Theory of fluorescence excitation spectra using anharmonic-coriolis coupling in S_1 and internal conversion to S_0. I. General formalism

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A treatment of one- or two-photon fluorescence excitation spectra is described using the vibration–rotation coupling of zeroth order states in the excited electronic state and nonadiabatic coupling to the ground state. Using perturbation theory, experimental harmonic frequencies, an anharmonic force field, and various theoretical Coriolis coupling constants, a quasistationary molecular eigenstate in an excited electronic state S_1 is first calculated. The S_1 eigenstate is then coupled via the nonadiabatic nuclear kinetic energy operator (internal conversion) to rovibronic states in the ground state manifold, the latter states approximated in a simple manner. A search algorithm is used to select the S_1 dark states and the S_0 states. Both the perturbation theory coefficient and the Franck–Condon factors are employed in the evaluation function used in the search. The results are applied in part II to the channel three problem in benzene.

I. INTRODUCTION

Radiationless transitions, internal conversion (IC), and intersystem crossing (ISC) in molecules have been the subject of numerous studies.[1–4] Both processes may compete with radiative decay channels, such as fluorescence from spin singlets and phosphorescence from spin triplets. The behavior of an isolated molecule under collision-free conditions is determined by the density of states at the energy of the prepared vibronic state in the initial electronic state, the density of states in the final electronic state at the same energy, and other more specific factors. The small, intermediate, and large molecule cases[2,3] result from the interplay of these state densities with the magnitude of the various couplings.

One of the systems where an increasingly detailed body of spectroscopic information has become available is benzene. In the benzene system, a "channel three" region occurs, namely, a region where the benzene fluorescence disappears rather suddenly with increasing excess energy in the first excited singlet state S_1. It occurs at an energy somewhat above 3000 cm^{-1}. The explanation most frequently invoked is that of internal conversion.[5–8] In early, vibrationally resolved studies below channel three, intersystem crossing was cited as the dominant channel for radiationless decay in benzene.[9] However, whereas the ISC rate is weakly dependent on the initial vibrational energy in S_1, the IC rate increases greatly with increasing vibrational energy.[10,11] Thereby, IC becomes the dominant decay channel at energies over 3000 cm^{-1}. In the past decade, the J and K dependencies of the fluorescence excitation spectra of various bands in benzene have been studied,[5–8] J referring to the total angular momentum and K to its component along the sixfold symmetry axis. Our own interest was prompted by these results and their relationship to more general questions such as intramolecular vibrational relaxation and "non-Rice–Ramsperger–Kassel–Marcus (RRKM)" behavior. In the present paper, a treatment of the problem is formulated, drawing on previous work. It is applied in part II[12] to the channel three problem.

In the present paper, the internal conversion and the fluorescence quantum yield and excitation spectra are treated. A vibrational–rotational perturbation expression is set up for a quasimolecular eigenstate in the excited electronic state S_1. The availability of a cubic anharmonic force field and various low and higher order Coriolis coefficients for benzene makes a detailed application appealing. Numerous states enter into the perturbation expression, and their relative importance for inclusion in the wave function is assessed using a search algorithm which weights the state according to its Franck–Condon factors for internal conversion and according to its coefficient in the perturbation expression. The S_1 quasimolecular eigenstate is then introduced into a "discrete state in a continuum formalism" to obtain the behavior of the resulting spectral line including its width and fluorescence intensity.

One question is whether or not, for the molecule and energy investigated, the bath of states in S_1 form a continuum, or a lumpy continuum, which is coupled to the light state and to the continuum of states in S_0. When there are about N important states per cm^{-1} in S_1 that couple significantly to the light state N as estimated later in this paper, the "molecular eigenstates" in S_1 in which the light zeroth order state has a significant contribution have a mean separation of $1/N$ cm^{-1}. When this separation is significantly larger than the experimental width of the rotational line of interest in S_1, one can use, as in the present paper, a single S_1 molecular eigenstate to treat the present phenomenon and couple it with the continuum of states in S_0. A procedure modified from that used here would be needed in cases where there are a number of S_1 molecular eigenstates involving the light state within the observed width of the rotational line. Furthermore, the presumption

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of a single light state is not essential, and the treatment can be extended to the more general case.

The outline of the paper is as follows: In Sec. II, the interaction of a quasieigenstate of a molecule in S_1 with a large number of states in S_0 is discussed, using the discrete state in a continuum formalism. Expressions for the fluorescence quantum yield and fluorescence excitation spectral intensity are given in Eqs. (2.1) and (2.2) for the one- and two-photon absorption cases, respectively. The nonradiative linewidth which appears in Eq. (2.3) is treated in Sec. III using a golden rule type formula, account being taken of the explicit S_1 and S_0 states to be summed over, as selected by an artificial intelligence (AI) search. Evaluation of matrix elements for the internal conversion is discussed there. In Sec. IV, the method used for determining terms in the quasieigenstate in S_1, which is dominantly the zeroth order light state in character, is described, using high order perturbation theory. In Sec. V, the selection of states in the dense manifold of S_0 states is discussed. A brief summary is given in Sec. VI.

II. FLUORESCENCE EXCITATION SPECTRUM

The model of a single state coupled to a quasicontinuum of states has been treated theoretically many times, e.g., Ref. 13–15. This model, which has also been applied to predissociation,[16,17] among other problems, is useful for treating the two-photon Doppler-free fluorescence excitation spectra of particular interest in part II. The density of states in the ground state electronic manifold S_0 is so high that it can be regarded as a quasicontinuum of those states at the energies of interest.[18,19]

In applying this formalism to the channel three benzene problem, the discrete state consists of the "light" state in S_1 perturbed by other (dark) zeroth order states in S_1, the light state in part II being $|14^1 1^2; J,K\rangle$. The most important dark states in part II typically differ from that state by five or six vibrational quanta.

In a fluorescence excitation spectrum, the total fluorescence intensity is measured at a given absorption frequency, upon integrating the fluorescence over all emission frequencies. In the present case, the fluorescence quantum yield under collision-free conditions ϕ_f in a simple kinetic prescription for a single rotational line is given by

$$\phi_f = k_f/(k_f+k_{\rm IC}+k_{\rm ISC}) \tag{2.1}$$

$$\approx k_f/(k_f+k_{\rm IC}) = \Delta_f/(\Delta_f+\Delta_{\rm IC}), \tag{2.2}$$

where k_f, $k_{\rm IC}$, and $k_{\rm ISC}$ are rate constants for the competing processes of fluorescence, internal conversion, and intersystem crossing, respectively, and the Δ's are the corresponding linewidths for the excited state eigenstates ($\Delta_{\rm IC} = k_{\rm IC}$ in Hertz). Equation (2.2) follows in the absence of intersystem crossing, which can be important in the decay of other vibronic bands, however.[20] The quantity k_f is known, in the case of benzene, from experiments in which the excitation is of vibronic bands in the S_1 state well below the onset of competing processes. A golden rule-like expression is given below for $k_{\rm IC}$ and is used in the subsequent detailed calculations.

The problem of a prepared light state interacting with a quasicontinuum of dark states has been treated previously,[14,15] and only the final results are given here, as specialized to the one- and two-photon absorption (TPA) cases. By the light state, we shall refer to a zeroth order rigid rotor–harmonic oscillator (RRHO) state that is accessible by one- or two-photon absorption from the ground state. A zeroth order dark state is dark with respect to absorption, i.e., not readily accessible from the ground state by absorption, but it is not dark with respect to emission. The focus of the present study is in the rotational state (J,K) dependence of the fluorescence excitation spectra. The fluorescence intensity I for a homogeneously broadened line is written as a Lorenzian function of excitation energy E, where E_{S_1} is the energy of the S_1 eigenstate by the proportionality[21,22]

$$\begin{aligned} I(E-E_{S_1}) \propto c_{\rm ls}^2(J',K')(|C_{\rm el}\cdot C_{\rm vib}C_{\rm rot}(J',K',J'',K'')|)^2 \\ \times(2J+1)f_{\rm nuc}(J'',K'')f_{\rm Boltz}(J'',K'') \\ \times[\Delta_f/(\Delta_f+\Delta_{\rm nr})] \\ \times\frac{\Delta_f+\Delta_{\rm nr}}{(E-E_{S_1})^2+(1/4)(\Delta_f+\Delta_{\rm nr})^2}. \end{aligned} \tag{2.3}$$

In Eq. (2.3), $c_{\rm ls}$ denotes the coefficient of the light state in the S_1 eigenstate. $C_{\rm el}$ is the electronic matrix element[22] for the relevant component of the electric dipole operator in the one-photon case, or of the two-photon absorption (TPA) tensor from state S_0 to S_1; in the two photon case, $C_{\rm vib}$ is the vibrational matrix element of the dipole moment operator (one photon), or of the appropriate component of the TPA tensor[22] (two photon) for the transition from the ground state vibrational level to the "light" vibrational state in the excited state,[22] $f_{\rm nuc}(J'',K'')$ is a nuclear spin statistical factor for the ground state species prior to excitation,[23–25] $f_{\rm Boltz}(J'',K'')$ is the Boltzmann weighting for the ground state at the rotational temperature of the experiment, and $C_{\rm rot}(J',K',J'',K'')$ is the rotational matrix element, possibly complex, of $\mathbf{J}_\alpha$ ($\alpha=0$ or ±1) in the one-photon case, or in the two-photon case, is a sum of rotational matrix elements for several components of the TPA tensor.[22] In Eq. (2.3), the $I(E-E_{S_1})$ contains both the above (J,K) dependent terms and others such as $\Delta_{\rm nr}$.

III. CALCULATION OF THE INTERNAL CONVERSION RATE $\Delta_{\rm nr}$

The statistical limit expression for the nonradiative linewidth $\Delta_{\rm nr}$ is given by a golden rule formula which allows for different magnitudes of the coupling matrix element V_{sl} between the state s in S_1 and background states $\{l\}$ in S_0,[26]

$$\Delta_{\rm nr} = 2\pi\sum_l |V_{sl}|^2\delta(E_s-E_l) \tag{3.1}$$

in units of $\hbar=1$. In our case, s is a quasimolecular eigenstate in S_1 (a product of electronic and vibration–rotation wave functions $\psi_{S_1}^{\rm el}\psi_{S_1}^{\rm vr}$), and l labels quasimolecular eigenstates in S_0.

For practical implementation, it is desirable to re-express Eq. (3.1) in terms of the zeroth order rigid rotor harmonic oscillator (RRHO) states $|i\rangle$ in S_0, instead of in terms of its eigenstates $|l\rangle$. If $\mathbf{H}$ denotes the electronic-rovibrational Hamiltonian for S_0, then introducing $E_l|l\rangle = \mathbf{H}|l\rangle$ and the completeness relation $\Sigma_l|l\rangle\langle l| = \mathbf{I}$ in Eq. (3.1), the latter can be rewritten as

$$\Delta_{nr} = 2\pi\langle s|\mathbf{V}_{IC}\delta(E_s - \mathbf{H})\mathbf{V}_{IC}|s\rangle$$
$$= -2\,\mathrm{Im}\langle s|\mathbf{V}_{IC}\mathbf{G}(E_s)\mathbf{V}_{IC}|s\rangle, \tag{3.2}$$

where $\mathbf{V}_{IC}$ is the perturbation operator responsible for the $S_1 \rightarrow S_0$ IC, $\mathbf{G}(E)$ is the Green's function

$$\mathbf{G}(E) = (E - \mathbf{H} + i\epsilon)^{-1} \tag{3.3}$$

and where the well-known relation[27]

$$\frac{1}{x \pm i\epsilon} = P\left(\frac{1}{x}\right) \mp i\pi\delta(x) \tag{3.4}$$

was used, P denoting "principal part of." Upon introducing before and after $\mathbf{G}$ in Eq. (3.2), the completeness relation $\Sigma_i|i\rangle\langle i| = \mathbf{I}$ for the zeroth order states in S_0, and assuming that in a statistical limit the phases in the off-diagonal (i,j) terms cancel in the double sum for Δ_{nr}, we have

$$\Delta_{nr} = -2\,\mathrm{Im}\sum_i |V_{si}|^2 G_{ii}(E_s), \tag{3.5}$$

where V_{si} and G_{ii} denote $\langle s|\mathbf{V}_{IC}|i\rangle$ and $\langle i|\mathbf{G}|i\rangle$.

Each zeroth order state $|i\rangle$ in S_0 can itself be regarded as a discrete state in a quasicontinuum. That formalism is then used to obtain a more convenient functional form for G_{ii}. Using the standard partitioning argument, summarized in Appendix A, where the approximations used are noted, it follows that in terms of the RRHO states $|i\rangle$ in S_0, we have

$$\Delta_{nr} = 2\pi\sum_i |\mathbf{V}_{si}|^2 \frac{\Gamma_i/2\pi}{(E_s - E_i^0 - \Lambda_i)^2 + (\Gamma_i/2)^2}. \tag{3.6}$$

Here, Γ_i represents the rate of disappearance of the state $|i\rangle$ due to intramolecular vibrational redistribution (IVR) in S_0. In effect, in the formalism this decay is treated as exponential. E_i^0 is the energy of the ith zeroth order state in S_0, and Λ_i represents the level shift of that state due to the interactions with the other zeroth order states in S_0.[28]

The quantity in parentheses in Eq. (3.6) serves as a smoothed delta function—it is peaked near E_s and yields unity upon integration over E_i $(=E_i^0+\Lambda_i)$, after neglecting the dependence of Γ_i and Λ_i on E and i. In applying Eq. (3.6) in part II, we shall use an essentially equivalent expression

$$\Delta_{nr} \approx \frac{2\pi}{\Delta}\sum_i{}' |\mathbf{V}_{si}|^2, \tag{3.7}$$

the prime indicating a sum over the states $|i\rangle$ in S_0 lying in a range Δ of energies comparable with Γ. If, as in the present case, the density of relevant states in S_0 is large enough, the right-hand side of Eq. (3.7) becomes independent of Δ in this range, the number of states $|i\rangle$ being proportional to Δ over a narrow range. The lack of detailed knowledge of Λ_i and Γ_i in Eq. (3.6) makes such a step necessary. For Eq. (3.7) to be meaningful, the density of relevant states in S_0 must be large enough that the result is, indeed, independent of the small Δ selected.

We consider next the evaluation of V_{si}. The state $|s\rangle$ denotes the eigenstate $\psi_{S_1}^{el}\psi_{S_1}^{vr}$ in S_1, while i denotes $\psi_{S_0}^{el}\psi_{S_0,i}^{vr}$, an electronic-RRHO (rovibronic) state in S_0. The perturbation operator $\mathbf{V}_{IC}$ is the usual nonadiabatic nuclear kinetic energy operator $-\frac{1}{2}\partial^2/\partial\mathbf{Q}^2$, and in the matrix element yields a term in which $\partial/\partial\mathbf{Q}$ operates once each on $\psi_{S_0}^{el}$ and $\psi_{S_0,i}^{vr}$, and another term where it operates twice on $\psi_{S_0}^{el}$. The latter contribution is smaller than the first[13] and so we write

$$V_{si} \approx -\langle\psi_{S_0}^{el}|\frac{\partial}{\partial\mathbf{Q}_p}|\psi_{S_1}^{el}\rangle\langle\psi_{S_0}^{vr}|\frac{\partial}{\partial\mathbf{Q}_p}|\psi_{S_1,i}^{vr}\rangle, \tag{3.8}$$

where mode Q_p is of the appropriate symmetry to induce the internal conversion.

In Eq. (3.8), the electronic matrix element is given by[13]

$$\langle\psi_{S_1}^{el}(\mathbf{r},\mathbf{Q})|\frac{\partial}{\partial\mathbf{Q}_p}|\psi_{S_0}^{el}(\mathbf{r},\mathbf{Q})\rangle = \frac{\langle\psi_{S_1}^{el}(\mathbf{r},\mathbf{Q})|[\partial U(\mathbf{r},\mathbf{Q})/\partial Q_p]|\psi_{S_0}^{el}(\mathbf{r},\mathbf{Q})\rangle}{E_{S_1}(\mathbf{Q}) - E_{S_0}(\mathbf{Q})}, \tag{3.9}$$

where in the Condon approximation it is estimated at some point, e.g., $\mathbf{Q}=\mathbf{Q}_0$, which may be removed from an equilibrium position (the "$\mathbf{Q}$-centroid approximation").[29] We next introduce the perturbation expression for $\psi_{S_1}^{vr}$ in terms of the zeroth order (RRHO) states in S_1,

$$\psi_{S_1}^{vr} = \sum_j c_j\psi_{S_1,j}^{vr}. \tag{3.10}$$

When mode Q_p is the inducing mode, the jth RRHO component of the S_1 eigenstate contributes a term

$$\langle\psi_{S_0,i}^{vr}|\frac{\partial}{\partial\mathbf{Q}_p}|\psi_{S_1,j}^{vr}\rangle = \langle\phi_{Q_p,i}^{S_0}|\frac{\partial}{\partial\mathbf{Q}_p}|\phi_{Q_p,j}^{S_1}\rangle \times \prod_{r\neq p}^{s}\langle\phi_{Q_r,i}^{S_0}|\phi_{Q_r,j}^{S_1}\rangle, \tag{3.11}$$

as the vibrational factor in Eq. (3.8). The product is over all vibrational modes Q_r, there being s such modes, except for that mode Q_p which induces the transition.[30] In Eq. (3.11), the usual approximation has been made that the vibrational wave function is a product of one-dimensional (or two-dimensional in the case of doubly degenerate modes) harmonic oscillator wave functions. The rotational matrix element in internal conversion gives unity. Overlap integrals for one- and two-dimensional harmonic oscillators were evaluated by standard means.[31–35] Any Duchinsky mixing of ground and excited state vibrational modes is neglected for simplicity in the present study.[8] In practice, some Duchinsky mixing could be included in the evaluation of the right-hand side of Eq. (3.9).

IV. DETERMINATION OF THE S_1 QUASIEIGENSTATE

The S_1 component of the prepared state, an eigenstate of the S_1 Born–Oppenheimer (BO) Hamiltonian, is written as

$$\Psi_{S_1}=\psi^{\rm el}_{S_1}\psi^{\rm vr}_{S_1}=\psi^{\rm el}_{S_1}\sum_j c_j\psi^{\rm vr}_{S_1,j}, \tag{4.1}$$

where $\psi^{\rm vr}_{S_1,j}$ is the jth RRHO state. In the spectral region of interest, the formulas simplify when one of these RRHO states in S_1 is the light state, i.e., carries the oscillator strength in the absorption (one or two photon) from the ground state. In a perturbation calculation, the remaining RRHO states in the above sum enter from vibrational and rotational coupling in S_1 with this light state. We next consider the vibration–rotation Hamiltonian, which permits calculation of c_j. The most important of these c_j's are determined using an "artificial intelligence" (AI) search, with an evaluation function given later by Eq. (5.7).

The well-known method for treating matrix elements and eigenvalues of vibrating–rotating molecules is used, which involves a perturbation expansion of the molecular Hamiltonian, with terms arranged according to the perturbation order of the vibrational and rotational operators[36–43]

$$\mathbf{H}=\sum_m\sum_n\lambda^{m+n-2}\mathbf{H}_{mn}. \tag{4.2}$$

Here, λ is a perturbation parameter, and m and n denote the degree of vibrational and rotational operators, respectively, $\mathbf{H}_{20}$ corresponding to the harmonic oscillator (HO) Hamiltonian and $\mathbf{H}_{02}$ to the rigid rotor (RR) one. The lowest order term containing Coriolis coupling $\mathbf{H}_{21}$ involves two normal modes Q_k and Q_l.[44,45] The higher order Coriolis terms $\mathbf{H}_{31}$ and $\mathbf{H}_{41}$ are also used.

The rovibrational energy of a planar oblate symmetric top, such as benzene, is given using RRHO and first order Coriolis terms by

$$E=E_{\rm vib}+B_e[J(J+1)-\tfrac{1}{2}K^2]\mp B_e\zeta_{\rm eff}K, \tag{4.3}$$

where $E_{\rm vib}$ denotes the rotational origin. The total rotational quantum number is J, K is the magnitude of the body-fixed component of the angular momentum along the sixfold symmetry axis, and B_e (replacing $2C_e$)[46,47] is the rotational constant (equilibrium configuration) for rotation about one of the in-plane axes. The Coriolis term on the right-hand side of Eq. (4.3) has a sign determined by the symmetry of the electronic state, and $\zeta_{\rm eff}$ is a coefficient which contains a sum over the degenerate vibrational modes which possess vibrational angular momenta $l_l\hbar$.[48]

In part II, the vibrational potential energy in the Hamiltonian is expanded as a polynomial in normal coordinates, while the kinetic energy has only terms quadratic in their conjugate momenta with coefficients which are constants. (Alternatively, the potential could be expanded in curvilinear coordinates.) *Ab initio* cubic curvilinear constants have been calculated for benzene,[49] e.g., and are equal to the corresponding cubic anharmonic constants in a normal mode (rectilinear) description, e.g., as noted in Ref. 50. They were obtained for the S_0 state so those for S_1, needed for calculation of $\psi^{\rm vr}_{S_1}$, are approximated by those in S_0 as before.[50]

The terms $\mathbf{H}_{mn}$ in Eq. (4.2) include those arising from expansion of the inverse inertia tensor μ which appears in the quantum-mechanical vibration–rotation Hamiltonian $\mathbf{H}$ (Ref. 51)

$$\mathbf{H}=\frac{1}{2}\sum_{\alpha,\beta}\mu_{\alpha\beta}(\mathbf{J}_\alpha-\mathbf{p}_\alpha)(\mathbf{J}_\beta-\mathbf{p}_\beta)+\frac{1}{2}\sum_k\mathbf{P}_k^2+\mathbf{U}(\mathbf{Q})$$
$$-\frac{1}{8}\hbar^2\sum_\alpha\mu_{\alpha\alpha}. \tag{4.4}$$

$\mathbf{J}_\alpha$ is a body-fixed component of the rotational angular momentum operator $\mathbf{J}$, with $\alpha=x, y, z$. $\mathbf{p}_\alpha$ is the αth component of the vibrational angular momentum operator

$$\mathbf{p}_\alpha=\sum_{k,\sigma_k,l,\sigma_l}\zeta^{(\alpha)}_{k,\sigma_k,l,\sigma_l}\mathbf{Q}_{k,\sigma_k}\mathbf{P}_{l,\sigma_l}, \tag{4.5}$$

where the σ subscripts label components of degenerate modes and are absent for nondegenerate modes, $\mathbf{Q}_{k,\sigma_k}$ is the operator for the (mass-weighted) normal mode (k,σ_k), $\mathbf{P}_{l,\sigma_l}$ is the momentum conjugate to $\mathbf{Q}_{l,\sigma_l}$, and $\zeta^{(\alpha)}_{k,\sigma_k,l,\sigma_l}$ is a Coriolis coupling coefficient. Its magnitude does not exceed unity.[52] The second and third terms on the right-hand side of Eq. (4.4) are the kinetic part of the normal mode energies and the harmonic plus anharmonic potential energy $U(\mathbf{Q})$, respectively. In its equilibrium nuclear configuration, the molecule has a principal axis system in which the inertia tensor is diagonal $\mu^{(0)}_{\alpha\beta}=\delta_{\alpha\beta}\mu^{(0)}_{\alpha\alpha}$. The rigid rotor Hamiltonian is recovered using $\mu^{(0)}_{\alpha\alpha}$ and neglecting vibrational angular momenta and vibrational anharmonicities.

The lowest order Coriolis interaction $\mathbf{H}_{21}$ arises from the cross terms in $\mathbf{J}$ and $\mathbf{p}$ in Eq. (4.4) upon substitution of $\mu^{(0)}_{\alpha\alpha}$ for $\mu_{\alpha\beta}$ there. As seen from Eqs. (4.4)–(4.5) $\mathbf{H}_{21}$ is a sum of terms, each of which contains two vibrational operators and one rotational operator. The terms $\mathbf{H}_{m1}$, $m\geqslant 3$ arise from the expansion of $\mu_{\alpha\beta}$ in Eq. (4.4) in normal mode coordinates. The $\mathbf{H}_{m1}$ terms contain m vibrational operators and one rotational operator. In particular, for $m=2$ and 3, we have

$$\mathbf{H}_{31}=-\frac{1}{2}\sum_{\alpha,\beta}\sum_{a,\sigma_a}(I^{(e)}_{\alpha\alpha}I^{(e)}_{\beta\beta})^{-1}\Omega^{(1)\alpha\beta}_{a,\sigma_a}(\mathbf{p}_\alpha\mathbf{Q}_{a,\sigma_a}+\mathbf{Q}_{a,\sigma_a}\mathbf{p}_\alpha)\mathbf{J}_\beta, \tag{4.6}$$

$$\mathbf{H}_{41}=-\frac{1}{2}\sum_{\alpha,\beta}\sum_{a,\sigma_a b,\sigma_b}(I^{(e)}_{\alpha\alpha}I^{(e)}_{\beta\beta})^{-1}\Omega^{(2)\alpha\beta}_{a,\sigma_a b,\sigma_b}$$
$$\times(\mathbf{p}_\alpha\mathbf{Q}_{a,\sigma_a}\mathbf{Q}_{b,\sigma_b}+\mathbf{Q}_{a,\sigma_a}\mathbf{Q}_{b,\sigma_b}\mathbf{p}_\alpha)\mathbf{J}_\beta, \tag{4.7}$$

where $\Omega^{(1)\alpha\beta}_{a,\sigma_a}$ and $\Omega^{(2)\alpha\beta}_{a,\sigma_a b,\sigma_b}$ are coefficients in the expansion of $\mu_{\alpha\beta}$,

$$\mu_{\alpha\beta}=(I^{(e)}_{\alpha\alpha}I^{(e)}_{\beta\beta})^{-1}\Big[I^{(e)}_{\alpha\beta}+\sum_{b,\sigma_b}\Omega^{(1)\alpha\beta}_{b,\sigma_b}Q_{b,\sigma_b}$$
$$+\sum_{b,\sigma_b}\sum_{c,\sigma_c}\Omega^{(2)\alpha\beta}_{b,\sigma_b c,\sigma_c}Q_{b,\sigma_b}Q_{c,\sigma_c}+\cdots\Big]. \tag{4.8}$$

The coordinates Q are defined so that they vanish at the equilibrium geometry. $\mathbf{H}_{31}$ and $\mathbf{H}_{41}$ are seen to reflect a vibrational dependence of the Coriolis term. All of these operators play a role in the ensuing calculation. Terms in $\mathbf{H}$ up to the order λ^3 of perturbation theory will be included in the application in part II,[53] so including, thereby, the $\mathbf{H}_{41}$ terms.

In first order, aside from the $\mathbf{H}_{21}$ Coriolis operator, the centrifugal distortion operator $\mathbf{H}_{12}$ is included, which consists of the linear coordinate dependence of the $\mu_{\alpha\beta}$ coefficient of the $\mathbf{J}_\alpha\mathbf{J}_\beta$ terms. $\mathbf{H}_{12}$ is readily calculable, since the same $\Omega^{(1)\alpha\beta}_{a,\sigma_a}$ coefficient enters as in $\mathbf{H}_{31}$.[53] The cubic anharmonicity contributions $\mathbf{H}_{30}$ are also terms first order in λ. An *ab initio* cubic force field is employed in the application in part II,[2] together with the other relevant molecular constants used.

In addition to the Coriolis operator $\mathbf{H}_{31}$, terms second order in λ include $\mathbf{H}_{22}$, $\mathbf{H}^{\mathbf{p}_\alpha\mathbf{p}_\beta}_{40}$, and $\mathbf{H}_{40}$, where $\mathbf{H}_{22}$ contains the quadratic coordinate term in the expansion of $\mu_{\alpha\beta}$ in the $\mathbf{J}_\alpha\mathbf{J}_\beta$ term, and is again immediately obtained. It involves the same $\Omega^{(2)\alpha\beta}_{a,\sigma_a b,\sigma_b}$ as that in $\mathbf{H}_{41}$.[54] The principal effect of $\mathbf{H}_{22}$ is to shift the RRHO levels. $\mathbf{H}^{\mathbf{p}_\alpha\mathbf{p}_\beta}_{40}$ is the term quadratic in vibrational angular momenta $\mathbf{p}_\alpha\mathbf{p}_\beta$ and by Eq. (4.5) is available from knowledge of the Coriolis coupling coefficients $\xi^{(\alpha)}_{k,\sigma_k,l,\sigma_l}$.[38] $\mathbf{H}_{40}$ is the quartic anharmonicity. In the absence of data on the quartic anharmonicities, they are neglected in part II.

Among the third order terms, one is quintic anharmonicity, which is neglected in part II. It is presently unavailable, and in any case, is expected to contribute relatively few paths to dark states differing in five or six quanta, as discussed in part II. The third order term analogous to $\mathbf{H}_{22}$ is $\mathbf{H}_{32}$. $\mathbf{H}_{32}$ has off-diagonal matrix elements whose magnitudes are very small, due a cubic coordinate dependence on the inertia tensor, and is neglected in part II. $\mathbf{H}^{\mathbf{p}_\alpha\mathbf{p}_s}_{40}$ is a second order operator having two rotational matrix elements that give inherently smaller couplings than when cubic anharmonic matrix elements alone are present. Its linear dependence on vibrational coordinates, which arises in third order, is neglected in part II. Thereby, the only third order term that is included there is the Coriolis operator $\mathbf{H}_{41}$.

The symmetry requirements for nonzero cubic force constants in $\mathbf{H}_{30}$ and for Coriolis coupling coefficients in $\mathbf{H}_{21}$ are well known.[54] The symmetry restrictions for the terms containing the $\Omega^{(1)\alpha\beta}_{Q_a,\sigma_a}$ and $\Omega^{(2)\alpha\beta}_{Q_a,\sigma_a Q_b,\sigma_b}$ coefficients for benzene, e.g., such as $\mathbf{H}_{31}$ and $\mathbf{H}_{41}$, have been derived individually and are given in Appendix B of Ref. 50. Because of the symmetry restrictions, the number of terms which are summed over in the perturbation expressions is greatly reduced.

To obtain RRHO energies, we use Eq. (4.3) (less the Coriolis energy which appears there), the vibrational energy being the sum of harmonic frequencies that appear in the combination required. [The Coriolis energy, formally $\mathbf{H}_{21}$ in the expansion (4.2), is added to the RRHO energy subsequently in the calculation.] The combination band origin has an energy slightly different from the simple sum of fundamental frequencies[50] because of extra anharmonic contributions. (The experimental fundamentals have some anharmonic contributions.) In the case of the S_1 state of benzene, use of the experimental fundamental frequencies[55,56] ν_i yields calculated combination band origins with an estimated accuracy of perhaps $\pm 10\ \mathrm{cm}^{-1}$. The figure of $\pm 10\ \mathrm{cm}^{-1}$ is based on comparison with calculated theoretical fundamental and combination band frequencies using the *ab initio* cubic anharmonic force field employed.[49]

Vibrational matrix elements, including those found in Coriolis operators, typically contain factors such as $\omega_i^{1/2}$ and $\omega_j^{-1/2}$, where these ω_i's are the harmonic frequencies. Since we use experimental frequencies instead of harmonic ones, an error is made in these terms, but it is small, much smaller than other error sources.

In employing perturbation theory to obtain, order by order, the corrections to the light state which will yield Ψ_{S_1} the S_1 component of the eigenstate, we note first that when the zeroth order light state is nondegenerate, nondegenerate perturbation theory may be used to expand $\psi^{\mathrm{vr}}_{S_1}$ in powers of the perturbation. For example, in part II, the $|14^1 1^2;J,K\rangle$ light state in benzene is nondegenerate, apart from doubling due to positive and negative k, since modes Q_1 and Q_{14} are both nondegenerate.[57,58]

The wave function $|\psi^{\mathrm{vr}}_{S_1}\rangle$ can be expressed in terms of a projection operator $\mathbf{P}$ and the unperturbed light state $|\psi^0_I\rangle$, where

$$|\psi^{\mathrm{vr}}_{S_1}\rangle = \mathbf{P}|\psi^0_I\rangle \tag{4.9}$$

and, in the case of nondegenerate perturbation theory,[59] the part of $\mathbf{P}$ operating on the $|\psi^0_I\rangle$ subspace is

$$\mathbf{P} = \mathbf{P}_0 + \frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{V}_{S_1}\mathbf{P}_0 + \frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{V}_{S_1}\frac{\mathbf{Q}_0}{\mathbf{a}}\mathbf{V}_{S_1}\mathbf{P}_0 + \cdots, \tag{4.10}$$

where $\mathbf{a}$ denotes $E^0_I - \mathbf{H}_0$, E^0_I is the eigenvalue for $|\psi^0_I\rangle$, $\mathbf{V}_{S_1}$ denotes the perturbation terms in the Hamiltonian for S_1, and $\mathbf{P}_0$ and $\mathbf{Q}_0$ are the projection operators

$$\mathbf{P}_0 = |\psi^0_I\rangle\langle\psi^0_I|, \tag{4.11}$$

$$\mathbf{Q}_0 = \sum_{i\neq I}|\psi^0_i\rangle\langle\psi^0_i|. \tag{4.12}$$

In Eq. (4.10), terms which do not end in $\mathbf{P}_0$ have been omitted, since $\mathbf{Q}_0|\psi^0_I\rangle = 0$. Terms in which $\mathbf{P}_0$ occurs more than once are present in Eq. (4.10), but make only a minor contribution.

This perturbation expansion for the S_1 wave function thereby involves multidimensional sums over "paths" which lead from the light state I to dark states in S_1. A path contains a series of these virtual states that are coupled sequentially by terms in the vibration–rotation Hamiltonian, states sometimes coupled by more than one path. In part II, the application to benzene involves paths that contain zero, one, and two Coriolis operators. A path with no Coriolis operator has only cubic anharmonic terms and, aside from shifts in energy levels, couples the light state to dark states in S_1 and, via internal conversion to the S_0

quasicontinuum, in a manner independent of J and K. Paths with a single Coriolis operator couple light and dark states with a matrix element proportional to K for parallel and to $[J(J+1)-K(K\pm1)]^{1/2}$ for perpendicular Coriolis coupling. Paths with two Coriolis operators couple in a more complicated fashion. Their inclusion in part II ensured that the calculations at high J were of an order consistent with the order used at low J.[38] The coefficients c_i for the components of $|\psi_{S_1}^{vr}\rangle$ in Eq. (4.1) were obtained from the results of the perturbation expansion in Eq. (4.10).

The individual matrix elements of the perturbation $\mathbf{V}_{S_1}$, which may be any of the operators through third order in the vibration–rotation Hamiltonian, are obtained in the usual way after factoring into vibrational and rotational matrix elements of the relevant vibrational and rotational operators. Matrix elements of vibrational operators for one- and two-dimensional harmonic oscillators are well known.[60] For matrix elements of rotational operators $\mathbf{J}_x$, $\mathbf{J}_y$, and $\mathbf{J}_z$, these latter are transformed to spherical tensor operators $\mathbf{J}_\pm$, and $\mathbf{J}_0$ and evaluated in the standard way.[43]

V. SELECTION OF STATES IN THE S_1 AND S_0 MANIFOLDS

In the present procedure, a method is used in which specific S_0 rovibronic states are selected for coupling with S_1 based on their having large Franck–Condon factors with states in S_1 having large coefficients c_i. The algorithm employed for the selection of these S_0 states is a directed search over S_0 states quasienergetic with the S_1 eigenenergy E_{S_1} (or really with the energy of the zeroth order light state). The range of energies is described below. Within the limitations imposed by energy and symmetry requirements discussed below, all S_0 states are searched in a fashion which, in the language of artificial intelligence algorithms, is termed a "depth-first" search.[61] Included in the search algorithm is the distinguishing between active vs inactive modes, an active mode Q_k being defined as any mode with a sizeable overlap integral for nonzero changes Δv_k in its principal vibrational quantum number for internal conversion. An inactive mode has by definition an appreciable overlap integral only when $\Delta v_k=0$. In general, a large change in frequency and, for totally symmetric modes, in displacement as well[31,32] between the excited and the ground states contribute to the activity of a normal mode from the resulting large overlap integral.

The selection rules in internal conversion for specific vibrational modes are determined by the molecular point group and the irreducible representations of the modes in question. When an active mode is totally symmetric and is an accepting mode [i.e., is not involved in the nonadiabatic operator in Eq. (3.8)], we have

$$\Delta v_k=0,\pm1,\pm2,... \tag{5.1}$$

with any change in degree of excitation allowed.[62] For nontotally symmetric active accepting modes

$$\Delta v_k=0,\pm2,\pm4,..., \tag{5.2}$$

while for inactive modes, by definition

$$\Delta v_k=0. \tag{5.3}$$

Finally, we have the additional restriction for degenerate modes

$$\Delta l_k=0, \tag{5.4}$$

since otherwise the angular integration over a coordinate ϕ in a two-dimensional (degenerate) harmonic oscillator representation yields zero. When the promoting mode Q_p is nondegenerate, Eq. (5.4) does not apply for the corresponding matrix element involving the operator $\partial/\partial\mathbf{Q}_p$. Equation (5.4) reduces a $3N-6$-dimensional search for S_0 states to a $(3N-6)-n_d$-dimensional search, where n_d is the number of degenerate modes (N is the number of atoms).

Since the quantum state for all inactive modes is specified, one need not search over these modes when searching for states in S_0 with large Franck–Condon overlap to a given RRHO basis state in the S_1 eigenvector. If n_i is the number of inactive modes, then the dimensionality of the search for S_0 states is further reduced to $n_a=(3N-6)-n_d-n_i$ and is equal to the number of active vibrational modes.

For these n_a active modes, an n-dimensional search in the S_0 manifold is performed, subject to the constraints imposed by Eqs. (5.1)–(5.4). A prospective rovibronic state in the S_0 manifold must satisfy several additional criteria in order to be selected.

(1) For internal conversion via the nuclear kinetic energy operator, $\Delta J=0$ and, when K exists, $\Delta K=0$.[63]

(2) The S_0 state should lie in a prespecified narrow energy range Δ centered about the S_1 energy E_{S_1}. In practice, it is sufficient to choose the energy center as the zeroth order energy of the RRHO state in S_1 that is the dominant contributor to the S_1 eigenvector, which is typically the light state. In the statistical limit, it should be immaterial where one places this energy "window." There is a large enough density of states in S_0, with similar numbers and coupling strengths, regardless of the placement of energy center.

(3) Symmetry criteria specific to the promoting modes should be satisfied. For example, if Q_a and Q_b are promoting modes of the appropriate symmetry, with Q_a active and Q_b inactive, then when Q_a is the promoting mode [a Q_p in Eq. (3.8)]

$$\Delta v_a=\pm1,\pm3,... \quad \text{and} \quad \Delta v_b=0, \tag{5.5}$$

since there is a $\partial/\partial\mathbf{Q}_a$ operator in the integrand of the mode Q_a overlap integral in Eq. (3.11), thereby switching the even-only rule in Eq. (5.2) to odd only, since mode Q_b is inactive. If Q_b is the promoting mode, then

$$\Delta v_a=0,\pm2,\pm4,... \quad \text{and} \quad \Delta v_b=\pm1, \tag{5.6}$$

since mode Q_a is active. Mode Q_b is subject to the odd-only rule due to the $\partial/\partial\mathbf{Q}_b$ operator, and being inactive, is further restricted to the smallest allowed changes in its quantum number, namely, ±1.

When there is more than one promoting mode, care must be taken to first sum over the allowed couplings to a given RRHO state in S_0 and then take the squared amplitude [cf. Eq. (3.7)]. If, as in the case of benzene, access to a given RRHO state in S_0 occurs via only one promoting mode, owing to the even–odd selection rules, this consideration is unnecessary. For the $S_1 \rightarrow S_0$ internal conversion in benzene, e.g., Q_a and Q_b correspond to modes Q_{14} (active) and Q_{15} (inactive), respectively.

(4) The tentative S_0 rovibronic state must have a large Franck–Condon overlap integral with the dark zeroth order state in the S_1 eigenvector to which it is coupled via internal conversion. A cut-off value for the magnitude of this overlap is employed, since consideration of all tentative S_0 states would be impractical. Specifically, an evaluation function (E.F.) is defined

$$\text{E.F.} = |c_i \langle \psi^{\text{vr}}_{S_1,i} | \partial/\partial \mathbf{Q}_p | \psi^{\text{vr}}_{S_0,j} \rangle| \tag{5.7}$$

for the coupling of the ith RRHO state in the S_1 eigenvector (with coefficient c_i there) to the jth RRHO state in the S_0 manifold. The state $|\psi^{\text{vr}}_{S_0,j}\rangle$ is accepted provided its E.F. equals or exceeds the predetermined minimal value and the other criteria (1)–(3) are also satisfied.

Let us suppose that N states in S_1 have been selected in the AI search. A diagonalization of these states determines the approximate S_1 "eigenstates," where the light state makes nonnegligible contributions. If those with a substantial light state content are rather sparse, there may only be one such eigenstate in the observed width of the rotational line. In that case, the formalism described in this paper is appropriate.

If there are two or more such light state rich eigenstates, e.g., because of a resonance between the light state and one or more dark states, there will be a splitting in the line, unless the broadening of each due to IC to S_0 is comparable with or exceeds the separation of these two or more S_1 eigenstates. In the application to a particular band in part II, the system treated has one S_1 eigenstate. If two S_1 eigenstates overlap because of the broadening arising from coupling to S_0, a two discrete state in a continuum formalism would be employed.[7]

VI. CONCLUDING REMARKS

A formalism is given for the calculation of fluorescence excitation spectra for systems in which a molecular eigenstate contains a first excited (S_1) electronic state component and components in S_0 due to internal conversion coupling, and is separated from other such states. The method is readily applicable to systems having vibration–rotation coupling and internal conversion, provided that detailed molecular parameters are available. The S_0 and S_1 states are selected using an AI search algorithm that accepts candidate states in S_0 and S_1 having the largest product of the coefficients in the perturbation expansion in S_1 and the Franck–Condon factors to the S_0 state, i.e., the terms with the largest E.F. defined by Eq. (5.7). The calculated fluorescence spectral lines are approximated as Lorentzians whose widths are determined by the effective coupling to the S_0 manifold, a coupling found by summation over the explicit couplings between the selected S_1 and S_0 states. The formalism is applied in part II to the channel three problem in benzene.

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APPENDIX A: DERIVATION OF EQ. (3.6) FOR Δ_{nr}

Each zeroth order state $|i\rangle$ in S_0 is treated as a discrete state in a quasicontinuum of the remaining states in S_0, $|j\rangle$, $j \neq i$. The usual partitioning formalism is employed.[59] Let $\mathbf{P}$ and $\mathbf{Q}$ denote the projection operators $|i\rangle\langle i|$ and $\Sigma_{j\neq i}|j\rangle\langle j|$, and $\mathbf{H}$ denote the Hamiltonian for S_0.

If $\mathbf{G}(E)$ denotes the resolvent operator $(E-\mathbf{H}+i\epsilon)^{-1}$, then inserting $\mathbf{P}+\mathbf{Q}$ into the identity

$$(E-\mathbf{H}+i\epsilon)\mathbf{G}(E)=\mathbf{I} \tag{A1}$$

before $\mathbf{G}$ and operating on the left by $\mathbf{P}$ and on the right by $\mathbf{P}$ to obtain Eq. (A2), and alternatively on the left by $\mathbf{Q}$ and on the right by $\mathbf{P}$ to obtain Eq. (A3), we have

$$(E-\mathbf{H}_{PP}+i\epsilon)\mathbf{G}_{PP}-\mathbf{H}_{PQ}\mathbf{G}_{QP}=\mathbf{P}, \tag{A2}$$

$$-\mathbf{H}_{QP}\mathbf{G}_{PP}+(E-\mathbf{H}_{QQ}+i\epsilon)\mathbf{G}_{QP}=0, \tag{A3}$$

where $\mathbf{H}_{PP}$, $\mathbf{G}_{PP}$,... denote $\mathbf{PHP}$, $\mathbf{PGP}$,... . Elimination of $\mathbf{G}_{QP}$ yields the well-known result

$$\mathbf{G}_{PP}=[E-\mathbf{H}_{PP}-\mathbf{H}_{PQ}(E-\mathbf{H}_{QQ}+i\epsilon)^{-1}\mathbf{H}_{QP}]^{-1}\mathbf{P}. \tag{A4}$$

Using Eq. (3.4), $\mathbf{H}_{PQ}(E-\mathbf{H}_{QQ}+i\epsilon)^{-1}\mathbf{H}_{QP}$ can be written in terms of its real χ_{PP} and imaginary $i\Gamma_{PP}/2$ parts

$$\mathbf{G}_{PP}=(E-\mathbf{H}_{PP}-\chi_{PP}+i\Gamma_{PP}/2)^{-1}\mathbf{P}, \tag{A5}$$

where

$$\chi_{PP}=P[\mathbf{H}_{PQ}(E-\mathbf{H}_{QQ})^{-1}\mathbf{H}_{QP}], \tag{A6}$$

$$\Gamma_{PP}/2=\pi\mathbf{H}_{PQ}\delta(E-\mathbf{H}_{QQ})\mathbf{H}_{QP}. \tag{A7}$$

$\mathbf{G}_{ii}$ the quantity defined in Eq. (3.5) of the text is equal to $\langle i|\mathbf{G}_{PP}|i\rangle$. Introducing the expressions for $\mathbf{P}$ and $\mathbf{Q}$, we then have

$$\chi_i=P\left(\sum_{k,k'} H_{ik}\left\langle k\left|\frac{1}{E-\mathbf{H}_{QQ}}\right|k'\right\rangle H_{k'i}\right), \tag{A8}$$

$$\Gamma_i=2\pi\sum_{k,k'} H_{ik}\langle k|\delta(E-\mathbf{H}_{QQ})|k'\rangle H_{k'i}, \tag{A9}$$

where P denotes the principal part, and χ_i and Γ_i denote $\langle i|\chi_{PP}|i\rangle$ and $\langle i|\Gamma_{PP}|i\rangle$. Strictly speaking, the evaluation of these expressions would involve diagonalization of the Hamiltonian $\mathbf{H}_{QQ}$, the $|k\rangle$'s being coupled by anharmonic and Coriolis interactions. If one assumes a phase averaging

when summing over k' at a fixed k and approximates the eigenvalues of $\mathbf{H}_{QQ}$ by their zeroth order values E_k^0, Eqs. (A8) and (A9) become

$$\chi_i \approx P\left(\sum_k \frac{|H_{ik}|^2}{E-E_k^0} \right), \tag{A10}$$

$$\Gamma_i \approx 2\pi \sum_k |H_{ik}|^2 \delta(E-E_k^0), \tag{A11}$$

where Eq. (A10) is to be understood as an integral over the k states in S_0, which are treated as a continuum.

We note that $\langle i|\mathbf{H}_{PP}+\chi_{PP}|i\rangle$ equals $E_i^0 + V_{S_0,ii} + \chi_i$ when $\mathbf{H}$ is written as $\mathbf{H}_0 + \mathbf{V}_{S_0}$, where $\mathbf{V}_{S_0}$ is the perturbation part of the S_0 vibrational–rotational Hamiltonian. One then sees from Eq. (A10) that this quantity represents the energy of the ith state up to and including second order of perturbation theory, its zeroth order nature being described by $|i\rangle$. In Eq. (A11), Γ_i represents the usual golden rule result for decay into a "prediagonalized" continuum (here, prediagonalized by neglecting the off-diagonal terms in $\mathbf{H}_{QQ}$). The Λ_i in Eq. (3.6) represents the shift $V_{S_0,ii} + \chi_i$ of the ith level E_i^0, due to the interactions, to second order, with the other states in S_0.

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