# COMMENTS ON THE VIBRONIC LINEWIDTH OF AN ISOLATED RESONANCE OF A HIGHER ELECTRONIC STATE

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The linewidth of a higher electronic transition interacting with a lower continuum of vibronic states is calculated using a simple model. The calculated linewidth is two orders of magnitude smaller than observed.

Experimental studies have established the fact that, with a few rare exceptions, radiative emission does not occur from excited states of large molecules higher than the lowest excited state of a given multiplicity. Many theories have been put forward to explain the channels of "radiationless transitions" responsible for this phenomenon.

An intimately related phenomenon is the diffuseness of the absorption spectra of these higher electronic transitions, traced by many authors to line broadening caused by vibronic interactions. Recently quantitative descriptions based on time-independent theory were proposed independently by Bixon and Jortner [1] and by Henry and Kasha [2], Rhodes [3], and Gardner and Kasha [4]. Experimentally encountered linewidths of individual vibronic transitions to higher excited electronic states are of the order of several hundred $\mathrm{cm}^{-1}$, so that any mechanism proposed has to account for this basic fact. Byrne and Ross [5] have shown that trivial effects as rotational broadening and superimposed hot bands, etc. do not account for the experimentally encountered width.

The above mentioned theories are based on a vibronic mechanism intrinsic to the isolated molecule. These theories attribute the line broadening to interaction between non-diagonal Born–Oppenheimer states.

In the present note, we estimate the line broadening predicted by these theories. We review the assumptions in the Bixon and Jortner model:

a) A Born–Oppenheimer (BO) vibronic states $\phi_s$ of an higher excited electronic state $\psi_2$ of a given multiplicity is imbedded in a manifold of BO vibronic states $\{\phi_l\}$ of a lower excited electronic state $\psi_1$. The matrix elements are assumed to be

$$\langle\phi_l|H|\phi_{l'}\rangle = \delta_{ll'}E_{l'}\,, \qquad \langle\phi_l|H|\phi_s\rangle = V \tag{1}$$

so that a constant interaction is assumed between the zeroth BO state $\phi_s$ and each of the manifold states $\{\phi_l\}$;

b) The manifold $\{\phi_l\}$ is assumed to consist of equally spaced states with an energy separation $\epsilon$; so that the density of states (i.e., the number of states per unit energy) is given simply by $\rho = \epsilon^{-1}$;

c) Intensity of absorption from the ground electronic state $\psi_g$ to the manifold is assumed to be negligible due to small Franck–Condon overlap factors. The only state which has oscillator strength is the state $\phi_s$; i.e.,

$$|\langle\psi_g|\mu|\phi_s\rangle|^2 \gg |\langle\psi_g|\mu|\phi_l\rangle|^2\,. \tag{2}$$

Mixing between the zero BO vibronic states gives vibronic eigenfunctions, $\psi_n$, of the form

$$\psi_n = a_s^n\,\phi_s + \sum_l b_l^n\,\phi_l\,. \tag{3}$$

The absorption intensity to these stationary states is proportional to $|a_s^n|^2$ according to assumption *c*. The diagonalization of the Hamiltonian matrix gives the following expression for $|a_s^n|^2$, assuming $V \gg \epsilon$

$$|a_s^n|^2 = \frac{V^2}{(E_n - E_s)^2 + (\pi V^2/\epsilon)^2} \tag{4}$$

so that the resulting line is a Lorentzian with a width, $\Delta$, given by:

$$\Delta = 2\pi V^2 \rho . \tag{5}$$

The interaction $V$ is traced to the nuclear kinetic energy operator $T(Q)$, the major contributing term is reasoned [1] to be the linear term given by the form

$$V = V_{1l,\,2s} = \sum_i \int \mathrm{d}Q \left\{ \langle \psi_1(q,Q) \,|\frac{\partial U(q,Q)}{\partial Q_i}|\, \psi_2(q,Q) \rangle_q \frac{1}{E_2(Q) - E_1(Q)} \chi_{1l}(Q) \frac{\partial}{\partial Q_i} \chi_{2s}(Q) \right\} , \tag{6}$$

where

$$\phi_s = \psi_2(q,Q)\, \chi_{2s}(Q) , \qquad \phi_l = \psi_1(q,Q)\, \chi_{1l}(Q)$$

are the zeroth order adiabatic wavefunctions in the usual representation. $U(q,Q)$ is the potential energy operator of the molecular Hamiltonian, and $E_1(Q)$ and $E_2(Q)$ are the adiabatic potential function of the states $\psi_1$ and $\psi_2$ respectively. (We have set $\hbar = 1$ for convenience.) Approximating the vibrational function $\chi(Q)$ as a product of the $3n-6$ vibrational functions and approximating the electronic part of the integral at the equilibrium configuration $Q_0$ of the second state, one finds

$$V = \sum_i \left\{ \frac{\langle \psi_1(q,Q_0) \,|[\partial U(q,Q)/\partial Q_i]_{Q_0}|\, \psi_2(q,Q_0) \rangle_q}{E_2(Q_0) - E_1(Q_0)} \int \mathrm{d}Q\, f_{1l}^*(Q_i) \frac{\partial}{\partial Q_i} f_{2s}(Q_i) \prod_{j \neq i} f_{1l}^*(Q_j) f_{2s}(Q_j) \right\} . \tag{7}$$

Although the summation is carried over all $3n-6$ normal coordinates the number of active normal modes is much smaller than $3n-6$, in fact, this number is usually about unity. Therefore, we can write $V$ as

$$V = \sum_i K_i S_i \cong KS , \tag{8}$$

where $K_i$ and $S_i$ are given by (for the lowest vibronic level of the upper electronic state)

$$K_i = \frac{\langle \psi_1(q,Q_0) \,|[\partial U(q,Q)/\partial Q_i]_{Q_0}|\, \psi_2(q,Q_0) \rangle_q}{E_2(Q_0) - E_1(Q_0)} \langle f_{1l}(Q_i) |\frac{\partial}{\partial Q_i}| f_{2s}(Q_i) \rangle ,$$

$$S_i = \prod_{j \neq i} \int \mathrm{d}Q_j\, f_{1l}^*(Q_j) f_{2s}(Q_j) . \tag{9}$$

Thus the linewidth is expressed by

$$\Delta \cong 2\pi K^2 S^2 \rho . \tag{10}$$

We now define two magnitudes

$$S_{\mathrm{g},1}^2(E_2)\rho(E_2) \qquad \text{and} \qquad S_{2,1}^2(E_2)\rho(E_2) ,$$

which express the square of the vibrational overlap (Franck–Condon factor) per unit energy between the ground BO state, $\phi_\mathrm{g} = \psi_\mathrm{g}\chi_{\mathrm{g}0}$, and the BO manifold $\{\phi_l\}$ at the energy $E_2$ and between the state $\phi_s$ and the manifold respectively. We assume that

$$\langle \chi_{\mathrm{g}0}(Q) | \chi_{1l}(Q) \rangle_Q \sim \langle \chi_{20}(Q) | \chi_{1l}(Q) \rangle_Q , \qquad S_{\mathrm{g},1}^2(E_2) \sim S_{2,1}^2(E_2) . \tag{11}$$

Multiplying expression (10) by $\Delta$ leads to

$$\Delta^2/K^2 = 2\pi \Delta \rho(E_2)\, S_{2,1}^2(E_2) . \tag{12}$$

One can immediately see that the linewidth $\Delta$ has to be smaller than $K$, otherwise an inconsistency with the basic assumptions of the theory results, along with the violation of a sum rule. The reasoning runs as follows:

if $\Delta \geqslant K$ it is clear from (12) that

$$\Delta\rho(E_2)S^2_{2,1}(E_2) > 1/2\pi\,,$$

so that by applying eq. (11) one gets

$$\Delta\rho(E_2)S^2_{g,1}(E_2) > 1/2\pi\,.$$

Now this term is proportional to the intensity of absorption from the ground state to the manifold per vibronic linewidth $\Delta$, so that the absorption intensity to the manifold $\{\phi_l\}$ per linewidth is of the same magnitude as the *intensity of absorption to the state $\phi_s$, which contradicts assumption* c *of the theory.*

Moreover, it violates the quantum mechanical sum rule as the summation of the $\rho S^2$ term over an electronic width which is of an order of magnitude larger than the width of a single vibronic line will lead to

$$10\,\Delta\rho S^2 > 1\,.$$

Therefore, one is forced to assume that $\Delta < K$. Estimation of $K$ can be obtained from theoretical and experimental data [6,7]. In fact*

$$K \approx \left[\langle\psi_1|\frac{\partial U}{\partial Q_i}|\psi_2\rangle\langle 1|Q_i|0\rangle\right]\frac{\omega_i}{E_2 - E_1}\,,$$

where the first bracketed expression is the term appearing in the Herzberg–Teller [8] and Jahn–Teller [9] theories and is of the order of 1000 $\mathrm{cm}^{-1}$**, and $\omega_i$ is the vibrational frequency of the $i$th mode in $\mathrm{cm}^{-1}$ so that $K \approx 100\ \mathrm{cm}^{-1}$. In the case of aromatic hydrocarbons like benzene, we estimate*** that $\rho S^2 \approx 10^{-5}$ for energies of 10000 $\mathrm{cm}^{-1}$ above the absorption maximum for the lower electronic state. This means that $\Delta \approx 1\ \mathrm{cm}^{-1}$, a factor of 100 smaller than observed experimentally in benzene, and other aromatic molecules.

*Thus, it seems that the present model cannot predict the observed widths.* We believe that the width is due to "vibronic" effects, and thus either the present *model* is too simplified (see assumptions a - c) or there is a more complicated mechanism operating.

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* We have written $\langle f_{1l}(Q_i)|\,\partial/\partial Q_i|f_{20}(Q_i)\rangle_{Q_i} = \langle f_{1l}(Q_i)\,|\omega_i Q_i|f_{20}(Q_i)\rangle_{Q_i}$ assuming $f_{20}(Q_i)$ to be nearly harmonic (it is *the lowest vibrational level of state $\psi_2$). Then we write* $\langle f_{1l}|Q_i|f_{20}\rangle \approx \langle 1|\,Q\,|0\rangle$, *where we have replaced the vi*brational wavefunctions by harmonic oscillator (ho) functions. Since we could expand $f_{1l}(Q_i)$ in terms of the ho functions, this represents an upper limit to the integral.

** The bracketed term represents the matrix element giving rise to intensity borrowing from state 2 to state 1. From typical aromatic hydrocarbon spectra (benzene), we estimate the matrix element between either of the two lowest singlet states and the $E_{1u}$ state to be $\approx 1000\ \mathrm{cm}^{-1}$. We take this as a good estimate of the magnitude in our case.

*** The estimate is made by noting that the integrated intensity 10000 $\mathrm{cm}^{-1}$ above the absorption maxima is less than 0.01 of the total intensity. Assuming that the electronic linewidth is 1000 $\mathrm{cm}^{-1}$ gives $\rho S^2 \approx 10^{-5}$.

## REFERENCES

[1] M. Bixon and J. Jortner, J. Chem. Phys. 48 (1968) 715.
[2] B. Henry and M. Kasha, Ann. Rev. Phys. Chem. 19 (1968) 161.
[3] W. Rhodes, J. Chem. Phys. 50 (1969) 2885.
[4] P. J. Gardner and M. Kasha, J. Chem. Phys. 50 (1969) 1543.
[5] J. P. Byrne and I. G. Ross, Can. J. Chem. 43 (1965) 3253.
[6] A. C. Albrecht, J. Chem. Phys. 33 (1960) 169.
[7] H. M. McConnell and A. D. McLachlan, J. Chem. Phys. 34 (1961) 1.
[8] G. Herzberg and E. Teller, Z. Physik Chem. B21 (1933) 410.
[9] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) A161 (1937) 220.