

Line shape of a molecular resonance

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In this paper we consider some implications of intramolecular electronic relaxation on the optical line shape of large molecules in the statistical limit. General expressions for the line shape were derived utilizing the Green's function formalism, which account both for interference with background absorption and for interference between resonances. The energy dependence of the line-width functions was elucidated. We have demonstrated that the line shape for an 'isolated' resonance is a fanian; however, as the line profile index is determined by the ratio of the level spacing to the non-radiative width, the corrections to the lorentzian line shape are small in this case. We have established the equivalence of the physical description utilizing a three-level crude adiabatic basis and a two-level adiabatic basis. In the case of overlapping resonances the line shape may be recast in terms of a modified Fano-type formula where the line profile index is energy dependent. The nature of interference effects in this case is determined by the ratio and the relative signs of projections of the transition moments on the polarization vector.

1. INTRODUCTORY COMMENTS

The diffuseness of spectral lines in the optical absorption spectra of large molecules [1] is intimately related to intramolecular electronic relaxation in these systems. Theoretical work [2-4] has established that in the statistical limit the near resonance non-adiabatic coupling between a zero-order state $|s\rangle$ and a quasi-continuum $\{|l\rangle\}$ results in a Breit-Wigner line shape

$$L(E) \sim \frac{\frac{1}{2}\Gamma(E_s)}{(E - E_s)^2 + (\frac{1}{2}\Gamma(E_s))^2} \quad (1.1)$$

exhibiting a differential lorentzian distribution of the intensity of the zero order $|s\rangle$ state, which is characterized by the energy E_s . The line-width function $\Gamma(E)$ is a slowly varying function of the energy in the vicinity of $E \approx E_s$, and this weak energy dependence may result in corrections to the lorentzian line shape. It is also worthwhile stressing that in the statistical limit the details of the level distribution in the $\{|l\rangle\}$ manifold and the variation of the interstate $s-l$ coupling terms are immaterial and do not affect the general conclusion concerning the lorentzian line shape of an 'isolated' molecular resonance.

The line width $\Gamma(E_s)$ was conventionally taken [2-4] to be determined by the intramolecular interstate coupling and by the density of states in the $\{|l\rangle\}$ quasi-continuum. There has recently been a lively controversy concerning the 'proper'

choice of a zero-order basis set and of the intramolecular coupling [5–10], whereupon the classical approach based on the non-adiabatic coupling between Born–Oppenheimer adiabatic (A) zero-order states was challenged, and an alternative approach on Herzberg–Teller coupling between crude adiabatic (CA) zero-order states was advocated [5, 6]. Obviously, the choice of a zero-order basis set is arbitrary and does not reflect on the physical features of the problem. Both untruncated and complete CA and A bases are adequate for describing the broadening and decay of a molecular resonance. We would like, however, to point out that the general conditions for the validity of equation (1.1) with Γ being given by

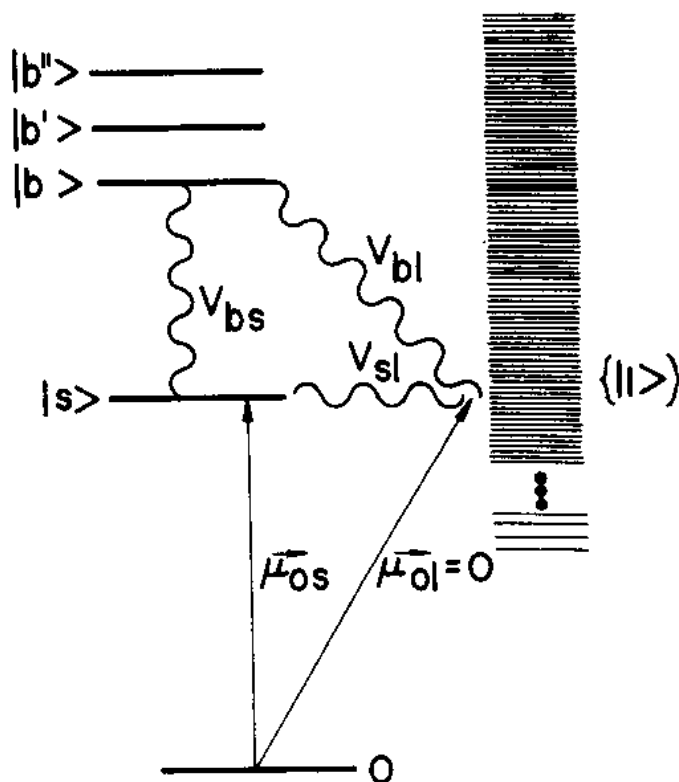


Figure 1. A schematic representation of the relevant molecular states and couplings. Arrows indicate dipole coupling via the interaction with the radiation field. Wavy lines represent intramolecular coupling.

the Fermi 'golden rule' are not satisfied either by the A or by the CA basis and in certain cases physically significant deviation may be encountered [10]. The basic physical model for a lorentzian line shape (and exponential intramolecular relaxation) in the statistical limit (see figure 1) rests on the following model:

(A) A single zero-order state $|s\rangle$ (i.e. a vibronic component of the excited electronic state) carries oscillator strength from the ground state $|0\rangle$.

(B) $|s\rangle$ is quasidegenerate with and coupled to a dense quasicontinuum $\{|l\rangle\}$ corresponding to a lower electronic configuration(s).

(C) The quasicontinuum $\{|l\rangle\}$ does not carry oscillator strength from the ground state.

(D) Other 'optically active' excited states $|b\rangle$, which may correspond to different vibronic components of the same electronic state as $|s\rangle$ or to other electronic configurations, are well separated from $|s\rangle$ (relative to their zero-order widths).

(E) Off-resonance coupling of the zero-order states $|s\rangle$ and $\{|l\rangle\}$ with other states $|b\rangle$ is negligible.

We should note in passing that if condition (C) is violated, a Fano-type line shape [2] will result, while if condition (D) or (E) does not hold interference effects between resonances [3 b] will be exhibited. Turning our attention now to the A and to the CA basis sets the following points are relevant [10 b]:

(a) The A basis minimizes the off-resonance couplings with $|b\rangle$ states, whereupon the line width (and decay) can be adequately described by a two-electronic-level (i.e. $|s\rangle$ and $\{|l\rangle\}$) system.

(b) The CA basis is adequate only provided that off resonance coupling with $|b\rangle$ states is included.

(c) The A basis cannot be specified in terms of symmetry classification of the zero-order states.

(d) The CA basis utilizes the basic symmetry properties of the zero-order molecular states, as the electronic wavefunctions are defined for a fixed nuclear configuration.

Thus points (a) and (b) establish the advantages of the A basis from the conceptual point of view. As far as the line shape problem is concerned, the symmetry properties of the CA basis are useful in view of:

(e) In the CA basis the symmetry selection rules (at least within the framework of the harmonic approximation applied to the promoting vibrational modes) imply that the quasicontinuum $\{|l\rangle\}$ is optically inactive.

(f) The A type quasicontinuum $\{|l\rangle\}$ does carry oscillator strength from the ground state.

We have just exposed the main theme of this paper. The use of the A basis does not (at least in principle) fulfil the basic condition (C); on the other hand, the CA basis, which satisfies condition (C), in turn violates condition (E). We may thus conclude that neither the A nor the CA basis can satisfy simultaneously conditions (A)–(E) and that molecular resonances encountered in an optical experiment exhibit deviations from equation (1.1). In the present paper we study the line shape of a molecular resonance, utilizing both the A and CA bases. We shall demonstrate that in general the line shape is a Fanoian, the Fano line index parameter being determined by the ratio of the molecular frequency to the non-radiative line width. For relatively small line widths $\Gamma \lesssim 10 \text{ cm}^{-1}$, the correction to the Lorentzian line shape is trivial. Apart from intrinsic theoretical interest, the techniques and results of the present study are relevant for the following reasons: (1) Many high extra-valence excitations in large molecules are characterized by line widths $\Gamma \sim 100\text{--}1000 \text{ cm}^{-1}$ and the role of the effects of background absorption is of physical interest. (2) The present results are of interest for the elucidation of the decay pattern of ultrafast molecular relaxation processes in the subpicosecond time domain.

2. GENERAL EXPRESSIONS FOR THE OPTICAL LINE SHAPE

Including the effects of the coupling with the radiation field up to first order, linear response theory yields the well known expression for the line shape [12]

$$L(E) = -\frac{1}{\pi} \text{Im} \langle 0 | \mu G(E) \mu | 0 \rangle, \quad (2.1)$$

where Im refers to the imaginary part, $\mu = (\boldsymbol{\mu} \cdot \boldsymbol{\epsilon})$ is the projection of the dipole operator $\boldsymbol{\mu}$ on the polarization vector, $\boldsymbol{\epsilon}$, of the electric field, while the Green operator

$$G(E) = (E - H + i\eta)^{-1}; \quad \eta \rightarrow 0^+ \quad (2.2)$$

is defined in terms of the molecular hamiltonian†. Performing an (arbitrary) separation of the hamiltonian into $H = H_0 + V$ one can display the line shape in terms of the eigenbasis $|\alpha\rangle$ of H_0 which satisfy $H_0|\alpha\rangle = E_\alpha|\alpha\rangle$. It is immediately apparent that the line shape is independent of the choice of the basis set as we have from (2.1).

$$L(E) = -\frac{1}{\pi} \text{Im} \sum_{\alpha} \sum_{\alpha'} \mu_{0\alpha} G_{\alpha\alpha'} \mu_{\alpha'0} \quad (2.3)$$

where $\mu_{0\alpha} = \langle 0|\mu|\alpha\rangle$ and $G_{\alpha\alpha'} = \langle \alpha|G(E)|\alpha'\rangle$. Making use of the Dyson equation

$$\begin{aligned} G &= (E - H + i\eta)^{-1} = (E - H_0 + i\eta)^{-1} + (E - H_0 + i\eta)^{-1} V (E - H + i\eta)^{-1} \\ &= G^0 + G^0 V G \end{aligned} \quad (2.4)$$

the relevant matrix elements of the Green operator can be displayed in the form

$$\begin{aligned} G_{\alpha\alpha'} &= G_{\alpha\alpha'}^0 + \sum_{\beta, \gamma} G_{\alpha\beta}^0 V_{\beta\gamma} G_{\gamma\alpha'} \\ &= \delta_{\alpha\alpha'} (E - E_\alpha + i\eta)^{-1} + (E - E_\alpha + i\eta)^{-1} \sum_{\gamma} V_{\alpha\gamma} G_{\gamma\alpha'}. \end{aligned} \quad (2.5)$$

Up to this point the basis set is completely arbitrary, however, an appropriate choice of the basis can result in closed expressions for the matrix elements of the Green's function. It will be advantageous at this point to recall one of the basic properties of both the A and the CA bases, that is that they are diagonal within the same electronic configuration [10 b]. At this stage we introduce two simplifying assumptions, first that the off-resonance coupling with the low lying ground state is negligible‡, and second that only a single $|b\rangle$ state (figure 1) is included§. The line shape from equations (2.1) and (2.5) for this model system both in the A and in the CA bases is

$$\begin{aligned} L(E) &= -\frac{1}{\pi} \text{Im} \left[\mu_{0s} G_{ss} \mu_{s0} + \mu_{0b} G_{bb} \mu_{b0} + \mu_{0s} G_{sb} \mu_{b0} + \mu_{0b} G_{bs} \mu_{s0} \right. \\ &\quad \left. + \sum_I \left(\sum_I \mu_{0I} G_{II} \mu_{I'0} + \mu_{0s} G_{sI} \mu_{I0} + \mu_{0I} G_{Is} \mu_{s0} + \mu_{0b} G_{bI} \mu_{I0} + \mu_{0I} G_{Ib} \mu_{b0} \right) \right]. \end{aligned} \quad (2.6)$$

† If the effects of the coupling with the radiation field were included to a higher order, the line width for an isolated resonance would be $\Gamma_t = \Gamma + \Gamma_R$ where Γ_R is the radiative while Γ is the non radiative width. When interference effects are encountered the radiative corrections are more complex [11]. These radiative contributions are neglected in the present study as we are interested in cases where $\Gamma \gg \Gamma_R$.

‡ The coupling matrix elements with the ground state may be easily included and may be of some importance when the CA basis is used [13], however, they do not affect the features of the line shape problem.

§ This assumption implies neglecting interference effects between different $|b\rangle$ states, which can be included, resulting in cumbersome expressions.

The first term in this equation provides the major contribution to the line shape around $E \approx E_s$, provided that the quasicontinuum is optically inactive, i.e. $\mu_{0l} = 0$ for all l , and the off-resonance coupling terms are small, i.e. $V_{bs} \approx 0$ and $V_{bl} \approx 0$. The second term in (2.6) taken at $E \approx E_s$, yields the contribution of the zero order state $|b\rangle$ to the absorption around $E \approx E_s$, and provided that the broadening of the resonances centred around $E \approx E_s$ and $E \approx E_b$ is large, interference effects will be exhibited by second order coupling via the manifold $\{l\}$. It is also worthwhile noting that when the CA basis is employed the second term in (2.6) will result in the conventional Herzberg-Teller contribution to the intensity [13, 14]. The third and fourth terms in equations (2.6) are non-vanishing for appreciable off-resonance coupling of $|s\rangle$ and/or $\{|l\rangle\}$ with $|b\rangle$, and exhibit the effect of interference between resonances. The fifth term in (2.6) contains the direct contribution to the background absorption (for $\mu_{0l} \neq 0$). Finally, the last four terms in this equation arise from interference effects with background absorption, and include both direct $|s\rangle - |l\rangle$ interference effects and also indirect interference via the off-resonance $|b\rangle$ state.

To complete this formal exposition we now utilize equation (2.4) with the condition $V_{ll'} = 0$ for $l \neq l'$ to recast the relevant matrix elements of the Green's function in the following form :

$$G_{sb} = G_{ss}V_{sb}(Z - E_b)^{-1} + \sum_l G_{sl}V_{lb}(Z - E_b)^{-1}, \quad (2.7 a)$$

$$G_{bs} = (Z - E_b)^{-1}V_{bs}G_{ss} + \sum_l (Z - E_b)^{-1}V_{bl}G_{ls}, \quad (2.7 b)$$

$$G_{sl} = G_{ss}V_{sl}(Z - E_l)^{-1} + G_{sb}V_{bl}(Z - E_l)^{-1}, \quad (2.7 c)$$

$$G_{ls} = (Z - E_l)^{-1}V_{ls}G_{ss} + (Z - E_l)^{-1}V_{lb}G_{bs}, \quad (2.7 d)$$

$$G_{lb} = (Z - E_l)^{-1}V_{lb}G_{bb} + (Z - E_l)^{-1}V_{ls}G_{sb}, \quad (2.7 e)$$

$$G_{bl} = G_{bb}V_{bl}(Z - E_l)^{-1} + G_{bs}V_{sl}(Z - E_l)^{-1}, \quad (2.7 f)$$

$$G_{ll'} = \delta_{ll'}(Z - E_l)^{-1} + (Z - E_l)^{-1}V_{ls}G_{ss}V_{sl'}(Z - E_{l'})^{-1} \\ + (Z - E_l)^{-1}V_{lb}G_{bb}V_{bl'}(Z - E_{l'})^{-1} + (Z - E_l)^{-1}V_{ls}G_{sb}V_{bl'}(Z - E_{l'})^{-1} \\ + (Z - E_l)^{-1}V_{lb}G_{bs}V_{sl'}(Z - E_{l'})^{-1}, \quad (2.7 g)$$

$$G_{bb} = (Z - E_b)^{-1} + (Z - E_b)^{-1}V_{bs}G_{sb} + (Z - E_b)^{-1} \sum_l V_{bl}G_{lb} \quad (2.7 h)$$

and finally

$$G_{ss} = (Z - E_s)^{-1} + (Z - E_s)^{-1} \sum_l V_{sl}G_{ls} + (Z - E_s)^{-1}V_{sb}G_{bs}, \quad (2.7 i)$$

where we have used the (complex) variable $Z = E + i\eta$. It will now be convenient to introduce several definitions of line widths and of level shifts in terms of the following complex functions :

$$A(E) = \alpha(E) - i\beta(E) = \sum_l \frac{V_{bl}V_{ls}}{Z - E_l}, \quad (2.8 a)$$

$$\tilde{A}(E) = \alpha(E)^* - i\beta(E)^* = \sum_l \frac{V_{sl}V_{lb}}{Z - E_l}, \quad (2.8 b)$$

where

$$\alpha(E) = PP \sum_l \frac{V_{bl}V_{ls}}{E - E_l}, \quad (2.8 c)$$

$$\beta(E) = \pi \sum_l V_{bl}V_{ls} \delta(E - E_l), \quad (2.8 d)$$

where PP represents the principal part of an integral. To keep track of the indices of the zero order vibronic levels we maintain the notation of a sum in (2.8), bearing in mind that in the statistical limit $\{|l\rangle\}$ is a quasicontinuum whereupon $\sum_l \rightarrow \int dE_l \rho_l$. Let us note that $\alpha(E)$ and $\beta(E)$ represent 'mixed type' level shifts and level widths which connect the zero order state $|s\rangle$ and $|b\rangle$ via the quasicontinuum.

The 'golden rule' level shifts, D_s and D_b and widths, Γ_s and Γ_b , of the zero order states $|s\rangle$ and $|b\rangle$ are defined by

$$S(E) = D_s(E) - i\Gamma_s(E) = \sum_l \frac{V_{sl}V_{sl}}{Z - E_s}, \quad (2.9)$$

where

$$D_s(E) = PP \sum_l \frac{V_{sl}V_{ls}}{E - E_s}, \quad (2.9 a)$$

$$\Gamma_s(E) = \pi \sum_l |V_{sl}|^2 \delta(E - E_s) \quad (2.9 b)$$

and

$$B(E) = D_b(E) - i\Gamma_b(E) = \sum_l \frac{V_{bl}V_{lb}}{Z - E_l}, \quad (2.10)$$

where

$$D_b(E) = PP \sum_l \frac{|V_{bl}|^2}{E - E_l}, \quad (2.10 a)$$

$$\Gamma_b(E) = \pi \sum_l |V_{bl}|^2 \delta(E - E_l). \quad (2.10 b)$$

It is important to note at this point that the (zero order) width $\Gamma_s(E)$ does not necessarily correspond to the total width $\Gamma(E)$ of the resonance located around $E \approx E_s$, as off-resonance coupling of terms will contribute to Γ .

Simple algebraic manipulations of equations (2.7 a)–(2.7 d) enable us to express these off diagonal matrix elements in terms of the diagonal element G_{ss} as follows:

$$G_{sb} = G_{ss} \frac{V_{sb} + \tilde{A}(E)}{Z - E_b - B(E)}, \quad (2.11 a)$$

$$G_{bs} = G_{ss} \frac{V_{bs} + A(E)}{Z - E_b - B(E)}, \quad (2.11 b)$$

$$G_{sl} = G_{ss} \left[\frac{V_{sl}}{Z - E_l} + \frac{V_{bl}}{Z - E_l} \left(\frac{V_{sb} + \tilde{A}(E)}{Z - E_b - B(E)} \right) \right], \quad (2.12 a)$$

$$G_{ls} = G_{ss} \left[\frac{V_{ls}}{Z - E_l} + \frac{V_{lb}}{Z - E_l} \left(\frac{V_{bs} + A(E)}{Z - E_b - B(E)} \right) \right]. \quad (2.12 b)$$

Making use of equation (2.11) the off diagonal terms (2.7 e) and (2.7 f) are

$$G_{lb} = \frac{V_{lb}}{Z - E_l} \left(\frac{1}{Z - E_b - B(E)} + \frac{(V_{bs} + A(E))(V_{sb} + \tilde{A}(E))}{(E - E_b - B(E))^2} G_{ss} \right) + \frac{V_{ls}}{Z - E_l} \left(\frac{V_{sb} + \tilde{A}(E)}{Z - E_b - B(E)} \right) G_{ss}, \quad (2.13 a)$$

$$G_{bl} = \frac{V_{bl}}{Z - E_l} \left(\frac{1}{Z - E_b - B(E)} + \frac{(V_{bs} + A(E))(V_{sb} + \tilde{A}(E))}{(E - E_b - B(E))^2} G_{ss} \right) + \frac{V_{ls}}{Z - E_l} \left(\frac{V_{sb} + \tilde{A}(E)}{Z - E_b - B(E)} \right) G_{ss}. \quad (2.13 b)$$

Utilizing equations (2.11)–(2.13) the diagonal matrix elements (2.7 h) and (2.7 i) take the form

$$G_{bb} = \frac{1}{Z - E_b - B(E)} + \frac{(V_{bs} + A(E))(V_{sb} + \tilde{A}(E))}{(E - E_b - B(E))^2} G_{ss} \quad (2.14 a)$$

which may also be recast in the alternative form

$$G_{bb} = \frac{Z - E_s - S(E)}{Z - E_b - B(E)} G_{ss} \quad (2.14 b)$$

and

$$G_{ss} = \left\{ Z - E_s - S(E) - \frac{(V_{bs} + A(E))(V_{sb} + \tilde{A}(E))}{E - E_b - B(E)} \right\}^{-1}. \quad (2.15)$$

From equations (2.14) and (2.15) it is apparent, as we have already pointed out, that the total widths of the resonances are not given by $\text{Im } B(E)$ and by $\text{Im } S(E)$, and that off resonance coupling terms are important. In particular, it will be useful to rewrite equation (2.15) in the form

$$G_{ss} = \{Z - E_s - D(E) + i\Gamma(E)\}^{-1}, \quad (2.15 a)$$

where the total level shift of s is

$$D(E) = \text{Re} \left\{ S(E) + \frac{(V_{bs} + A(E))(V_{sb} + \tilde{A}(E))}{E - E_b - B(E)} \right\}. \quad (2.16)$$

The corresponding total line width is given from (2.15), (2.8), and (2.9)

$$\Gamma(E) = \Gamma_s(E) - \text{Im} \frac{(V_{bs} + \alpha - i\beta)(V_{sb} + \alpha^* - i\beta^*)}{E - E_b - D_b(E) + i\Gamma_b(E)}. \quad (2.17)$$

We have already pointed out [10 b] that equation (2.17) can be recast in a manner which is similar to the Fano line shape formula [2] taken at a single energy $E \approx E_s$. Defining the auxiliary parameters :

$$\tilde{\epsilon}(E) = \frac{E - E_b - D_b(E)}{T_b(E)}, \quad (2.18 a)$$

$$\tilde{q}(E) \exp(i\theta(E)) = \frac{V_{bs} + \alpha(E)}{\beta(E)}, \quad (2.18 b)$$

we get

$$\begin{aligned} \Gamma(E) &= \Gamma_s(E) + \frac{|\beta(E)|^2 \tilde{q}(E)^2 - 1 + 2\tilde{\epsilon}(E)\tilde{q}(E) \cos \theta}{\Gamma_b(E) (1 + \tilde{\epsilon}(E)^2)} \\ &= \Gamma_s(E) \frac{\tilde{q}(E)^2 + \tilde{\epsilon}(E)^2 + 2\tilde{q}(E)\tilde{\epsilon}(E) \cos \theta}{1 + \tilde{\epsilon}(E)^2}, \end{aligned} \quad (2.19)$$

where we have utilized the relation $|\beta(E)|^2 = \Gamma_b(E)\Gamma_s(E)$ which originates from equations (2.8), (2.9) and (2.10). It is interesting to note that when non degenerate electronic states are involved, then both for internal conversion (V_{bs} , $\beta(E)$ and $\Gamma(E)$ all real) and for intersystem crossing (V_{bs} , $\beta(E)$ and $\alpha(E)$ all complex) we have $\theta = 0$ in (2.18) and equation (2.19) is further simplified to yield the familiar expression

$$\Gamma(E) = \Gamma_s(E) \frac{(\tilde{q} + \tilde{\epsilon})^2}{(1 + \tilde{\epsilon})^2}, \quad (2.19 a)$$

This last result† can be recast in a somewhat more detailed form

$$\begin{aligned} \Gamma(E) &= [\Gamma_b(E)(V_{sb} + \alpha(E))^2 + 2(E - E_b - D_b(E))\beta(E)(V_{sb} + \alpha(E)) \\ &\quad + \Gamma_s(E)(E - E_b - D_b(E))^2] / [(E - E_b - D_b(E))^2 + \Gamma_b(E)^2]. \end{aligned} \quad (2.19 b)$$

We have considered G_{ss} in such detail, as the line shape can be expressed in our model in terms of the functions $A(E)$, $B(E)$, (which are determined by the coupling terms V_{sl} and V_{bl} with the quasicontinuum), the interstate coupling term V_{sb} and by the matrix element G_{ss} (equation (2.19)). The following points are now pertinent :

(a) As we are interested in the resonance centred around $E \approx E_s$, then in the statistical limit one can assert that the functions $A(E)$, (equation (2.8 a)), $\tilde{A}(E)$, (equation (2.8 b)), [or $\alpha(E)$ and $\beta(E)$, equations (2.8 c) and (2.8 d)], $S(E)$, (equation 2.9) [or $D_s(E)$ and $\Gamma_s(E)$, (equations (2.9 a) and (2.9 b))], $B(E)$, (equation (2.10), [or $D_b(E)$ and $\Gamma_b(E)$, (equations (2.10 a) and (2.10 b))], and finally, $D(E)$, (equation (2.16)) and $\Gamma(E)$, (equation (2.19)) are all weakly varying functions of the energy in the vicinity of $E \approx E_s$. Thus for reasonable estimates of the line shape, all these functions can be taken at a fixed energy. If the details of the level distributions and the coupling strength within the quasicontinuous manifold $\{|I\rangle\}$ are known,

† A cursory examination of equation (2.19 a) might indicate that the linewidth can vanish due to interference when $\tilde{\epsilon} = -\tilde{q}$ [15]. However, it is meaningless to consider a simple exponential decay in this case, and consequently to regard Γ as a reciprocal decay time or a line width, as Γ is strongly dependent on E .

the energy dependence of these generalized width and level shifts can be estimated. In § 3 we shall demonstrate that for $|E - E_s| \ll \hbar\omega_M$ (where ω_M is the totally symmetric vibration of maximum frequency) the correction to the line width function (due to its energy dependence) is trivial, while for $|E - E_s| \sim \hbar\omega_M$ this correction is of the order of 30–50 per cent.

(b) The level shifts $\alpha(E)$, (equations (2.8 c)), $D_b(E)$, (equation (2.10 a)) and $D(E)$, (equation (2.16)) which are also weakly dependent on the energy in the vicinity of $E \approx E_s$ will be incorporated in the zero order energies in the form

$$\tilde{E}_s = E_s + D(E), \quad (2.20)$$

$$\tilde{E}_b = E_b + D_b(E). \quad (2.21)$$

Note that in this definition the correction term to the energy of the zero order s state includes the whole contributions (2.16) while the energy of the E_b state includes just the first order corrections due to the interaction with the quasicontinuum.

(c) The general width $\Gamma(E)$ (equation (2.19)) could be derived in an alternative manner by invoking the formal relation

$$\Gamma(E) = \text{Im} \langle S | R(E) | S \rangle, \quad (2.22)$$

where $R(E)$ is the level shift operator [16]. We believe that the present derivation is somewhat more transparent.

(d) Equation (2.19) for the generalized width $\Gamma(E)$ implies that $\Gamma(E) \neq \Gamma_s(E)$ (where $\Gamma_s(E)$ is given by equation (2.9 b)). When off-resonance coupling terms are appreciable, the width (and the relaxation time) cannot be described in terms of the Fermi 'Golden rule' expression but rather by (2.22). This point brings up a 'convenience principle' for the choice of the A basis set to describe electronic relaxation processes.

(e) In principle the general line shape for a molecular resonance (equation (2.6)) is expected to exhibit deviation from a lorentzian (characterized by the width $\Gamma(E_s)$) due to the energy dependence of $\Gamma(E)$. This energy dependence can be traced to two factors: first, the intervention of the state $|b\rangle$ and secondly the correction discussed in (a) above and in § 3.

This completes our formal discussion of the line shape problem, without referring to any specific approximations except the use of the model system (figure 1) and the mild restriction on the basis set which is diagonal within a given electronic configuration. Two cases of physical interest will now be encountered. (1) The zero order states $|s\rangle$ and $|b\rangle$ correspond to the same electronic configuration. In this case $V_{bs} = 0$, while the energy separation $|E_s - E_b| \sim \hbar\omega$ is small. In this case (provided that $\alpha(E)$ is neglected) the line width function (2.19 a) will be given by

$$\Gamma(E) = \Gamma_s(E) \frac{\tilde{\epsilon}(E)^2}{1 + \tilde{\epsilon}(E)^2}$$

(2) The zero order $|s\rangle$ and $|b\rangle$ states correspond to different electronic configurations. Now, $V_{sb} \neq 0$, while the energy spacing $E_s - E_b \approx \Delta E_{sb}$ is large corresponding roughly to the electronic energy gap between the s and b states. If $\Gamma_b(E_s) \ll \Delta E_{sb}$ the line width function takes the form $\Gamma(E) = \Gamma_s(E)(1 + V_{sb}/(E - E_b))$ for $E \approx E_s$. The latter result corresponds to a simple perturbation expansion.

3. COMMENTS ON THE ENERGY DEPENDENCE OF THE NON-RADIATIVE WIDTHS

The energy dependence of the non-radiative widths $\Gamma_s(E)$ and $\Gamma_b(E)$ and of the 'mixed width' $\beta(E)$ can be estimated by invoking the theory of multiphonon processes in large molecules [17-19]. As it is well known, these functions can be expressed in terms of a Fourier transform of a generating function and the integral can be handled by the steepest descent method, resulting in a generalized 'energy gap law' equation [18-19].

To obtain a reasonable estimate it will be sufficient to focus attention on a model molecule which we take to be characterized by displaced harmonic potential surfaces. The calculations of

$$\Gamma_s(E) = \pi \sum_l |V_{sl}|^2 \delta(E - E_l), \quad (3.1)$$

$$\Gamma_b(E) = \pi \sum_l |V_{bl}|^2 \delta(E - E_l) \quad (3.2)$$

and

$$\beta(E) = \pi \sum_l V_{bl} V_{ls} \delta(E - E_l) \quad (3.3)$$

may all be performed on equal footing by evaluating the appropriate generating functions [17-19] $J_{ss}(t)$, $J_{bb}(t)$ and $J_{bs}(t)$, in terms of which we have

$$\Gamma_s(E) = \frac{1}{\hbar} \int_{-\infty}^{\infty} J_{ss}(t) dt, \quad (3.4)$$

$$\Gamma_b(E) = \frac{1}{\hbar} \int_{-\infty}^{\infty} J_{bb}(t) dt \quad (3.5)$$

and

$$\beta(E) = \frac{1}{\hbar} \int_{-\infty}^{\infty} J_{bs}(t) dt. \quad (3.6)$$

Now, provided that the promoting modes are identical in the electronic states $|s\rangle$, $|l\rangle$ and $|b\rangle$, the generating functions can be displayed in the form [18, 19]

$$J_{bs}(t) = \sum_{k=1}^p \frac{C_{bl} C_{ls}}{8} \hbar \omega_k \exp \left[-i(E - E_l^0) \frac{t}{\hbar} \right] \\ \times [(v_k + 1) \exp(i\omega_k t) + v_k \exp(-i\omega_k t)] \prod_{\mu \neq k} g_{\mu}^{bs}(t), \quad (3.7)$$

where b and s are assumed to possess the same electronic symmetry and also to be characterized by equal occupation numbers v_k of the promoting modes k . C_{bl} and C_{ls} are electronic coupling matrix elements and E_l^0 will represent the electronic origin of the l th state ($i = s, l$ or b). Finally $g_{\mu}^{bs}(t)$ in (3.7) is given by [20]

$$g_{\mu}^{bs}(t) = \langle v_{b\mu} | \exp(iP_{\mu}(0)\Delta_{b\mu}) \exp(-iP_{\mu}(t)\Delta_{s\mu}) | v_{s\mu} \rangle, \quad (3.8)$$

where $\Delta_{b\mu}$ and $\Delta_{s\mu}$ are the normalized (reduced) components of the shifts of the b and s potential surfaces relative to the l potential surface. $P_{\mu}(t)$ is the Heizenberg

IE NON-RADIATIVE WIDTHS

the $\Gamma_s(E)$ and $\Gamma_b(E)$ and of the theory of multiphonon promotion, these functions can be written as a generating function and the integral representation in a generalized energy

to focus attention on a model of harmonic potential surfaces.

$$(1), \quad (3.1)$$

$$(2), \quad (3.2)$$

$$(3), \quad (3.3)$$

using the appropriate generating function which we have

$$(4), \quad (3.4)$$

$$(5), \quad (3.5)$$

$$(6), \quad (3.6)$$

valid in the electronic states $|s\rangle$, and in the form [18, 19]

$$(-i\omega_k t) \prod_{\mu \neq k} g_{\mu}^{bs}(t), \quad (3.7)$$

where $g_{\mu}^{bs}(t)$ is the generating function for the μ mode, and C_{b_i} and C_{s_i} will represent the electronic shifts. Equation (3.7) is given by [20]

$$iP_{\mu}(t)\Delta_{s\mu}|v_{s\mu}\rangle, \quad (3.8)$$

where $\Delta_{s\mu}$ and $\Delta_{b\mu}$ are the components of the shifts of the b potential surface. $P_{\mu}(t)$ is the Heisenberg

representation of the reduced momentum of the μ mode, expressed in terms of creation, a_{μ}^+ and annihilation a_{μ} operators for this mode

$$P_{\mu}(0) = \frac{i}{\sqrt{2}} (a_{\mu}^+ - a_{\mu}), \quad (3.9 a)$$

$$P_{\mu}(t) = \frac{i}{\sqrt{2}} (a_{\mu}^+ \exp(i\omega_{\mu}t) - a_{\mu} \exp(-i\omega_{\mu}t)). \quad (3.9 b)$$

Utilizing elementary commutation relations [20, 21] equation (3.8) can be recast in the form:

$$g_{\mu}^{bs}(t) = \exp \left[-\frac{1}{4} (\Delta_{b\mu}^2 + \Delta_{s\mu}^2) - \frac{1}{2} \Delta_{s\mu} \Delta_{b\mu} \exp(i\omega_{\mu}t) \right] \times \frac{1}{\sqrt{(v_{s\mu}! v_{b\mu}!)}} \langle 0 | (a - \lambda_{b_s}^{\mu}(t))^{v_{b\mu}} (a^+ + \lambda_{s_s}^{\mu}(t))^{v_{s\mu}} | 0 \rangle, \quad (3.10)$$

where

$$\lambda_{b_s}^{\mu}(t) = \frac{1}{\sqrt{2}} (\Delta_{b\mu} - \Delta_{s\mu} \exp(-i\omega_{\mu}t)) \quad (3.11)$$

applying the binomial expansion, equation (3.10) yields after some algebraic manipulations

$$g_{\mu}^{bs}(t) = \exp \left[-\frac{1}{4} (\Delta_{b\mu}^2 + \Delta_{s\mu}^2) - \frac{\Delta_{s\mu} \Delta_{b\mu}}{2} \exp(i\omega_{\mu}t) \right] \times \sqrt{(v_{s\mu}! v_{b\mu}!)} \sum_{r=0}^{\min(v_{s\mu}, v_{b\mu})} (-1)^{v_{b\mu}-r} \times \frac{(\lambda_{b_s}^{\mu}(t))^{v_{s\mu}} (\lambda_{s_s}^{\mu}(t))^{v_{b\mu}} |\lambda_{b_s}^{\mu}(t)|^{-2r}}{r! (v_{s\mu}-r)! (v_{b\mu}-r)!}. \quad (3.12)$$

In the calculation of a diagonal matrix element whereupon s and b correspond to the same potential surface we have to set $\Delta_{b\mu} = \Delta_{s\mu}$ and $v_{s\mu} = v_{b\mu}$. If we want to calculate a width, say $\Gamma_s(E)$, the relevant generating function $J_{ss}(t)$ will contain the diagonal matrix elements $g_{\mu}^{ss}(t)$. As is evident from equation (3.7) and (3.12) the functional form of energy dependence of a real width [equation (3.4) and (3.5)], or of a 'mixed width', [equation (3.6)] is identical. All the pertinent information is contained in the generating functions. Thus equations (3.4)–(3.6) together with (3.7) and (3.12) exhibit the general energy dependence of the relevant width functions. To consider a specific example let us focus attention on the 'mixed width' for the case $v_{s\mu} = 0$ and $v_{b\mu} = 1$ where all the other occupation numbers are zero. In this case equation (3.12) takes the form

$$g_{\mu}^{0,1}(t) = -\exp \left[\left(-\frac{\Delta_{b\mu}^2 + \Delta_{s\mu}^2}{4} \right) - \frac{\Delta_{s\mu} \Delta_{b\mu}}{2} \exp(i\omega_{\mu}t) \right] \times \left[\frac{\Delta_{b\mu}}{\sqrt{2}} - \frac{\Delta_{s\mu}}{\sqrt{2}} \exp(i\omega_{\mu}t) \right]. \quad (3.13)$$

From this simple result and from the general relations (3.7) and (3.12) it is apparent that for small vibrational occupation numbers (such that $E - E_i^0 \gg v\hbar\omega$) the problem

of the energy dependence of the width is reduced to the problem of the energy dependence of integrals of the form

$$I = \int_{-\infty}^{\infty} \exp\left(-i\Delta E \frac{t}{\hbar}\right) \exp(\Delta \exp(i\omega t)), \quad (3.14)$$

where Δ is of the order of magnitude of $\sum \frac{1}{2} \Delta_{\mu}^2$ and $\Delta E = E - E_i^0$. Integrals of this type have been commonly encountered in the theory of multiphonon processes and have been evaluated [18-19] by the saddle point approximation to yield

$$I \sim \exp\left(-\gamma \frac{\Delta E}{\hbar\omega_M}\right) = \exp\left(-\frac{\gamma}{\hbar\omega_M} (E - E_i^0)\right), \quad (3.15)$$

where ω_M is the maximum molecular frequency and γ is of the order of unity.

Equation (3.15) provides us with a reasonable approximation for the energy dependence of the non radiative widths. As a relevant example let us consider the width of the zero order state s , which is given by

$$\Gamma_s(E) \sim \exp\left[-\frac{\gamma}{\hbar\omega_M} (\Delta E_{si} + (E - E_s))\right], \quad (3.16)$$

where $\Delta E_{si} = E_s - E_i^0$ representing the electronic energy gap between s and the l manifolds. Thus the energy dependence of the non radiative widths is

$$\Gamma_s(E) = \Gamma_s(E_s) \exp\left(\frac{\gamma}{\hbar\omega_M} (E_s - E)\right). \quad (3.17)$$

Similar equations will result from the energy dependence of $\Gamma_b(E)$ and $\beta(E)$ in the vicinity of $E \approx E_s$. The numerical estimates in § 2 are based on equation (3.17).

The general criterion for the weak energy dependence of a line width function $I(E)$ (equations (3.14) and (3.15)) is given by the simple relation

$$\left|\frac{dI}{dE}\right|_{E_c} \ll 1, \quad (3.18)$$

where E_c corresponds to the centre of the line, for the case under consideration $E_c \approx E_s$. Thus for $\Gamma_s(E)$ (equation 3.16)) we have

$$\left|\frac{d\Gamma_s(E)}{dE}\right|_{E=E_s} = \Gamma_s(E_s) \frac{\gamma}{\hbar\omega_M} \ll 1. \quad (3.18 a)$$

As $\gamma \sim 1$ the weak energy dependence of the line width function will imply

$$\Gamma_s(E_s) \ll \hbar\omega_M. \quad (3.19)$$

Thus we expect that the energy dependent corrections to the line width function are small provided that interference (i.e. overlap) between adjacent resonances is negligible.

We shall now proceed to consider the features of the line shape in the A and in the CA basis, limiting our considerations to the case of internal conversion. Apart

from the point made preceding equation (2.19 a) the case of the (spin orbit induced) intersystem crossing is simple and does not add any new physical features to the problem.

4. THE LINE SHAPE IN THE CA BASIS

The most useful feature of the CA basis involves the preservation of the molecular symmetry properties, as the electronic wavefunctions are chosen at a fixed nuclear configuration \mathbf{Q}_0 which corresponds to the equilibrium ground state :

$$\left. \begin{aligned} |S^{(CA)}\rangle &= \varphi_s(\mathbf{r}, \mathbf{Q}_0) \chi_{si}^{(CA)}(\mathbf{Q}), \\ |I^{(CA)}\rangle &= \varphi_I(\mathbf{r}, \mathbf{Q}_0) \chi_{Ij}^{(CA)}(\mathbf{Q}), \\ |b^{(CA)}\rangle &= \varphi_b(\mathbf{r}, \mathbf{Q}_0) \chi_{bk}^{(CA)}(\mathbf{Q}), \end{aligned} \right\} \quad (4.1)$$

where φ represent the eigenfunctions of the electronic hamiltonian for variable electronic coordinates at the fixed nuclear configuration \mathbf{Q}_0 , while $\chi^{(CA)}(\mathbf{Q})$ are the crude adiabatic vibrational wavefunctions (which differ in principle from the adiabatic vibrational wavefunctions). Now, provided that $|s^{(CA)}\rangle$ is accessible by optical excitation from the vibrationless level of the ground state, $\chi_{si}^{(CA)}(\mathbf{Q})$ will in the harmonic approximation involve only totally symmetric vibrational modes. In the weak electronic vibrational coupling limit the off-diagonal near resonance matrix elements in this basis are $\langle S^{(CA)} | \sum_k (\partial U(\mathbf{r}, \mathbf{Q}) / \partial Q_k)_0 Q_k | I^{(CA)} \rangle$ where $U(\mathbf{r}, \mathbf{Q})$ is the molecular potential. Let us further assume that the electronic states $\varphi_s(\mathbf{r}, \mathbf{Q}_0)$ and $\varphi_I(\mathbf{r}, \mathbf{Q}_0)$ are characterized by different symmetry. Then the well-known rules for vibronic coupling [17] imply that the vibrational states $\{\chi_{Ij}^{(CA)}(\mathbf{Q})\}$ of the effective quasicontinuum have to contain a non-totally symmetric promoting mode. Thus

$$\mu_{0I}^{(CA)} = \langle 0 | \mu | \varphi_I(\mathbf{r}, \mathbf{Q}_0) \chi_{Ij}^{(CA)}(\mathbf{Q}) \rangle = 0$$

for all j . It is safe to assert that the relevant states in the $\{|I\rangle\}$ manifold do not carry oscillator strength from the ground state.

The line shape function (2.6) now takes the simplified form :

$$\begin{aligned} L(E) = -\frac{1}{\pi} \text{Im} \{ & \mu_{0s}^{(CA)} G_{ss}^{(CA)} \mu_{s0}^{(CA)} + \mu_{0b}^{(CA)} G_{bb}^{(CA)} \mu_{b0}^{(CA)} \\ & + \mu_{0s}^{(CA)} G_{sb}^{(CA)} \mu_{b0}^{(CA)} + \mu_{0b}^{(CA)} G_{bs}^{(CA)} \mu_{b0}^{(CA)} \}. \end{aligned} \quad (4.2)$$

Utilizing equations (2.11 a), (2.11 b) and (2.14 a) we get

$$\begin{aligned} L(E) = -\frac{1}{\pi} \text{Im} \left[& G_{ss}^{(CA)} |\mu_{0s}^{(CA)}|^2 + \frac{|\mu_{0b}^{(CA)}|^2}{E - \tilde{E}_b^{(CA)} + i\Gamma_b^{(CA)}(E)} \right. \\ & + |\mu_{0b}^{(CA)}|^2 \left(\frac{V_{bs}^{(CA)} + A^{(CA)}(E)}{E - \tilde{E}_b^{(CA)} + i\Gamma_b^{(CA)}(E)} \right)^2 G_{ss}^{(CA)} \\ & + \mu_{0s}^{(CA)} \mu_{b0}^{(CA)} \left(\frac{V_{sb}^{(CA)} + \tilde{A}^{(CA)}(E)}{E - \tilde{E}_b^{(CA)} + i\Gamma_b^{(CA)}(E)} \right) G_{ss}^{(CA)} \\ & \left. + \mu_{0b}^{(CA)} \mu_{s0}^{(CA)} \left(\frac{V_{bs}^{(CA)} + A^{(CA)}(E)}{E - \tilde{E}_b^{(CA)} + i\Gamma_b^{(CA)}(E)} \right) G_{ss}^{(CA)} \right]. \end{aligned} \quad (4.3)$$

This form is particularly useful when discussing the influence of the state $|b\rangle$ on the lineshape in the vicinity of E_s , when $E - E_b \gg \Gamma(E)$, i.e. when $|b\rangle$ corresponds to a different electronic configuration. Equation (4.3) can be now displayed in a more transparent form

$$L(E) = \frac{1}{\pi} \frac{|\mu_{0b}^{(CA)}|^2 \Gamma_b^{(CA)}(E)}{(E - \tilde{E}_b^{(CA)})^2 + (\Gamma_b^{(CA)}(E))^2} - \frac{1}{\pi} \operatorname{Im} \left\{ \frac{1}{E - \tilde{E}_s^{(CA)} + i\Gamma^{(CA)}(E)} [\mu_{0s} + \mu_{0b}(\varphi(E) - i\eta(E))] \times [\mu_{s0} + \mu_{b0}(\varphi^*(E) - i\eta^*(E))] \right\}, \quad (4.4)$$

where we have defined the auxiliary functions

$$\varphi(E) = \frac{(V_{bs}^{(CA)} + \alpha^{(CA)})(E - \tilde{E}_b) - \beta^{(CA)}(E)\Gamma_b^{(CA)}(E)}{(E - \tilde{E}_b)^2 + (\Gamma_b^{(CA)})^2}, \quad (4.5 a)$$

$$\eta(E) = \frac{\beta^{(CA)}(E)(E - \tilde{E}_b) + \Gamma_b^{(CA)}(E)(V_{bs}^{(CA)} + \alpha^{(CA)})}{(E - \tilde{E}_b)^2 + (\Gamma_b^{(CA)})^2}. \quad (4.5 b)$$

For the case $E - E_b \gg \Gamma_b(E)$ these functions exhibit a weak energy dependence in the vicinity of $E \approx E_s$.

For internal conversion the functions (4.5) are real. We can now define the energy dependent reduced effective energy $\epsilon(E)$ and the line index $q(E)$ in the form

$$\epsilon(E) = \frac{E - E_s}{\Gamma^{(CA)}(E)}, \quad (4.6 a)$$

$$q(E) = \frac{\mu_{0s}^{(CA)} + \mu_{0b}^{(CA)}\varphi(E)}{\mu_{0b}^{(CA)}\eta(E)} \quad (4.6 b)$$

to get a generalized Fano type [2] equation

$$L(E) = \frac{1}{\pi} \frac{|\mu_{0b}^{(CA)}|^2 \Gamma_b^{(CA)}(E)}{(E - \tilde{E}_b)^2 + (\Gamma_b^{(CA)}(E))^2} + \frac{|\mu_{0b}^{(CA)}|^2 (\eta(E))^2}{\pi \Gamma^{(CA)}(E)} \times \frac{q^2(E) - 1 + 2q(E)\epsilon(E)}{1 + \epsilon(E)^2}. \quad (4.7)$$

From equation (4.7) we conclude that interference effects in the line shape will be always exhibited. However, the magnitude of these effects depends on the specific cases to be now considered :

(a) Interstate s - b coupling, φ_s and φ_b correspond to different symmetry of the molecular point group. In this case $\alpha(E) = \beta(E) = 0$ for all E as $|b\rangle$ is not coupled to the same quasicontinuum as $|s\rangle$. Now equation (4.4) will yield just a superposition of two lorentzians

$$L(E) = \frac{\Gamma^{(CA)}(E) \left(\mu_{0s}^{(CA)} + \mu_{0b}^{(CA)} \frac{V_{bs}}{E_s - E_b} \right)^2}{(E - \tilde{E}_s)^2 + \Gamma^{(CA)}(E)^2} + \frac{|\mu_{0b}^{(CA)}|^2 \Gamma_b^{(CA)}(E)}{(E - \tilde{E}_b)^2 + \Gamma_b^{(CA)}(E)^2} \quad (4.8)$$

namely the lorentzian corresponding to the s resonance seated on the background of the lorentzian which corresponds to the $|b\rangle$ state. Note that this simple result accounts both for symmetry allowed and symmetry forbidden transitions. We thus conclude that electronic states of different electronic symmetry will not contribute to interference effects in the line shape. However, these states may contribute to the total line with, $\Gamma(E)$, provided that V_{sb} is appreciable.

(b) Interstate s - b coupling, φ_s and φ_b correspond to the same symmetry. In this case we can usually assume that $|\tilde{E}_s - \tilde{E}_b| \gg \Gamma_b(E)$ (otherwise the general equation (4.4) has to be used). Under this condition $\varphi(E) \approx V_{bs}^{(CA)}/(E - \tilde{E}_b)$ and $\eta(E) \approx \beta^{(CA)}/(E - \tilde{E}_b)$ whereupon

$$q = \frac{\mu_{0s}^{(CA)} + \mu_{0b}^{(CA)} V_{bs}/(E - \tilde{E}_b)}{\mu_{0b}^{(CA)} [\beta^{(CA)}/(E - \tilde{E}_b)]} \quad (4.9)$$

and†

$$L(E) = \frac{|\mu_{0b}^{(CA)}|^2 \Gamma_b^{(CA)}(E)}{(E - \tilde{E}_b)^2} + \frac{|\beta^{(CA)}(E)|^2}{\Gamma^{(CA)}(E)} |\mu_{0b}^{(CA)}|^2 \frac{q^2 + 2\epsilon q - 1}{1 + \epsilon^2}. \quad (4.10)$$

Now for a symmetry allowed $|0\rangle \rightarrow |s\rangle$ transition the line profile index is

$$q \approx \frac{\Delta E_{sb} \mu_{0s}^{(CA)}}{\Gamma_s^{(CA)}(E_s) \mu_{0b}^{(CA)}}. \quad (4.10 a)$$

(Note that $\beta \sim \Gamma_s$.) The ratio of the transition moments is ~ 0.1 - 10.0 while $\Delta E_{sb}/\Gamma_s \sim 10^4$ - 10^2 , thus the line profile index $q \gtrsim 10$ and only small deviation from lorentzian line shape is exhibited, expect, of course, for a small ΔE_{sb} energy gap.

Consider now the case where $|s\rangle$ and $|b\rangle$ correspond to the same electronic configuration. In this case $V_{bs} = 0$. We should note that the form of equation (4.7) is misleading, as $q(E)$ is now strongly energy dependent. Still we can express the line shape function in a simple alternative form, taking advantage of the fact that V_{bs} vanishes. Assuming also that α may be neglected equation (4.3) yields after some algebraic manipulations.

$$L(E) = \frac{1}{\pi} \frac{2\beta^{(CA)}(E) \mu_{0s}^{(CA)} \mu_{0b}^{(CA)} (E - \tilde{E}_s)(E - \tilde{E}_b) + \mu_{0s}^{(CA)2} \Gamma_s^{(CA)}(E)(E - \tilde{E}_b)^2 + \mu_{0b}^{(CA)2} \Gamma_b^{(CA)}(E)(E - \tilde{E}_s)^2}{[(E - \tilde{E}_s)(E - \tilde{E}_b)]^2 + \{[\Gamma_s^{(CA)}(E)(E - \tilde{E}_b) + \Gamma_b^{(CA)}(E)(E - \tilde{E}_s)]\}^2} \quad (4.11)$$

where the matrix elements are again taken to be real.

It is convenient now to define the parameter

$$\delta(E) = \frac{E - \tilde{E}_s}{E - \tilde{E}_b} \quad (4.12)$$

in terms of which equation (4.11) may be recast in the form

$$L(E) = \frac{1}{\pi} \frac{(\mu_{0b}^{(CA)}) \sqrt{[\Gamma_b^{(CA)}(E)]} \delta(E) + (\text{sign } \beta) \mu_{0s}^{(CA)} \sqrt{[\Gamma_s^{(CA)}(E)]}}{(E - \tilde{E}_s)^2 + (\Gamma_s^{(CA)}(E) + \Gamma_b^{(CA)}(E) \delta(E))^2}, \quad (4.13)$$

† Note that $|\beta|^2 = \Gamma_b \Gamma_s$ so that only when $\Gamma_s = \Gamma$ (i.e. $V_{bs} = 0$) equation (4.10) is reduced to the conventional Fano formula [2].

where we have utilized the relation $\beta(E) = \pm \sqrt{[\Gamma_b(E)\Gamma_s(E)]}$ and $\text{sign}(\beta) = \pm 1$. From equation (4.13) it is immediately apparent that we shall encounter destructive interference (i.e. $L(E) = 0$) either between \tilde{E}_s and \tilde{E}_b or outside the energy region enclosed by \tilde{E}_s and \tilde{E}_b , depending on the sign of β . The condition for a dip in the lineshape is

$$\delta(E) = -\text{sign}(\beta) \frac{\mu_{0s}^{(CA)}}{\mu_{0b}^{(CA)}} \sqrt{\left(\frac{\Gamma_s^{(CA)}(E)}{\Gamma_b^{(CA)}(E)}\right)}. \quad (4.14)$$

The following comments are now in order :

(1) The nature of the interference effect does not depend on the phases of zero order wavefunctions as may be seen from the original expression, equation (2.6), where every wavefunction appears with its complex conjugate. In equation (4.4) the sign of the wavefunctions (which had been chosen to be real) does not influence the result.

(2) The condition (4.14) for destructive interference is determined by the relative sign of μ_{0s} and μ_{0b} which in turn depend on the molecular parameters. For example suppose that s and b denote the zero and first vibrational levels of an excited electronic state whose potential surface is shifted relative to that of the ground electronic state by an amount Δ . The vibrational overlap Franck-Condon

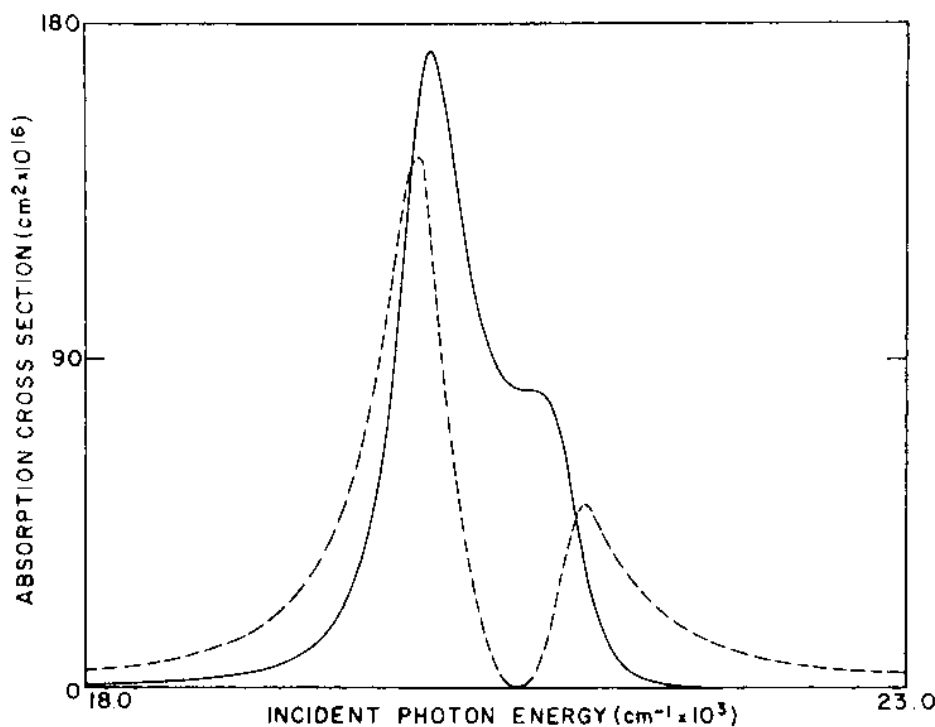


Figure 2. Absorption lineshapes in a system of two overlapping resonances. This particular example corresponds to the absorption from the vibrationless level of the ground electronic state of an harmonic molecule into the vibrationless and the first excited vibronic states of the excited electronic state, whose potential surface is displaced relative to that of the ground electronic state. The electronic energy gap is $20\,000\text{ cm}^{-1}$, the relevant molecular frequency is 100 cm^{-1} and the non radiative widths are taken to be 500 cm^{-1} while the electronic dipole matrix element is chosen so that the radiative widths of the two states will be 10^{-3} cm^{-1} . The (normalized) displacement of the electronic states is $+0.8$ for the solid line and -0.8 for the dotted line.

† In these figures we included also the radiative corrections which cause the absorption in the dip to be different from zero [22].

factors will cause μ_{0s}/μ_{0b} to be either positive or negative, depending on the sign of Δ . In figures 2 and 3 we present the results of numerical calculations demonstrating this fact†.

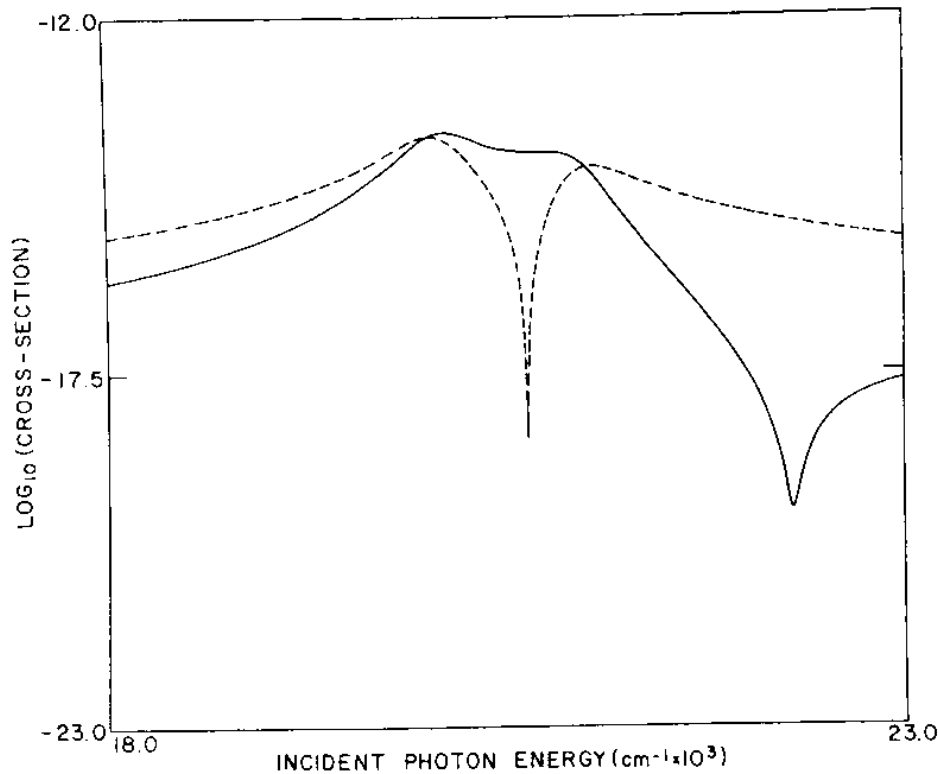


Figure 3. Logarithmic plots of the absorption line profiles which are presented in figure 2.

(3) If the r.h.s. of equation (4.14) is negative that means that dip in the lineshape will be encountered between the energies \tilde{E}_s and \tilde{E}_b (see figure 1 and 2). If the r.h.s. of equation (4.14) is positive the dip will generally not be amenable to experimental observation (see figure 2) as $\delta(E)$ is of the order of magnitude of unity, whereupon complete destructive interference will be exhibited in a region where the absorption is practically zero.

(4) When the widths $\Gamma_b(E)$ and $\Gamma_s(E)$ are small relative to $\tilde{E}_s - \tilde{E}_b$ the lineshape in the vicinity of $E = \tilde{E}_s$ will be fanian [2]. To demonstrate this point we shall rewrite equation (4.13) in the form

$$L(E) = \frac{1}{\pi} \left(\frac{\mu_{0b} \sqrt{[\Gamma_b^{(CA)}(E)]}}{E - \tilde{E}_b} \right)^2 \frac{(\epsilon + q)^2}{\epsilon^2 + 1}, \quad (4.15)$$

where

$$\epsilon = \frac{E - E_s}{\Gamma_s^{(CA)}(E)}, \quad (4.16 a)$$

$$q = \pm \frac{\mu_{0s}^{(CA)}}{\mu_{0b}^{(CA)}} \frac{E - \tilde{E}_b}{\sqrt{[\Gamma_b^{(CA)}(E)\Gamma_s^{(CA)}(E)]}} \quad (4.16 b)$$

and where in the vicinity of \tilde{E}_s , $\delta(E)$ in the denominator may be neglected, and $E - \tilde{E}_b$ (and q) may be regarded as weakly varying functions of the energy. This case is equivalent to the interstate coupling situation discussed above. Note that for the present case $\mu_{0s} \sim \mu_{0b}$, $\Gamma_s \sim \Gamma_b$ while $E - \tilde{E}_b \sim \tilde{E}_s - \tilde{E}_b = \hbar\omega$ (where ω is a totally symmetric vibrational frequency) so that

$$q \sim \frac{\hbar\omega}{\Gamma_s}. \quad (4.17)$$

This result is valid for intrastate coupling when the widths are small.

5. INTERFERENCE EFFECTS IN THE ADIABATIC REPRESENTATION

Following early work in the field it was conventionally assumed that in the A basis the quasicontinuum is optically inactive. For the case of internal conversion the usual argument that the quasicontinuum is characterized by unfavourable Franck-Condon factors (for transitions from the ground state) is not entirely convincing, in view of the large density of states in this manifold. To examine this problem somewhat more closely let us consider the adiabatic wavefunctions

$$\left. \begin{aligned} |S^{(A)}\rangle &= \varphi_s(\mathbf{r}, \mathbf{Q}) \chi_i^{(A)}(\mathbf{Q}), \\ |I^{(A)}\rangle &= \varphi_l(\mathbf{r}, \mathbf{Q}) \chi_j^{(A)}(\mathbf{Q}), \\ |b^{(A)}\rangle &= \varphi_b(\mathbf{r}, \mathbf{Q}) \chi_k^{(A)}(\mathbf{Q}), \end{aligned} \right\} \quad (5.1)$$

where $\varphi(\mathbf{r}, \mathbf{Q})$ represent the (nuclear coordinates \mathbf{Q} dependent) electronic wavefunctions while $\chi^{(A)}$ correspond to the vibrational wavefunctions obtained from the adiabatic potential surfaces. To establish the dependence of the electronic A type wavefunctions on the nuclear coordinates it is not sufficient to apply first order perturbation theory as usually done. We have previously demonstrated [9] that the electronic adiabatic wavefunctions can be expanded in terms of the Wigner-Brillouin perturbation series in the weak electronic vibrational limit. As in the adiabatic representation the role of off-resonance coupling terms is small we can focus attention on a two electronic level system. In this case the energy denominator in the Wigner-Brillouin perturbation expansion is given by the difference between the adiabatic energy surfaces corresponding to the s and l states [9]. Thus the quasicontinuum adiabatic electronic wavefunction takes the form

$$\varphi_l(\mathbf{r}, \mathbf{Q}) = \varphi_l(\mathbf{r}, \mathbf{Q}_0) + \frac{\langle \varphi_s(\mathbf{r}, \mathbf{Q}_0) | V | \varphi_l(\mathbf{r}, \mathbf{Q}_0) \rangle \varphi_s(\mathbf{r}, \mathbf{Q}_0)}{E_l(\mathbf{Q}) - E_s(\mathbf{Q})}. \quad (5.2)$$

In the weak electronic-vibrational coupling limit $E_l(\mathbf{Q}) - E_s(\mathbf{Q})$ is the (\mathbf{Q} dependent) difference between the adiabatic energy surfaces. For this limit the perturbation operator in (5.2) is $V = \sum_k (\partial U / \partial Q_k)_0 Q_k$ where U is the molecular potential and the sum is taken over all normal modes.

Now invoking the conventional symmetry classification for the vibrational $\chi^A(\mathbf{Q})$ wavefunctions [17, 23], we assert that for internal conversion $\chi_{si}^A(\mathbf{Q})$ is totally symmetric, while $\chi_{lj}^A(\mathbf{Q})$ contains a nontotally symmetric mode whereupon

$\langle \chi_{00}^{(A)} | \chi_{ij}^{(A)} \rangle = 0$ so that the first term in (5.2) does not contribute to the transition moment. The electronic transition moment to the quasicontinuum is

$$\begin{aligned} \mu_{0i}^{(A)} &= \langle \varphi_0(\mathbf{r}, \mathbf{Q}_0) | \mu | \varphi_s(\mathbf{r}, \mathbf{Q}_0) \rangle \\ &\times \left(\chi_{00}^{(A)}(\mathbf{Q}) \left| \frac{\sum_k \langle \varphi_s \left| \left(\frac{\partial U}{\partial Q_k} \right)_0 \right| \varphi_i \rangle Q_k}{E_i(\mathbf{Q}) - E_s(\mathbf{Q})} \right| \chi_{ij}^{(A)}(\mathbf{Q}) \right) \\ &= \frac{\mu_{0s}^{(CA)}}{F_{0s}} \left(\chi_{00}^{(A)}(\mathbf{Q}) \left| \frac{\sum_k \langle \varphi_s \left| \left(\frac{\partial U}{\partial Q_k} \right)_0 \right| \varphi_i \rangle Q_k}{E_i(\mathbf{Q}) - E_s(\mathbf{Q})} \right| \chi_{ij}^{(A)}(\mathbf{Q}) \right), \quad (5.3) \end{aligned}$$

where $\langle \rangle$ and $()$ represent integration over electronic and nuclear coordinates respectively. F_{0s} is the Franck-Condon vibrational overlap factor for the $|0\rangle \rightarrow |s\rangle$ optical transition. The calculation of the nuclear integrals in (5.3) cannot be performed by invoking the Condon approximation. Numerical calculations have demonstrated [10 a] that these integrals take the following form for near resonance coupling

$$\begin{aligned} &\sum_k \left(\chi_{00}^{(A)}(\mathbf{Q}) \left| \frac{\langle \varphi_s \left| \left(\frac{\partial U}{\partial Q_k} \right)_0 \right| \varphi_i \rangle Q_k}{E_s(\mathbf{Q}) - E_i(\mathbf{Q})} \right| \chi_{ij}^{(A)}(\mathbf{Q}) \right) \\ &= \sum_k \langle \varphi_s \left| \left(\frac{\partial U}{\partial Q_k} \right)_0 \right| \varphi_i \rangle \left(\chi_{00}^{(A)}(\mathbf{Q}) \left| \frac{Q_k}{E_s(\mathbf{Q}) - E_i(\mathbf{Q})} \right| \chi_{ij}^{(A)}(\mathbf{Q}) \right) \\ &\approx \eta_1 \sum_p \frac{\langle \varphi_s \left| \left(\frac{\partial U}{\partial Q_p} \right)_0 \right| \varphi_i \rangle}{\Delta E_{si}} \langle Q_p \rangle \tilde{F}_{0i}, \quad (5.4) \end{aligned}$$

where ΔE_{si} is the electronic energy gap, the index p refers to the promoting modes, $\langle Q_p \rangle$ is the matrix element of the normal coordinate of the promoting mode between the states specified by the vibrational quantum numbers $v_p=0$ and $v_p=1$, and finally \tilde{F}_{0i} is a reduced Franck-Condon vibrational overlap factor, which excludes the promoting mode. The numerical correction factor, η_1 , is of the order $\eta_1 \approx \Delta E_{si}/\hbar\omega$. Thus we get in the A representation

$$\begin{aligned} \mu_{0i}^{(A)} &\approx \frac{\mu_{0s}^{(CA)}}{F_{0s}} \sum_p \left\langle \varphi_s(\mathbf{r}, \mathbf{Q}_0) \left| \left(\frac{\partial U}{\partial Q_p} \right)_0 \right| \varphi_i(\mathbf{r}, \mathbf{Q}_0) \right\rangle \langle Q_p \rangle \frac{\tilde{F}_{0i}}{\hbar\omega} \\ &\approx \mu_{0s}^{(CA)} \frac{V_{si}^{(CA)}}{\hbar\omega}, \quad (5.5) \end{aligned}$$

where $V_{si}^{(CA)}$ is the CA interstate coupling, provided that the ground and the s state are not shifted in energy. It is worthwhile to note that a straightforward application of first order perturbation theory for near resonance $s-1$ coupling would have resulted in a term which is smaller by $\eta_1 \sim \Delta E_{si}/\hbar\omega$. Our final result (5.5) for the transition moment in the A basis has a simple physical interpretation.

In view of the nuclear dependence of the A electronic functions the symmetry forbidden $\{l\}$ vibronic components have a small allowed vibrational component, and their intensity is determined by $\mu_{0s}^{(CA)}$ and by a (small) Franck-Condon vibrational overlap factor.

The major advantage of the A basis is that off-resonance coupling terms can be disregarded. Setting $V_{sb}^{(A)} \approx 0$ and $V_{bl}^{(A)} \approx 0$ the line shape (apart from a 'background' due to the b state) takes the simple form

$$L(E) = \frac{1}{\pi} \text{Im} \left\{ |\mu_{0s}^{(A)}|^2 G_{ss}^{(A)} + \sum_l \left(\sum_{l'} \mu_{0l}^{(A)} G_{ll'}^{(A)} \mu_{l'0}^{(A)} + \mu_{0s}^{(A)} G_{sl}^{(A)} \mu_{l0}^{(A)} + \mu_{0l}^{(A)} G_{ls}^{(A)} \mu_{s0}^{(A)} \right) \right\}. \quad (5.6)$$

Now utilizing equations (2.7)–(2.19) for the Green's function matrix elements in the A basis our result takes the form

$$L(E) = \sum_l |\mu_{0l}^{(A)}|^2 \delta(E - E_l) + \frac{1}{\pi} \text{Im} \left\{ G_{ss}^{(A)} (\mu_{0s}^{(A)} + J^{(A)} - iI^{(A)}) \times (\mu_{s0}^{(A)} + J^{*(A)} - iI^{*(A)}) \right\}, \quad (5.7)$$

where the 'transition level shift' is

$$J^A(E) = PP \sum_l \frac{\mu_{0l}^{(A)} V_{ls}^{(A)}}{E - E_l} \quad (5.8)$$

while the corresponding mixed width is given by

$$I^A(E) = \pi \sum_l \mu_{0l}^{(A)} V_{ls}^{(A)} \delta(E - E_l). \quad (5.9)$$

We can assume that I and J are real. Now defining the line profile index

$$q^A = \frac{\mu_{0s}^{(A)} + J^{(A)}}{I^{(A)}} \quad (5.10)$$

and the reduced energy

$$\epsilon^A = \frac{E - \tilde{E}_s^{(A)}}{\Gamma_s^{(A)}}. \quad (5.11)$$

The line shape takes the form

$$L(E) = \sum_l |\mu_{0l}^{(A)}|^2 \delta(E - E_l) \frac{(\epsilon^A + q^A)^2}{1 + (\epsilon^A)^2}. \quad (5.12)$$

Now consider the line index parameter in somewhat greater detail. Making use of (5.5) and (5.9) the denominator of equation (5.10) is

$$I^A \approx \mu_{0s}^{(CA)} \sum V_{sl}^{(CA)} V_{ls}^{(A)} \delta(E - E_l) \approx \mu_{0s}^{(CA)} [\Gamma_s^A(E) \Gamma_s^{(CA)}(E)]^{1/2} \approx \mu_{0s}^{(CA)} \Gamma^{(A)}(E) \quad (5.13)$$

whereupon the line index parameter is $q^{(A)} \approx \hbar\omega/\Gamma^A(E_s)$. This result obtained in the A basis utilizing a two-level system is identical to the result obtained in § 4 equation (4.17) for the CA basis utilizing intrastate coupling in a three-level system.

We have just demonstrated that the interference effects in the A and in the CA representations are of the same order of magnitude. However, we did not establish the full equivalence between these two representations. The difficulty lies in the fact that in the A basis the continuum carries oscillator strength via the interaction of the $|s\rangle$ and $|l\rangle$ CA functions, while in the CA basis transitions from the ground state to the continuum occur by second order processes via the state b . A case in which the equivalence between the two representations may be fully established is encountered when $\mu_{0b} \gg \mu_{0s}$ so that also in the adiabatic representation the interaction V_{bl} leads to a major contribution to the continuum oscillator strength. In this case we may express $\varphi_l(\mathbf{r}, \mathbf{Q})$ by an expansion of the form

$$\begin{aligned} \varphi_l(\mathbf{r}, \mathbf{Q}) = & \varphi_l(\mathbf{r}, \mathbf{Q}_0) + \frac{\langle \varphi_s(\mathbf{r}, \mathbf{Q}_0) | V | \varphi_l(\mathbf{r}, \mathbf{Q}_0) \rangle}{E_l(\mathbf{Q}) - E_s(\mathbf{Q})} \varphi_s(\mathbf{r}, \mathbf{Q}_0) \\ & + \frac{\langle \varphi_b(\mathbf{r}, \mathbf{Q}_0) | V | \varphi_l(\mathbf{r}, \mathbf{Q}_0) \rangle}{E_l^0(\mathbf{Q}) - E_b^0(\mathbf{Q})} \varphi_b(\mathbf{r}, \mathbf{Q}_0), \end{aligned} \quad (5.14)$$

where the coefficient of $\varphi_b(\mathbf{r}, \mathbf{Q}_0)$ may not be expressed in a manner analogous to that of the near resonance coupling of $\varphi_s(\mathbf{r}, \mathbf{Q}_0)$ to $\varphi_l(\mathbf{r}, \mathbf{Q}_0)$; so that we apply the simple Raleigh-Shrodinger perturbation expansion for this coupling. Equation (5.3) will be now replaced by

$$\begin{aligned} \mu_{0l}^A = & \langle \varphi_0(\mathbf{r}, \mathbf{Q}_0) | \mu | \varphi_b(\mathbf{r}, \mathbf{Q}_0) \rangle \\ & \times \frac{1}{\Delta E_{bl}} \left(\chi_{00}^{(A)}(\mathbf{Q}) \left| \sum_k \left\langle \varphi_s \left| \frac{\partial U}{\partial Q_k} \right| \varphi_l \right\rangle Q_k \right| \chi_{lj}^{(A)}(\mathbf{Q}) \right), \end{aligned} \quad (5.15)$$

where the contribution of the s state has been neglected as $\mu_{0b} \gg \mu_{0s}$. Utilizing the same procedure which lead to equation (5.5) we now obtain

$$\mu_{0l}^{(A)} = \frac{\mu_{0b}^{(CA)} V_{sl}^{(CA)}}{\Delta E_{bl}} \quad (5.16)$$

which leads the equation (5.12) for the lineshape where now the lineshape index is given by

$$q^{(A)} \approx \frac{\mu_{0b}^{(CA)}}{\mu_{0s}^{(CA)}} \frac{\Delta E_{bl}}{\Gamma^{(A)}(E_s)}. \quad (5.17)$$

This result is analogous to the expression for q obtained for interstate coupling in the CA representation (equation (4.10 a)).

6. DISCUSSION

In this paper we have presented a detailed study of the optical molecular line shape in the statistical limit. We have demonstrated that apart from the energy dependence of the line width function $\Gamma(E)$ Fano type interference effects can modify the lorentzian line shape. Within the framework of the CA basis other

vibronic components of same optically active electronic manifold will contribute to the line asymmetry. In our three electronic level CA basis the line index is $q \approx \hbar\omega/\Gamma(E_s)$. Within the framework of the conventional adiabatic representation we have challenged the conventional assumption that the zero order quasicontinuum is optically inactive and within the framework of the two adiabatic electronic levels system we were able to demonstrate that again the line shape index is $q \approx \hbar\omega/\Gamma(E_s)$. It is gratifying that both different lines of attack on the problem yield identical results, thus providing a physical demonstration of the equivalence of the basis sets.

Several experimental implications of the present study are of interest. As pointed out by Byrne and Ross in their recent authoritative review [1] two sources of experimental data are available concerning the line broadening of electronic spectra which arises from electronic relaxation. (a) The gas phase data are apparently hopeless as far as quantitative analysis is concerned. If the line broadening exceeds $\sim 0.1 \text{ cm}^{-1}$ rotational lines will overlap while if the line broadening exceeds $\sim 5 \text{ cm}^{-1}$ sequence bands will overlap. (b) Low temperature spectra of molecules embedded in some mixed crystals and in Shpolskii matrices [24] (i.e. hydrocarbons or solid rare gases) may yield information concerning the upper limit due to intramolecular relaxation broadening. To extract the physical information concerning the intramolecular relaxation broadening of a molecule imbedded in a medium, one has to correct for the gaussian distribution of trapping sites and for the line broadening due to quadratic terms in the molecule-lattice coupling. The total experimental linewidth cannot be rigorously considered as composed of additive contributions of non radiative widths and lattice contributions, and more elaborate methods such as used in solid state physics are required to extract the intramolecular relaxation contribution to the line shape for $\Gamma(E_s) \lesssim 10 \text{ cm}^{-1}$. For large widths the experimental data will be adequate provided that it will be demonstrated that linear terms in molecular phonon coupling are negligible. The present theoretical results demonstrate that

(a) For intramolecular relaxation broadening $\Gamma(E_s) \lesssim 10 \text{ cm}^{-1}$ (i.e. resonance decay times of $\gtrsim 3 \text{ ps}$) the line shape is lorentzian as previously proposed.

(b) For intermediate intramolecular broadening of $\Gamma(E_s) \approx 50\text{--}200 \text{ cm}^{-1}$ the line shape can be described in terms of a fanian. Gas phase data are not useful in this respect, however, low temperature mixed crystal data, when they become available for such transitions will be amenable to a proper interpretation.

(c) For large line widths $\Gamma(E_s) \approx 200\text{--}1000 \text{ cm}^{-1}$, interference effects between resonances have to be taken into account. In this case, we should use the general equation (2.6), and it will be further advisable to utilize this equation in the A basis where off-resonance interstate coupling is negligible (so that the $|b\rangle$ state(s) correspond just to the same electronic configuration as $|s\rangle$). Furthermore the energy dependence of $\Gamma(E)$ and $q(E)$ will have to be included explicitly. When reliable line shapes (for broad lines) in low temperature mixed crystal data become available, the results of the present study can be directly applied to this problem. It should be noted that for this physically interesting case the original Bizon-Jortner model [3] has to be modified.

Finally, let us point out that relaxation line broadening characterized by $\Gamma(E) \sim 1000 \text{ cm}^{-1}$ (relaxation time $\tau \sim 10^{-15} \text{ s}$) can be encountered in real life, although the relaxation time exceeds the period of the molecular vibrations

(10^{-14} s). In this case the zero order states are just a mathematical artifact while the real excited states of the system are so strongly scrambled that they completely lose their identity.

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