

A semiclassical model for intramolecular vibrational relaxation of local mode overtone in polyatomic molecules

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A combination of the semiclassical perturbation (SCP) approximation and a kinetic coupling model gives rise to simple analytic formulae for the description of local mode overtone absorption spectra and the associated intramolecular vibrational relaxation in polyatomic molecules. Application to the CH(CD) stretch local mode overtones of C_6H_6 (C_6D_6) gives results which are in reasonable agreement with experimental observations. The SCP-kinetic coupling model is thus seen to provide a very useful description of this intramolecular dynamics.

Key words: Semiclassical perturbation approximation — Kinetic coupling model — Local mode overtone absorption spectra — Intramolecular vibrational relaxation

1. Introduction

Intramolecular vibrational relaxation (IVR) is an important feature of the dynamics of polyatomic molecular systems; it plays a central role, for example, in the description of multiphoton excitation and mode specific chemistry. A particularly clear and dramatic example of IVR is manifest in the overtone spectra of CH stretch local modes observed in a number of polyatomic molecules. Because the phenomenon is so ubiquitous, it has attracted considerable experimental [1–5] and theoretical [6–12] attention.

We have earlier [13] shown how a simple semiclassical approach, the semiclassical perturbation (SCP) approximation, provides a *qualitative* description of the line shapes of the CH overtones – and thus the related time decay of the initially excited local mode state – and the purpose of the present paper is to present a more detailed analysis and to show that the description is also quantitatively useful. The SCP approximation [14, 15], which is essentially a perturbative

approximation to “classical S-matrix” theory [16], has been usefully applied to a number of phenomena – vibrationally [17] and rotationally [18] inelastic scattering, diffraction of atoms and molecules from crystal surfaces [19], phonon inelastically in atom/molecule scattering from surfaces [20], curvature corrections to reactive tunneling probabilities [13] – and this is another example of this very simple and widely applicable dynamical model.

Our preliminary discussion [13] of overtone line widths was based on the reaction path Hamiltonian [21] but in the present work we have utilized the kinetic coupling model [11, 22, 23] originally proposed by Gribov [24] to describe the polyatomic molecule. In this model internal displacement coordinates, i.e., the changes in bond lengths and bond angles, are used. One of the most important advantages of using internal displacement coordinates is that in low orders of approximation the anharmonic potential coupling terms between the local modes and the remaining degrees of freedom of molecule, which are extremely difficult to determine, can be neglected, since in the internal coordinate frame the kinetic coupling terms resulting from the coordinate dependence of the effective mass for the internal coordinate motion provide the dominant coupling responsible for the overtone line widths [11, 25]. In contrast with the potential coupling, it is a rather trivial matter to calculate the kinetic coupling terms. In the present work the SCP approximation plus the kinetic coupling model gives simple, analytical expressions for the time correlation function which characterizes the relaxation of the local mode overtone states and their related absorption spectrum.

Section 2 first gives a brief review of the SCP description of local mode overtone absorption spectra. The kinetic coupling model that we use is described in Section 3, and its application to local mode overtone spectra is carried out in Section 4. Numerical results for the CH(CD) overtones in benzene (perdeuterobenzene) are discussed in Section 5, and Section 6 concludes.

2. The SCP formula for absorption spectra

Consider a molecular system of F degrees of freedom, one of which is a large amplitude motion coordinate s of special interest and characterized by the action-angle variables (n_s, q_s) . The remaining $(F - 1)$ molecular degrees of freedom are a set of the harmonic modes with frequencies $\{\omega_k\}$, $k = 1, \dots, F - 1$, and characterized by a set of the action-angle variables (\mathbf{n}, \mathbf{q}) . The classical Hamiltonian of the system has the form

$$H(n_s, q_s, \mathbf{n}, \mathbf{q}) = H_0(n_s, \mathbf{n}) + H_1(n_s, q_s, \mathbf{n}, \mathbf{q}) \quad (2.1)$$

with

$$H_0(n_s, \mathbf{n}) = \varepsilon_s(n_s) + \sum_{k=1}^{F-1} (n_k + \frac{1}{2}) \hbar \omega_k. \quad (2.2)$$

The corresponding quantum Hamiltonian operator is given by

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \quad (2.3)$$

where

$$\hat{H}_0 = \hat{h}_s + \sum_{k=1}^{F-1} \hat{h}_k. \quad (2.4)$$

$|n_s\rangle$ and $|n_k\rangle$, $k=1, \dots, F-1$, are the eigenstates of \hat{h}_s and \hat{h}_k with eigenvalue $\varepsilon_s(n_s)$ and $\hbar\omega_k(n_k + \frac{1}{2})$, respectively; i.e.,

$$\begin{aligned} \hat{h}_s |n_s\rangle &= \varepsilon_s(n_s) |n_s\rangle \\ \hat{h}_k |n_k\rangle &= \hbar\omega_k(n_k + \frac{1}{2}) |n_k\rangle, \quad k=1, \dots, F-1. \end{aligned} \quad (2.5)$$

If the molecule is initially in state $|n_s=0\rangle|\mathbf{n}\rangle$, where $|\mathbf{n}\rangle \equiv |n_1, \dots, n_{F-1}\rangle$ (the state $|\mathbf{n}\rangle$ will usually also be taken to be the ground state $|0\rangle$), then the absorption spectrum $I(\omega)$ is given by [26]

$$I(\omega) = \int_{-\infty}^{\infty} dt e^{i(E_0 + \hbar\omega)t/\hbar} \langle 0, \mathbf{n} | \hat{\mu} e^{-i\hat{H}t/\hbar} \hat{\mu} | 0, \mathbf{n} \rangle, \quad (2.6)$$

where

$$E_0 = \varepsilon_s(n_s) + \sum_{k=1}^{F-1} \hbar\omega_k(n_k + \frac{1}{2}),$$

and $\hat{\mu}$ is the dipole moment operator of the molecule. As is usual, one assumes that $\hat{\mu}$ is a function only of the s degree of freedom, so that insertion of complete sets of states before and after the propagator in Eq. (2.6) gives

$$\langle 0, \mathbf{n} | \hat{\mu} e^{-i\hat{H}t/\hbar} \hat{\mu} | 0, \mathbf{n} \rangle = \sum_{n_s, n'_s} \langle 0 | \hat{\mu} | n_s \rangle \langle n_s, \mathbf{n} | e^{-i\hat{H}t/\hbar} | n'_s, \mathbf{n} \rangle \langle n'_s | \hat{\mu} | 0 \rangle \quad (2.7)$$

If one neglects mode mixing—i.e., the term $n'_s \neq n_s$ in Eq. (2.7), then the absorption spectrum associated with the $0 \rightarrow n_s$ overtone of mode s takes the form [13]

$$I_{n_s,0}(\omega) = |\langle n_s | \hat{\mu} | 0 \rangle|^2 \int_{-\infty}^{\infty} dt e^{-i\Delta\omega t} C(t) \quad (2.8a)$$

with

$$\Delta\omega = \omega - \omega_{n_s,0} \quad (2.8b)$$

where $\omega_{n_s,0}$ is the zeroth-order position of the $0 \rightarrow n_s$ overtone absorption line

$$\omega_{n_s,0} = \varepsilon_s(n_s) - \varepsilon_s(0) \quad (2.8c)$$

and the correlation function $C(t)$ is

$$C(t) = e^{iE_{n_s,n}t/\hbar} \langle n_s, \mathbf{n} | e^{-i\hat{H}t/\hbar} | n_s, \mathbf{n} \rangle \quad (2.9a)$$

with

$$E_{n_s,n} = \varepsilon_s(n_s) + \sum_{k=1}^{F-1} \hbar\omega_k(n_k + \frac{1}{2}). \quad (2.9b)$$

To this point the description is exact: the overtone line shape, Eq. (2.8), is given by the Fourier transform of $C(t)$, and the task is to calculate this correlation

function from Eq. (2.9). To do this the SCP approximation is used for the matrix elements of the propagator in Eq. (2.9a), whereby the expression for the correlation function becomes

$$C(t) = \int_0^{2\pi} \frac{dq_s}{2\pi} \int_0^{2\pi} \frac{dq}{(2\pi)^{F-1}} \exp[-i\Delta\Phi(t)/\hbar] \quad (2.10a)$$

where the action integral $\Delta\Phi$ is given by

$$\Delta\Phi(t) = \int_0^t dt' H_1(n_s, q_s + \omega_s t', \mathbf{n}, \mathbf{q} + \boldsymbol{\omega} t') \quad (2.10b)$$

$$\boldsymbol{\omega} = \{\omega_k\}, k = 1, \dots, F-1, \quad (2.10c)$$

and

$$\omega_s = \frac{\partial \varepsilon_s(n_s)}{\partial n_s} = \varepsilon'_s(n_s). \quad (2.10d)$$

Eqs. (2.8) and (2.10) provide the working formulae of the SCP description of the overtone lineshape. It is thus necessary to express the perturbation H_1 in terms of the zeroth order action-angle variables and then to average over the angle variables as in Eq. (2.10a). $|C(t)|^2$ has the interpretation as the *survival probability* of the excited zeroth order state $|n_s, \mathbf{n}\rangle$, and the Fourier transform of $C(t)$ gives the absorption lineshape.

Because the SCP approximation is a type of exponential first-order perturbation theory it will be accurate for short times but less so for longer times. The initial decay of $|C(t)|^2$ should thus be described correctly, so that the overall line shape of the $0 \rightarrow n_s$ band will be obtained correctly. Fine structure of the overtone line shape, and certainly the limit of individual lines, requires the long time behavior of $C(t)$ and will thus not be described well by the SCP approximation to $C(t)$.

3. The kinetic coupling model for local mode overtone dynamics

An essential difference of local mode overtone dynamics from a normal mode study is that one has to be concerned with large amplitude motion. Anharmonic couplings among the modes must thus be taken into account, at least approximately. In Cartesian coordinates the kinetic energy is diagonal and all anharmonic couplings are in the potential energy, whose determination requires tremendous computational effort. In contrast, in internal coordinates the kinetic energy has the form [28]

$$T = \frac{1}{2} \sum_{i,j=1}^F g_{ij}(\mathbf{x}) p_i p_j, \quad (3.1)$$

where $\mathbf{x} \equiv \{x_i\}$, $i = 1, \dots, F$, are the internal displacement coordinates, i.e., the changes in bond lengths and bond angles, p_i are the momenta conjugate to x_i and $g_{ij}(\mathbf{x})$ are the Wilson G matrix elements which, in general, depend on the displacement coordinates \mathbf{x} and have been tabulated [28]. The $g_{ij}(\mathbf{x})$ can be

expanded in a Taylor series expansion in the internal displacement coordinates \mathbf{x} about the equilibrium geometry $\mathbf{x} = \mathbf{0}$

$$g_{ij}(\mathbf{x}) = g_{ij}^0 + \sum_{k=1}^F (\partial g_{ij} / \partial x_k)_{x=\mathbf{0}} x_k + \dots, \quad (3.2)$$

where $g_{ij}^0 \equiv g_{ij}(\mathbf{0})$ are determined by the atomic masses and the equilibrium geometry of the molecule. Eq. (3.2) gives the kinetic energy to the first order as

$$T \cong T^0 + \frac{1}{2} \sum_{i,j,k}^F (\partial g_{ij} / \partial x_k)_{x=\mathbf{0}} x_k p_i p_j = T^0 + T_1, \quad (3.3)$$

where

$$T^0 = \frac{1}{2} \sum_{i,j}^F g_{ij}^0 p_i p_j, \quad (3.4a)$$

and

$$T_1 = \frac{1}{2} \sum_{i,j,k}^F (\partial g_{ij} / \partial x_k)_{x=\mathbf{0}} x_k p_i p_j. \quad (3.4b)$$

If the internal coordinate x_s corresponds to the local mode of interest, which is described as an oscillator with Morse potential

$$V_s = D(1 - e^{-\alpha x_s})^2, \quad (3.5)$$

then the total potential energy can be expanded as

$$V(\mathbf{x}) = V_s + \sum_{i \neq s} \left(\sum_j C_{ij} x_i x_j + \sum_{j,k} C_{i,j,k} x_i x_j x_k + \dots \right), \quad (3.6)$$

where the potential energy at equilibrium geometry has been chosen as zero. The classical Hamiltonian to the first order thus reads

$$w = H_0 + H_1, \quad (3.7a)$$

where

$$H_0 = h_s + h \quad (3.7b)$$

with

$$h_s = \frac{1}{2} g_{ss}^0 p_s^2 + V_s, \quad (3.7c)$$

$$h = \sum_{i,j \neq s} [C_{ij} x_i x_j + \frac{1}{2} g_{ij}^0 p_i p_j],$$

and

$$H_1 = \sum_{i \neq s} C_{is} x_s x_i + \sum_{ij \neq s} C_{ijs} x_i x_j x_s + \frac{1}{2} \sum_{i \neq s} g_{is}^0 p_i p_s + \frac{1}{2} \sum_{j,i,k} (\partial g_{ij} / \partial x_k)_{x=\mathbf{0}} x_k p_i p_j. \quad (3.7d)$$

In internal coordinates the anharmonic *potential* couplings (the second term on the right side of Eq. (3.7d)) are usually much smaller than the *kinetic* couplings

(the fourth term on the right side of Eq. (3.7d)) [23]. In the kinetic coupling model the anharmonic potential couplings are totally neglected, so that Eq. (3.7d) becomes

$$H_1 \cong \sum_{i \neq s} C_{is} x_i x_s + \frac{1}{2} \sum_{i \neq s} g_{is}^0 p_i p_s + \frac{1}{2} \sum_{i,j,k} (\partial g_{ij} / \partial x_k)_{x=0} x_k p_i p_j. \quad (3.7e)$$

The coefficients C_{ij} in Eq. (3.7c) and Eq. (3.7e) are determined from the molecular (harmonic) force constants, so that with this kinetic coupling model the classical Hamiltonian is completely determined and relatively simple.

One now carries out a normal mode analysis [28] for the Hamiltonian h of Eq. (3.7c) to find the normal mode coordinates Q_k , the corresponding eigenvalues ω_k^2 and eigenvectors L_k with the elements L_{ik} , $i=1, \dots, F-1$. The internal coordinates are expressed in terms of the normal mode coordinates by

$$x_i = \sum_k L_{ik} Q_k \quad (3.8)$$

and the momenta p_i are given by

$$p_i = \sum_k (L^{-1})_{ik}^\dagger \dot{Q}_k \quad (3.9a)$$

where the dot denotes time derivative.

Substituting Eq. (3.8) and Eqs. (3.9) into Eqs. (3.7) gives

$$H = H_0 + H_1 \quad (3.10a)$$

with

$$H_0 = \frac{1}{2} g_{ss} p_s^2 + D(1 - e^{-\alpha x_s})^2 + \frac{1}{2} \sum_{l=1}^{F-1} (\dot{Q}_l^2 + \omega_l^2 Q_l^2) \quad (3.10b)$$

and

$$\begin{aligned} H_1 = & \sum_{i \neq s} \left[\sum_{l=1}^{F-1} C_{is} L_{il} Q_l x_s + \frac{1}{2} \sum_{l=1}^{F-1} g_{is}^0 (L^{-1})_{il}^\dagger \dot{Q}_l p_s \right] \\ & + \frac{1}{2} \sum_{l,m=1}^{F-1} \left[\sum_{i,j \neq s} (\partial g_{ij} / \partial x_s)_{x=0} (L^{-1})_{il}^\dagger (L^{-1})_{jm}^\dagger \dot{Q}_l \dot{Q}_m x_s \right. \\ & \left. + (\partial g_{is} / \partial x_j)_{x=0} L_{jl} (L^{-1})_{im}^\dagger Q_l \dot{Q}_m p_s \right] \\ & + \frac{1}{2} \sum_{l,m,n=1}^{F-1} \left[\sum_{i,j,k \neq s} (\partial g_{ij} / \partial x_k)_{x=0} L_{kn} (L^{-1})_{il}^\dagger (L^{-1})_{jm}^\dagger Q_n \dot{Q}_l \dot{Q}_m \right]. \quad (3.10c) \end{aligned}$$

This Hamiltonian, Eq. (3.10), is now precisely the form of that in Section 2, so that the SCP approach can be readily applied: H_0 consists of a Morse oscillator for the local mode and a normal mode ‘‘bath’’ for the remaining degrees of freedom, and H_1 provides the couplings between them.

It is well known from time-dependent perturbation theory that the importance of the terms in H_1 depends on the frequency difference between the local mode and the bath normal modes. If the frequency of the local mode s is close to the

frequencies of the bath normal modes, then the first two terms in H_1 are much more important than the last three. For CH stretch local modes, though, it is well-known [8, 11, 13] that the most significant coupling is to the corresponding CH *bend* modes, which have a frequency about half that of the stretch modes; the third and fourth terms in Eq. (3.10c) describes this interaction. The fifth term in Eq. (3.10c) describes coupling between the bath normal modes and will usually be neglected in low order approximations.

4. The SCP-kinetic coupling model for local mode overtones

To use the SCP formula in Section 2 one carries out a canonical transformation from the local mode and normal mode coordinates to action-angle variables (n_s, q_s) and (n, q) ,

$$(n, q) = (n_k, q_k), k = 1, \dots, F-1. \quad (4.1)$$

In terms of action-angle variables the normal mode coordinates are given by

$$Q_k = \sqrt{\frac{2n_k + 1}{\omega_k}} \sin q_k \quad (4.2a)$$

$$\dot{Q}_k = \sqrt{(2n_k + 1)\omega_k} \cos q_k, \quad (4.2b)$$

and the local mode coordinate and momentum x_s and p_s are given in terms of (n_s, q_s) by [27]

$$x_s = \alpha^{-1} \log \{ \lambda^{-2} [1 - (1 - \lambda^2)^{1/2} \cos q_s] \} \quad (4.3a)$$

and

$$P_s = \frac{1}{g_{ss}} \frac{\omega_s}{\alpha} \frac{(1 - \lambda^2)^{1/2} \sin q_s}{[1 - (1 - \lambda^2)^{1/2} \cos q_s]} \quad (4.3b)$$

with

$$\lambda = 1 - (n_s + \frac{1}{2})\alpha / (2D/g_{ss})^{1/2}, \quad (4.3c)$$

$$\omega_s = \frac{\partial \varepsilon_s(n_s)}{\partial n_s} = \alpha \lambda \sqrt{2Dg_{ss}}, \quad (4.3d)$$

and

$$\varepsilon_s(n_s) = -D\lambda^2 \quad (4.3e)$$

where units have been used such that $\hbar = 1$. If the overtone states of interest are not too high, then Eq. (4.3) can be approximated as

$$x_s \approx -\frac{1}{\alpha} (1 - \lambda^2)^{1/2} \cos q_s \quad (4.4a)$$

and

$$p_s \approx \frac{\omega_s}{g_{ss}\alpha} (1 - \lambda^2)^{1/2} \sin q_s. \quad (4.4b)$$

With Eqs. (4.2)-(4.4) one can now express the perturbation H_1 of the kinetic coupling model, Eq. (3.10), in terms of the zeroth order action-angle variables. The local mode overtone spectrum is thus given by Eqs. (2.8) and (2.10), where the action $\Delta\Phi(t)$ of Eq. (2.10b) is expressed as the sum of three terms,

$$\Delta\Phi(T) = I + II + III, \quad (4.5)$$

where

$$I = \int_0^t dt \sum_{l=1}^{F-1} \left\{ - \sum_{i \neq s} C_{is} L_{il} \frac{(1+\lambda^2)^{1/2}}{\alpha} \sqrt{\frac{(2n_l+1)}{\omega_l}} \sin(q_l + \omega_l t') \cos(q_s + \omega_s t') \right. \\ \left. + \sum_{i \neq s} g_{is}^0 (L^{-1})_{il}^\dagger \frac{\omega_s (1-\lambda^2)^{1/2}}{g_{ss} \alpha} \sqrt{(2n_l+1) \omega_l} \cos(q_l + \omega_l t') \sin(q_s + \omega_s t') \right\},$$

which may be approximated by keeping only the term involving the difference frequency,

$$I \approx \sum_{l=1}^{F-1} W_l \sin(q_s - q_l + \delta_l), \quad (4.6a)$$

with

$$W_l = \sqrt{(2n_l+1) \omega_l} \frac{(1-\lambda^2)^{1/2}}{2\alpha} \frac{\sin\left(\frac{\omega_s - \omega_l}{2} t\right)}{\omega_s - \omega_l} \\ \times \sum_{i \neq s} \left[\frac{C_{is} L_{il}}{\omega_l} + \frac{g_{is}^0}{g_{ss}} (L^{-1})_{il}^\dagger \omega_s \right] \quad (4.6b)$$

and

$$\delta_l = \pi + \frac{\omega_s - \omega_l}{2} t; \quad (4.6c)$$

$$II = \int_0^t dt' \frac{1}{2} \sum_{l,m=1}^{F-1} \left\{ \sum_{i,j \neq s} (\partial g_{ij} / \partial x_s)_{x=0} [-(L^{-1})_{il}^\dagger (L^{-1})_{jm}^\dagger] \frac{(1-\lambda^2)^{1/2}}{\alpha} \right. \\ \times \sqrt{(2n_l+1)(2n_m+1) \omega_l \omega_m} \cos(q_s + \omega_s t') \cos(q_l + \omega_l t') \\ \times \cos(q_m + \omega_m t') + (\partial g_{is} / \partial x_j)_{x=0} L_{jl} (L^{-1})_{im}^\dagger \frac{\omega_s (1-\lambda^2)^{1/2}}{g_{ss} \alpha} \\ \left. \times \sqrt{\frac{\omega_m}{\omega_l} (2n_l+1)(2n_m+1)} \sin(q_s + \omega_s t') \sin(q_l + \omega_l t') \cos(q_m + \omega_m t') \right\}, \quad (4.7a)$$

which is similarly approximated as

$$II \approx \sum_{l,m=1}^{F-1} Z_{lm} \sin(q_s - (q_l + q_m) + \beta_{lm}),$$

with

$$Z_{lm} = \sqrt{(2n_l+1)(2n_m+1)\omega_l\omega_m} \frac{(1-\lambda^2)^{1/2}}{4\alpha} \frac{\sin \frac{\omega_s - (\omega_l + \omega_m)}{2} t}{\omega_s - (\omega_l + \omega_m)} \\ \times \left\{ \sum_{i,j \neq s} \left[-(\partial g_{ij}/\partial x_s)_{x=0} (\mathbf{L}^{-1})_{il}^\dagger (\mathbf{L}^{-1})_{jm}^\dagger \right. \right. \\ \left. \left. + (\partial g_{is}/\partial x_j)_{x=0} L_{jl} (\mathbf{L}^{-1})_{im}^\dagger \frac{\omega_s}{\omega_l g_{ss}} \right] \right\}, \quad (4.7b)$$

and

$$\beta_{lm} = \frac{\pi}{2} + \frac{\omega_s - (\omega_l + \omega_m)}{2} t; \quad (4.7c)$$

$$III = \int_0^t dt' \frac{1}{2} \sum_{l,m,n=1}^{F-1} \sum_{i,j,k \neq s} (\partial g_{ij}/\partial x_k)_{x=0} \\ \times L_{kn} (\mathbf{L}^{-1})_{il}^\dagger (\mathbf{L}^{-1})_{im}^\dagger \sqrt{\frac{(2n_l+1)(2n_m+1)(2n_n+1)\omega_l\omega_m}{\omega_n}} \\ \times \sin(q_n + \omega_n t') \cos(q_m + \omega_m t') \cos(q_l + \omega_l t')$$

which may be approximated as

$$III \simeq \sum_{l,m,n=1}^{F-1} Y_{lmn} \left\{ \frac{\sin \left(\frac{\omega_n - \omega_l + \omega_m}{2} t \right)}{\omega_n - \omega_l + \omega_m} \sin(q_n - q_l + q_m + \gamma_1) \right. \\ \left. + \frac{\sin \left(\frac{\omega_n + \omega_l - \omega_m}{2} t \right)}{\omega_n + \omega_l - \omega_m} \sin(q_n + q_l - q_m + \gamma_2) \right. \\ \left. + \frac{\sin \left(\frac{\omega_n - \omega_l - \omega_m}{2} t \right)}{\omega_n - \omega_l - \omega_m} \sin(q_n - q_l - q_m + \gamma_3) \right\} \quad (4.8a)$$

with

$$Y_{lmn} = \frac{1}{4} \sum_{i,j,k \neq s} (\partial g_{ij}/\partial x_k)_{x=0} L_{kn} (\mathbf{L}^{-1})_{il}^\dagger (\mathbf{L}^{-1})_{jm}^\dagger \\ \times \sqrt{\frac{\omega_l\omega_m}{\omega_n} (2n_l+1)(2n_m+1)(2n_n+1)} \quad (4.8b)$$

$$\gamma_1 = \frac{\omega_n - \omega_l + \omega_m}{2} t, \quad (4.8c)$$

$$\gamma_2 = \frac{\omega_n + \omega_l - \omega_m}{2} t, \quad (4.8d)$$

and

$$\gamma_3 = \frac{\omega_n - \omega_l - \omega_m}{2} t. \quad (4.8e)$$

In many cases Eq. (4.5) can be simplified further. For example, if the local node frequency is close to the frequencies of the normal modes, then term I in Eq. (4.5) provides the dominant contribution. So that the correlation function $C(t)$ takes the form

$$C(t) = \int_0^{2\pi} \frac{dq_s}{2\pi} \int_0^{2\pi} \frac{dq}{(2\pi)^{F-1}} \prod_{l=1}^{F-1} \exp[-iW_l \sin(q_s - q_l + \delta_l)]. \quad (4.9)$$

Introducing a new variable

$$\theta_l = q_s - q_l$$

and using the identity

$$1 = \int_0^{2\pi} \frac{d\theta_l}{2\pi} \sum_{k_l=-\infty}^{\infty} e^{ik_l(\theta_l - q_s + q_l)}$$

one can perform the integrals in Eq. (4.9) and obtain a very simple, analytic expression for $C(t)$

$$\begin{aligned} C(t) &= \int_0^{2\pi} \frac{dq_s}{2\pi} \int_0^{2\pi} \frac{dq}{(2\pi)^{F-1}} \prod_{l=1}^{F-1} \sum_{k_l=-\infty}^{\infty} e^{-ik_l(q_s - q_l)} \\ &\quad \times \int_0^{2\pi} \frac{d\theta_l}{2\pi} e^{ik_l\theta_l} e^{-iW_l \sin(\theta_l + \delta_l)} \\ &= \int_0^{2\pi} \frac{dq_s}{2\pi} \int_0^{2\pi} \frac{dq}{(2\pi)^{F-1}} \prod_{l=1}^{F-1} \sum_{k_l=-\infty}^{\infty} e^{-ik_l q_s} e^{-ik_l q_l} e^{-ik_l \delta_l} J_{k_l}(W_l) \\ &= \prod_{l=1}^{F-1} J_0(W_l) \end{aligned} \quad (4.10)$$

where the relation

$$\int_0^{2\pi} \frac{dq}{2\pi} e^{inq} = \delta_{n,0}$$

has been used. Similarly if the local mode frequency is about twice those of the normal modes, then term II in Eq. (4.5) is dominant, so that

$$\begin{aligned} C(t) &\simeq \int_0^{2\pi} \frac{dq_s}{2\pi} \int_0^{2\pi} \frac{dq}{(2\pi)^{F-1}} \prod_{l,m=1}^{F-1} \exp\{-iZ_{lm} \sin[q_s(q_l + q_m) + \delta_{lm}]\} \\ &= \prod_{l,m=1}^{F-1} J_0(Z_{lm}) \end{aligned} \quad (4.11)$$

where the same trick as that above has been used.

5. Sample calculation: the CH(CD) stretch local mode overtone spectra of benzene (perdeuterobenzene)

To demonstrate the use of the SCP kinetic coupling model the CH(CD) stretch local mode overtone spectra of benzene (perdeuterobenzene) have been studied. Benzene is one of the most highly studied molecules. The normal mode fundamental frequencies and the force constants are available in literature [10, 28, 30]. In benzene, as in most hydrocarbons, the hydrogen atoms vibrate along the direction of the CH bonds without much other motion in the molecule. So to a good approximation the hydrogen vibrational motions along the CH bonds can be treated as local modes. In addition, since the six CH bonds do not have a common atom, the kinetic couplings between the six CH stretch local mode motions are to first order zero, and it is also reasonable that the quadratic off-diagonal terms between the six CH stretch motions in the potential energy in terms of internal coordinates are negligible. Thus to a good approximation the six stretch local modes can be treated as the six uncoupled anharmonic Morse oscillators with Morse potential $V(x_s) = D[1 - \exp(\alpha x_s)]^2$, where D is the CH bond dissociation energy and α is the scaling parameter. Furthermore, the benzene molecule has the D_{6h} symmetry and the six CH bonds are equivalent. Thus, the problem can be further simplified to considering only a single CH oscillator interacting with the ring modes.

The Hamiltonian for the problem of the CH local mode overtone thus reads

$$H = H_0 + H_1, \quad (5.1a)$$

with

$$H_0 = \frac{1}{2} g_{\text{CH}} p_{\text{CH}}^2 + D[1 - \exp(-\alpha x_{\text{CH}})]^2 + \frac{1}{12} \sum_{k=1}^{15} (\dot{Q}_k^2 + \omega_k^2 Q_k^2)$$

and

$$g_{\text{CH}} = \frac{1}{\mu_{\text{H}} + \mu_{\text{C}}}, \quad \mu_{\text{H}} = \frac{1}{m_{\text{H}}}, \quad \mu_{\text{C}} = \frac{1}{m_{\text{C}}} \quad (5.1b)$$

where only the fifteen in-plane normal ring modes are included because there are no coupling between the CH stretch local mode and the out-plane normal modes. Also, since the CH stretch frequency ($\sim 3000 \text{ cm}^{-1}$) is much larger than any of the other in-plane frequencies ($\sim 600\text{--}1600 \text{ cm}^{-1}$), the action $\Delta\Phi$ of Eq. (4.5) is well-approximated by term II alone. The in-plane internal coordinates which are kinetically coupled to the CH stretch x_{CH} are: the extension of the CC stretch coordinates x_1, x_6 and the in-plane CCH wag $x_w = X_{\text{CH}_0} \beta = X_{\text{CH}_0} [(\phi_6 - \phi_1)/2]$, where ϕ_1 and ϕ_6 are the CCH bond angles and X_{CH_0} is the equilibrium length of the CH bond (see Fig. 1). By using the general formulae for the Wilson G -matrix elements in Table VI-1 of reference [28], the kinetic coupling H_1 reads (for the details, see the Appendix)

$$H_1 = A_1 x_{\text{CH}} p_w^2 + A_2 x_{\text{CH}} (p_6 - p_1) p_w + A_3 x_w (p_6 - p_1) p_{\text{CH}} \quad (5.2a)$$

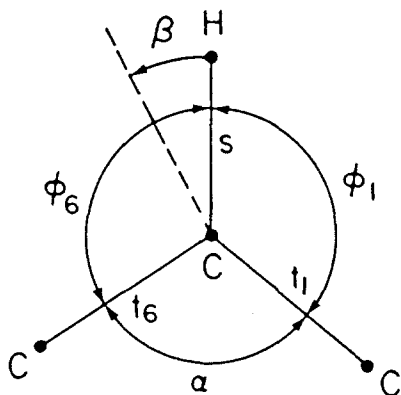


Fig. 1. Numbering of in-plane coordinates which are kinetically coupled with stretch x_{CH} : $s = x_{\text{CH}} + X_{\text{CH}_0}$ is CH bond length; $t_1 = x_1 + X_0$ and $t_6 = x_5 + X_0$ are CC bond lengths; $\beta = (\phi_6 - \phi_1)/2$, where ϕ_6 and ϕ_1 are CCH bond angles; α are CCC bond angles; X_{CH_0} and X_0 are equilibrium bond lengths of CH bond and CC bond, respectively

with

$$A_1 = -\left(\frac{\mu_{\text{H}}}{X_{\text{CH}_0}} + \frac{\mu_{\text{C}}}{X_{\text{CH}_0}} + \frac{\mu_{\text{C}}}{2X_0}\right) \quad (5.2b)$$

$$A_2 = -\sqrt{3}/(4X_{\text{CH}_0}) \cdot \mu_{\text{C}} \quad (5.2c)$$

$$A_3 = \sqrt{3}/(4X_{\text{CH}_0}) \cdot \mu_{\text{C}} \quad (5.2d)$$

where p_w , p_1 and p_6 are the momenta conjugate to x_w , x_1 and x_6 , respectively, and X_0 is the equilibrium bond length of CC bond.

With the interaction Hamiltonian H_1 given by Eqs. (5.2) the SCP correlation function takes the form given by Eq. (4.11)

$$C(t) = \prod_{l,m=1}^{15} J_0(Z_{lm}) \quad (5.3a)$$

with

$$\begin{aligned} Z_{lm} = & A_1(L^{-1})_{wl}^\dagger (L^{-1})_{wm}^\dagger + A_2(L^{-1})_{wm}^\dagger [(L^{-1})_{6l}^\dagger - (L^{-1})_{1l}^\dagger] \\ & + A_3 \frac{1}{g_{\text{CH}}} \frac{\omega_{\text{CH}}}{\omega_m} \cdot L_{wm} [(L^{-1})_{6l}^\dagger - (L^{-1})_{1l}^\dagger] \\ & \times \sqrt{(2n_l+1)(2n_m+1)} \omega_l \omega_m \frac{(1-\lambda^2)^{1/2}}{2\alpha} \frac{\sin\left(\frac{\omega_{\text{CH}} - \omega_l - \omega_m}{2} t\right)}{\omega_{\text{CH}} - (\omega_l + \omega_m)} \\ & \omega_{\text{CH}} = \alpha \sqrt{2Dg_{\text{CH}}} \cdot \lambda \end{aligned} \quad (5.3b)$$

and

$$\lambda = 1 - (n_{\text{CH}} + \frac{1}{2}) / \sqrt{2D/g_{\text{CH}}} \quad (5.3c)$$

where the Morse potential parameters $D = 0.0199$ (0.218) a.u. and $\alpha = 0.9386$ (0.898) a.u. for benzene (perdeuterobenzene C_6D_6) are determined such that the energy eigenvalues for the CH(CD) stretch Morse oscillator $h_{\text{CH}}(n_{\text{CH}}) = -D\lambda^2$

Table 1. Energy spacings between successive CH and CD overtones in C_6H_6 and C_6D_6 respectively

n	$\Delta\nu_{n-1,n}$ (cm^{-1}) CH ^a	CD ^b
1	3043	2294
2	2929	2209
3	2814	2153
4	2700	2097
5	2586	2040
6	2472	1984
7	2358	1928
8	2245	1871
9	2129	1815

^a Calculated by using the formula for the observed spacing in the CH stretch overtone spectrum [1].

$$\nu(cm^{-1}) = 3157.1(n + \frac{1}{2}) - 57.1(n + \frac{1}{2})^2$$

^b Calculated by using the formula for the observed spacing in the CD stretch overtone spectrum [1].

$$\nu(cm^{-1}) = 2322.3(n + \frac{1}{2}) - 28.2(n + \frac{1}{2})^2$$

Table 2. The ring normal modes of C_6H_6 and C_6D_6 and the coefficients in Eqs. (5.3)^a

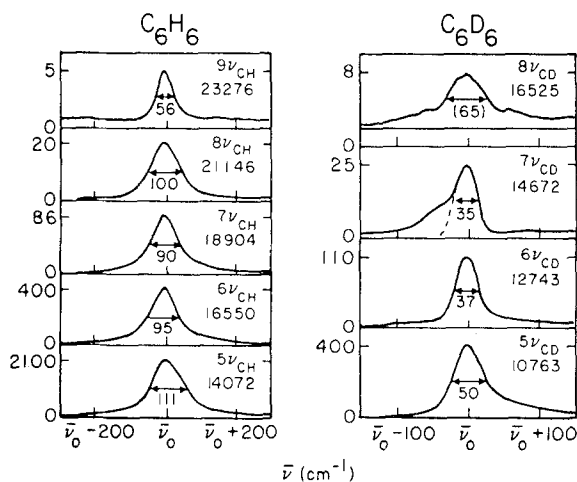
symmetry	$\nu(cm^{-1})$		$(L^{-1})_{wi}^{\dagger} {}^b [(L^{-1})_{6i}^{\dagger} - (L^{-1})_{1i}^{\dagger}] {}^b L_{wi} {}^c$					
	C_6H_6	C_6D_6	CH	CD	CH	CD	CH	CD
A_{1g}	993	945	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
A_{2g}	1350	1059	0.3644	0.4685	0.0000	0.0000	0.4574	0.3557
E_{2g}	606	579	0.0874	0.2314	1.7068	1.4389	0.0784	0.1041
$E_{2gb'}$	1599	1557	-0.1828	0.1157	-1.609	1.8256	-0.3894	0.2687
E_{2gb}	1178	869	-0.5430	0.7773	-1.621	-1.825	-0.4699	0.3565
B_{1u}	1010	970	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
B_{2u}	1309	1282	0.1656	0.0637	1.2968	1.549	0.2738	0.1488
B_{2u}	1146	824	0.3740	-0.5759	-1.100	0.8446	0.3229	-0.2730
E_{1ub}	1037	814	-0.4140	-0.7258	0.8338	0.8023	-0.2533	-0.289
E_{1ub}	1482	1333	0.3892	0.3098	0.3588	0.5746	0.5865	0.3949

^a Results taken from Reference [11]

^b In square root of atomic weight mass unit

^c In (1/square root of atomic weight mass) unit

Fig. 2. The experimental absorption spectra of C_6H_6 (C_6D_6) of reference [1]. Each panel contains: spectral assignments where n indicates the number of quanta of CH (CD) stretch excitation, positions of band maxima or band centers (ν_0 values in the upper right-hand corners of the panels, in cm^{-1}), and FWHM bandwidths in cm^{-1} . Ordinates are absorption cross sections (σ values, in Millibarns ($mb = 10^{-27} cm^2$)) and abscissae are spectral shifts relative to the band maxima



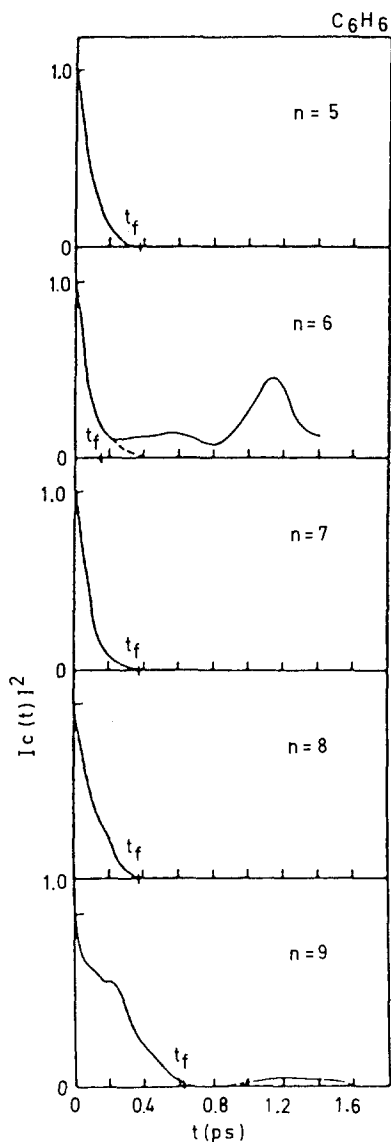


Fig. 3. The square of absolute value of the correlation function $|C(t)|^2$ for CH stretch local mode overtones $n=5-9$ in C_6H_6 as a function of time. The dashed line corresponds to $\tilde{C}(t)$ defined by Eqs. (5.4)

fit the experimental CH(CD) overtone spacing listed in Table 1, the transformation matrix elements $(L^{-1})_{wl}^\dagger$, $[(L^{-1})_{6l}^\dagger - (L^{-1})_{1l}^\dagger]$, and L_{wm} , $l, m=1, \dots, 10$ are given in Table 2, and the fact that only ten modes have different frequencies (five modes are doubly degenerated) has been used. The overtone spectrum of the CH(CD) stretch local mode $I_{n_{CH,0}}(\omega)$ can then be determined by Fourier transform of the correlation function $C(t)$, i.e., Eq. (2.8). Since $Z_{lm}(t) \sim \sin[(\omega_{CH} - \omega - \omega_m)t/2]$ is an odd function of time t , $J_0(Z_{lm})$ is an even function of Z_{lm} and the spectra thus symmetric.

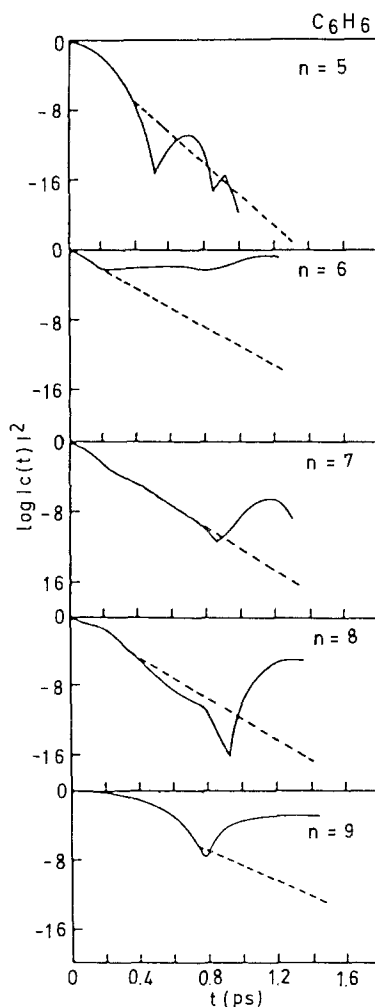


Fig. 4. The logarithm of $|C(t)|^2$ as a function of time for CH stretch local mode overtones $n=5-6$ in C_6H_6 . The dashed line corresponds to $\tilde{C}(t)$ defined by Eqs. (5.4)

The results for the CH stretch local mode overtones, $n=5-9$, in benzene C_6H_6 are shown as the solid line curves in Fig. 3-5. For comparison the experimental results [1] are presented in Fig. 2. In Fig. 3 the square of absolute value of the correlation function $|C(t)|^2$ plotted as a function of t . The $\log |C(t)|^2$ as a function of t is plotted in Fig. 4. The calculated absorption spectra of benzene are given in Fig. 5.

In Fig. 3 it is seen that $|C(t)|^2$ decays monotonically to (essentially) zero in a fraction of a picosecond; Fig. 4 shows that this decay is not strictly exponential, though this is of no great consequence. One also sees that except for $n=6$, there are no significant recurrences (i.e., where $|C(t)|^2$ rises above $\sim 10^{-2}$ for times up to ~ 2 picoseconds). Thus the overtone absorption spectra are broad and featureless, in agreement with the experimental results in Fig. 2. In order to demonstrate

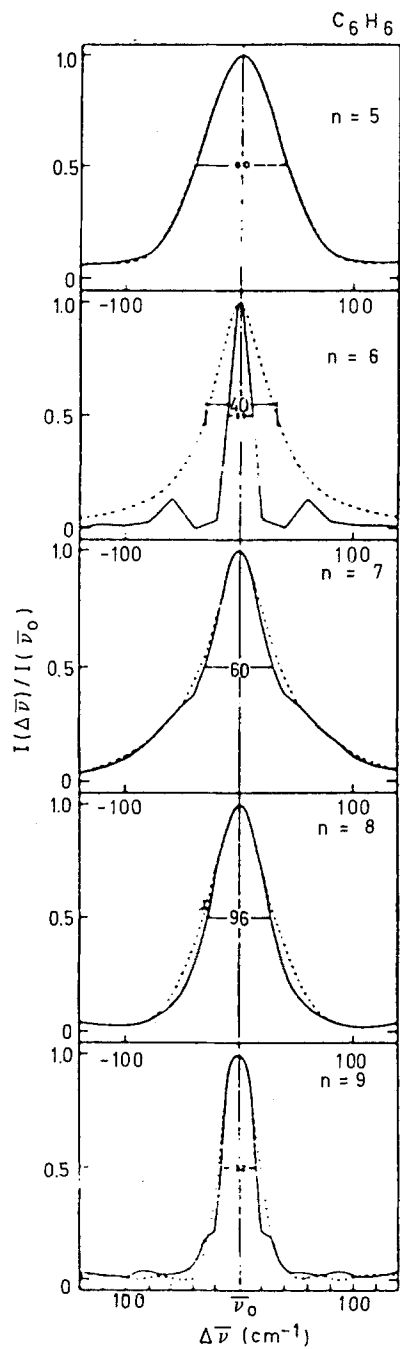


Fig. 5. The absorption spectra $I(\Delta\bar{\nu})/I(\bar{\nu})$ for CH stretch local mode overtones $n=5-9$ in C_6H_6 . The dashed line corresponds to $\tilde{C}(t)$ defined by Eqs. (5.4)

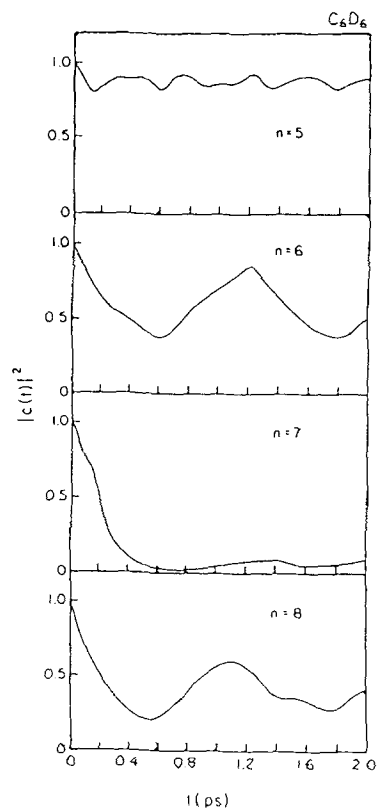


Fig. 6. The square of absolute value of the correlation function $|C(t)|^2$ for the CD stretch local mode overtones $n=5-9$ in C_6D_6 as a function of time

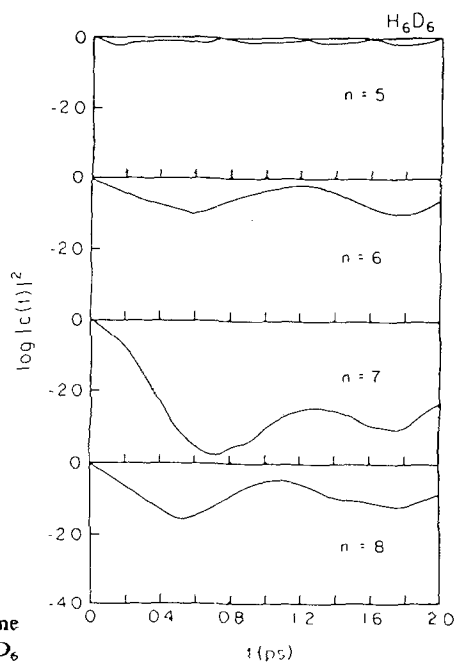


Fig. 7. The logarithm of $|C(t)|^2$ as a function of time for CD stretch local mode overtone $n=5-7$ in C_6D_6

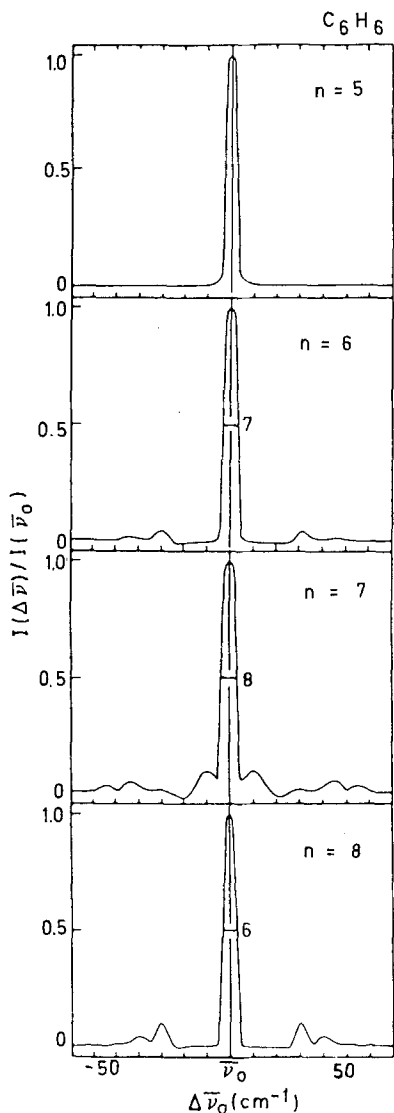


Fig. 8. The absorption spectra $I(\Delta\tilde{\nu})/I(\tilde{\nu}_0)$ for CD stretch local mode overtones $n = 5-6$ in C_6D_6 .

this even more clearly, in Fig. 3-5 we have also plotted the curves (dashed line) for $|\tilde{C}(t)|^2$, $\log |\tilde{C}(t)|^2$ and the corresponding spectra $\tilde{I}(\Delta\omega)/\tilde{I}(\omega^0)$, where $\tilde{C}(t)$ is defined by

$$\tilde{C}(t) = C(t) \text{ for } 0 \leq t \leq t_F \text{ and } \tilde{C}(t) = \exp(-t/t_F) \text{ for } t > t_F \quad (5.4a)$$

with

$$t_F = -t_F / \log [C(t_F)]. \quad (5.4b)$$

Here the time t_F indicated in Fig. 3-5 is the time at which the $|C(t)|^2$ has decayed to about 0.01 (except for $n=6$, for which t_F is about the end time of the initial

Table 3. Linewidth of (CD) stretch overtone of benzene(perdeuterobenzene C_6D_6)

n_{CH}	FWHM(cm^{-1})			
	Exp. ^a	CH SCPKC ^b	Exp. ^a	CD SCPKC ^b
5	111	82	50	
6	95	23-60	37	>7
7	90	60	≈35>	>8
8	100	56	65	>6
9	56	32		

^a Reference [1]^b Present work—SCP kinetic coupling model

rapid decay). In Fig. 5 it is seen that except for $n = 6$, the dashed line very closely follows the solid line. Thus the initial rapid decay of $|C(t)|^2$ determines the main features of the absorption spectrum so long as $|C(t)|^2$ is small ($\sim < 0.01$) for later time. For $n = 6$ CH stretch overtone there are strong recurrences, and as a consequence the absorption spectrum has some structure. The dashed line is different from the solid one, the former being the envelope of the latter.

Similar results for C_6D_6 are shown in Fig. 6–8. Fig. 6 and Fig. 7 show that for the CD stretch $|C(t)|^2$ decays approximately exponentially for short times (except for $n = 5$, which decays very little at all), though more slowly than for C_6H_6 and also with more significant recurrences. The spectra in Fig. 8 thus all show an extremely narrow peak.

The linewidths of the CH(CD) overtones of $C_6H_6(C_6D_6)$ taken from calculated spectra are listed in Table 3 where the experimental results are also included. The agreement is reasonable, realizing that the experimental results include rotational structure and also possible thermal inhomogeneities. It is particularly gratifying that our model reproduces the *narrowing* of the overtone line width for the highest overtones. This has been discussed before [11, 13] as being due to the overtone frequency (i.e., level spacing) becoming out of resonance with two quanta of the CH bend mode as n becomes $\approx 6-7$.

6. Concluding remarks

The present results show that the semiclassical perturbation model is capable of providing the correct description of short time dynamics in polyatomic molecules. They also provide additional evidence that the kinetic coupling model is the principal source of coupling of CH stretch vibrations to other modes in the molecule.

Agreement with the experimental line shapes of the CH stretch overtones in C_6H_6 is reasonably good. The calculated absorption lines for the C_6D_6 case are substantially narrower than the observed spectra, but since the experimental line widths

for C_6D_6 are much smaller (\sim half) than those for C_6H_6 it is quite likely that the observed widths for C_6D_6 are largely due to unresolved rotational structure.

It is encouraging that so simple a dynamical model as SCP is capable of providing a semi-quantitative description of the microscopic dynamics in a polyatomic molecule. One expects that it should be useful in other situations where it is the short time dynamics which determines the phenomena of interest.

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Appendix: The first derivatives of Wilson G matrix elements

For the internal coordinates of benzene defined in Fig. 1 the relevant Wilson G-matrix elements can be determined from Table VI-1 of reference [28]

$$g_w = g_{\beta\beta} X_{CH}^2 = X_{CH_0}^2 \frac{\mu_H}{(X_{CH_0} + x_{CH})^2} + \frac{1}{(X_{CH_0} + x_{CH})X_0} + \frac{3}{4X_0} \mu_C, \quad (A.1)$$

$$g_{w_{t_6}} = \frac{X_{CH_0}}{2} (g_{\phi_1 t_1} - g_{\phi_6 t_6}) = \frac{\mu_C X_{CH_0}}{2} \frac{\sqrt{3}}{(X_{CH_0} + x_{CH})} + \frac{3}{4} \mu_C \quad (A.2)$$

$$g_{w_{t_1}} = \frac{X_{CH_0}}{2} (g_{\phi_1 t_1} - g_{\phi_6 t_1}) = -\frac{\mu_C X_{CH_0}}{2} \frac{\sqrt{3}}{(X_{CH_0} + x_{CH})} + \frac{3}{4} \mu_C \quad (A.3)$$

$$g_{t_6 s} = \mu_C \cos(\phi - \beta) \quad (A.4)$$

$$g_{t_1 s} = \mu_C \cos(\phi + \beta) \quad (A.5)$$

$$g_{s\alpha} = -\frac{\mu_C}{X_0} \frac{2}{\sqrt{3}} \left[\frac{3}{2} \cos(\phi + \beta) + \frac{3}{2} \cos(\phi - \beta) \right] \quad (A.6)$$

with

$$\mu_C = \frac{1}{m_C}, \quad \mu_H = \frac{1}{m_H} \quad (A.7)$$

where m_C and m_H are the masses of atom C and atom H. Then the relevant derivatives are

$$\left. \frac{\partial g_w}{\partial x_{CH}} \right|_{x=0} = - \left[\frac{2\mu_H}{X_{CH_0}} + \frac{2\mu_C}{X_{CH_0}} + \frac{\mu_C}{X_0} \right] \quad (A.8)$$

$$\left. \frac{\partial g_{w_{t_6}}}{\partial x_{CH}} \right|_{x=0} = - \frac{\sqrt{3} \mu_C}{2X_{CH_0}} \quad (A.9)$$

$$\left. \frac{\partial g_{w_{t_1}}}{\partial x_{CH}} \right|_{x=0} = \frac{\sqrt{3}}{2} \frac{\mu_C}{X_{CH_0}} \quad (A.10)$$

$$\left. \frac{\partial g_{t_6 s}}{\partial x_w} \right|_{x=0} = \frac{\sqrt{3}}{2} \frac{\mu_C}{X_{CH_0}} \quad (A.11)$$

$$\left. \frac{\partial g_{ls}}{\partial x_w} \right|_{x=0} = -\frac{\sqrt{3}}{2} \frac{\mu_C}{X_{CH_0}} \quad (\text{A.12})$$

$$\left. \frac{\partial g_{s\alpha}}{\partial x_w} \right|_{x=0} = 0. \quad (\text{A.13})$$

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