

## VIBRONIC LINE BROADENING OF AN ISOLATED RESONANCE \*

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The vibronic line broadening theory is formulated in the "crude adiabatic approximation".

A quantitative theory for line broadening in higher excited electronic states of polyatomic molecules, was recently formulated by Bixon and Jortner [1] and by Kasha and Henry [2]. According to this model, the line broadening of an isolated resonance is brought about by vibronic interactions [3, 4] between a zeroth order Born-Oppenheimer vibronic state  $\phi_S$  of a higher excited electronic state and the manifold  $\{\phi_I\}$  of quasi degenerate vibronic levels of a lower electronic state of the same multiplicity. Assuming a constant interaction  $V$  and constant separation  $\epsilon$ , for the manifold levels  $\{\phi_I\}$ , the linewidth  $\Delta$  of the resulting Lorentzian line, is given by  $\Delta = 2\pi V^2 \rho$  (where  $\rho$  is the density of states in the manifold, given by  $\rho = \epsilon^{-1}$ ) provided that  $V\rho \gg 1$ . The interaction  $V$  was approximated to be of the form  $V \cong K \cdot S$ , where  $S$  is the Franck-Condon overlap and  $K$  is the vibronic interaction term, reasoned to be given by vibronic terms involving the kinetic energy operator [1]. These terms were approximated using approximate adiabatic wavefunctions [1] (Herzberg-Teller [5] functions). In a recent paper [6] we have estimated the upper limit for line broadening through this proposed procedure, and have shown that the estimated linewidth using the above mentioned wavefunction is of the order of  $1 \text{ cm}^{-1}$  whereas experimentally encountered linewidths are up to several hundred  $\text{cm}^{-1}$ .

In the following we discuss this discrepancy and show that the vibronic broadening can be properly described through the "crude adiabatic approximation" [7,8] whereas the procedure based on the adiabatic functions can be misleading if proper care is not taken\*\*\*. Since both of these methods employ complete sets of states, an exact calculation could start from either procedure, and, obviously, produce the same (correct) result. The purpose of this note is to point out the advantages of the procedure based on the "crude" adiabatic wavefunctions in the specific problem of line broadening. First we will briefly compare the two methods. The Hamiltonian for the molecular system is given by

$$H = T(Q) + T(q) + U(q, Q) = T(Q) + H_{\text{elec}}(q, Q). \quad (1)$$

The adiabatic procedure is based on the functions  $\Phi_{n\lambda}^A(q, Q) = \phi_n(q, Q) \chi_{n\lambda}^A(Q)$  where  $\phi_n(q, Q)$  is an eigenfunction of  $H_{\text{elec}}(q, Q)$  with eigenvalue  $E_n(Q)$  and  $\chi_{n\lambda}^A(Q)$  satisfies

$$H_n^A(Q) \chi_{n\lambda}^A = \{T(Q) + E_n(Q)\} \chi_{n\lambda}^A = \epsilon_{n\lambda}^A \chi_{n\lambda}^A. \quad (2)$$

The "crude" adiabatic procedure is based on the functions  $\Phi_{n\lambda}^C(q, Q) = \phi_n(q, Q_0) \chi_{n\lambda}^C(Q)$  where  $Q_0$  is the equilibrium position of the ground state and where  $\chi_{n\lambda}^C(Q)$  satisfies

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\*\*\* Robinson and Burland [9] have also found this to be the case in a similar study of this problem. We would like to thank Professor Robinson for informing us of this prior to publication.

$$H_n^C(Q) \chi_{n\lambda}^C = \langle \phi_n(qQ_0) | H | \phi_n(qQ_0) \rangle_q \chi_{n\lambda}^C = \{T(Q) + E_n'(Q)\} \chi_{n\lambda}^C = \epsilon_{n\lambda}^C \chi_{n\lambda}^C. \quad (3)$$

It is important to note that the equilibrium position of the nuclei in each state is in general different even though the electronic states are taken at  $Q_0$ . It is clear that both  $\{\Phi_{n\lambda}^A\}$  and  $\{\chi_{n\lambda}^C\}$  are complete sets of orthonormal states. The matrix elements of  $H$  between states in the A-representation are given by

$$\begin{aligned} \langle \Phi_{n\lambda}^A | H | \Phi_{m\mu}^A \rangle &= \delta_{nm} \delta_{\mu\lambda} \epsilon_{n\lambda}^A + (1 - \delta_{nm}) \int dQ \chi_{n\lambda}^{A*}(Q) \{ \langle \phi_n(qQ) | T(Q) | \phi_m(qQ) \rangle_q \\ &\quad - \hbar^2 \sum_K \langle \phi_n(qQ) | \frac{\partial}{\partial Q_K} | \phi_m(qQ) \rangle_q \frac{\partial}{\partial Q_K} \} \chi_{m\mu}^A(Q), \end{aligned} \quad (4)$$

while those in the C-representation are given by

$$\langle \Phi_{n\lambda}^C | H | \Phi_{m\mu}^C \rangle = \delta_{nm} \delta_{\mu\lambda} \epsilon_{n\lambda}^C + (1 - \delta_{nm}) \int \chi_{n\lambda}^{C*}(Q) \{ \langle \phi_n(qQ_0) | U(qQ) - U(qQ_0) | \phi_m(qQ_0) \rangle_q \} \chi_{m\mu}^C(Q). \quad (5)$$

The obvious advantage of the C-representation is that the electronic functions are all based on the ground state equilibrium position and hence have the symmetries associated with the symmetry group of that position. Thus, the selection rules based on this group are rigorously held to in the C basis set. The A functions do not have this property, and for example, the mixing of states via the Herzberg-Teller [5] mechanism is already included in these functions; thus the optical intensities of the A state are difficult to know.

We will be concerned with line broadening of an electronic state of a large molecule due to vibronic interactions between that state and a lower electronic state of the same multiplicity. In a previous note [6] we estimated the off-diagonal matrix elements causing this line broadening in the A-representation, and showed that in the first approximation, the calculated line broadening was two orders of magnitude smaller than the observed broadening. In the present note, we perform the same calculation in the crude adiabatic approximation and find a numerical result in agreement with experiment. We will also present arguments for the reasons why we believe the estimation based on the adiabatic functions gives the wrong result.

The line broadening is due to the off-diagonal matrix elements of  $H$  between nearly degenerate vibronic levels [1, 2]. We will make a model calculation assuming that there are only 2 electronic states,  $\phi_n(qQ_0)$  and  $\phi_m(qQ_0)$ , and that

$$\langle \phi_n(qQ_0) | T(q) + U(qQ) | \phi_m(qQ_0) \rangle_q = E_n'(Q) \delta_{nm} + (1 - \delta_{nm}) Q_K \langle \phi_n(qQ_0) | \left( \frac{\partial U}{\partial Q_K} \right)_0 | \phi_m(qQ_0) \rangle_q \quad (6)$$

(i.e., that there is one active vibrational mode, and that the linear term in  $U(q, Q)$  is the only nonvanishing off-diagonal term). Then

$$V^C \equiv H_{no, m\mu}^C = \langle \phi_n(qQ_0) | \left( \frac{\partial U}{\partial Q_K} \right)_0 | \phi_m(qQ_0) \rangle_q \int dQ \chi_{no}^{C*} Q_K \chi_{m\mu}^C. \quad (7)$$

This is related to the usual Herzberg-Teller matrix element. Using the same numerical estimates as before [6], we arrive at a line broadening of  $\approx 100 \text{ cm}^{-1}$  in accord with experiment.

If we try to estimate the line broadening in the adiabatic procedure based on the same assumptions about  $U(q, Q)$  we must first find the adiabatic wavefunctions. These wavefunctions are the eigenfunctions of  $T(q) + U(q, Q)$  and the adiabatic potentials are the eigenvalues of  $T(q) + U(q, Q)$ . Using the matrix elements given above, we find that the eigenvalues of  $H_{elec}$  are

$$E_{n,m}(Q) = \frac{1}{2}(E_n'(Q) + E_m'(Q)) \pm \left[ \frac{1}{4}(E_n'(Q) - E_m'(Q))^2 + \gamma^2 Q_K^2 \right]^{1/2}, \quad (8)$$

where

$$\gamma = \langle \phi_n(qQ_0) | \left( \frac{\partial U}{\partial Q_K} \right)_0 | \phi_m(qQ_0) \rangle_q \quad (9)$$

and the eigenfunctions are

$$\phi_n(qQ) = [(E'_m(Q) - E_n(Q))^2 + \gamma^2 Q_K^2]^{-1/2} [(E'_m(Q) - E_n(Q)) \phi_n(qQ_0) - \gamma Q_K \phi_m(qQ_0)] \quad (10a)$$

and

$$\phi_m(qQ) = [(E'_m(Q) - E_n(Q))^2 + \gamma^2 Q_K^2]^{-1/2} [(E'_m(Q) - E_n(Q)) \phi_m(qQ_0) + \gamma Q_K \phi_n(qQ_0)]. \quad (10b)$$

It is clear that the evaluation of  $H_{no, m\lambda}^A$  is a very difficult if not impossible task. Previous authors [1, 2] have approximated these functions as

$$\tilde{\phi}_n(qQ) = \phi_n(qQ_0) + \frac{\gamma Q_K}{E_n(Q_0) - E_m(Q_0)} \phi_m(qQ_0), \quad (11a)$$

$$\tilde{\phi}_m(qQ) = \phi_m(qQ_0) - \frac{\gamma Q_K}{E_n(Q_0) - E_m(Q_0)} \phi_n(qQ_0). \quad (11b)$$

It should be pointed out that these functions are of course not the *true* adiabatic functions, and therefore the Hamiltonian has comparatively large off-diagonal matrix elements. In fact calculating the off-diagonal matrix element of  $H$  using these functions, we find

$$\begin{aligned} \tilde{V}^A &= \langle \tilde{\phi}_n^A \chi_{n0} | H | \tilde{\phi}_m^A \chi_{m\mu} \rangle = \langle \chi_{n0} | \langle \phi_n + (\gamma Q_K / \Delta E) \phi_m | H | \phi_m - (\gamma Q_K / \Delta E) \phi_n \rangle | \chi_{m\mu} \rangle \\ &= \langle \chi_{n0} | \gamma Q_K - \frac{\gamma^3 Q_K^3}{(\Delta E)^2} + \left( \frac{\gamma Q_K}{\Delta E} \right) T(Q) - T(Q) \left( \frac{\gamma Q_K}{\Delta E} \right) + \frac{\gamma Q_K}{\Delta E} (E'_m(Q) - E'_n(Q)) | \chi_{m\mu} \rangle \\ &\cong [\gamma + (\gamma / \Delta E) (\epsilon_{m\lambda} - \epsilon_{n0})] \langle \chi_{n0} | Q_K | \chi_{m\mu} \rangle. \end{aligned} \quad (12)$$

Therefore  $\tilde{V}^A = V^C$  when  $\epsilon_{m\mu} \cong \epsilon_{n0}$ . (Notice that when  $\epsilon_{m\lambda} - \epsilon_{n0} \cong -\Delta E$ , we find  $\tilde{V}^A$  small and when  $\epsilon_{m\lambda} - \epsilon_{n0} = -\Delta E + \omega_K$  we find  $\tilde{V}^A = (\gamma \omega_K / \Delta E) \langle \chi_{n0} | Q_K | \chi_{m\mu} \rangle$  whereas  $V^C$  is large, so that in this limit the approximate adiabatic wavefunctions (11a) and (11b) which in fact are the electronic wavefunctions appearing in the Herzberg-Teller theory are better chosen wavefunctions than the crude adiabatic.) Thus, using these approximate wavefunctions for the case in which  $\epsilon_{m\mu} = \epsilon_{n0}$  gives the *same result* as the crude adiabatic procedure, and consequently a line broadening of  $\approx 100 \text{ cm}^{-1}$ .

An insight into why previously suggested approximations lead to a wrong value of  $V$  can be gotten from noting that the relevant integral was approximated in the following way [1].

$$\int \chi_{n0}^{A*} \frac{\langle \phi_n(qQ) | (\partial U / \partial Q_K) | \phi_m(qQ) \rangle_Q}{E_n(Q) - E_m(Q)} \frac{\partial}{\partial Q_K} \chi_{m\mu}^A dQ \approx \frac{\langle \phi_n(qQ_0) | (\partial U / \partial Q_K) | \phi_m(qQ_0) \rangle_Q}{E_n(Q_0) - E_m(Q_0)} \langle \chi_{n0} | \frac{\partial}{\partial Q_K} | \chi_{m\mu} \rangle. \quad (13)$$

However, this "zeroth order" approximation may be severely in error particularly in replacing  $E_n(Q) - E_m(Q)$  by  $E_n(Q_0) - E_m(Q_0)$ . To see this, we note that

$$\int \chi_{n0}^{A*} (E_n(Q) - E_m(Q)) \chi_{m\mu}^A dQ = (\epsilon_{n0} - \epsilon_{m\mu}) \langle \chi_{n0}^A | \chi_{m\mu}^A \rangle \quad (14a)$$

but the zeroth order approximation gives

$$\int \chi_{n0}^{A*} (E_n(Q) - E_m(Q)) \chi_{m\mu}^A dQ \approx [E_n(Q_0) - E_m(Q_0)] \langle \chi_{n0}^A | \chi_{m\mu}^A \rangle, \quad (14b)$$

a very different result when  $\chi_{m\mu}$  is a highly excited vibrational state (but a good approximation if  $\chi_{m\mu}$  is not an excited vibrational state).

The main conclusion of this note is that one must be extremely careful in approximating these vibronic coupling matrix elements in the above manner when one is dealing with highly excited vibrational states. We also would like to suggest that the crude adiabatic procedure, while not free of dangers, can be used in a straightforward way to calculate these same matrix elements, and it has the tremendous advantage of keeping track of all the intensity in a simple way, as was pointed out above.

## REFERENCES

- [1] M. Bixon and J. Joriner, *J. Chem. Phys.* 48 (1968) 715.
- [2] B. Henry and M. Kasha, *Ann. Rev. Phys. Chem.* 19 (1968) 161.
- [3] M. Born and R. Oppenheimer, *Ann. Phys.* 84 (1927) 457.
- [4] M. Born and K. Huang, *Dynamical theory of crystal lattices* (Oxford University Press, London and New York, 1954).
- [5] G. Herzberg and E. Teller, *Z. Physik. Chem.* B21 (1933) 410.
- [6] B. Sharf and R. Silbey, *Chem. Phys. Letters* 4 (1969) 423.
- [7] H. C. Longuet-Higgins, *Advan. Spectry.* 2 (1961) 429.
- [8] W. D. Hobey and A. D. McLachlan, *J. Chem. Phys.* 33 (1960) 1694.
- [9] Robinson and Burland, *Proc. Natl. Acad. Sci.*, to be published.