Coupling of Electronic and Vibrational Motions in Molecules[†]

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I. Brief History of Vibronic Coupling

The quantum-mechanical treatment of coupling between the electronic and vibrational motions in molecules (vibronic coupling) was first given by Born and Oppenheimer (BO) in 1927.[1] They showed that there exist states of molecules which can be approximately represented by products of electronic and nuclear functions

$$\psi_{nv}(x,Q) \approx \theta_n(x,Q)\chi_{nv}(Q) \qquad (1)$$

where $\theta_n(x,Q)$ is an eigenfunction of the electronic Hamiltonian

$$H(x,Q)\theta_n(x,Q) = E_n(Q)\theta_n(x,Q) \qquad (2)$$

and the vibrational function satisfies the differential equation

$$[T_N + E_n(Q)]\chi_{nv} = W_{nv}\chi_{nv} \qquad (3)$$

Here T_N and W_{nv} are nuclear and vibronic energies, respectively.

A necessary (but not sufficient) condition for the validity of approximation 1 is that the electronic function $\theta_n(x,Q)$ must be nondegenerate at any point in the relevant Q-space (e.g., displacements attained during zero-point vibrations). Description of electronically degenerate states (dynamical Jahn–Teller (JT) and Renner effects[2-4] proceeded along different lines than those proposed by BO for nondegenerate states. Techniques of dealing with the degenerate states were also applied to the so-called pseudo-Jahn–Teller effect[5,6] where several closely spaced (but nondegenerate) states are assumed to behave in a similar manner as the JT states. Further generalization leads to a whole series of problems ranging from the "strong" (JT) to the "weak" (BO) coupling cases. A smooth transition in the theories of these two limiting behaviors is expected. This, however, did not materialize satisfactorily and is the source of much confusion which exists today about the nature of vibronic coupling.[7]

It is worthwhile to elaborate on the procedures used to handle the (pseudo) JT problem. The standard approach has been to assume an expansion of the vibronic wave function in terms of a small number of fixed electronic states, $\theta_k^0(x) = \theta_k(x,Q_0)$, with energies $E_k^0 = E_k(Q_0)$, where Q_0 represents the symmetrical configuration of the nuclei.[2,5,6,8-12] Then the electronic basis is $[\theta_1^0,\theta_2^0]$, and the vibronic wave function for two (nearly) degenerate functions at Q_0 is

$$\psi^{CA}(x,Q) = \theta_1^0(x)\chi_1^{CA}(Q) + \theta_2^0(x)\chi_2^{CA}(Q) \qquad (4)$$

where following the usual terminology the superscript CA stands for "crude adiabatic".[2,7,13] The vibrational functions are determined by a pair of coupled equations whose potential terms are the matrix elements of H in the basis $[\theta_1^0,\theta_2^0]$:

$$H_{kl}(Q) = \int \theta_k^0(x)^* H(x,Q)\theta_l^0(x)\,dx \quad k, l = 1, 2 \qquad (5)$$

The method derives its appeal from these matrix elements whose functional form in Q may be deduced by an expansion of H into nuclear displacements around Q_0. Symmetry aspects of this analysis are well known from the Herzberg–Teller (HT) theory of forbidden transitions.[14]

One source of confusion can be traced to the application of usual perturbation methods to the solution of the coupled equations. Thus under the "weak-coupling" condition

$$|H_{12}/\Delta E_{21}^0| \ll 1 \qquad (6)$$

one has

$$\psi_{1v}^{CA} = \theta_1^0(x)\chi_{1v}^{CA}(Q) \qquad (7)$$

$$[T_N + H_{11}(Q)]\chi_{1v}^{CA} = W_{1v}^{CA}\chi_{1v}^{CA} \qquad (8)$$

The "crude-adiabatic" approximation for nondegenerate states as summarized by eq 7 and 8 is frequently listed as a possible starting point for the treatment of vibronic interactions.[7,13,15] Under the same conditions, the dominant part of the BO wave function 1 is $\psi_{1v} \approx \theta_1^0\chi_{1v}$, where χ_{1v} is determined from eq 3. It appears that the weak coupling condition 6 amounts to approximating the adiabatic potential $E_1(Q)$ by $H_{11}(Q)$. Explicit numerical calculations[16] show that this assumption is not even qualitatively correct. To see where the problem lies, write E_1 in the following form[17]

$$E_1(Q) = H_{11} - \frac{H_{12}^2}{\Delta E_{21}^0} - \sum_{k\neq 1,2}\frac{H_{1k}^2}{\Delta E_{k1}^0} + \text{order } (Q - Q_0)^3 \qquad (9)$$

valid whenever E_1 can be developed into a Taylor series in displacements around Q_0. Since the second term(s) of (9) may be of the same order of magnitude as H_{11} (actually $H_{11} - E_1^0$) without violating condition 6, conventional perturbation methods cease

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to be applicable. In section III, we show how this dilemma can be removed by passing from the coupled equations to the effective eigenvalue equation (3).

Similarly, the reasoning behind truncating the electronic basis for the JT problem to just two states, as in eq 4, is based on assumptions similar to (6). But we have seen that a coupling which is weak on the scale of electronic energies (condition 6) may not be so on the scale of vibrational energies (eq 9). The influence of the weakly coupled electronic states on the vibrational levels must then be incorporated into the equations describing the (pseudo) JT effect.

A refinement in the theory for the case of exact degeneracy was made by Moffitt and Liehr.[18] The accuracy of their equations is comparable with that of the BO eq 3 for nondegenerate states. However, they did not give much detail, and it is unclear how to deal with nearly degenerate states. Lack of detail and a cumbersome notation seem to be the reasons why this paper never received the recognition it deserves. The Moffitt–Liehr equations will be derived in section IV.

A number of treatments[2,19–22] of the (pseudo) JT effect start with a truncated Born expansion[23] for the wave function. The method consists of replacing the fixed basis $[\theta_1^0, \theta_2^0]$ by the corresponding adiabatic basis $[\theta_1(x,Q), \theta_2(x,Q)]$. Instead of the wave function 4,

$$\psi(x,Q) = \theta_1(x,Q)\chi_1(Q) + \theta_2(x,Q)\chi_2(Q) \qquad (10)$$

The simple appearance of (10) is deceiving, for it is difficult to predict the Q dependence of the electronic matrix elements which appear in the coupled equations for the vibrational motion. The major difficulty is associated with the rapid variation in θ_1 and θ_2 with Q for nearly degenerate states. According to Longuet-Higgins,[24] they even become singular in case of exact degeneracy. Consequently, a semiempirical formulation of the problem (which is the main attraction of the CA method) is not straightforward since power series expansions of the matrix elements cannot be assumed.

There have been several attempts to introduce adiabatic potentials into the theory of the (pseudo) JT effect. A common feature of all of these formulations is the use of "crude adiabatic" results at some point in the procedure. The eigenvalues and eigenfunctions of the 2 × 2 matrix 5 define the "crude adiabatic" potentials and electronic functions

$$E_{1,2}^{\mathrm{CA}} = \tfrac{1}{2}(H_{11} + H_{22}) \mp \tfrac{1}{2}[(H_{22} - H_{11})^2 + 4H_{12}^2]^{1/2} \qquad (11)$$

and

$$\theta_1^{\mathrm{CA}}(x,Q) = C_1(Q)\theta_1^0(x) + C_2(Q)\theta_2^0(x) \qquad (12a)$$

$$\theta_2^{\mathrm{CA}}(x,Q) = -C_2(Q)\theta_1^0(x) + C_1(Q)\theta_2^0(x) \qquad (12b)$$

In the immediate neighborhood of the point Q_0, the functions 12a,b have a singular behavior similar to the exact adiabatic states. On the other hand, when the inverse of the transformation in (12a,b) is applied to $[\theta_1^{\mathrm{CA}}, \theta_2^{\mathrm{CA}}]$, the singularity disappears since the fixed functions $[\theta_1^0, \theta_2^0]$ are regenerated. McLachlan[19] used this property to obtain equations of the "crude adiabatic" type by subjecting the coupled equations of the Born[23] method to the (unitary) inverse transformation of (12a,b). Unfortunately, the matrix elements in the original Born equations are not known. Hence one cannot be sure about the conditions which render the nonadiabatic matrix elements (i.e., those involving T_N) in the transformed equations negligible.

A different approach had been taken earlier by Renner,[4] Sponer and Teller,[22] and Longuet-Higgins.[2] Starting with the Born equations, they appear to have evaluated the matrix elements of T_N directly. However, as pointed out in ref 21, this part of the calculation is based on the functions 12a,b, while matrix elements of the electronic Hamiltonian are found using the exact adiabatic functions $\theta_1(x,Q)$ and $\theta_2(x,Q)$ (i.e., exact potential surfaces are assumed). Such use of different basis sets to calculate different parts of a Hamiltonian is not completely satisfactory.

In a recent series of papers[25–34] Siebrand and co-workers criticize the usual power series taken for the Q dependence of the off-diagonal matrix element H_{12} and suggest that a better functional form for H_{12} can be obtained by solving the pair of eq 11. This procedure gives H_{12} in terms of H_{11}, H_{22}, E_1^{CA}, and E_2^{CA}. The latter two functions are subsequently replaced by the exact adiabatic potentials. Thus this approach suffers from the limitations of the crude adiabatic model. An additional problem arises from the use of the usual power series for the diagonal elements H_{11} and H_{22}. Since the Q dependence of H_{kl} is entirely due to the Hamiltonian, their procedure, which results in different analytical properties of the off-diagonal vs. diagonal elements, would seem to need further study.

II. Scope of Review

By the above history, we have hoped to convince the reader that the nature of vibronic interactions is not as clearly understood today as it seemed to be half a century ago when Born and Oppenheimer published their famous paper, and Herzberg and Teller applied their results to spectroscopic transitions! The objective of this article is to develop a unified treatment of the coupling between vibrational and electronic motions. This is carried out by a simple reinterpretation of the ideas of BO using ordinary perturbation theory. Such an approach leads to a consistent theory, for it handles nondegenerate and (nearly) degenerate states on an equal footing. It also throws new light into the nature of the BO method itself.

Section III presents a new derivation of the BO approximation. The vibronic Schrodinger equation is formulated in the fixed electronic basis $\{\theta_k(x,Q_0)\}$ leading to an infinite set of coupled differential equations. We next attempt an iterative solution of these equations and show that under weak coupling conditions the original equation system may be replaced by the BO eq 3.

Unlike the BO κ method, extension of this procedure to deal with the (pseudo) JT problem is straightforward. A general formulation of vibronic interactions is presented in section IV using the multidimensional partitioning technique well known in ordinary perturbation theory.[35]

The intent of this article is not an encylopedic review. Our goal is to provide a clearer insight into the conditions of validity of the BO approximation and remove some of the misconceptions present in the literature on vibronic coupling. As an illustration of the coupled equations, a two-state, two-mode vibronic coupling model involving nontotally symmetric and Franck-Condon modes for the triplet states of aromatic aldehydes is discussed in section V. Exact solutions are obtained for a wide range of the triplet state energy gap and compared with the BO solutions.

A selective list of reviews on vibronic coupling includes the following. Longuet-Higgins[2] discusses the dynamical JT and Renner effects. The term "crude adiabatic" is first introduced in this paper. A very extensive treatment of the JT effect, along with many examples, may be found in Englman's book.[36] Various approaches to vibrational borrowing of intensity are reviewed by Ballhausen and Hansen.[13] Some ambiguities associated with the term "vibronic coupling" are pointed out by Azumi and Matsuzaki.[7]

III. The Born-Oppenheimer Approximation

A. Preliminary Formulation

Neglecting spin-dependent terms, the vibronic Hamiltonian of a molecule consists of two parts:

$$\mathcal{H} = T_N + H(x,Q) \qquad (13)$$

where T_N is the nuclear kinetic energy operator, and H is the electronic Hamiltonian. So defined, H contains the kinetic energy operator for the electrons, their potential energy in the field of the nuclei, and the mutual repulsions of the electrons and the nuclei. The symbols x and Q denote the set of electronic and nuclear variables, respectively. The Schrödinger equation is

$$\mathcal{H}(x,Q)\psi(x,Q) = W\psi(x,Q) \qquad (14)$$

For each value of Q, the electronic Hamiltonian has a set of eigenfunctions (assumed normalized to unity), defined by eq 2. At a given Q, they presumably form a complete set in the configuration space of the electrons.

In this section, the BO approximation for electronically nondegenerate states is rederived. To be definite, it is assumed that the nth electronic state is under consideration. Let Q_0 be an arrangement of the nuclei where $E_n(Q)$ takes a minimum value. Solutions of (2) at Q_0 are designated by the special symbols:

$$\theta_k^0(x) \equiv \theta_k(x,Q_0) \qquad (15a)$$

$$E_k^0 = E_k(Q_0) \qquad (15b)$$

The functions θ_k^0 are independent of nuclear displacements and have well-defined symmetry properties pertinent to the configuration Q_0.

The exact wave function ψ can be expanded in the form

$$\psi(x,Q) = \sum_k \theta_k^0(x)\chi_k(Q) \qquad (16)$$

Substituting (16) into (14), one obtains a system of linear differential equations, determining the vibrational amplitudes

$$(T_N + H_{nn})\chi_n + \sum_{k \neq n} H_{nk}\chi_k = W\chi_n \qquad (17a)$$

$$H_{kn}\chi_n + (T_N + H_{kk})\chi_k + \sum_{l \neq k,n} H_{kl}\chi_l = W\chi_k \qquad (17b)$$

and so on. Here

$$H_{kl}(Q) = \int \theta_k^0(x)\,^*H(x,Q)\theta_l^0(x)\,\mathrm{d}x \equiv \langle \theta_k^0 | H | \theta_l^0 \rangle \qquad (18a)$$

Following Born and Oppenheimer,[1] $H(x,Q)$ is expanded into a power series in nuclear displacements around Q_0. This gives the analytical Q dependence of $H_{kl}(Q)$ as

$$H_{kl}(Q) = E_l^0\delta_{kl} + H_{kl}^{(1)} + H_{kl}^{(2)} + \ldots \qquad (18b)$$

where $H_{kl}^{(p)}(Q)$ are homogeneous functions (degree indicated by the superscript p) of the displacements. Explicitly,

$$H_{kl}^{(1)} = \sum_r H_{kl}^r Q_r \qquad (19a)$$

$$H_{kl}^{(2)} = \tfrac{1}{2} \sum_{r,s} H_{kl}^{rs} Q_r Q_s \qquad (19b)$$

etc. The constants H_{kl}^r, H_{kl}^{rs}, *etc., are defined as*

$$H_{kl}^r = \left\langle \theta_k^0 \middle| \left(\frac{\partial H}{\partial Q_r}\right)_0 \middle| \theta_l^0 \right\rangle \qquad (20a)$$

$$H_{kl}^{rs} = \left\langle \theta_k^0 \middle| \left(\frac{\partial^2 H}{\partial Q_r \partial Q_s}\right)_0 \middle| \theta_l^0 \right\rangle \qquad (20b)$$

and so on. The subscript zero indicates that the derivatives are to be evaluated at Q_0. In eq 19a,b, summation is over the ($3N - 6$) internal displacement coordinates Q_r (measured relative to Q_0), which may be taken to be the symmetry coordinates of the configuration Q_0.

It proves convenient to explicitly separate the electronic energies E_k^0 from the diagonal matrix elements H_{kk}. For this purpose we introduce the notation

$$\hat{H}_{kk}(Q) = H_{kk}(Q) - H_{kk}(Q_0) = H_{kk}^{(1)} + H_{kk}^{(2)} + \ldots \qquad (21)$$

so that $H_{kk} = E_k^0 + \hat{H}_{kk}$.

A perturbation approach to solutions of eq 17 can be formulated by splitting the exact molecular wave function, ψ into $\psi^0 + \psi^1$, where

$$\psi^0 = \theta_n^0\chi n \qquad (22a)$$

$$\psi^1 = \sum_{k \neq n} \theta_k^0 \chi_k \qquad (22b)$$

We now look for solutions of eq 17 assuming the "weak coupling" condition

$$\langle \psi^1 | \psi^1 \rangle \ll \langle \psi^0 | \psi^0 \rangle \qquad (23)$$

Equation 17b may be formally solved for χ_k ($k \neq n$)

$$\chi_k = \frac{1}{W - T_N - H_{kk}} H_{kn}\chi_n + \frac{1}{W - T_N - H_{kk}} \sum_{l \neq k_1 n} H_{kl}\chi_l \qquad (24)$$

Our present goal is to determine the primary vibrational function χ_n and total energy W. Unfortunately, eq 24 as it stands is of little use for that purpose because of the presence of the differential operator T_N and the unknown energy W in the denominator. Equation 24 will be discussed in section III.D.

B. Solutions of the Basic Equations by Iteration

A manageable equation for χ_n and W can be obtained from (24) by rearranging the terms. If the total energy is measured relative to E_n^0 by $W = E_n^0 + \epsilon_n$ (where ϵ_n is a purely vibrational energy), the desired change in the form of (24) will be obtained by means of the identity

$$\begin{aligned} \frac{1}{W - T_N - H_{kk}} &= \frac{1}{\Delta E_{nk}^0 - (T_N + \hat{H}_{kk} - \epsilon_n)} \\ &= \frac{1}{\Delta E_{nk}^0} + \frac{1}{\Delta E_{nk}^0}\left(\frac{T_N + \hat{H}_{kk} - \epsilon_n}{W - T_N - H_{kk}}\right) \end{aligned} \qquad (25)$$

The notation of eq 21, and $\Delta E_{nk}^0 = E_n^0 - E_k^0$ has been employed.

Using eq 25 in 24 gives ($k \neq n$)

$$\chi_k = \frac{H_{kn}}{\Delta E_{nk}^0}\chi_n + \frac{1}{\Delta E_{nk}^0}\sum_{l \neq k_1 n} H_{kl}\chi_l + \frac{1}{\Delta E_{nk}^0}(T_N + \hat{H}_{KK} - \epsilon_n)\chi_k \qquad (26)$$

This equation is now iterated by means of the formula

$$\chi_k^{(p+1)} = \frac{H_{kn}}{\Delta E_{nk}^0}\chi_n + \frac{1}{\Delta E_{nk}^0}\sum_{l \neq k_1 n} H_{kl}\chi_l^{(p)} + \left(\frac{T_N + \hat{H}_{kk} - \epsilon_n}{\Delta E_{nk}^0}\right)\chi_k^{(p)} \qquad (27a)$$

$$k \neq n;\ p = 0, 1, 2, \ldots$$

starting with

$$\chi_k^{(0)} = 0 \qquad k \neq n \qquad (27b)$$

For example,

$$\chi_k^{(1)} = \frac{H_{kn}}{\Delta E_{nk}^0}\chi_n \qquad (28a)$$

$$\chi_k^{(2)} = \left[1 + \frac{T_N + \hat{H}_{kk} - \epsilon_n}{\Delta E_{nk}^0}\right]\frac{H_{kn}}{\Delta E_{nk}^0}\chi_n + \left[\frac{1}{\Delta E_{nk}^0}\sum_{l \neq k_1 n}\frac{H_{kl}H_{ln}}{\Delta E_{nl}^0}\right]\chi_n \qquad (28b)$$

and so on.

By means of the iteration process, the small components χ_k of the wave function are expressed in terms of the (yet unknown) unperturbed vibrational function χ_n and energy ϵ_n.[37] The latter two quantities are determined by substituting the pth iterate $\chi_k^{(p)}$ into eq 17a:

$$[T_N + \hat{H}_{nn}]\chi_n + \sum_{k \neq n} H_{nk}\chi_k^{(p)} \approx \epsilon_n \chi_n \tag{29}$$

This is an effective eigenvalue equation for the vibrational motion of the molecule in its nth electronic state. Using the first iterate 28a for χ_k, retaining up to quadratic terms in $\hat{H}_{nn}$, and the linear term in H_{nk}, it yields the well-known harmonic approximation for vibrational levels

$$K^0_{nn}\chi^0_n = \epsilon^0_n \chi^0_n \tag{30a}$$

where $K^0_{nn} = T_N + E_n^{(2)}$, and

$$E_n^{(2)} = H_{nn}^{(2)} + \sum_{k \neq n} \frac{|H_{nk}^{(1)}|^2}{\Delta E^0_{nk}} \tag{30b}$$

is the quadratic part of the adiabatic potential.[1a,17]

In higher orders of the iteration process, eq 29 must be solved by perturbation theory as the unknown energy ϵ_n and nuclear kinetic energy operator T_N appear in a complicated manner. It will become apparent that the procedure based on eq 27 and 29 is equivalent to the BO expansion method.

In order to obtain the energy correct to fourth-order terms in the BO parameter κ[39] the third iterate χ^3_k is used in eq 29, giving

$$[K^0_{nn} + K^1_{nn}(\epsilon_n)]\chi_n = \epsilon_n \chi_n \tag{31}$$

where K^0_{nn} is the harmonic Hamiltonian, and $K^1_{nn}(\epsilon_n)$ denotes the remaining terms in eq 29 with $p = 3$. Taking K^0_{nn} as the unperturbed Hamiltonian, the energy in the next two approximations is given by

$$\epsilon_{nv} \simeq \epsilon^0_{nv} + \langle \chi^0_{nv} | K^1_{nn}(\epsilon^0_{nv}) | \chi^0_{nv} \rangle + \sum_{v' \neq v} \frac{\langle \chi^0_{nv'} | K^1_{nn}(\epsilon^0_{nv}) | \chi^0_{nv} \rangle^2}{\epsilon^0_{nv} - \epsilon^0_{nv'}} \tag{32}$$

where the vibrational quantum number v has been introduced to distinguish between different eigenvectors of K^0_{nn} (assuming that χ^0_{nv} is normalized to unity). We will show that ϵ_{nv}, taken to κ^4 terms, is the same result as obtained by Born and Oppenheimer.

An analysis of the explicit expression for K^1_{nn} shows, by comparison with the formulas given in ref 17, that the term cubic in displacements is just the cubic part $E_n^{(3)}$ of the adiabatic potential. The quartic part $E_n^{(4)}$ also appears if, in the function $K^1_{nn}(\epsilon^0_{nv})\chi^0_{nv}$, the terms involving T_N and ϵ^0_{nv} are rearranged:

$$(T_N + \hat{H}_{kk} - \epsilon^0_{nv})H_{kn}\chi^0_{nv} = [\hat{H}_{kk} - E_n^{(2)}]H_{kn}\chi^0_{nv} + [T_N, H_{kn}]\chi^0_{nv} \tag{33}$$

where $[\ldots, \ldots]$ denotes the commutator. Proceeding in this manner, one concludes that

$$K^1_{nn}(\epsilon^0_{nv})\chi^0_{nv} = [E_n^{(3)} + E_n^{(4)}]\chi^0_{nv} + \left(\sum_{k \neq n} \frac{H_{kn}^{(1)}}{\Delta E^{02}_{nk}} [T_N, H_{kn}^{(1)}]\right)\chi^0_{nv} + \ldots \tag{34}$$

valid to fourth order terms in κ. Use of (34) in eq 32 yields the BO result for the energy:

$$\epsilon_{nv} \simeq \epsilon^0_{nv} + C_n + \langle x^0_{nv} | E_n^{(4)} | \chi^0_{nv} \rangle + \sum_{v' \neq v} \frac{\langle \chi^0_{nv'} | E_n^{(3)} | \chi^0_{nv} \rangle^2}{\epsilon^0_{nv} - \epsilon^0_{nv'}} + \ldots \tag{35}$$

where C_n is the diagonal correction to the energy arising through the nuclear kinetic energy,

$$C_n = \left\langle \chi^0_{nv} \middle| \sum_{k \neq n} \frac{H_{kn}^{(1)}}{\Delta E^{02}_{nk}} [T_N, H_{kn}^{(1)}] \middle| \chi^0_{nv} \right\rangle = \sum_r \frac{\hbar^2}{2M_r} \left\langle \frac{\partial \theta_n}{\partial Q_r} \middle| \frac{\partial \theta_n}{Q_r} \right\rangle_0$$

Higher order corrections to the vibrational function χ_n can be similarly expressed in terms of the matrix elements of the adiabatic potential. We apply standard perturbation theory to solve eq 31 for χ_n to second order in $K^1_{nn}(\epsilon^0_{nv})$, and use relation 34. Omitting the terms which are of third and higher order in the BO parameter κ, the result may be written

$$\chi_{nv} = \chi^0_{nv} + \chi^{(1)}_{nv} + \chi^{(2)}_{nv} + Z_{nv} \tag{36}$$

where

$$\chi^{(1)}_{nv} = \sum_{v' \neq v} \frac{\langle \chi^0_{nv'} | E_n^{(3)} | \chi^0_{nv} \rangle}{\epsilon^0_{nv} - \epsilon^0_{nv'}} \chi^0_{nv'} \tag{37a}$$

$$\chi^{(2)}_{nv} = \sum_{v' \neq v} \frac{\langle \chi^0_{nv'} | E_n^{(4)} | \chi^0_{nv} \rangle}{\epsilon^0_{nv} - \epsilon^0_{nv'}} \chi^0_{nv'} + \sum_{v' \neq v} \frac{\langle \chi^0_{nv'} | E_n^{(3)} | \chi^{(1)}_{nv} \rangle}{\epsilon^0_{nv} - \epsilon^0_{nv'}} \chi^0_{nv'} \tag{37b}$$

and

$$Z_{nv} = -\tfrac{1}{2} \sum_{v' \neq v} \left\langle \chi^0_{nv'} \middle| \sum_{k \neq n} \left(\frac{H_{kn}^{(1)}}{\Delta E^0_{nk}} \right)^2 \middle| \chi^0_{nv} \right\rangle \chi^0_{nv'} \tag{37c}$$

The function Z_{nv} is a contribution coming from the last term in eq 34. In arriving at eq 37c the identities

$$H_{kn}^{(1)} [T_N, H_{kn}^{(1)}] = \tfrac{1}{2}[T_N, H_{kn}^{(1)2}] - \tfrac{1}{2}[[T_N, H_{kn}^{(1)}], H_{kn}^{(1)}]$$

(the double commutator is simply C_n when summed over k), and

$$[T_N, H_{kn}^{(1)2}]\chi^0_{nv} = (K^0_{nn} - \epsilon^0_{nv})H_{kn}^{(1)2}\chi^0_{nv}$$

are used.

C. The Complete Wave Function

The total wave function is

$$\psi_{nv} = \psi^0_{nv} + \psi^1_{nv} \tag{38}$$

Now that the primary function χ_{nv} and ϵ_{nv} are determined, the vibrational amplitudes χ_k of ψ^1_{nv} can be evaluated from eq 28. In the lowest approximation keeping only the linear term in H_{kn},

$$\chi_k \simeq \frac{H_{kn}^{(1)}}{\Delta E^0_{nk}} \chi^0_{nv} \quad k \neq n \tag{39}$$

from eq 28a. Using eq 22a,b with $\chi_{nv} \simeq \chi^0_{nv}$, eq 38 becomes

$$\psi_{nv} \simeq \left[\theta^0_n + \sum_{k \neq n} \theta^0_k \frac{H_{kn}^{(1)}}{\Delta E^0_{nk}}\right] \chi^0_{nv} \tag{40}$$

yielding the (first-order) HT form of the wave function.[14]

Higher order approximations to χ_k are found from eq 28b and similar equations for $p > 2$. The results are conveniently expressed by ordering the matrix elements according to the powers of κ.[39] Through terms of order κ^2, eq 28b gives (noting that in $(T_N + \hat{H}_{kk} - \epsilon^0_{nv})H_{kn}$, only $H_{kk}^{(1)}H_{kn}^{(1)}$ contributes to the κ^2 terms)

$$\chi_k \approx \frac{H_{kn}^{(1)}}{\Delta E^0_{nk}} (\chi^0_{nv} + \chi^{(1)}_{nv}) + \frac{1}{\Delta E^0_{nk}} \left\{ H_{kn}^{(2)} + \sum_{l \neq n} \frac{H_{kl}^{(1)}H_{ln}^{(1)}}{\Delta E^0_{nl}} \right\} \chi^0_{nv}, \quad k \neq n$$

The coefficients of χ^0_{nv} in this equation have a simple interpretation. We display the Taylor series of the adiabatic electronic function $\theta_n(x,Q)$ around Q_0 as $\theta_n = \theta^0_n + \theta^{(1)}_n + \theta^{(2)}_n + \ldots$, where $\theta^{(1)}_n = \Sigma_r(\partial\theta_n/\partial Q_r)_0 Q_r$, $\theta^{(2)}_n = \tfrac{1}{2}\Sigma_{r,s}(\partial^2\theta_n/\partial Q_r \partial Q_s)_0 Q_r Q_s$, etc. It may be verified (e.g., from ref 17) that $H_{kn}^{(1)}/\Delta E^0_{nk} = \langle \theta^0_k | \theta^{(1)}_n \rangle$ and that the coefficient of χ^0_{nv} quadratic in Q is simply $\langle \theta^0_k | \theta^{(2)}_n \rangle$, $k \neq n$. The total wave function 38 becomes

$$\psi_{nv} = N\left\{\theta^0_n(\chi^0_{nv} + \chi^{(1)}_{nv} + \chi^{(2)}_{nv} + Z_{nv}) + (\chi^0_{nv} + \chi^{(1)}_{nv}) \times \sum_{k \neq n} \theta^0_k \langle \theta^0_k | \theta^{(1)}_n \rangle + \chi^0_{nv} \sum_{k \neq n} \theta^0_k \langle \theta^0_k | \theta^{(2)}_n \rangle \right\} \tag{41}$$

where N is a normalization constant. As $\langle\theta_n^0|\theta_n^{(1)}\rangle = 0$, the first sum in braces is $\theta_n^{(1)}$, follows from the completeness of $\{\theta_k^0\}$. The constant $N = \{\langle\chi_{nv}|\chi_{nv}\rangle + \Sigma_{k\neq n}\langle\chi_k|\chi_k\rangle\}^{-1/2}$ correct to terms of order κ^2 is $N = 1 - {}^1\!/_2\langle\chi_{nv}^{(1)}|\chi_{nv}^{(1)}\rangle - {}^1\!/_2\langle\chi_{nv}^0|\Sigma_{k\neq n}(H_{kn}^{(1)}/\Delta E_{nk}^0)^2|\chi_{nv}^0\rangle$. The third term in N when multiplied by $\theta_n^0\chi_{nv}^0$ and added to $\theta_n^0 Z_{nv}$ (cf. eq 37c) yields a function which may be identified as $\langle\theta_n^0|\theta_n^{(2)}\rangle\chi_{nv}^0\theta_n^0$. Adding the latter to the second sum in (41) gives $\theta_n^{(2)}\chi_{nv}^0$. Thus the normalized wave function through terms of order κ^2 is

$$\psi_{nv} = (\chi_{nv}^0 + \chi_{nv}^{(1)})(\theta_n^0 + \theta_n^{(1)}) - {}^1\!/_2\langle\chi_{nv}^{(1)}|\chi_{nv}^{(1)}\rangle\theta_n^0\chi_{nv}^0 + \chi_{nv}^{(2)}\theta_n^0 + \chi_{nv}^0\theta_n^{(2)} \qquad (42)$$

in agreement with the BO result.[1b,17]

In the BO classification[39] with respect to the powers of κ, T_N and ϵ_{nv} contribute toward the third-order approximation for χ_k. Here one uses relation 33 to separate the adiabatic (the first term on the right side of eq 33) from the nonadiabatic terms. The details are left to the reader.

D. Discussion

We now examine the limitations of the method. Basic to the procedure is the "weak coupling" condition. In a first approximation, (39) is used to express condition 23 in the form

$$\langle\chi_{nv}^0|\sum_{k\neq n}\left|\frac{H_{kn}^{(1)}}{\Delta E_{nk}^0}\right|^2|\chi_{nv}^0\rangle \ll 1 \qquad (43)$$

imposing constraints on the constants H_{kn}^r, which occur in the power series expression for $H_{kn}^{(1)}$ (cf. eq 18–20). Implicit in (43) is the slowly varying nature of the adiabatic function $\theta_n(x,Q)$ with nuclear displacements.

Condition 43 does not necessarily imply that the harmonic potential $E_n^{(2)}$ can be approximated by the crude potential $H_{nn}^{(2)}$ as $\Sigma_{k\neq n}H_{kn}^{(1)2}/\Delta E_{nk}^0$ may be comparable to $H_{nn}^{(2)}$. Weak interactions among electronic states can lead to strong perturbations in the vibrational states because of the disparity between the vibrational and electronic energy differences. Calculations[16] show that the approximation $E_n^{(2)} \approx H_{nn}^{(2)}$ is not valid even for the ground state, normally well separated from the other electronic states.

In arriving at the BO results 35 and 42, perturbation theory has been used at two points. The first application, displayed in the iteration formula 27, resulted in an approximate decoupling of equation system 17, and led to the effective equation 29. Condition 43 provides a rough justification for this step. The method of successive approximations was again applied to find solutions of eq 29 using the harmonic Hamiltonian as the unperturbed Hamiltonian. This is justified only if anharmonicities in the adiabatic potential $E_n(Q)$ are sufficiently small in the neighborhood of its minimum. In summary, we expect the BO method to work if the adiabatic function $\theta_n(x,Q)$ is a slowly varying function of nuclear displacements, and the potential $E_n(Q)$ is a smooth function of displacements around Q_0.

It is important to understand clearly that the procedure employed solves the vibronic Schrödinger equation only in a *very limited region* in Q space. This is the essence of the BO method, and is suggested by the classical concepts of molecular structure and infinitesimal vibrations of the nuclei from an equilibrium structure Q_0 (see Woolley and Sutcliffe[40]). Wave functions which result from the theory are localized around Q_0. In general, Q_0 is neither unique nor are the exact wave functions localized about any preferential point in Q space.[40] Thus the exact wave functions have the full symmetry of the vibronic Schrödinger equation, whereas our localized functions belong to the (much smaller) molecular point group. A plausible explanation of this apparent contradiction is to represent the exact wave function as a linear superposition of BO functions localized around equivalent conformations. If overlap between different "structure" functions is small, localized and delocalized descriptions of the molecule are equivalent (note the implication of a multitude of accidental degeneracies in the exact eigenvalues). These considerations are consistent with the assumptions about the power series expansions of $E_n(Q)$ and $\theta_n(x,Q)$. Candidates which fulfill the above conditions are "rigid" molecules, the minima of whose potential surfaces are separated by high barriers. In systems exhibiting the (pseudo) JT effect, the hypothesis of a localized wave function needs to be relaxed (section IV).

The perturbed part of the wave function is needed in the discussion of forbidden electronic transitions.[41–45] Provided the primary vibrational function χ_n and energy ϵ_n are known, a more accurate expression for the remaining amplitudes χ_k ($k \neq n$) may be obtained from eq 24 by a perturbation formula analogous to eq 27. Thus in a first approximation, the contribution of the sum in eq 24 is neglected to obtain

$$\chi_k \approx \frac{1}{W_{nv}^0 - T_N - H_{kk}}H_{kn}\chi_{nv}^0 = \sum_{v'}\frac{\langle\phi_{kv'}|H_{kn}|\chi_{nv}^0\rangle}{\Delta E_{nk}^0 + \epsilon_{nv}^0 - \lambda_{kv'}}\phi_{kv'} \qquad (44)$$

where $(T_N + \hat{H}_{kk})\phi_{kv} = \lambda_{kv}\phi_{kv}$, and $W_{nv}^0 = E_n^0 + \epsilon_{nv}^0$. Here it is assumed that the interaction H_{kn} is sufficiently small so that it is legitimate to calculate χ_n and W via eq 30a.

IV. Strong Vibronic Coupling

A. Generalized Iteration Solution by the Partitioning Method

A powerful method of finding approximate solutions of equation system 17 is provided by the partitioning technique.[35] It will be seen below that the iteration formulas 27 and 29 leading to eq 35 and 42 are special cases of this more general formalism.

The procedure is best described by collecting the functions χ_k into a column vector χ. Equations 17 can then be compactly written

$$[T_N\mathbf{1} + \mathbf{H}]\chi = W\chi \qquad (45)$$

where $\mathbf{1}$ is the unit matrix and elements of the matrix $\mathbf{H}$ are given by eq 18.

In a molecule with closely spaced interacting electronic states, we desire to treat the coupling among these nearby states by an exact method. For this purpose, it is convenient to divide the basis set $\{\theta_k^0\}$ into two subsets (a) and (b). A finite number, say L, of strongly interacting states are placed in subset (a) in ascending order of energy. For practical reasons L is a small number, rarely exceeding 3. Because it is convenient to measure the vibrational energy relative to E_n^0 (see below), this is designated as the lowest energy member of this subset. The remaining (infinite number of) functions are contained in subset (b). The idea is to treat the coupling between the two groups (a) and (b) by perturbation methods, while fully taking into account interactions within the primary group (a). To this end, the unperturbed and perturbed parts of the molecular wave function are split as before, with

$$\psi^0 = \sum_{k \text{ in (a)}}\theta_k^0\chi_k \qquad (46a)$$

and

$$\psi^1 = \sum_{k \text{ in (b)}}\theta_k^0\chi_k \qquad (46b)$$

Since the groups (a) and (b) are disjoint, $\langle\psi^0|\psi^1\rangle = 0$. E.g., if $L = 1$ so that (a) contains only one function, χ_n, we have the weak coupling case, and eq 46 reduces to eq 22. Similarly, for $L = 2$ subset (a) consists of θ_n^0 and θ_m^0 ($E_m^0 \geqslant E_n^0$, $H_{mn} \neq 0$), and

$$\psi^0 = \theta_n^0\chi_n + \theta_m^0\chi_m \qquad (47a)$$

and

$$\psi^1 = \sum_{k \neq n,m} \theta_k^0 \chi_k \tag{47b}$$

The unperturbed wave function ψ^0 will be normalized to unity

$$\langle \psi^0 | \psi^0 \rangle = \sum_{k \text{ in (a)}} \langle \chi_k | \chi_k \rangle = 1 \tag{48a}$$

For the coupling between the two groups of states (a) and (b) to be characterized as weak, the perturbed part ψ^1 of the wave function must be small when compared to ψ^0, i.e., $\langle \psi^1 | \psi^1 \rangle \ll 1$. Using eq 46b, the condition

$$\sum_{k \text{ in (b)}} \langle \chi_k | \chi_k \rangle \ll 1 \tag{48b}$$

should be satisfied. When $L = 1$, conditions 48 reduce to 23.

With the division of the basis set into two groups (a) and (b), matrices $T_N \mathbf{1}$, $\mathbf{H}$, and the column vector χ are partitioned according to

$$T_N \mathbf{1} = T_N \begin{pmatrix} \mathbf{1}_a & 0 \\ 0 & \mathbf{1}_b \end{pmatrix}, \quad \mathbf{H} = \begin{pmatrix} \mathbf{H}_{aa} & \mathbf{H}_{ab} \\ \mathbf{H}_{ba} & \mathbf{H}_{bb} \end{pmatrix}, \quad \chi = \begin{pmatrix} \chi_a \\ \chi_b \end{pmatrix} \tag{49}$$

Subscripts a and b on all submatrices indicate their dimensions. Thus $\mathbf{H}_{aa}$ is a $L \times L$ matrix, and $\mathbf{H}_{ab} = \mathbf{H}_{ba}^\dagger$ contains L rows and an infinite number of columns. Where a matrix is diagonal only one subscript is kept. The column vector χ_a contains the L unperturbed vibrational functions in eq 46a, and χ_b has all of the remaining amplitudes entering into the definition of eq 46b.

Using eq 49, eq 45 may be displayed as

$$[T_N \mathbf{1}_a + \mathbf{H}_{aa}] \chi_a + \mathbf{H}_{ab} \chi_b = W \chi_a \tag{50a}$$

$$\mathbf{H}_{ba} \chi_a + [T_N \mathbf{1}_b + \mathbf{H}_{bb}] \chi_b = W \chi_b \tag{50b}$$

Formally solving (50b) for χ_b gives

$$\chi_b = \frac{1}{W \mathbf{1}_b - T_N \mathbf{1}_b - \mathbf{H}_{bb}} \mathbf{H}_{ba} \chi_a \tag{51}$$

Substituting eq 51 into eq 50a results in a pseudo-eigenvalue equation for χ_a

$$\mathbf{K}_{aa} \chi_a = W \chi_a \tag{52}$$

where

$$\mathbf{K}_{aa} = T_N \mathbf{1}_a + \mathbf{H}_{aa} + \mathbf{H}_{ab} \frac{1}{W \mathbf{1}_b - T_N \mathbf{1}_b - \mathbf{H}_{bb}} \mathbf{H}_{ba} \tag{53}$$

The matrix operator $(W \mathbf{1}_b - T_N \mathbf{1}_b - \mathbf{H}_{bb})$ is nonsingular if W is different from all eigenvalues of $(T_N \mathbf{1}_b + \mathbf{H}_{bb})$, in which case its inverse exists. We shall assume this to be the case and look for perturbation solutions of eq 51 and 52 subject to conditions 48a,b. As in section III.B, it is convenient to separate the vibrational energy ϵ from W, and we set

$$W = E_n^0 + \epsilon \tag{54}$$

The electronic index n is dropped from ϵ, because when $L > 1$ (strong coupling of θ_n^0 to other states), n is no longer a good quantum number.

Equations 51 and 52 are exact. Perturbation aspects of the problem emerge in the calculation of $(W \mathbf{1}_b - T_N \mathbf{1}_b - \mathbf{H}_{bb})^{-1}$. For this purpose, we use the iteration formula:

$$\begin{aligned} \frac{1}{\mathbf{A} - \mathbf{B}} &= \frac{1}{\mathbf{A}} + \frac{1}{\mathbf{A}} \mathbf{B} \frac{1}{\mathbf{A} - \mathbf{B}} \\ &= \frac{1}{\mathbf{A}} + \frac{1}{\mathbf{A}} \mathbf{B} \frac{1}{\mathbf{A}} + \frac{1}{\mathbf{A}} \mathbf{B} \frac{1}{\mathbf{A}} \mathbf{B} \frac{1}{\mathbf{A} - \mathbf{B}} \\ &\vdots \\ &= \frac{1}{\mathbf{A}} \sum_{k=0}^{\infty} \left(\mathbf{B} \frac{1}{\mathbf{A}} \right)^k \end{aligned} \tag{55}$$

valid for any two square matrices $\mathbf{A}$ and $\mathbf{B}$ with identical dimensions.[46] The pth approximation to $(\mathbf{A} - \mathbf{B})^{-1}$ is defined as the expression obtained by retaining the first p terms in the geometric series in eq 55, where $p = 1, 2, 3, \ldots$. Clearly, formula 55 is useful only if $\mathbf{A}^{-1}$ is known. In the particular problem at hand, it will be necessary to choose $\mathbf{A}$ diagonal and independent of nuclear variables. Employing an obvious generalization of the notation introduced in eq 18b and 21, power series of the matrices $\mathbf{H}_{aa}$, $\mathbf{H}_{bb}$, and $\mathbf{H}_{ab}$ around Q_0 are

$$\mathbf{H}_{aa} = \mathbf{E}_a^0 + \mathbf{H}_{aa}^{(1)} + \mathbf{H}_{aa}^{(2)} + \ldots = \mathbf{E}_a^0 + \hat{\mathbf{H}}_{aa} \tag{56a}$$

$$\mathbf{H}_{bb} = \mathbf{E}_b^0 + \mathbf{H}_{bb}^{(1)} + \mathbf{H}_{bb}^{(2)} + \ldots = \mathbf{E}_b^0 + \hat{\mathbf{H}}_{bb} \tag{56b}$$

and

$$\mathbf{H}_{ab} = \mathbf{H}_{ab}^{(1)} + \mathbf{H}_{ab}^{(2)} + \ldots \tag{56c}$$

Here $\mathbf{E}_a^0$ and $\mathbf{E}_b^0$ are diagonal matrices whose diagonal entries are the electronic energies of the states belonging to groups (a) and (b), respectively.

Using definitions 54 and 56b, we now apply eq 55 to calculate $(W \mathbf{1}_b - T_N \mathbf{1}_b - \mathbf{H}_{bb})^{-1}$ with $A = E_n^0 \mathbf{1}_b - \mathbf{E}_b^0$

$$\begin{aligned} &\frac{1}{W \mathbf{1}_b - T_N \mathbf{1}_b - \mathbf{H}_{bb}} \\ &\quad = \frac{1}{(E_n^0 \mathbf{1}_b - \mathbf{E}_b^0) - (T_N \mathbf{1}_b + \hat{\mathbf{H}}_{bb} - \epsilon \mathbf{1}_b)} = \frac{1}{E_n^0 \mathbf{1}_b - \mathbf{E}_b^0} \\ &+ \frac{1}{E_n^0 \mathbf{1}_b - \mathbf{E}_b^0} (T_N \mathbf{1}_b + \hat{\mathbf{H}}_{bb} - \epsilon \mathbf{1}_b) \frac{1}{W \mathbf{1}_b - T_N \mathbf{1}_b - \mathbf{H}_{bb}} \end{aligned} \tag{57}$$

The pth iterate of the small components χ_k (k in (b)) of the wave function is obtained by using the pth approximation to $(W \mathbf{1}_b - T_N \mathbf{1}_b - \mathbf{H}_{bb})^{-1}$ in eq 51. For example,

$$\chi_b^{(1)} = \frac{1}{E_n^0 \mathbf{1}_b - \mathbf{E}_b^0} \mathbf{H}_{ba} \chi_a \tag{58a}$$

$$\begin{aligned} \chi_b^{(2)} &= \frac{1}{E_n^0 \mathbf{1}_b - \mathbf{E}_b^0} \\ &\quad \times \left\{ 1 + (T_N \mathbf{1}_b + \hat{\mathbf{H}}_{bb} - \epsilon \mathbf{1}_b) \frac{1}{E_n^0 \mathbf{1}_b - \mathbf{E}_b^0} \right\} \mathbf{H}_{ba} \chi_a \end{aligned} \tag{58b}$$

etc. For $L = 1$, $\chi_a \equiv \chi_n$ and eq 58a,b reduce to the perturbation formulas 28.

The basic problem is the determination of the unperturbed vibrational functions χ_k (k in (a)) through eq 52. Once χ_a is found, it is a relatively straightforward matter to calculate the remaining components via eq 58 to any desired degree of accuracy. In order to extract a tractable yet sufficiently accurate equation out of (52), we use expansion 57 to rewrite the pseudo-Hamiltonian $\mathbf{K}_{aa}$ (eq 53) as

$$\begin{aligned} \mathbf{K}_{aa} = T_N \mathbf{1}_a &+ \mathbf{H}_{aa} + \mathbf{H}_{ab} \frac{1}{E_n^0 \mathbf{1}_b - \mathbf{E}_b^0} \mathbf{H}_{ba} \\ &+ \mathbf{H}_{ab} \frac{1}{E_n^0 \mathbf{1}_b - \mathbf{E}_b^0} (T_N \mathbf{1}_b + \hat{\mathbf{H}}_{bb} - \epsilon \mathbf{1}_b) \\ &\times \frac{1}{\mathrm{W} \mathbf{1}_b - T_N \mathbf{1}_b - \mathbf{H}_{bb}} \mathbf{H}_{ba} \end{aligned} \tag{59}$$

A zero-order vibrational Hamiltonian, $\mathbf{K}_{aa}^0$, will be defined on the basis of the first three terms on the right side of (59), namely:

$$T_N \mathbf{1}_a + \mathbf{H}_{aa} + \mathbf{H}_{ab} \frac{1}{E_n^0 \mathbf{1}_b - \mathbf{E}_b^0} \mathbf{H}_{ba} \tag{60}$$

We set

$$\mathbf{K}_{aa}^0 = T_N \mathbf{1}_a + \mathbf{U}_{aa} \tag{61}$$

and define the $L \times L$ matrix potential $\mathbf{U}_{aa}$ using the second and third terms in (60) truncated at quadratic terms in their power-series expansions (cf. eq 56):

$$\mathbf{U}_{aa} = \mathbf{E}_a^0 + \mathbf{H}_{aa}^{(1)} + \mathbf{H}_{aa}^{(2)} + \mathbf{H}_{ab}^{(1)} \frac{1}{E_n^0 \mathbf{1}_b - \mathbf{E}_b^0} \mathbf{H}_{ba}^{(1)} \tag{62}$$

Elements of the matrix $\mathbf{U}_{aa}$ have the explicit form

$$U_{kl} = E_l^0\delta_{kl} + H_{kl}^{(1)} + H_{kl}^{(2)} + \sum_{j \text{ in } (b)} \frac{H_{kj}^{(1)}H_{jl}^{(1)}}{\Delta E_{nj}^0} \tag{63}$$

where both subscripts k and l refer to electronic states belonging to group (a).

Equation 52 may now be written as

$$[K_{aa}^0 + K_{aa}^1(\epsilon)]\chi_a = W\chi_a \tag{64}$$

where $K_{aa}^1(\epsilon) = K_{aa} - K_{aa}^0$ will be assumed to be a small perturbation. Zero-order solutions of (64) are determined by solving L simultaneous differential equations (in the JT problem, where all E_k^0 (k in (a)) are the same; these are the Moffitt–Liehr equations[18])

$$K_{aa}^0\chi_a^0 = W^0\chi_a^0 \tag{65}$$

where $W^0 = E_n^0 + \epsilon^0$. The next energy correction is $\Delta\epsilon_v = \langle \chi_{av}^0|K_{aa}^1(\epsilon_v^0)|\chi_{av}^0\rangle$, where the vibrational quantum number v distinguishes between the different solutions of eq 65.[47]

An important feature of the present formulation is the unified treatment it provides in handling both nondegenerate (weak coupling) and nearly degenerate (strong coupling) problems on an equal footing. The method guarantees that as the coupling matrix elements become sufficiently small, there will be a smooth transition between these two limiting cases.

The usual procedure of finding solutions of the vibronic Schrödinger equation in the strong coupling case is based on the variational method using the L electronic functions of subset (a) as a truncated basis set.[2,5,6,8–12] The matrix potential in this approach is $\mathbf{H}_{aa}$, which ignores all interactions between groups (a) and (b). As pointed out in section III in the comparison of crude, H_{nn}, vs. adiabatic, E_n, potentials, these terms have considerable influence on the vibrational energy levels and wave functions. Therefore, they should be included in the definition of the zero-order Hamiltonian. Note, however, that eq 65, whose matrix potential is $\mathbf{U}_{aa}$, has precisely the same structure as the crude adiabatic model with potential $\mathbf{H}_{aa}$.[19–21] In other words, both $\mathbf{U}_{aa}$ and $\mathbf{H}_{aa}$ are power series in displacements differing only in the definition of their respective expansion coefficients. Thus the results of all (parametrized) vibronic coupling calculations, which were based on the crude adiabatic model, can be carried over here with a simple reinterpretation of the parameters.

B. Two-State Interaction

In the weak coupling limit ($L = 1$), eq 64 leads to the BO results 35 and 42 as explained in section III. For strong coupling ($L = 2$), the dominant part of the wave function is given by eq 47a. To a first approximation, the vibrational functions χ_n^0 and χ_m^0 are calculated by means of eq 65:

$$(T_N + U_{nn})\chi_n^0 + U_{nm}\chi_m^0 = W\chi_n^0 \tag{66a}$$

$$U_{mn}\chi_n^0 + (T_N + U_{mm})\chi_m^0 = W\chi_m^0 \tag{66b}$$

where from eq 63

$$U_{nn} = E_n^0 + H_{nn}^{(2)} + \sum_{j\neq n,m} \frac{|H_{nj}^{(1)}|^2}{\Delta E_{nj}^0} \tag{67a}$$

$$U_{mm} = E_m^0 + H_{mm}^{(1)} + H_{mm}^{(2)} + \sum_{j\neq n,m} \frac{|H_{mj}^{(1)}|^2}{\Delta E_{nj}^0} \tag{67b}$$

and

$$U_{nm} = H_{nm}^{(1)} + H_{nm}^{(2)} + \sum_{j\neq n,m} \frac{H_{nj}^{(1)}H_{jm}^{(1)}}{\Delta E_{nj}^0} = U_{mn}^* \tag{67c}$$

The absence of the linear terms $U_{nn}^{(1)} = H_{nn}^{(1)} = E_n^{(1)}$ from U_{nn} is due to Q_0 being chosen as the minimum of $E_n(Q)$.[48]

A feature of the BO equation 35, useful in ab initio calculations, is the possibility of obtaining the adiabatic potential E_n directly by means of eq 2. This simplifying aspect of the BO theory is, in general, lost upon going to the coupled equations 66a,b. However, it may be possible to avoid definitions 67a,b, and calculate U_{nn} and U_{mm} from a knowledge of the potentials E_n, E_m, and the interaction $H_{nm}^{(1)}$ if there is symmetry.

Comparing eq 67a with eq 30b, it is seen that $U_{nn}^{(2)} = E_n^{(2)} - |H_{nm}^{(1)}|^2/\Delta E_{nm}^0$, provided $|\Delta E_{nm}^0| \neq 0$. Therefore, the difference between $U_{nn}^{(2)}$ and $E_n^{(2)}$ arises in their dependence on the coupling modes[49] (i.e., those coordinates Q_r for which $H_{nm}^r \neq 0$).

As an example, consider the case where the functions θ_n^0 and θ_m^0 belong to different irreducible representations. Then the interaction $H_{nm}^{(1)}$ has no dependence on the totally symmetric coordinates Q_{sym}, i.e., $H_{nm}^{(1)} = H_{nm}^{(1)}(Q_{\text{asym}})$, where Q_{asym} denotes the set of nontotally symmetric (asymmetric) coordinates. The functional dependence of $U_{nn}^{(2)}$ (and $E_n^{(2)}$) on nuclear displacements is

$$U_{nn}^{(2)} = U_{nn}^{(2)}(Q_{\text{sym}}) + U_{nn}^{(2)}(Q_{\text{asym}}) \tag{68}$$

where $U_{nn}^{(2)}(Q_{\text{sym}}) = U_{nn}^{(2)}(Q)|_{Q_{\text{asym}}=0}$. $U_{nn}^{(2)}(Q_{\text{asym}})$ is similarly defined. Since $H_{nm}^{(1)}$ is a function of Q_{asym} only,

$$U_{nn}^{(2)}(Q_{\text{sym}}) = E_n^{(2)}(Q_{\text{sym}}) \tag{69a}$$

and

$$U_{nn}^{(2)}(Q_{\text{asym}}) = E_n^{(2)}(Q_{\text{asym}}) - (|H_{nm}^{(1)}|^2/\Delta E_{nm}^0) \tag{69b}$$

$$\Delta E_{nm}^0 \neq 0$$

The other diagonal potential term, $\hat{U}_{mm} = U_{mm}^{(1)} + U_{mm}^{(2)}$, can be similarly related to the adiabatic potential $\hat{E}_m = E_m^{(1)} + E_m^{(2)} + \ldots$ if the strongly coupled states θ_n^0 and θ_m^0 are well separated from the remaining states θ_j^0. That is, when $|\Delta E_{nm}^0| \ll |\Delta E_{nj}^0|$ ($j \neq n, m$) in eq 67b, E_n^0 may be replaced by E_m^0, and hence

$$U_{mm}^{(2)}(Q_{\text{sym}}) \approx E_m^{(2)}(Q_{\text{sym}}) \tag{70a}$$

and

$$U_{mm}^{(2)}(Q_{\text{asym}}) \approx E_m^{(2)}(Q_{\text{asym}}) + |H_{nm}^{(1)}|^2/\Delta E_{nm}^0 \tag{70b}$$

$$|\Delta E_{nm}^0| \neq 0$$

The exact relation $U_{mm}^{(1)} = E_m^{(1)}$ holds for the linear term.

In an experimental situation described by eq 66a,b, the observed energies will have no connection with either of the adiabatic potentials E_n or E_m. Consequently, relations 69a,b and 70a,b have only theoretical significance.

C. Forbidden Transitions

We define a transition between the ground and an excited state represented by wave functions $\psi_g^0 = \theta_g^0\chi_g$ and $\psi = \psi^0 + \psi^1$, respectively, as electronically forbidden if matrix elements of M (the electronic dipole moment operator) between θ_g^0 and the electronic functions in ψ^0 are zero (or very small; i.e., $\langle\theta_g^0|M|\theta_n^0\rangle \simeq 0$ and $\langle\theta_g^0|M|\theta_m^0\rangle \simeq 0$ when ψ^0 is given by eq 47a). Then the intensity of the transition is largely governed by ψ^1 (there will also be contributions from the HT components of the ground electronic state). In the lowest approximation, the vibrational amplitudes ($k \neq n, m$) of ψ^1 are given by eq 58a. Using the vector

$$\chi_{av}^0 = \begin{pmatrix} \chi_{nv}^0 \\ \chi_{mv}^0 \end{pmatrix} \tag{71}$$

in eq 58a yields

$$\chi_k^{(1)} = \frac{1}{\Delta E_{nk}^0}(H_{kn}\chi_{nv}^0 + H_{km}\chi_{mv}^0) \tag{72}$$

$$k \neq n, m$$

The total wave function is thus (cf. eq 47a,b)

TABLE I. Parameters Used in Vibronic Calculations for Benzaldehyde Triplet States

	ω_7[a]	ω_{25}[a]	ω_{26}[a]	ω_{36}[a]	D_7[b]	D_{25}[b]
S_0[c]	1700	215	1000	110	...	...
$T_1(n\pi^*)$[c]	1300	185	425	115	1.7	0.3
$T_2(\pi\pi^*)$[d]	1700	250	1000	140	0.9	0.8

$H_{12}^a(\hbar/2\omega_a)^{1/2} = 100\ \mathrm{cm}^{-1}$ where $a = \nu_{26}$ or ν_{36}.[e,f]

[a] In cm^{-1}. [b] Dimensionless displacement parameters obtained from Franck–Condon factors using the experimental intensity ratio of the origin band and the first member of the progression. (Formal definition: $D_s(k) = H_{kk}^s/\hbar\omega_s(k)(\hbar/\omega_s(k))^{1/2}$, where $k = T_1$ or T_2, and $s = \nu_7$ or ν_{25}.) [c] Data from ref 57 for the gaseous free molecule. [d] Data for ν_{25} and ν_{36} from unpublished work of M. Koyanagi and L. Goodman. These values are from solid-state spectra with application of crystal to gas shift correction. The frequencies for ω_7 and ω_{26} are assumed unchanged from the ground-state values. [e] H_{12}^a is as defined in eq 20a where Q_a is taken to be a (mass-weighted) normal coordinate. [f] References 53 and 58.

$$\psi_v \simeq \left(\theta_n^0 + \sum_{k\neq n,m} \theta_k^0 \frac{H_{kn}}{\Delta E_{nk}^0}\right) \chi_{nv}^0 + \left(\theta_m^0 + \sum_{k\neq n,m} \theta_k^0 \frac{H_{km}}{\Delta E_{nk}^0}\right) \chi_{mv}^0 \quad (73)$$

Vibronic wave function 73 is the appropriate generalization of the HT wave function 40 to the strong coupling case (with $L = 2$).

Spin-dependent terms have been omitted from the vibronic Hamiltonian. By making the replacement $H_{kl} \rightarrow H_{kl} + H_{kl}^{\mathrm{so}}$ in all foregoing formulas, the spin-orbit (H^{so}) interactions may be included. In molecules containing light atoms such as the aromatic hydrocarbons, spin-orbit forces are much weaker than vibronic interactions.[50] Consequently, their effect on the energy levels and the zero-order wave functions may be neglected. Intensities of transitions between states of different multiplicities may then be accounted for by including the matrix elements H_{kl}^{so} in the perturbed part ψ^1 of the wave function. E.g., if the two closely coupled states θ_n^0 and θ_m^0 are triplets, intensity of the transitions to the singlet ground state will be determined by the following part of ψ^1

$$\left(\sum_k \theta_k^0 \frac{H_{kn}^{\mathrm{so}}}{\Delta E_{nk}^0}\right) \chi_{nv}^0 + \left(\sum_k \theta_k^0 \frac{H_{km}^{\mathrm{so}}}{\Delta E_{nk}^0}\right) \chi_{mv}^0 \quad (74)$$

where the electronic index k runs over singlets only.

D. Vibronic Calculations

The ideas presented in sections III and IV are illustrated in a series of model calculations,[51] and in the chemical application described in the next section. The parametrization necessary to carry out computations using eq 66 is described in ref 51.

V. Application. Vibronic Coupling between the Triplet States of Aromatic Aldehydes

A. $^3n\pi^*$ Spectrum of Benzaldehyde

The purpose of this section is to compare the exact solutions of (66) with the BO solutions in an example that passes from the weak to strong coupling cases. There has been extensive interest in vibronic coupling between the lowest triplet states of aromatic aldehydes,[52-56] the problem having both photochemical and spectroscopic ramifications. There is no intent to review the literature or to relate the calculations to detailed experiments here. The lowest energy triplet (T_1) state for the simplest aromatic aldehyde, benzaldehyde, is $^3n\pi^*$ in the free (assumed planar) molecule. Two weak out-of-plane (nontotally symmetric) vibrational bands are observed in the phosphorescence spectrum: ν_{26} and ν_{36} corresponding to modes largely involving the aldehyde out-of-plane hydrogen wagging and CHO torsional motions (ground-state frequencies near 1000 and 110 cm^{-1}), respectively.[57] Details of the spectrum suggest that these modes are active because of vibronic interaction with a triplet $\pi\pi^*$ state (T_2) lying some 1000 cm^{-1} above T_1 in the free molecule.[53-56]

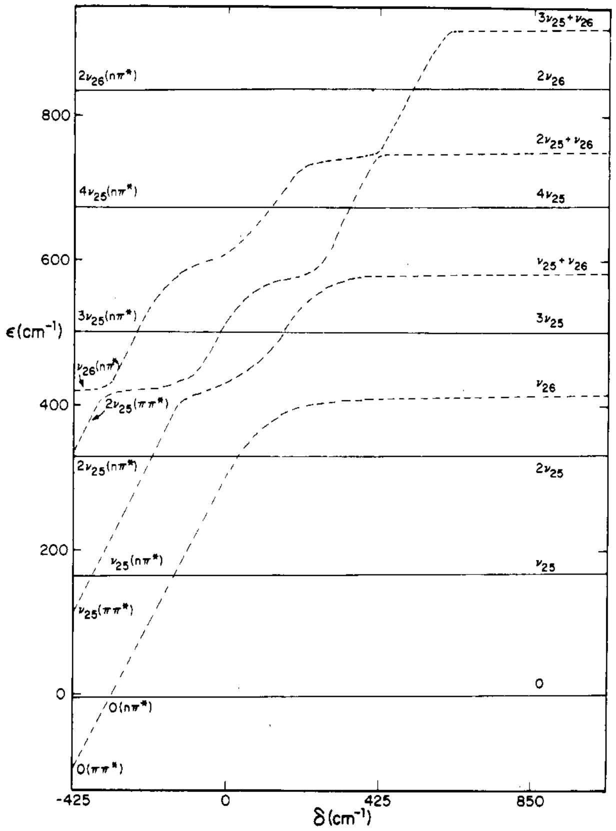

Figure 1. First ten eigenvalues of eq 66 involving coupling mode ν_{26} and totally symmetric mode ν_{25}, as a function of the T_1–T_2 energy gap δ.[63] Level designations refer to weak vibronic coupling: —, even parity levels; - - -, odd parity levels.[65]

The two most prominently observed Franck-Condon modes in the $T_1 \rightarrow S_0$ spectrum are ν_7 and ν_{25}, largely corresponding to the C=O stretching and the CHO in-plane wagging vibrations observed in the free molecule spectrum near 1700 and 215 cm^{-1}, respectively. These modes persist in other aromatic aldehyde spectra, but the energy gap between T_1 and T_2 is changeable including inversion of the two triplets. Different solid-state environments may also vary or invert the T_1–T_2 gap.

We consider the solutions of (66) as a function of the energy gap between T_1 and T_2 within an idealized (two-mode) model consisting of coupling modes ν_{36} or ν_{26}, and totally symmetric modes ν_{25} or ν_7.

We presume at the outset that the coupling is weak in free benzaldehyde. The coupling matrix element H_{12} has been estimated ~100 cm^{-1} from phosphoresence microwave double resonance studies.[53,58] Conclusions drawn from the calculations are not affected by reasonable variations from this value, although applications to specific molecules in specific situations might be. In addition we make the simplifying assumption that H_{12} is insensitive to the energy gap. The necessary parameters are assembled in Table I.

B. Energy Levels

The first few eigenvalues of eq 66 are displayed vs. the T_2–T_1 gap δ[63] in Figures 1-3. Even though the coupling matrix element is the same for both ν_{26} and ν_{36}, the interaction of the two states through each of these modes is quite different owing to the

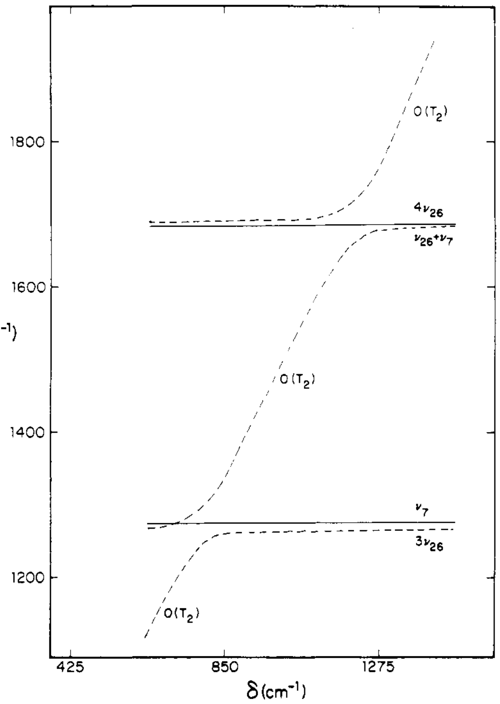

Figure 2. Several eigenvalues of eq 66 around resonance points, in the coupling model comprised of ν_{26} and the totally symmetric mode ν_7. Level designations refer to weak vibronic coupling: —, even parity levels; - - -, odd parity levels.

disparity in their frequencies (115 cm^{-1} (ν_{36}) vs. 425 cm^{-1} (ν_{26})).

Figures 1 and 2, where ν_{26} is the active mode, are examples of the weak coupling case. Except for values where the vibronic energies are nearly degenerate ($W_{1v} \approx W_{2v'}$), the two states behave independently of each other. Around the resonance points, there is a weak breakdown of the BO approximation.[59] The splittings are predictable via degenerate perturbation theory, taking into account only the levels which are in resonance.

The basic features of strong vibronic coupling are brought out in Figure 3. Here the two states are coupled through the CHO torsional mode ν_{36}, and the Franck-Condon mode ν_{25}. At large energy gaps ($\delta \gtrsim 800$ cm^{-1} corresponding to the weak coupling region), the BO approximation is valid. The two modes independently form their harmonic progressions. Note, however, that the frequency of ν_{36} is lower than its value at infinite separation of the two states. E.g., at $\delta = 920$ cm^{-1}, $\omega_{36} = 96$ cm^{-1} as compared with 115 cm^{-1} in the absence of the coupling. The frequency at finite (but large) δ values is accurately given by the harmonic approximation as $\omega_{36}(T_1) = 115(1 - 2l^2/\Delta E_{21}^0)^{1/2}$ cm^{-1}, where l is the dimensionless interaction parameter, and $\Delta E_{21}^0 = \delta + 1/2fD^2\beta_s^2$, the vertical energy gap in units of $\hbar\omega_{36}^0 = 115$ cm^{-1}.[60]

When the gap approaches 500 cm^{-1}, strong breakdown of the BO approximation occurs, with the harmonic approximation completely failing at $\delta = 330$ cm^{-1}. At this energy gap, the force constant of ν_{36} becomes zero. A strong negative anharmonicity in the overtones of ν_{36} appears, which may be qualitatively understood on the basis of positive quartic terms in the associated adiabatic potential.[61,62]

Owing to the rather small shift in the origin of T_2 relative to T_1 ($D \simeq 0.4$), and similar values in the frequency of ν_{25} ($\omega_{25}(T_2)/\omega_{25}(T_1) = 1.3$), the Franck-Condon mode ν_{25} behaves quite regularly throughout Figure 3. The frequency of ν_{25} in the progression $36_0{}^1 + 25_0{}^n$ is somewhat higher (within 4 cm^{-1}) than in the progression $0 + 25_0{}^n$. This is qualitatively in agreement with the BO approximation for large δ, when the anharmonic terms are taken into account, since $\omega_{25}(T_2) > \omega_{25}(T_1)$. The only exceptions occur around $\delta \simeq 0$ (where $\omega_{25}(T_1)$ has to pass into $\omega_{25}(T_2)$ and vice versa), and where overtones of ν_{36} are nearly degenerate with the harmonics of ν_{25}. In the latter case, the two modes are scrambled, not unlike the mixing of the two states in Figures 1 and 2 around resonance regions. The behavior of several levels from Figure 3 around such points are compared in Figure 4 with solutions of the one-mode problem involving only ν_{36}.

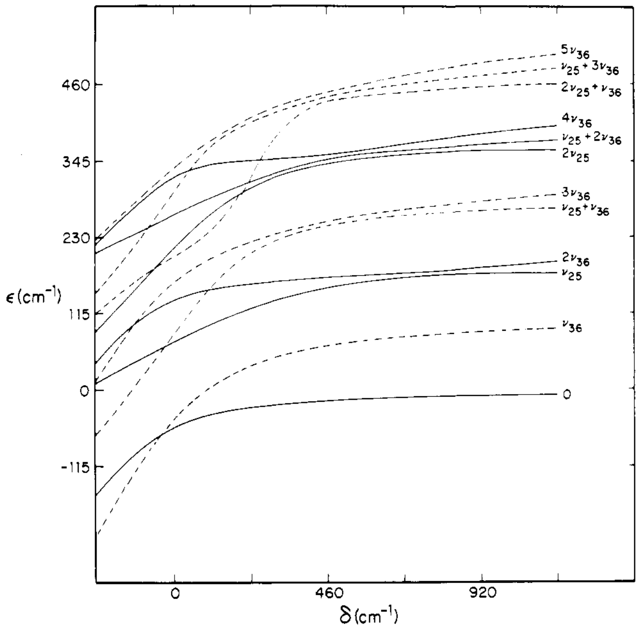

Figure 3. Low-lying eigenvalues of eq 66 involving coupling mode ν_{36} and totally symmetric mode ν_{25}, as a function of the T_1–T_2 energy gap, δ. Level designations refer to weak vibronic coupling, i.e., large δ. At the left the modes are too scrambled to allow designation: —, even parity levels; - - -, odd parity levels.

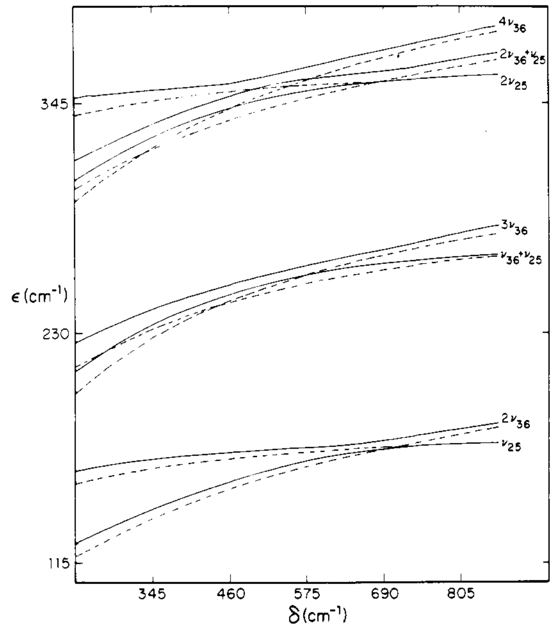

Figure 4. Comparison of several levels from Figure 3 with solutions of a one-mode (ν_{36}) problem around Fermi resonance regions: —, two-mode eigenvalues of eq 66 involving ν_{36} and ν_{25}; - - -, single-mode eigenvalues of eq 66 involving ν_{36}. Combination levels have been constructed using harmonic energies of ν_{25}.

Thus the weak coupling assumption made for free benzaldehyde ($\delta \simeq 1000$ cm^{-1}) is basically valid; however, the calculated ω_{36} would be depressed by about 15 cm^{-1} to 98 cm^{-1} from the parameters in Table I.

Replacement of the hydrogen atom at the aldehyde position

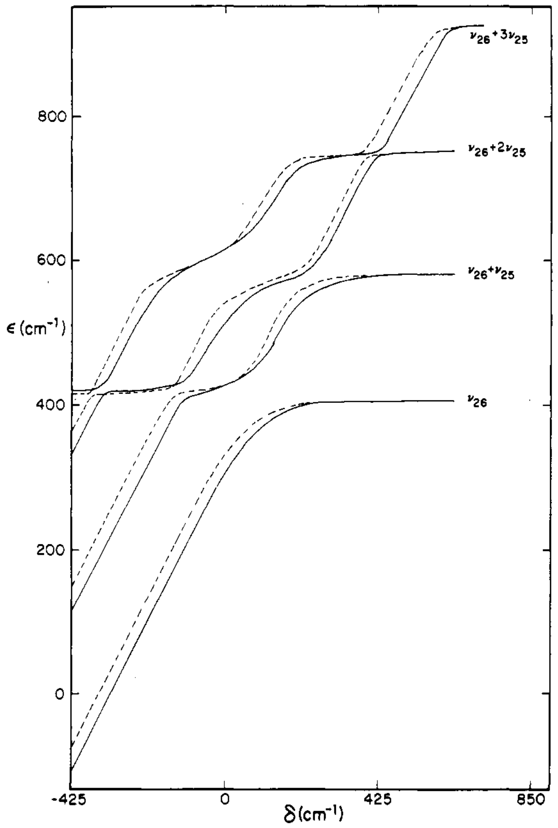

Figure 5. Deuterium effect on several eigenvalues of eq 66 involving ν_{25} and ν_{26} as a function of the T_1–T_2 energy gap, δ. Level designations refer to weak vibronic coupling: —, normal aldehyde; - - -, CDO molecule.

by deuterium drops the ν_{26} frequency from 425 to 310 cm^{-1} in the $^3n\pi^*$ state of free benzaldehyde,[57] nearly the value for pure hydrogen motion. A possibility then exists for an important deuterium effect involving the ν_{26} coupling mode. Such is not the case for ν_{36} since the corresponding reduction in its frequency is small.[57]

The first few eigenvalues involving ν_{26} are compared for the CDO and CHO systems in Figure 5. The only significant differences are in the resonance region in accord with the weak coupling brought about by ν_{26}. In the 100–200 cm^{-1} gap region the ν_{26} frequency is predicted to be less depressed by vibronic interaction in the CDO molecule than in the normal one. The progression $\nu_{26} + n\nu_{25}$ is also predicted to suffer sizable perturbations upon deuteration.

Extensions of these considerations to the excited state dipole moments for the various vibronic levels and to band intensities for emission and absorption of aromatic aldehydes have recently been made.[55,64]

VI. Partial List of Symbols and Abbreviations

BO: Born-Oppenheimer
HT: Herzberg–Teller
JT: Jahn–Teller
vibronic: vibrational-electronic
nonadiabatic: interactions that arise due to the nonnegligibility of the nuclear kinetic energy operator
x: electronic coordinate
Q: nuclear coordinate
Q_0: a minimum point of $E_n(Q)$
$H(x,Q)$: electronic Hamiltonian
T_N: nuclear kinetic energy operator
$\mathcal{H} = H + T_N$: vibrational-electronic Hamiltonian (exclusive of the translational and rotational energies)
$\psi = \psi^0 + \psi^1$: exact vibronic wave function
$\theta_k(x,Q)$: eigenfunction of $H(x,Q)$
$E_k(Q)$: eigenvalue of $H(x,Q)$ (kth adiabatic potential surface)
$E_k^0 = E_k(Q_0)$
$E_k^{(2)}$: harmonic (quadratic) part of the kth adiabatic potential surface
$\Delta E^0_{nk} = E^0_n - E^0_k$
χ_k: vibrational function
$\chi_k^{(p)}$: pth (p = 1, 2, . . .) approximation to χ_k
ϵ: vibrational energy
$W = E_n^0 + \epsilon$: total energy
$H_{kl} = \langle\theta_k^0|H|\theta_l^0\rangle$
$H_{kl}^r = \langle\theta_k^0|(\partial H/\partial Q_r)_0|\theta_l^0\rangle$
$H_{kl}^{rs} = \langle\theta_k^0(\partial^2 H/\partial Q_r\partial Q_s)_0|\theta_l^0\rangle$, etc.
H: matrix element
Taylor series of an arbitrary function F about an arbitrary point Q_0 is displayed as $F(Q) = F(Q_0) + F^{(1)} + F^{(2)} + \ldots$
The Q-dependent portion of a power series is denoted by $\hat{F} = F^{(1)} + F^{(2)} + \ldots = F(Q) - F(Q_0)$
$K^0_{nn} = T_N + E_n^{(2)}$: harmonic Hamiltonian
$K_{nn}(\epsilon) = K^0_{nn} + K^1_{nn}(\epsilon)$: projection of the exact vibronic Hamiltonian into the subspace spanned by the single function $\theta_n^0(x)$
$U_{kl}(Q)$, where k, l = 1, 2, . . . , L: projection of the electronic
$U_{kl}(Q)$, where k, l = 1, 2, . . . , L: projection of the electronic Hamiltonian into the subspace spanned by the L electronic functions $\theta_k^0(x)$, k = 1, 2, . . . , L
κ: (electron mass/average nuclear mass)$^{1/4}$

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(37) It should be noted that even in this nondegenerate case, we are in effect applying the multidimensional (in fact, infinite dimensional) partitioning technique[35] (also see section IV). If a complete set of vibrational functions were introduced, each of the functions χ_k would be represented by a column matrix containing the (infinite number of) expansion coefficients. Equations 28a,b would then be matrix relations.

(38) Reference 1b, p 405.

(39) The BO ordering of the terms in the Hamiltonian with respect to κ is formally obtained by putting $Q_r \rightarrow \kappa Q_r$ (so that, e.g., $H_{kl}^{(P)} \rightarrow \kappa^P H_{kl}{}^{(P)}$), and $T_N \rightarrow \kappa^2 T_N$. At the end of the calculation, set $\kappa = 1$.

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(47) When $L > 1$, this matrix element is evaluated by observing the following rules. One first calculates (formally) $\chi_a^+ \mathbf{K}_{aa}^1 \chi_a$ using ordinary matrix multiplication rules, and then integrates over the nuclear variables.

(48) In order to obtain the BO approximation (with no linear terms in the potential) for $L = 1$, and to avoid possible confusions in the definition of matrix elements, we have not changed the fixed basis $\{\theta_k(x, Q_0)\}$ by retaining Q_0 as a minimum point of the potential $E_n(Q)$. Actually, in the strong coupling problem at hand, it is preferable (for better convergence) to take Q_0 as the average position of the minima of the L adiabatic potentials E_k, k in (a). For example, in the JT effect Q_0 will be the symmetrical "crossing" point of the adiabatic potentials (this is the usual practice). Employment of this slightly different basis will generally result in nonvanishing linear terms in all diagonal elements $U_{kk}(Q)$, k in (a) (i.e., including U_{nn}).

(49) Whereas $U_{nn}^{(2)}$ and $E_n^{(2)}$ are functions of all ($3N - 6$) internal symmetry coordinates, $H_{nm}^{(1)} = \sum_r H_{nm}^r Q_r$ is a function of a smaller number of variables. $U_{nn}^{(1)}$ and $E_n^{(2)}$ can be expressed as a sum of terms, each of which is a function of only those coordinates which belong to a given irreducible representation of the molecular symmetry group. The interaction, H_{nm}, on the other hand, is a function of only those coordinates whose symmetry species is contained in the direct-product representation of the electronic functions θ_n^0 and θ_m^0. Dependence of the $U_{nn}^{(2)}$ on those displacements which do not appear in $H_{nm}^{(1)}$ is identical with the projection of $E_n^{(2)}$ along these variables.

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(65) Because in planar aromatic aldehydes the two triplet states have different electronic symmetries, the coupling mode must be nontotally symmetric leading to even and odd parity vibronic states.