{a} \rangle = 2i\hbar \sum_{e\neq g} \sum_{A} \frac{\langle \psi_{g}{}^{0} | m_{\beta}{}^{E} | \psi_{e}{}^{0} \rangle \langle \psi_{e}{}^{0} | (\partial \psi_{g} / \partial \mathrm{R}_{A,\alpha})_{0} \rangle s_{A\alpha,a} \langle \phi_{g1}{}^{a} | P_{a} | \phi_{g0}{}^{a} \rangle}{E_{e}{}^{0} - E_{g}{}^{0}} \tag{38}$$

and the electronic contribution to the AAT is given by

$$I_{\alpha\beta}{}^{A} = 2i\hbar \sum_{e\neq g} \sum_{A} \frac{\langle \psi_{g}{}^{0} | m_{\beta}{}^{E} | \psi_{e}{}^{0} \rangle \langle \psi_{e}{}^{0} | (\partial \psi_{g} / \partial R_{A,\alpha})_{0} \rangle}{E_{e}{}^{0} - E_{g}{}^{0}} \tag{39}$$

Here, only the imaginary part of eq 19 contributes and the BO contribution vanishes. Thus, at this level of vibronic detail, there is complete separation between BO and non-BO contributions to the electric-dipole and magnetic-dipole transition moments for pure vibrational transitions.

IV. Lowest-Order Vibronic Theory Including LLESs

From the equations above, it is clear that IR and VCD intensities can be written as perturbation expressions involving sums over all electronic states. In particular, the electronic APTs in eqs 34 and 36 and the electronic AAT in eq 39 that describe the electronic contributions to the electric-dipole and magnetic-dipole moments, respectively, are expressed, directly or indirectly, with perturbation terms that contain energy denominators of the difference between the equilibrium-position energy of the excited electronic state s and the originating electronic state e. It is also clear, as a result of the omission of vibronic detail in the energy denominators, that these expressions break down in the limit where the energy of one or more LLESs s approaches the state e or lies very close to, or within, the manifold of vibration transitions being measured.

Equation 18 can be rewritten with retained vibronic detail in the non-BO term as

$$\Psi_{ev}(\mathbf{r}, \mathbf{R}) = \psi_{e}{}^{0}(\mathbf{r})\, \phi_{ev}(\mathbf{R}) + \sum_{s\neq e} \sum_{A} \langle \psi_{s}{}^{0} | (\partial \psi_{e} / \partial R_{A,\alpha})_{0} \rangle R_{A\alpha,a} \psi_{s}{}^{0}(\mathbf{r})\, \phi_{ev}(\mathbf{R}) + i\hbar \sum_{su\neq ev} \sum_{A} \frac{\langle \psi_{s}{}^{0} | (\partial \psi_{e} / \partial R_{A,\alpha})_{0} \rangle \langle \phi_{su} | \dot{R}_{A,\alpha} | \phi_{ev} \rangle}{E_{su}{}^{0} - E_{ev}{}^{0}} \psi_{s}{}^{0}(\mathbf{r})\, \phi_{su}(\mathbf{R}) \tag{40}$$

This wave function can be used to obtain more general expressions for the transition moments in eqs 33, 35, and 38 that represent fundamental vibrational transitions of normal mode *a* in the ground electronic state labeled g, where state e will now be taken to represent an excited electronic state. The required wave functions, taking into account the complex nature of eq 40 and dropping the explicit functional dependence of the electronic and vibrational wave functions, are

$$\Psi_{g0}{}^{a} = \psi_{g}{}^{0} \phi_{g0}{}^{a} + \sum_{e\neq g} \sum_{A} \langle \psi_{e}{}^{0} | (\partial \psi_{g} / \partial R_{A,\alpha})_{0} \rangle \partial R_{A\alpha,a} \psi_{e}{}^{0} \phi_{g0}{}^{a} + i\hbar \sum_{ev\neq g0} \sum_{A} \frac{\langle \psi_{e}{}^{0} | (\partial \psi_{g} / \partial R_{A,\alpha})_{0} \rangle \langle \phi_{ev} | P_{a} | \phi_{g0}{}^{a} \rangle s_{A\alpha,a}}{E_{ev}{}^{0} - E_{g0}{}^{0}} \psi_{e}{}^{0} \phi_{ev} \tag{41}$$

$$\Psi_{g1}{}^{a*} = \psi_{g}{}^{0} \phi_{g1}{}^{a} + \sum_{e\neq g} \sum_{A} \langle \psi_{e}{}^{0} | (\partial \psi_{g} / \partial R_{A,\alpha})_{0} \rangle Q_{a} s_{A\alpha,a} \psi_{e}{}^{0} \phi_{g1}{}^{a} + i\hbar \sum_{ev\neq g1} \sum_{A} \frac{\langle \psi_{e}{}^{0} | (\partial \psi_{e} / \partial R_{A,\alpha})_{0} \rangle \langle \phi_{g1}{}^{a} | P_{a} | \phi_{ev} \rangle s_{A\alpha,a}}{E_{ev}{}^{0} - E_{g1}{}^{0}} \psi_{e}{}^{0} \phi_{ev} \tag{42}$$

Insertion of these wave functions into the electronic contribution of eq 20 for the electric-dipole transition moment yields

$$\langle \Psi_{g1}{}^{a} | \mu_{B}{}^{E} | \Psi_{g0}{}^{a} \rangle = \Bigg[2 \sum_{e\neq g} \sum_{A} \langle \psi_{g}{}^{0} | \mu_{\beta}{}^{E} | \psi_{e}{}^{0} \rangle \langle \psi_{e}{}^{0} | (\partial \psi_{g} / \partial R_{A,\alpha})_{0} \rangle \langle \phi_{g1}{}^{a} | Q_{a} | \phi_{g0}{}^{a} \rangle + i\hbar \sum_{ev\neq g0} \sum_{A} \frac{\langle \psi_{g}{}^{0} | \mu_{\beta}{}^{E} | \psi_{e}{}^{0} \rangle \langle \psi_{e}{}^{0} | (\partial \psi_{g} / \partial R_{A,\alpha})_{0} \rangle \langle \phi_{g1}{}^{a} | \phi_{ev} \rangle \langle \phi_{ev} | P_{a} | \phi_{g0}{}^{a} \rangle}{E_{ev}{}^{0} - E_{g0}{}^{0}} + i\hbar \sum_{ev\neq g0} \sum_{A} \frac{\langle \psi_{g}{}^{0} | (\partial \psi_{e} / \partial R_{A,\alpha})_{0} \rangle \langle \psi_{e}{}^{0} | \mu_{\beta}{}^{E} | \psi_{g}{}^{0} \rangle \langle \phi_{g1}{}^{a} | P_{a} | \phi_{ev} \rangle \langle \phi_{ev} | \phi_{g0}{}^{a} \rangle}{E_{ev}{}^{0} - E_{g1}{}^{0}} \Bigg] s_{A\alpha,a} \tag{43}$$

In contrast to eq 33, this equation contains three terms instead of one. The first arises from within the BO approximation, and the next two are due to non-BO contributions that normally do not appear at the lowest level of the position form of the electric-dipole transition moment. For the two non-BO terms, the first arises from substitution of the non-BO part of eq 41 for the initial vibronic state, g0, whereas the second term represents substitution of the non-BO part of eq 42 for the final state, g1. In the absence of LLESs where the separation between excited electronic states is large compared to the vibronic sublevel energies, eq 43 reduces to the standard expression given in eq 33. This is accomplished by removing vibronic detail from the denominators in eq 43 and summing over excited vibronic states to closure. The two non-BO terms, when the electronic matrix elements are put in the same form (see the following), have opposite signs, cancel, and make no contribution.

The corresponding expression for the velocity form of the electric-dipole transition moment starting from the electronic part of eq 21 is given by

$$\langle \Psi_{g1}{}^{a}|\dot{\mu}_{B}{}^{E}|\Psi_{g0}{}^{a}\rangle = i\hbar \sum_{ev\neq g0}\sum_{A}\left[\frac{\langle \psi_{g}{}^{0}|\dot{\mu}_{B}{}^{E}|\psi_{e}{}^{0}\rangle\langle \psi_{e}{}^{0}|(\partial\psi_{g}/\partial R_{A,\alpha})_{0}\rangle\langle \phi_{g1}{}^{a}|\phi_{ev}\rangle\langle \phi_{ev}|P_{a}|\phi_{g0}{}^{a}\rangle}{E_{ev}{}^{0}-E_{g0}{}^{0}} + \frac{\langle \psi_{g}{}^{0}|(\partial\psi_{e}/\partial R_{A,\alpha})_{0}\rangle\langle \psi_{e}{}^{0}|\dot{\mu}_{B}{}^{E}|\psi_{g}{}^{0}\rangle\langle \phi_{g1}{}^{a}|P_{a}|\phi_{ev}\rangle\langle \phi_{ev}|\phi_{g0}{}^{a}\rangle}{E_{ev}{}^{0}-E_{g1}{}^{0}}\right]s_{A\alpha,a} \quad (44)$$

Here, the two non-BO terms in this equation do not cancel when the vibronic detail is removed and the electronic matrix elements are brought into the same form. Both represent the entire corrected contribution to the transition moment. The corresponding two terms in eq 43 serve only to correct the main BO term.

Similarly, substitution of eqs 41 and 42 into the electronic contribution of eq 27 for the magnetic-dipole transition moments yields

$$\langle \Psi_{g1}{}^{a}|m_{B}{}^{E}|\Psi_{g0}{}^{a}\rangle = i\hbar \sum_{ev\neq g0}\sum_{A}\left[\frac{\langle \psi_{g}{}^{0}|m_{B}{}^{E}|\psi_{e}{}^{0}\rangle\langle \psi_{e}{}^{0}|(\partial\psi_{g}/\partial R_{A,\alpha})_{0}\rangle\langle \phi_{g1}{}^{a}|\phi_{ev}\rangle\langle \phi_{ev}|P_{a}|\phi_{g0}{}^{a}\rangle}{E_{ev}{}^{0}-E_{g0}{}^{0}} + \frac{\langle \psi_{g}{}^{0}|(\partial\psi_{e}/\partial R_{A,\alpha})_{0}\rangle\langle \psi_{e}{}^{0}|m_{B}{}^{E}|\psi_{g}{}^{0}\rangle\langle \phi_{g1}{}^{a}|P_{a}|\phi_{ev}\rangle\langle \phi_{ev}|\phi_{g0}{}^{a}\rangle}{E_{ev}{}^{0}-E_{g1}{}^{0}}\right]s_{A\alpha,a} \quad (45)$$

This equation closely follows the velocity form of the electric-dipole transition moment in eq 44. Equations 44 and 45 reduce to the standard expressions given in eqs 35 and 38, respectively, by eliminating the vibronic detail in the denominators, as was described for the reduction of eq 43 to eq 33.

V. Vibronic Energy Approximation

The expressions for the electric- and magnetic-dipole transition moments can be simplified by invoking an approximation regarding the nature and energy of the excited-state vibrational wave functions. This approximation holds well for LLESs that, as a result of their small energy denominators, have the potential to make large contributions to the transition moment. It can be argued that any excited electronic state that lies above the ground electronic state by a small energy is not likely to have potential energy surfaces that differ significantly from those of the ground state. This is particularly true for metal-centered *d*−*d* or *f*−*f* transitions that have little effect on the vibrational motion of the molecule. A possible exception to this assumption may arise for molecules whose metal center possesses enough symmetry that the ground electronic state or the LLESs are degenerate. Under this circumstance, the molecule will distort its geometry in the degenerate state such that the degeneracy is broken by the Jahn−Teller effect. Under the assumption that the Jahn−Teller effect is not large compared to the splitting imposed by the coordination geometry of the complex, the following approximation can be invoked:

$$\phi_{ev} = \phi_{ev}{}^{a} = \phi_{gv}{}^{a} \quad (46)$$

This approximation may still work well for many vibrational modes in molecules with Jahn−Teller distortion, but only direct comparisons between theory and experiment will be able to address this point. Using the approximation of eq 46 in eq 43 and invoking harmonic oscillator selection rules yields

$$\langle \Psi_{g1}{}^{a}|\mu_{\beta}{}^{E}|\Psi_{g0}{}^{a}\rangle = \left[2\sum_{e\neq g}\sum_{A}\langle \psi_{g}{}^{0}|\mu_{\beta}{}^{E}|\psi_{e}{}^{0}\rangle\langle \psi_{e}{}^{0}|(\partial\psi_{g}/\partial R_{A,\alpha})_{0}\rangle\langle \phi_{g1}{}^{a}|Q_{a}|\phi_{g0}{}^{a}\rangle + i\hbar\sum_{e\neq g}\sum_{A}\frac{\langle \psi_{g}{}^{0}|\mu_{\beta}{}^{E}|\psi_{e}{}^{0}\rangle\langle \psi_{e}{}^{0}|(\partial\psi_{g}/\partial R_{A,\alpha})_{0}\rangle\langle \phi_{g1}{}^{a}|\phi_{g1}{}^{a}\rangle\langle \phi_{g1}{}^{a}|P_{a}|\phi_{g0}{}^{a}\rangle}{E_{e}{}^{0}-E_{g}{}^{0}+\hbar\omega_{a}} + i\hbar\sum_{e\neq g}\sum_{A}\frac{\langle \psi_{g}{}^{0}|(\partial\psi_{e}/\partial R_{A,\alpha})_{0}\rangle\langle \psi_{e}{}^{0}|\mu_{\beta}{}^{E}|\psi_{g}{}^{0}\rangle\langle \phi_{g1}{}^{a}|\phi_{g1}{}^{a}|P_{a}|\phi_{g0}{}^{a}\rangle\langle \phi_{g0}{}^{a}|\phi_{g0}{}^{a}\rangle}{E_{e}{}^{0}-E_{g}{}^{0}-\hbar\omega_{a}}\right]s_{A\alpha,a} \quad (47)$$

where we can explicitly evaluate the vibronic energy difference in the denominator. This expression can be simplified further by converting the electronic matrix elements to the same form by interchanging wave functions, with a change of sign of the nuclear-derivative matrix element but not the dipole-moment matrix element, and taking into account of the normalization of the vibrational wave functions,

$$\langle \Psi_{g1}{}^{a}|\mu_{\beta}{}^{E}|\Psi_{g0}{}^{a}\rangle = \left[2\sum_{e\neq g}\sum_{A}\langle \psi_{g}{}^{0}|\mu_{\beta}{}^{E}|\psi_{e}{}^{0}\rangle\langle \psi_{e}{}^{0}|(\partial\psi_{g}/\partial R_{A,\alpha})_{0}\rangle\langle \phi_{g1}{}^{a}|Q_{a}|\phi_{g0}{}^{a}\rangle + i\hbar\sum_{e\neq g}\sum_{A}\langle \psi_{g}{}^{0}|\mu_{\beta}{}^{E}|\psi_{e}{}^{0}\rangle\langle \psi_{e}{}^{0}|(\partial\psi_{g}/\partial R_{A,\alpha})_{0}\rangle \times \left(\frac{1}{E_{eg}{}^{0}+\hbar\omega_{a}} - \frac{1}{E_{eg}{}^{0}-\hbar\omega_{a}}\right)\langle \phi_{g1}{}^{a}|P_{a}|\phi_{g0}{}^{a}\rangle\right]s_{A\alpha,a} \quad (48)$$

It is now even easier to see that this equation reduces to eq 33 when the energy difference between the excited and the ground electronic states is large compared to vibrational energy spacings. The non-BO term simply vanishes. Despite the simplifying nature of the approximation leading to eq 48, the combination of excited-state energies and particular vibrational normal-mode frequencies mixes the contributions of the electrons and nuclei to the transition moment in a nonseparable way, in keeping with the spirit of the non-BO nature of the included correction terms for LLESs. The BO and non-BO terms in eq 48 can be brought into closer form in the following way. The momentum (velocity) vibrational matrix element in the non-BO term can be converted to the position form of this matrix element by using eq 32. After combining the energy terms over a common denominator, one obtains

$$\langle \Psi_{g1}{}^{a}|\mu_{\beta}{}^{E}|\Psi_{g0}{}^{a}\rangle = 2\sum_{e\neq g}\sum_{A}\langle \psi_{g}{}^{0}|\mu_{\beta}{}^{E}|\psi_{e}{}^{0}\rangle\langle \psi_{e}{}^{0}|(\partial\psi_{g}/\partial R_{A,\alpha})_{0}\rangle s_{A\alpha,a} \times \left[1+\frac{\omega_{\alpha}{}^{2}}{(\omega_{eg}{}^{0})^{2}-\omega_{a}{}^{2}}\right]\langle \phi_{g1}{}^{a}|Q_{a}|\phi_{g0}{}^{a}\rangle \quad (49)$$

One further algebraic simplification yields

$$\langle \Psi_{g1}{}^{a}|\mu_{\beta}{}^{E}|\Psi_{g0}{}^{a}\rangle = 2\sum_{e\neq g}\sum_{A}\langle \psi_{g}{}^{0}|\mu_{\beta}{}^{E}|\psi_{e}{}^{0}\rangle\langle \psi_{e}{}^{0}|(\partial\psi_{g}/\partial R_{A,\alpha})_{0}\rangle s_{A\alpha,a}\left[\frac{(\omega_{eq}{}^{0})^{2}}{\omega_{eg}{}^{0\,2}-\omega_{a}{}^{2}}\right] \times \langle \phi_{g1}{}^{a}|Q_{a}|\phi_{g0}{}^{a}\rangle \quad (50)$$

In eq 49, the first term is the BO contribution and the second is the non-BO correction. In the limit where the electronic energy spacing is large relative to the vibrational energy spacing, the correction term vanishes and this expression again reduces to the standard vibronic expression given by eq 33. Equation 50 is the generalized expression for the position form of the electric-dipole transition moment taking into account the possible close approach of an excited electronic state to the energy region of vibrational transitions. Equations 49 and 50 represent two equivalent algebraic ways of expressing the frequency-dependent correction associated with the presence of a LLES. One is the standard term plus a correction term, and the other is a modified standard term in a more compact representation.

From eq 50, it is now possible to write a generalization of the electronic ATP given in eq 34 as

$$E_{r,\alpha\beta}{}^{A}(\omega_a) = 2\sum_{\mathrm{e}\neq\mathrm{g}}\langle\psi_{\mathrm{g}}{}^{0}|\mu_\beta{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{e}}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle\left[\frac{(\omega_{\mathrm{eg}}{}^{0})^2}{(\omega_{\mathrm{eg}}{}^{0})^2-\omega_a{}^2}\right] \quad (51)$$

Here, the ATP is no longer independent of the normal modes of the molecule as indicated by its parametric dependence on the vibrational frequency of the *a*th normal mode. As mentioned above, inclusion of vibronic detail in BO correction terms introduces an interdependence of the vibrational motion on the electronic response of the molecule. Thus, in the presence of LLESs, one must envision a *set* of electronic ATPs for each atom *A* in the molecule, one for each normal mode *a*, instead of just one such ATP for each atom as in eq 34. The factor in brackets in eq 51 depends on both the frequencies of the excited electronic states and the individual vibrational modes in a nonseparable way.

Similar steps can be carried out for the electronic contribution to the velocity form of the electric-dipole transition moment. Here, both the matrix elements of the dipole velocity and nuclear derivative change sign upon interchange of electronic wave functions needed to bring the two non-BO terms of eq 44 into the same form,

$$\langle\Psi_{\mathrm{g}1}{}^{a}|\dot{\mu}_\beta{}^{\mathrm{E}}|\Psi_{\mathrm{g}0}{}^{a}\rangle = i\hbar\sum_{\mathrm{e}\neq\mathrm{g}}\sum_{A}\langle\psi_{\mathrm{g}}{}^{0}|\dot{\mu}_\beta{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{e}}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle s_{A\alpha,a} \times \left(\frac{1}{E_{\mathrm{eg}}{}^{0}+\hbar\omega_a}+\frac{1}{E_{\mathrm{eg}}{}^{0}-\hbar\omega_a}\right)\langle\phi_{\mathrm{g}1}{}^{a}|P_a|\phi_{\mathrm{g}0}{}^{a}\rangle \quad (52)$$

Combining the energy denominators and factoring out the pure electronic energy difference yields

$$\langle\Psi_{\mathrm{g}1}{}^{a}|\dot{\mu}_\beta{}^{\mathrm{E}}|\Psi_{\mathrm{g}0}{}^{a}\rangle = 2i\hbar\sum_{\mathrm{e}\neq\mathrm{g}}\sum_{A}\frac{\langle\psi_{\mathrm{g}}{}^{0}|\dot{\mu}_\beta{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{e}}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle s_{A\alpha,a}}{E_{\mathrm{eg}}{}^{0}} \times \left[\frac{(\omega_{\mathrm{eg}}{}^{0})^2}{(\omega_{\mathrm{eg}}{}^{0})^2-\omega_a{}^2}\right]\langle\phi_{\mathrm{g}1}{}^{a}|P_a|\phi_{\mathrm{g}0}{}^{a}\rangle \quad (53)$$

Here the same correction factor appears that is present in eq 50 where the reduction to the standard expression in eq 35 follows in the same way. The corresponding expression for the velocity form of the electronic ATP given is

$$E_{\mathrm{v},\alpha\beta}{}^{A}(\omega_a) = 2i\hbar\sum_{\mathrm{e}\neq\mathrm{g}}\frac{\langle\psi_{\mathrm{g}}{}^{0}|\dot{\mu}_\beta{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{e}}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle}{E_{\mathrm{eg}}{}^{0}}\left[\frac{(\omega_{\mathrm{eg}}{}^{0})^2}{(\omega_{\mathrm{eg}}{}^{0})^2-\omega_a{}^2}\right] \quad (54)$$

The hypervirial equation given in eq 37 exactly converts the new generalized expressions for the velocity form of the APT in eq 54 to the corresponding position form in eq 51 and vice versa. Neglecting the vibrational frequency term in the denominators of these expressions reduces them to their standard forms in eqs 34 and 36.

The generalized expressions for the electronic contribution to the magnetic-dipole transition moment follow closely the corresponding expressions for the velocity form of the electric-dipole transition moment.

$$\langle\Psi_{\mathrm{g}1}{}^{a}|m_\beta{}^{\mathrm{E}}|\Psi_{\mathrm{g}0}{}^{a}\rangle = \left[i\hbar\sum_{\mathrm{e}\neq\mathrm{g}}\sum_{A}\langle\psi_{\mathrm{g}}{}^{0}|m_\beta{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{e}}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle \times \left(\frac{1}{E_{\mathrm{eg}}{}^{0}+\hbar\omega_a}+\frac{1}{E_{\mathrm{eg}}{}^{0}-\hbar\omega_a}\right)\langle\phi_{\mathrm{g}1}{}^{a}|P_a|\phi_{\mathrm{g}0}{}^{a}\rangle\right] \quad (55)$$

Combining the two energy terms over a common denominator and factoring out the pure electronic energy difference, one obtains

$$\langle\Psi_{\mathrm{g}1}{}^{a}|m_\beta{}^{\mathrm{E}}|\Psi_{\mathrm{g}0}{}^{a}\rangle = 2i\hbar\sum_{\mathrm{e}\neq\mathrm{g}}\sum_{A,\alpha}\frac{\langle\psi_{\mathrm{g}}{}^{0}|m_\beta{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{e}}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle s_{A\alpha,a}}{E_{\mathrm{eg}}{}^{0}} \times \left[\frac{(\omega_{\mathrm{eg}}{}^{0})^2}{(\omega_{\mathrm{eg}}{}^{0})^2-\omega_a{}^2}\right]\langle\phi_{\mathrm{g}1}{}^{a}|P_a|\phi_{\mathrm{g}0}{}^{a}\rangle \quad (56)$$

Finally, the general form of the electronic contribution to the AAT is given by

$$I_{\alpha\beta}{}^{A}(\omega_a) = 2i\hbar\sum_{\mathrm{e}\neq\mathrm{g}}\frac{\langle\psi_{\mathrm{g}}{}^{0}|m_\beta{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{e}}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle}{E_{\mathrm{eg}}{}^{0}}\left[\frac{(\omega_{\mathrm{eg}}{}^{0})^2}{(\omega_{\mathrm{eg}}{}^{0})^2-\omega_a{}^2}\right] \quad (57)$$

This expression reduces to the traditional form given in eq 39 upon neglect of the vibrational frequency term in the denominator of eq 57.

VI. Bandwidth of Electronic Transitions

The generalized expressions for the transition moments and tensors given above possess a resonance denominator that becomes 0 when frequency separation between the excited and ground electronic state equals that of the vibrational transition. To avoid this unrealistic outcome, the bandwidth of the associated states needs to be taken into account. The ground electronic state has negligible bandwidth, compared to any of the excited electronic states, because it cannot decay to a lower state. The excited states in general appear to have large bandwidths compared to individual vibrational transitions. To avoid infinities in the resonance denominator, an imaginary

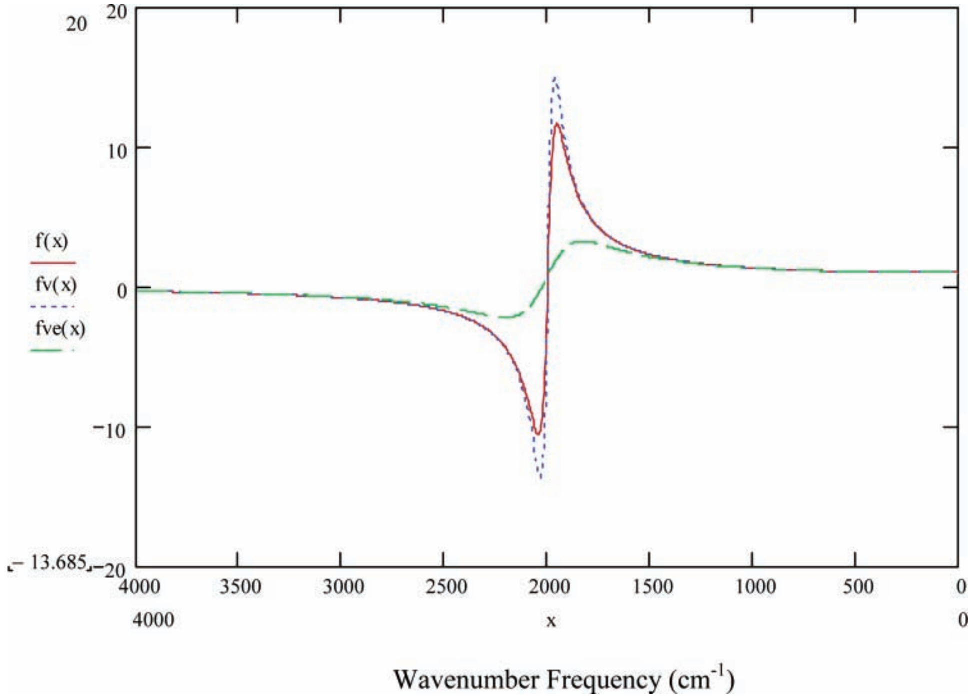

Figure 1. The real part of the frequency-dependent expression in the square brackets of eqs 58 and 59 as a function of vibrational frequency in wavenumbers. All three curves refer to a LLES at 2000 cm^{-1}. The curve $f(x)$ uses an electronic damping factor of 50 cm^{-1} and a vibrational damping factor 5 cm^{-1}. For $fv(x)$, these values change to 50 and 15 cm^{-1}, respectively, while the corresponding values for $fve(x)$ are 200 and 15 cm^{-1}

damping term, $i\Gamma_e$, is added to each occurrence of the electronic frequency difference between the electronic states e and g, and a damping term $i\gamma_a$ is added to each occurrence of the vibration frequency for mode a. Thus, for the electronic contribution to the position form of the electric-dipole transition moment one writes

$$\langle \Psi_{g1}{}^{a}|\mu_\beta{}^{E}|\Psi_{g0}{}^{a}\rangle = 2\sum_{e\neq g}\langle\psi_g{}^0|\mu_\beta{}^E|\psi_e{}^0\rangle\langle\psi_e{}^0|(\partial\psi_g/\partial Q_a)_0\rangle \times \left[1+\frac{(\omega_a+i\gamma_a)^2}{(\omega_{eg}{}^0+i\Gamma_e)^2-(\omega_a+i\gamma_a)^2}\right]\langle\phi_{g1}{}^a|Q_a|\phi_{g0}{}^a\rangle \quad (58)$$

Similarly, for the magnetic-dipole transition moment, the expression is

$$\langle \Psi_{g1}{}^{a}|m_\beta{}^{E}|\Psi_{g0}{}^{a}\rangle = 2i\hbar\sum_{e\neq g}\frac{\langle\psi_g{}^0|m_\beta{}^E|\psi_e{}^0\rangle\langle\psi_e{}^0|(\partial\psi_g/\partial Q_a)_0\rangle}{E_{eg}{}^0+i\hbar\Gamma_e} \times \left[1+\frac{(\omega_a+i\gamma_a)^2}{(\omega_{eg}{}^0+i\Gamma_e)^2-(\omega_a+i\gamma_a)^2}\right]\langle\phi_{g1}{}^a|P_a|\phi_{g0}{}^a\rangle \quad (59)$$

The resonance frequency expression between the excited electronic states and the vibrational state, in the large brackets, is written as the sum of unity, representing the standard expression, plus a correction term that vanishes when the excited-state energy is much larger than the vibrational energy. Another interesting limit is when the energy of a LLES goes to 0. In this case, the correction term has a limit of −1 that cancels the +1 representing the standard expression, and the contribution of that state to the transition moment vanishes. If the vibrational frequency is higher in energy than that of the LLES, the correction term is negative, and when vibrational frequency is lower in energy relative to the LLES, the correction term in positive. A plot of the real part of one plus the correction term (the quantity in square brackets in eqs 58 and 59) as a function of vibrational frequency for different choices of electronic and vibrational bandwidths for a LLES at 2000 cm^{-1} is shown in Figure 1. The expressions for the transition moments given in eqs 58 and 59 can be inserted into the expressions for the dipole strength and rotational strength given above to calculate IR and VCD intensities.

VII. Low-Lying Magnetic-Dipole-Allowed Excited Electronic States

The expressions developed above do not depend on the nature of the excited electronic states. An interesting and relatively common case is when a LLES is electric-dipole forbidden and magnetic-dipole allowed. This occurs for the $d-d$ transitions in transition metals with unfilled d levels, and similarly for the $f-f$ transition in rare earth elements. In the limit of pure magnetic-dipole character, there is no effect of these LLES transitions on the electric-dipole transition moments, ATPs, or IR intensities. On the other hand, the magnetic-dipole transition moments will be significantly affected, and the more general expressions just developed must be utilized to calculate the corresponding AATs and VCD intensities.

When considering low-lying electronic $d-d$ or $f-f$ transitions, the formalism developed in this paper could be rederived starting from degenerate, rather than nondegenerate, Rayleigh−Schrödinger perturbation theory. However, little value is seen at this time from this approach because for most chiral coordination-geometry perturbations, necessary for VCD, the symmetry of the degenerate metal-centered states is usually broken well beyond any electronic degeneracy and carrying that notation would serve little purpose. There may be some relatively rare cases of twofold- or threefold-symmetric chiral metal complexes where such an approach might prove useful in the description of the LLESs.

The generalized expression for the electronic contribution to the AAT given in eq 57 written as a sum of the conventional, frequency-independent term, $I_{\alpha\beta}{}^{A}$, given in eq 39, plus a frequency-dependent correction term and omitting the bandwidth terms, is given by

$$I_{\alpha\beta}{}^{A}(\omega_a) = 2i\hbar\sum_{\mathrm{e}\neq\mathrm{g}}\frac{\langle\psi_{\mathrm{g}}{}^{0}|m_{\beta}{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{e}}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle}{E_{\mathrm{eg}}{}^{0}} \times \left[1 + \frac{\omega_a{}^2}{(\omega_{\mathrm{eg}}{}^{0})^2 - \omega_a{}^2}\right] \quad (60)$$

The correction term in eq 60 is less than a 1% correction for electronic states when the transition energy for state e is 1 order of magnitude, or more, greater than the vibrational energy of the *a*th normal mode of the molecule. As a result, as a reasonable approximation, it is necessary to include the correction term only for LLESs. The standard term and the correction term are written in terms of AAT symbols in eq 61 where the primed term is the frequency-dependent correction term.

$$I_{\alpha\beta}{}^{A}(\omega_a) = I_{\alpha\beta}{}^{A} + I_{\alpha\beta}{}'^{A}(\omega_a) \quad (61)$$

An approximation for the correction term is given in eq 62 where only LLESs labeled e′ are included in the summation.

$$I_{\alpha\beta}{}'^{A}(\omega_a) \cong 2i\hbar\sum_{\mathrm{e}'}\frac{\langle\psi_{\mathrm{g}}{}^{0}|m_{\beta}{}^{\mathrm{E}}|\psi_{\mathrm{e}}{}^{0}\rangle\langle\psi_{\mathrm{e}'}{}^{0}|(\partial\psi_{\mathrm{g}}/\partial R_{A,\alpha})_0\rangle}{E_{\mathrm{e}'\mathrm{g}}{}^{0}}\left[\frac{\omega_a{}^2}{(\omega_{\mathrm{e}'\mathrm{g}}{}^{0})^2 - \omega_a{}^2}\right] \quad (62)$$

Another division of these equations that is useful to consider is to separate further the standard AAT tensor, $I_{\alpha\beta}{}^{A}$, into terms involving electronic states that are far from vibrational energies from the state or states that are low-lying and needed for the correction term in eq 62. This expression for the AAT is given by

$$I_{\alpha\beta}{}^{A}(\omega_a) = I_{\alpha\beta}{}^{A}(\mathrm{e}\neq\mathrm{e}') + I_{\alpha\beta}{}^{A}(\mathrm{e}') + I_{\alpha\beta}{}'^{A}(\omega_a) \quad (63)$$

Here, the first two terms depend only on the electronic energies in the usual way, and the last term is the same as that in eq 62. For the case of two molecules that possess identical bonding properties but differ in the presence or absence of LLESs, say transition metal complexes with these properties, the first term in eq 64 applies to the molecule with no LLESs, whereas two correction terms apply to an otherwise identical molecule with LLESs. The first correction term can be calculated using standard VCD algorithms, whereas the second correction term must be added for each LLES and each vibrational mode under consideration.

If only the magnetic-dipole transition moment needs correction for a LLES, this separation of correction carries directly forward to the rotational strength in a linear manner. Thus, using the same notation as used for the AAT, the rotational strength can be written as

$$R_{\mathrm{g1,g0}}{}^{a}(\omega_a) = R_{\mathrm{g1,g0}}{}^{a}(\mathrm{e}\neq\mathrm{e}') + R_{\mathrm{g1,g0}}{}^{a}(\mathrm{e}') + R_{\mathrm{g1,g0}}{}'^{a}(\omega_a) \quad (64)$$

and no corrections are needed for the ATPs and the dipole strength.

VII. Discussion

The expressions for the transition moments and tensors developed for IR and VCD intensities represent generalizations of the standard expressions that take into account the possible occurrence of LLESs in molecules. The standard expressions will show intensity enhancement in the IR, VCD, or both, depending on the nature of the LLES. The new terms derived here provide a source of additional intensity enhancement from the vibronic detail in the denominators of the BO correction terms, which are normally neglected as unimportant.

Previous expressions for VCD through the magnetic-dipole transition moment and IR intensity through the velocity form of the electric-dipole transition moment involve corrections terms to the BO approximation as explained previously. The final expressions, through the reasonable approximation of no vibronic detail for excited electronic states, are factorable contributions of the electronic and nuclear motion to the electronic part of the transition moment. This is the essence of the CA approximation where one uses expressions that are non-BO in origin but adiabatic in the factored separation of electronic and nuclear contributions. The new correction terms from LLESs introduced in this paper involve terms that are both non-BO and nonadiabatic in the sense that contributing electronic excited states and excited vibrational states appear together in the same terms in a nonfactorable form. This prevents the clean definition of the electronic ATPs and AATs in terms of pure electronic properties. Rather, these tensors now carry a frequency dependence for the particular vibrational mode considered, and the ATPs and AATs change in their contributions from one vibrational mode to another. This dependence of the AAT on the frequency of the vibrational mode is plotted in Figure 1.

Several interesting features can be discerned from the dependence of the AAT correction term on the frequency of the vibrational mode shown in Figure 1. It is clear that, independent of choices of bandwidth for the electronic or vibrational states, there is a dramatic rise in intensity as resonance is approached followed by a sigmoidal change in sign passing through zero at exact resonance. This makes the VCD intensity very sensitive to the transition energy of the LLES, when comparing experiment to theoretical calculation. The magnitude of the correction term relative to unity is modulated by the choice of bandwidths. The final AAT is obtained by adding the nuclear contribution to the AAT that also modifies the effect of the correction term. Clearly from the correction term, increases in the size of the electronic contribution to the AAT can be realized by up to an order of magnitude over the size of the AAT without the correction term. And it is clear that even without the correction term, considerable increase in the size of the AAT can be present from the energy denominator that is part of the standard expression for the AAT.

As expressed by eqs 63 and 64, one can envision three levels of contribution to the electronic part of an AAT or the rotational strength when a magnetic-dipole-allowed LLES is present in a molecule: (1) There is the contribution that would be present in the absence of such a state. In the case of LLES from *d*−*d* or *f*−*f* transitions in transition or rare earth elements, respectively, one can consider a molecule containing such metal atoms where the *d* shell or *f* shell is filled or high-spin half-filled, and where such transitions cannot occur. (2) There is the contribution due to a LLES that arises routinely within the standard formalism. Both contribution 1 and contribution 2 can be calculated with existing programs on the basis of the standard theory of VCD because such programs depend explicitly or implicitly on all the excited electronic states defined by the calculational scheme. In particular, use of the MFP VCD calculations produce contributions for each of these two sources. (3) The third contribution is the new correction term that depends on the relative sizes of the squares of the frequencies of the LLES and the vibrational mode of the molecule. This contribution is currently not present in any existing VCD calculational formalism. Most likely, it cannot be calculated using the existing MFP methodology. From the present perspective, it appears that this contribution may only be calculated by an approach where the contributions of individual LLESs and particular vibrational transitions are explicitly taken into account.

Several examples of VCD bands or spectra enhanced by the presence of LLESs have been reported in the literature. The clearest example is that of the transition metal complexes of sparteine, first observed by Mason and co-workers in 1980 for CH stretching vibrations[13] and most recently in our laboratory repeated and extended to the mid-IR vibrational frequency range using Fourier transform instrumentation.[14] In these cases, VCD spectra from three different sparteine complexes were measured. The Zn(II) complex has no LLESs, whereas the corresponding Co(II) and Ni(II) complexes have LLESs that are strongly magnetic-dipole-allowed. These complexes have nearly identical IR spectra but dramatically different VCD spectra. The first term in eq 63 corresponds to the AAT for the Zn(II) complex. The second term carries the contributions that can be calculated using the conventional AAT expression in eq 39 due to the presence of the LLESs of the Co(II) and Ni(II) complexes, and the last term in eq 63 is the new correction term derived in this paper. This term provides an additional correction that depends on both the electronic energy of the LLES and the vibrational energy of the transition in question. If the spacing between the electronic and vibrational states becomes sufficiently small, electronic and vibrational bandwidth terms need to be included as shown in eq 59.

Examples such as the one just cited may allow for isolation of VCD enhancement contributions from those of the ordinary VCD intensity. In particular, it is noted that the second and third enhancement terms in eq 63 differ term by term only by the frequency correction factor and that comparing VCD experimental spectra to calculated VCD with and without LLESs may permit the modeling of correction terms currently not included in any theoretical formalisms.

Although the need to introduce imaginary damping terms in the frequency correction factors to avoid infinities in the frequency denominators has been described in eqs 58 and 59, a complete bandwidth formalism, including the background electronic CD intensity, has not been developed at this time. Such considerations could also lead to interferences between electronic CD and VCD intensity, sometimes referred to as Fano terms,[17] as previously noted in a theoretical study of electronic CD intensities.[18]

It is clear from the development of this paper that VCD spectra under the conditions of intensity enhancement from LLESs have contributions from existing theoretical formalism, from new formalism as derived in this paper, and possibly from interference effects between electronic CD and VCD as the strong resonance between electronic and vibrational transitions is approached and realized.

VIII. Conclusion

In this paper, an extension of the standard theoretical expressions for IR and VCD intensities is presented. The more general expressions for the APT and AAT contain a frequency-dependent correction term that is unity in the absence of LLESs, but for such states large intensity enhancements may arise as resonance between the LLES energy and the vibrational energy is approached. For a sufficiently close approach, damping terms for the electronic and vibrational states must be included to avoid vanishing energy denominators in the correction terms. Interference between VCD intensity of electronic and vibrational origin occurring at the same point in the spectrum is also possible that would produce distorted vibrational band shapes.

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