Monte Carlo simulation of solvent effects on vibrational and electronic spectra\textsuperscript{a)}

Michael F. Herman\textsuperscript{b)}

\textit{Department of Chemistry, Tulane University, New Orleans, Louisiana 70118}

Bruce J. Berne

\textit{Department of Chemistry, Columbia University, New York, New York 10027}

(Received 22 July 1982; accepted 11 August 1982)

Solvent effects on vibrational states are treated in the Born–Oppenheimer approximation. A Monte Carlo procedure is devised for simulating a system in which the vibrations are treated as quantum degrees of freedom and all other degrees of freedom are treated classically. The key to this method is the use of a restructured perturbation theory for solving the vibrational Schrödinger equation at each of the solvent configurations sampled. This method also is used to compute Franck–Condon factors. The methods developed are applied to two different problems. First, solvent effects on vibrational transitions in the ground electronic state are considered. It is found that the frequency shift from the gas phase frequency is to the red at low solvent densities, but to blue at high solvent densities. Secondly, the heterogeneous electronic absorption and emission line shapes are simulated in a variety of model solute-solvent systems and the results are discussed in terms of a simple theoretical model.

I. INTRODUCTION

Monte Carlo\textsuperscript{1} and molecular dynamics\textsuperscript{2} techniques are valuable tools for the calculation of equilibrium and non-equilibrium statistical mechanical and thermodynamic quantities for classical systems. Currently, Monte Carlo procedures are being developed for semical\textsuperscript{3} and quantum mechanical systems\textsuperscript{5}\textsuperscript{–}\textsuperscript{6} as well. However, there are many systems of chemical interest for which classical mechanics provides an accurate description of the motion of nearly all the degrees of freedom, except for a small number (possibly only one) of coordinates that require a quantum mechanical description.\textsuperscript{9} Application of a fully quantum method to these problems would be an inefficient route to take.

In this paper, we consider a simple system of this type: a diatomic molecule in a monatomic solvent. The vibrational motion is not classical at ordinary temperatures. On the other hand, classical mechanics is certainly adequate for the analysis of the translational degrees of freedom. Furthermore, it is assumed throughout that the moment of inertia of the diatomic is sufficiently large so that the classical description of the rotational motion is valid. This classical rotation approximation will break down at low and moderate temperatures for diatomics which contain H, and possibly D, due to their low moments of inertia. Thus, these diatomics are excluded from consideration in this work, although the possible extension to include quantum rotations is discussed briefly in Sec. IV.

Because little is known about the true intermolecular potential energy, we adopt the following model here. The intramolecular potential of the solute is taken to be the RKR potential\textsuperscript{10} for the isolated molecule corresponding to the electronic state of interest. The diatomic is assumed to consist of two sites, and the solvent molecules are each assumed to consist of several sites (one if they are monatomic). Each site on the diatomic interacts through a central potential with each site on every solvent molecule. Thus, we invoke a site-site model. In addition, the sites on different solvent molecules interact with each other. To model electrostatic interaction, charges (and polarizabilities, etc.) can be ascribed to sites and the Coulomb terms can be summed. In general, the potential parameters for the solute site-solvent site interactions and the charges on the diatomic sites will be different for different electronic states of the solute. These parameters are also expected to depend on the instantaneous bond length of the diatomic molecule. The choice of electronic state dependent parameters allows us to study solvent effects on electronic absorption and emission spectra.

Starting with the Schrödinger equation for all the degrees of freedom, the Born–Oppenheimer approximation\textsuperscript{11} is made, effectively separating the "fast" vibrational motion from the "slow" rotations and translations. The classical limit\textsuperscript{6,12} is applied to the quantum mechanical canonical density matrix in such a way that the vibrational factor remains quantum mechanical while the rotational and translational parts go over to their respective classical forms, thus yielding a mixed quantum-classical density matrix. The distribution function is a product of a classical \(\exp(-\beta V)\) factor and a quantum-vibrational distribution function, which depends parametrically on the values of the coordinates for the slow motions, as would be expected intuitively. This mixed quantum-classical distribution function can be employed as a sampling function for the ordinary Metropolis Monte Carlo procedure.\textsuperscript{13}

This formulation requires the determination of the vibrational energies and corresponding eigenfunctions.
for every sampled solvent configuration. This is the time consuming part of the simulation. We show how this can be done efficiently by using a reorganized perturbation theory that is shown to be rapidly convergent for the determination of the states, energies, and Franck-Condon factors for the low lying vibrational states. In a subsequent paper we extend this approach using wave packet dynamics.

The adiabatic approximation is considered in Sec. II A and the procedure for application of the mixed quantum-classical Monte Carlo and molecular dynamics simulation is presented. The perturbative method for the solution of the vibrational Schrödinger equation with the solvent-dependent potential is presented in detail in Sec. II B. A method for simulating electronic absorption and emission spectra is outlined in Sec. II C.

The results of Monte Carlo simulations for a model of Br$_2$ dissolved in Ar are discussed in Sec. III A for various densities. The observed density dependent shifts in the average vibrational frequency and the nonsymmetric shapes of the frequency distributions are particularly interesting. The average frequency decreases at moderate densities (relative to the gas phase frequency), while at higher densities it increases. This behavior is very reminiscent of the density dependence of the frequency shift that is experimentally observed in many systems. The interaction potential employed includes a specific model for the bond length dependence of the Ar–Br$_2$ interaction. It has been suggested that this bond length dependence has important effects on the equilibrium properties of the oscillator, and we find that the red shift in the average frequency at moderate densities is essentially absent if this aspect of the potential is not included in the model. The density dependence of the peak position and shape of the frequency distributions are analyzed in terms of a simplified model in Sec. III A. In Sec. III B methods developed in Sec. II are used to simulate the electronic absorption and emission spectra of a model diatomic for several different solvent–solute potentials. The observed solvent induced shifts are readily understood on the basis of simple arguments. Finally, in Sec. IV the major results of this work are summarized and possible extensions of these approaches are discussed.

II. THEORY

A. Adiabatic approximation for an oscillator in a solvent

In this section, we treat systems consisting of one diatomic molecule in a dense monatomic fluid. The time scale for vibrational motion is, in most cases, orders of magnitude faster than the other motions present. These other slow motions include rotation and translation of the diatomic, and translation of the solvent particles. This separation of time scales suggests a Born–Oppenheimer approximation.

Let $\mathbf{r}$ be the vibrational coordinate (bond length) and let the set $\{\mathbf{X}\}$ represent all the slow coordinates. The Hamiltonian for our systems is

\[
H = T_G + T_f + V(\mathbf{r}, \{\mathbf{X}\})
\]

\[
= T_G + H_f
\]  

where $T_G$ and $T_f$ are kinetic energy operators for the slow and fast variables, respectively. The wave function for the entire system can be approximated as

\[
\Psi(\mathbf{r}, \{\mathbf{X}\}) = \psi(\mathbf{r} | \mathbf{X}) \phi(\mathbf{X}),
\] 

where $\psi(\mathbf{r} | \mathbf{X})$ is an eigenfunction of $H_f$, the Hamiltonian for the fast degree of freedom at fixed $\{\mathbf{X}\}$, i.e.,

\[
H_f \psi(\mathbf{r} | \mathbf{X}) = E_f(\mathbf{X}) \psi(\mathbf{r} | \mathbf{X}).
\] 

The adiabatic approximation consists of substitution of Eqs. (2.2) and (2.3) into Eq. (2.1) and ignoring the terms involving derivatives of $\psi(\mathbf{r} | \mathbf{X})$ with respect to the slow variables. This approximation yields the following equation for the slow variables:

\[
\{T_G + E_f(\mathbf{X})\} \phi(\mathbf{X}) = E_f \phi(\mathbf{X}),
\] 

where $E_f$ is the total energy of the full system. The vibrational energy levels, $E_f(\mathbf{X})$, calculated for fixed $\{\mathbf{X}\}$, act as the potential energy surfaces which govern the evolution of the slow variables.

As is usually the case, we assume that the spacings of energy levels corresponding to the slow degrees of freedom is much smaller than $k_B T$. If this is the case, then classical mechanics provides an accurate description for these motions. Thus, the rotational and translational motions evolve classically according to Hamilton’s equations of motion,

\[
\dot{X}_G = \frac{\partial H}{\partial P_G},
\]

\[
\dot{P}_G = - \frac{\partial H}{\partial X_G},
\] 

where the Hamiltonian for the slow degrees of freedom is

\[
H_S = T_G + E_f(\mathbf{X})
\] 

and $\{P_{S} \}$ is the set of generalized momenta conjugate to the positions $\{X\}$,

\[
P_{S_G} = \frac{\partial T_S}{\partial \dot{X}_G}.
\] 

Note that the potential surface $E_f(\mathbf{X})$ also depends on the quantum state of the oscillator, and the trajectory of the slow variables will differ for different vibrational levels.

This situation is, of course, exactly analogous to the usual Born–Oppenheimer separation of the electronic and nuclear motions. Adiabatic electronic energy surfaces are obtained for fixed nuclear configurations. The nuclear motions take place on these surfaces. The classical limit corresponds to running classical trajectories for the nuclear degrees of freedom on a given electronic surface.

For many purposes, only thermally averaged quantities are desired, as opposed to dynamical information about the evolution of the system subject to specific initial conditions. In this case, the quantity of interest is the canonical density matrix. In an earlier publica-
tion, we have shown that, after the classical limit has been taken for the slow variables, the density matrix in the position representation is,

\[ \rho(r, r'; \beta | X) = A(\beta) \sum_{\mathbf{x}} \psi_{s}(r | \mathbf{x}) \bar{\psi}_{s}(r' | \mathbf{x}) e^{i \mathbf{L} \cdot \mathbf{X}}. \]  

(2.8)

In Eq. (2.8), \( \psi_{s} \) and \( E_{s} \) are the wave function and energy for the \( s \)-th vibrational state at the fixed values of the rotational and translational coordinates, \( \{ \mathbf{X} \} \), \( \beta = (k_{B}T)^{-1} \), \( k_{B} \) is the Boltzmann constant, \( T \) is the temperature, and \( A(\beta) \) is a temperature dependent constant arising from the integrations over the momenta \( \{ \mathbf{P}_{s} \} \) conjugate to the slow variables. For the particular case of a diatomic in a monatomic fluid,

\[ A(\beta) = (2\pi m k_{B} T / h^{2})^{3/2}(2\pi m k_{B} T / h)^{3/2} (2\pi 1k_{B} T / h)^{3/2}, \]

(2.9)

where \( N \) is the number of solvent particles and \( k \) is Planck's constant. \( M \), \( m \), and \( I \) are, respectively, the mass of a solvent particle, the reduced mass of the diatomic, and the moment of inertia of the diatomic, respectively. In order to facilitate the integrations over the momenta conjugate to the diatomic rotational angles \( \theta \) and \( \phi \), the term \( L^{2}/2m \) in \( T_{s} \) is replaced with \( L^{2}/2I \), where \( I = m r_{e}^{2} \) and \( r_{e} \) is the equilibrium bond length for the isolated diatomic.

A number of ensemble averaged quantities are of interest. For example, the average bond length is given by

\[ \langle r \rangle = \int d\mathbf{X} \int d\mathbf{r} \rho(r, r' | \beta | \mathbf{X}) = \int d\mathbf{X} \int d\mathbf{r} \rho_{s}(r | \mathbf{r} | \beta | \mathbf{X}) \rho_{s}(r' | \mathbf{r} | \beta | \mathbf{X}) e^{i \mathbf{L} \cdot \mathbf{X}}. \]

(2.10)

The average total energy of the system is given by

\[ \langle E \rangle = \left\{ \frac{3N+5}{2} \right\} k_{B} T + \int d\mathbf{X} \int d\mathbf{r} \left[ H_{s}(r, r'; \beta | \mathbf{X}) \right]_{\rho_{s}|r=r_{e}}. \]

(2.11)

The term \( \{3N+5/2\} k_{B} T \) is the average kinetic energy \( T_{s} \), in the classical limit. It contains contributions of \( 3Nk_{B} T/2 \), and \( 3k_{B} T/2 \) and \( k_{B} T \), from the translations of the solvent particles, the translations of the diatomic center of mass and the rotations of the diatomic, respectively. The second term on the right in Eq. (2.11) can obviously be rewritten as \( \int d\mathbf{X} \sum_{\mathbf{r}_e} E_{s}(\mathbf{X}) \times \exp( - \beta E_{s}(\mathbf{X})) \).

For some purposes, it may be desirable to average over an ensemble which corresponds to a diatomic in one particular vibrational state, while the translations and rotations are distributed according to an equilibrium canonical distribution. In this case, the appropriate constrained density matrix to be averaged over is

\[ \rho_{s}(r, r'; \beta | \mathbf{X}) = A(\beta) \psi_{s}(r | \mathbf{X}) \bar{\psi}_{s}(r' | \mathbf{X}) e^{i \mathbf{L} \cdot \mathbf{X}}. \]

(2.12)

It is possible to study ensemble average properties in systems such as those we have been discussing by using the standard Metropolis Monte Carlo sampling procedure\(^{13}\) to generate a set of points which are distributed, in the limit of a large sample, according to \( e^{-\beta \mathbf{H}} \rho(r, r'; \beta | \mathbf{X}) \) or \( Z_{s}^{-1} \rho_{s}(r, r'; \beta | \mathbf{X}) \), \( \{ Z_{s} = \int d\mathbf{X} \int d\mathbf{r} \rho_{s}(r, r'; \beta | \mathbf{X}) \} \). It is also possible to determine the distribution function of the solvent atoms around a solute molecule in a given vibrational state, irrespective of its bond length by sampling from

\[ P_{s}(\mathbf{X}) = \int d\mathbf{r} \rho_{s}(r, r'; \beta | \mathbf{X}) \]

(2.13)

[or from \( P(\mathbf{X}) \), obtained by replacing \( \rho_{s} \) by \( \rho \) in Eq. (2.13)].

Since the details of the particular sampling procedure that we employ are straightforward and have been presented elsewhere,\(^{3} \) we do not restate them here. The point that is worth emphasizing again, however, is that this method required solving the adiabatic (fixed configuration) vibrational Schrödinger equation (2.3) a large number of times. Thus, it is imperative that the method of solution of this differential equation be organized so that it is as efficient as possible for the problem at hand. The method that we employ is described in detail in Sec. II B. Given that such a fast and accurate procedure is available, the method that has been discussed in the present section allows for the realistic, detailed study of the effects of a classical solvent on the quantum vibrational motion of the diatomic.

The procedure outlined in Sec. II B for solving the vibrational Schrödinger equation can also yield the derivatives of the vibrational state energies with respect to the slow variables. These are needed to calculate the forces required to run trajectories in the phase space of the translation and rotations, according to Eq. (2.6). Therefore, molecular dynamics calculations for the mixed quantum-classical systems are also feasible. Since the vibrational degree of freedom is treated quantum mechanically, the time step chosen for the classical trajectory need reflect only the time scales of the motions of the slow variables, and not the (possibly much shorter) time scale appropriate for the vibrational motion.

B. Solution of the vibrational Schrödinger equation

In this section we examine the perturbative solution procedure of the Morse oscillator where

\[ V_{\psi}(r) = D_{\psi}(1 - \exp(-\alpha(r - r_{e})))^{2} \]

(2.13)

is a prototype for the general vibrational potential. The reference Hamiltonian is the harmonic oscillator Hamiltonian where the harmonic frequency \( \omega \) is chosen to be

\[ \omega = \left[ 2D_{\psi} \alpha^{2} / \hbar \right]^{1/2}, \]

(2.14)

\( m \) is the reduced mass of the oscillator. With this choice for \( \omega \), the second derivatives of \( V_{\psi}(r) \) and the harmonic oscillator potential \( V_{HO}(r) = m \omega^{2}(r - r_{e})^{2}/2 \) agree at \( r_{e} \).

Expanding the perturbation in a power series we have

\[ V_{\psi}(r) - V_{HO}(r) = \hbar \omega \sum_{n=0} \delta_{n} y_{n}, \]

(2.15)

where the dimensionless length is defined as \( y = (m \omega / \hbar)^{1/2}(r - r_{e}) \), and \( \delta_{n} \) is given by

\[ J. Chem. Phys., Vol. 78, Part II, No. 6, 15 March 1983 \]
\[ d_n = \frac{1}{n! \hbar \omega} \left( \frac{\hbar}{\mu \omega} \right)^{n/2} \left( \frac{d^n V}{dr^n} \right)_{\omega} \]  

(2.16)

The derivatives are evaluated at \( \omega \). Noting that the \( n \)th derivative of \( V \) is proportional to \( D_n \), \( d_n \) is a simple task to show that \( d_n \) is of order \( \lambda^{-n} \) where \( \lambda = (\hbar \omega / D_1)^{1/2} \). For typical chemical bonds, \( \lambda \) is a small quantity and Eq. (2.16) provides us with a small expansion parameter for developing a perturbation theory. This expansion in \( \lambda \) is easily obtained by rearranging the familiar Rayleigh-Schrödinger perturbation theory (RSPT) expansion.

Computationally useful expressions are obtained by dividing the reference Hamiltonian and the perturbation by \( \hbar \omega \). The state energies are simply calculated by multiplying the scaled perturbation expansion by \( \hbar \omega \). The scaled reference Hamiltonian is simply

\[ H_R = -\frac{1}{2} (d^2 / dy^2) + \frac{y}{2} \]  

(2.17)

The zeroth order energies of the Morse oscillator are given by \( (n + 1/2) \hbar \omega \). The first order \( (n \lambda) \) contributions to the energies are

\[ E_{n1} = d_n (n | y | n) \hbar \omega \]  

(2.18)

which vanish due to symmetry.

The second order corrections are

\[ E_{n2} = \left[ d_n (n | y | n) + \frac{1}{2} \sum_{m \neq n} | \langle m | y | n \rangle |^2 (n - k) \right] \hbar \omega \]  

(2.19)

The first term in the brackets in Eq. (2.19) comes from first order RSPT, while the other term comes from second order RSPT. The matrix elements \( \langle n | y | k \rangle \) are evaluated using the states of the reference Hamiltonian \( H_R \). The denominator \( (n - k) \) is merely the difference of zeroth order energies of \( H_R \).

If the expressions for \( d_n \), \( d_n \), and the matrix elements \( \langle n | y | m \rangle \) and \( \langle n | y | k \rangle \) are inserted into Eq. (2.19) (recall \( \langle m | y | m \rangle \neq 0 \) only if \( m = n \pm 1, \pm 3 \)) we find (after a little work)

\[ E_{n1} + E_{n2} = (n + 1/2) \hbar \omega - (n + 1/2)^2 \hbar \omega / 4 D_1 \hbar \omega \]  

(2.20)

which is the exact result for the Morse oscillator energies.\(^{13}\) Therefore, all higher order terms in \( \lambda \) must be identically zero. For instance, the fourth order term in \( \lambda \) has many contributions which are individually nonzero but which can be shown to exactly cancel. One of these terms arises in first order in ordinary RSPT, another in second order, another in third, and the remaining terms in fourth order. By arranging the perturbation expansion in orders of \( \lambda \) we take advantage of this cancellation. For the general anharmonic oscillator, there is not an exact cancellation. Nevertheless, the cancellation should be considerable if in Eqs. (2.15) and (2.16) \( d_n \) is evaluated by replacing \( V \) with the real potential \( V \) and the derivatives are evaluated at the potential minimum.

Sprandel and Kern\(^{19}\) have numerically studied the convergence of various perturbation expansions for anharmonic oscillator systems. Their work provides evidence of the superior convergence of a perturbation expansion which treats the cubic term in the Taylor series of the perturbation potential \( \{ Eq. (2.15) \} \) as order one, the quartic term as order two, etc. We feel that the analysis of the Morse oscillator presented here provides added insight into this problem.

Every term in the energy expansion can be separated into two factors, one which depends on the solvent configuration and one which does not. The configuration dependent factors are products of \( \hbar \omega \) and a number of \( d_n \) 's. These depend on the derivatives of the total potential evaluated at the equilibrium bond length. The remaining factors consist of products of matrix elements of the scaled reference Hamiltonian \( \langle n | y | m \rangle \) divided by scaled energy differences \( (n - k) \). These may involve summations of the states of \( H_R \). Since these factors only depend on \( H_R \), they remain constant as the solvent configuration changes. Therefore, they need to be evaluated once in the course of a simulation. The computational advantage arises from the fact that these configuration independent factors contain the time consuming portion of the perturbation calculation, the matrix elements and sums over states. A similar analysis applies to the expansion for the wave functions.

Fourth order perturbation theory \( \langle n \lambda \rangle \) is employed in the Monte Carlo simulations discussed in the next section. At each step in the calculation the minimum of the total potential must be located with respect to bond length. Defining \( r_m(X) \) to be this configuration dependent equilibrium bond length, \( V(r_m, X) \) and the first six derivatives of \( V \) with respect to \( r \) must be evaluated at \( r_m(X) \) in order to obtain the needed \( d_n \). The perturbation expansion for the state energies measured relative to the potential minimum \( V(r_m, X) \) are then evaluated as just described. In molecular dynamics simulations or in force biased Monte Carlo simulations the forces are needed. This involves differentiation with respect to solvent coordinates of \( V(r_m, X) \) and the perturbation expansion for the vibrational energy levels.

Care must be taken to correctly account for the fact that \( r_m \) also changes as \( X \) varies. Thus the total rate of change of some quantity \( A \) with respect to \( X \) is given by

\[ \frac{\partial A}{\partial X} = \frac{\partial A}{\partial X_m} r_m \left( \frac{\partial A}{\partial r} \right) X \left( \frac{\partial r_m}{\partial X} \right), \]  

(2.21)

where \( X_m \) and \( r \) are treated as independent variables on the right-hand side of Eq. (2.21). \( \partial A / \partial X_m \) is obtained from the condition that \( \{ \partial V / \partial r \} / \partial X \) = 0 which follows from the definition of \( r_m \). Thus, the total rate of change of \( \partial V / \partial r \) with respect to variations in \( X \) must vanish. When inserted into Eq. (2.21) this gives the condition

\[ 0 = \frac{\partial V}{\partial X} + \frac{\partial V}{\partial X} \frac{\partial r_m}{\partial X}, \]  

(2.22)

where the derivatives of \( V \) are evaluated at \( r_m \). Eq. (2.22) can be solved for \( \partial r_m / \partial X \).

C. Electronic spectra

Consider two electronic states of a diatomic molecule labeled \( A \) and \( B \), where state \( A \) is the ground state and state \( B \) is some excited state. In the isolated molecule,
the nuclear potentials for these states are given by
RKR potential curves. Given the potential models
described in the introduction, each configuration of
the solvent produces two new potential curves. Because the
solvent is being treated classically, the modulation of
these curves is adiabatic and no transitions are induced
by solvent fluctuations, only the curves and the associated
vibrational states and energies are changed. For
each solvent configuration, we can use the methods de-
veloped in Sec. II B to compute the low-lying vibra-
tional states and energies for the two potentials and
thereby the transition energies. To compute the strength
of the transition, we must be able to compute the ac-
companying Franck-Condon factors—a problem we re-
turn to shortly. For each solvent configuration, we thus
obtain the transition energies and Franck-Condon fac-
tors. If we sample the initial solvent configuration
using our Monte Carlo algorithm (Sec. II A) with the
molecule being in the ground electronic state, we have
all the information required to compute the electronic
absorption spectrum within the scope of the model.
On the other hand, if the solvent configurations are sampled
with the molecule initially in the excited electronic state,
the resulting spectrum is the fluorescence spectrum.
In time resolved fluorescence, the molecule is ex-
cited by a pulse of light on a time scale short compared
to the relaxation times of the fluid, but because emis-
sion takes place on a nanosecond time scale, the fluo-
rescence spectrum taken at intervals of time after ex-
citation will show an evolution from a spectrum consis-
tent with solvent configurations in equilibrium with the
ground electronic state of the molecule to a spectrum
consistent with the fluid being in equilibrium with the
excited electronic state of the molecule. The present
study gives both the initial and final fluorescence spec-
tra, but not the time evolution of the spectra. The time
evolution can, nevertheless, be simulated. This is ac-
complished by sampling initial solvent configurations
with the molecule in its ground state. Each of these
configurations provides an initial state for a molecular
dynamics simulation where the forces are computed
using the excited state potential surface. The time
evolution of the solvent then generates the new con-
figurations for the computations of energies and Franck-
Condon factors, and thus for the computation of the
time evolution of the fluorescence spectra.

There is yet another possibility which will be fol-
lowed up in a subsequent study. Instead of solving the
vibrational problem, we can adopt the methods de-
veloped by Heller for studying wave packet dynamics.
Given an initial fluid configuration—sampled by Monte
Carlo—the molecular dynamics of the wave packet and
fluid can be solved. This requires three classical tra-
jectories for each initial configuration (including packet
state). The beauty of this technique is that it enables
us to study transitions involving highly excited states—
states that are otherwise not obtainable by the perturba-
tion techniques described above.

The procedure used to compute the Franck-Condon
factors is as follows. The vibrational wave functions
(for a given configuration) on surface A are

\[ |\phi_n^A = \sum_k C_{km}^A |\phi_m^A \rangle, \]

where \( |\phi_m^A \rangle \) are harmonic oscillator states on surface
A. The Franck-Condon factors are then

\[ \langle \phi_n^A | |\phi_m^A \rangle = \sum_k C_{km}^A C_{mn}^B \langle \phi_k^A | \phi_n^B \rangle. \]

The coefficients are computed perturbatively as outlined
in Sec. II B. The harmonic overlaps,

\[ F_{mn}^{AB} = \langle \phi_n^A | \phi_m^B \rangle \]

depend on the harmonic frequencies \( \omega_A, \omega_B \) of the two
electronic surfaces, and also on the difference in the
equilibrium bond lengths, \( \Delta = r_{A,B} - r_{A,A} \). \( \omega_A, \omega_B, \)
and \( \Delta \), and, concomitantly, the harmonic overlap, vary with
fluid configuration. To avoid evaluating the overlap for
every configuration, it was convenient to adopt the fol-
lowing procedure. First, we note that the overlaps are functions of \( \omega_A \) and \( \omega_B \) through the parameters \( \gamma_A, \gamma_B, \)

\[ F_{mn}^{AB} = F_{mn}(\gamma_A, \gamma_B; \Delta) \]

where \( \gamma_A = (m\omega_A/\hbar)^{1/2} \) and \( \gamma_B = (m\omega_B/\hbar)^{1/2} \) define har-
monic length scales in the two surfaces. By simple
change of scale of the integral defining \( F_{mn}^{AB} \), it can be shown

\[ F_{mn}(\gamma_A, \gamma_B; \Delta) = (1/\gamma_A) F_{mn}(1, \gamma_B/\gamma_A, \gamma_A \Delta) \]

The approach employed in the simulations was to expand
\( F_{mn}^{AB}(1, x, y) \) in a Taylor series up to quadratic order
around some average value for \( x_0, y_0 \). The matrices
\( F_{mn}(1, x_0, y_0); \partial F_{mn}/\partial x(1, x_0, y_0); \partial^2 F_{mn}/\partial x^2(1, x_0, y_0);
\partial^2 F_{mn}/\partial y^2(1, x_0, y_0); \partial^2 F_{mn}/\partial x\partial y(1, x_0, y_0); \)
and \( \partial F_{mn}/\partial y(1, x_0, y_0) \) are then evaluated before the simula-
tion is initiated. Then \( F_{mn}^{AB} \) can be evaluated at each step of the simulation, from the
quadratic expansion for each new \( x, y \). The average
values of \( x_0, y_0 \) are found from small trial runs. The
fluctuation of \( x \) and \( y \) around \( x_0 \) and \( y_0 \) is monitored. In
all cases reported, the fluctuations are sufficiently
small that this Taylor series approximation should be
accurate. If in other cases the fluctuations become
too large, more than one such expansion point can be
chosen. Then as the run proceeds for each new sol-
vent configuration, the closest expansion point \( (x_1, y_1) \)
could be seen.

III. RESULTS

A. Solvent effects on vibrational spectrum

In this section, we report the results of a number of
Monte Carlo simulations of a model system consisting
of Br\(_2\) dissolved in Ar. Br\(_2\) in Ar is a somewhat unusual
system in that the vibrational period for Br\(_2\) is about
10^{-13} s, which is quite slow as vibrational motions go.
At 300 K, the temperature at which our Monte Carlo
simulations are run, a free Ar atom travels about 0.3
Å per vibrational period on the average. Thus, we
would expect the adiabatic approximation to break down,
with the consequence that solvent induced vibrational
relaxation may be rapid. The present work makes no
attempt to calculate this nonadiabatic vibrational relaxa-
tion. Furthermore, it assumes that the mixed quantum-
classical density matrix based upon the separation of


Downloaded 30 Dec 2003 to 128.59.114.15. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp
vibrational and rotational-translation motions provides a reasonable description for the calculation of static properties of this system. The question of solvent induced, nonresonant vibrational relaxation and the effect it has on the statistical properties of a system is a very interesting subject which we hope to address in future work.

The intramolecular Br2 interaction is modeled by a Morse potential with \(D_e = 23100 \text{ K} \), \(\alpha = 1.94 \text{ Å}^{-1}\) and \(r_e = 2.28 \text{ Å}\). The solvent (Ar) atoms interact with each other via a Lennard-Jones (LJ) potential with \(\epsilon_{\text{Ar}} = 120 \text{ K} \) and \(\sigma_{\text{Ar}} = 3.42 \text{ Å}\). The Ar atoms interact pairwise additively with each Br atomic center through an LJ potential. In one model, designated the fixed epsilon (FE) model, the Ar–Br LJ parameters are those of Freaser et al.,\(^{21}\) \(\epsilon_{\text{ArBr}} = 143 \text{ K} \), \(\sigma_{\text{Br}} = 3.51 \text{ Å}\). Since the electron density in Br2 certainly depends on bond length, it is more realistic to use parameters in the Ar–Br potential which are dependent on \(r\). Pratt and Chandler\(^{3} \) and Oxtoby\(^{18}\) have suggested that the variation of the strength of \(V_{\text{ArBr}}\) with changing Br bond length is an important feature that must be taken into account in order to correctly reproduce the solvent effects on the oscillator. Since the molecular static polarizability is generally an increasing function of bond length, Pratt and Chandler\(^{15}\) suggest replacing the constant \(\epsilon_{\text{Ar}}\) in \(V_{\text{ArBr}}\) with an \(\epsilon_{\text{Ar}}\) which is a linear function of \(r\). (Because it is the attractive part of the LJ potential that should depend on the Br2 polarizability, Pratt and Chandler opt for including the bond length dependence in \(V_{\text{ArBr}}\) only. Here \(V_{\text{ArBr}}\) is the attractive part of the total potential \(V_{\text{ArBr}} = V_{\text{Ar}} + V_{\text{Br}} + V_{\text{ArBr}}\) as defined by Weeks, Andersen, and Chandler.\(^{21}\) However, this leads to changes in this parameter, and give the same overall length. Furthermore, there is no reason to believe that the repulsive potential \(V_{\text{ArBr}}\) is independent of bond length. Therefore, we employ a modified bond length dependent \(\epsilon_{\text{Ar}}\) for the total potential \(V_{\text{ArBr}}\).) We adopt an \(\epsilon_{\text{Ar}}(r)\) which is nearly linear near \(r_e\) but which goes to constant values at large and small \(r\). This avoids the possibility of spurious effects due to having a potential well which increases in depth without bound as \(r\) increases. The functional form employed is\(^8\)

\[
\epsilon_{\text{Ar}} = \epsilon_1 - \epsilon_2 \exp\left(\alpha'(r - b)^2\right).
\]

The parameters \(\epsilon_1, \epsilon_2, \alpha',\) and \(b\) are fit so that \(\epsilon_{\text{Ar}} = 143 \text{ K} \), \((d\ln \epsilon_{\text{Ar}}/d\rho)^1 = 1 \text{ Å}^{-1}\) (this is the same slope as that used by Pratt and Chandler\(^{15}\)) and \(d^2\epsilon_{\text{Ar}}/d\rho^2 = 0\) at \(r_e\). This last condition ensures that \(\epsilon_{\text{Ar}}\) is approximately linear near \(r_e\). Given these parameters, there is one free parameter in our functional form for \(\epsilon_{\text{Ar}}(r)\), namely, \(r_e - b\). By choosing a sufficiently large value for this parameter, the region of approximately linear behavior of \(\epsilon_{\text{Ar}}(r)\) near \(r_e\) can be adjusted to be suitably large. In all variable epsilon (VE) studies reported below, \(r_e - b = 0.5 \text{ Å}\). \(r_e - b = 1.0 \text{ Å}\) has also been tested and the results of the simulations found to be insensitive to changes in this parameter, and give the same results as \(r_e - b = 0.5 \text{ Å}\).

The Ar–Ar and the Ar–Br potentials are spherically truncated and shifted at pair distances \(R_{\text{Ar-Ar}}^2\) and \(R_{\text{Ar-Br}}^2\), respectively. At these cutoffs, both potentials are 1 K—with the proviso that Br2 is at its equilibrium bond length. The introduction of the cutoffs leads to discontinuities in the derivatives of the potentials at the cutoff distances, but the cutoffs are at sufficiently large distances that these discontinuities cause no problems in practice.

Following Freaser et al.,\(^{21}\) we report the density of the various simulations in terms of an effective excluded volume fraction, defined as

\[
\chi = \pi(\rho_{\text{Ar}} \sigma_{\text{Ar}}^2 + \rho_{\text{Br}} \sigma_{\text{Br}}^2)/6,
\]

where \(\rho_{\text{Ar}}\) and \(\rho_{\text{Br}}\) are the number densities of Ar and Br atoms in the simulation, respectively.

The details of the Monte Carlo simulation procedure are the same as presented in an earlier publication\(^9\) and are not discussed here. Runs have been performed for \(\chi = 0.3, 0.4, 0.5, \) and 0.6, using the variable epsilon model for the Br–Ar interaction. For comparison, a fixed epsilon run has also been performed at \(\chi = 0.3\). All runs are performed at 300 K. The initial configuration for each run is taken to be the final configuration of some previous simulation, and the system is allowed to relax further for at least \(5.4 \times 10^5\) moves. Each run consists of \(5.4 \times 10^5\) moves, in addition to the moves which are discarded at the beginning of the simulation. Some tests of the accuracy of the statistics for the simulations have been made. These are discussed below and they indicate that these simulations are sufficiently long to provide accurate results.

A number of quantities have been determined. Among these are the bond length distribution, the distribution of energies \(\{\epsilon(X)\}\) in individual oscillator strates, and the distribution of harmonic frequencies of the vibrational potential defined as \(\omega(x) = [1/(m\hbar^2)]^{1/2} V(x)/\rho(x)^{3/2}\). The solvent effect on the bond length is fairly small in all cases, as demonstrated by the results in Table I. Run I (\(\chi = 0.3\), constant \(\epsilon_{\text{Ar}}\)) shows essentially no effect on the average bond length as compared with the isolated molecule. \((\rho)\) increases somewhat, 0.009 Å, when the bond length dependence is added to \(\epsilon_{\text{Br}}(r)\) at this density, in agreement with the prediction of Pratt and Chandler.\(^{14}\) At high density \((\chi = 0.6)\) with \(\rho\)-dependent \(\epsilon_{\text{Ar}}\), there is a 0.013 Å reduction in the bond length compared with the \(\rho\) for the Morse potential alone. As a check of the accuracy of these results, a second simulation \((\chi = 0.3, \) variable \(\epsilon_{\text{Ar}}(r)\) has been performed. The average bond length differed by only 0.0002 Å between these two runs, indicating that good statistics have been

---

**TABLE I.** Average quantities for Br2 in Ar model system evaluated from mixed quantum-classical Monte Carlo simulations.

<table>
<thead>
<tr>
<th>(\langle r \rangle \text{ (Å)})</th>
<th>(\langle \omega \rangle \text{ (cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. (\chi = 0.3, \epsilon_{\text{ArBr}}) is constant</td>
<td>2.242</td>
</tr>
<tr>
<td>II. (\chi = 0.3, \epsilon_{\text{ArBr}}) is a function of (r)</td>
<td>2.2953</td>
</tr>
<tr>
<td>III. (\chi = 0.3, \epsilon_{\text{ArBr}}) is a function of (r)</td>
<td>2.7278</td>
</tr>
<tr>
<td>Isolated Br2 Morse potential</td>
<td>2.2861</td>
</tr>
</tbody>
</table>
achieved. (The statistics for the highest density $\chi = 0.6$ simulation appear to be poorer. For instance, if separate subaverages of the bond length are taken at this density for the first $2.7 \times 10^4$ moves and for the last $2.7 \times 10^4$ moves, these averages differ by nearly 0.01 Å. Presumably, these poor statistics are the result of decreased efficiency of sampling at the higher density due to smaller step sizes and to increased difficulty of reaching all other configurations from a given configuration because of the tight packing. Even with the poorer statistics, the qualitative trends discussed are certainly still significant.)

In contrast to the bond length, properties that are related to the internal vibrational state energies of the diatomic $\epsilon_i(X)$ are indeed sensitive to density, and also to the inclusion of the bond length dependence in $\epsilon_{\text{br}}(r)$. The same trends are apparent whether one views the average values and distribution functions for the harmonic frequency $\omega(X)$, or for internal oscillator state energies, or for differences in state energies. This is not surprising, since the internal state energies are just $(n+1/2)\hbar\omega$ in lowest order. Only the data for $\omega(X)$ is discussed here in detail. The distribution functions of the harmonic frequencies are presented for three simulations in Fig. 1. Two of these are at $\chi = 0.3$. The $\epsilon_{\text{br}}$ differ in that in one, $\epsilon_{\text{br}}$ is held constant, while in the other $\epsilon_{\text{br}}(r)$ depends on bond length [Eq. (3.1)]. The third simulation also includes the variable $\epsilon_{\text{br}}(r)$, but is at the higher density, $\chi = 0.6$. For run I ($\chi = 0.3$, fixed $\epsilon_{\text{br}}$), $\langle \omega \rangle = 60.54$ ps$^{-1}$, lies very close to the frequency for the isolated Morse potential, 60.15 ps$^{-1}$.

Addition of the bond length dependence in $\epsilon_{\text{br}}(r)$ gives $\langle \omega \rangle = 58.90$ ps$^{-1}$, and in fact induces a red shift in agreement with the qualitative prediction of Pratt and Chandler$^{15}$ and the quantitative studies of various systems by Schweitzer and Chandler.$^{16}$ The frequency distributions rise sharply on the low frequency side and tail off more slowly at high frequencies. The distribution function for the $\chi = 0.6$ simulation is much broader, blue shifted, and it does not rise as fast on the low frequency side as the $\chi = 0.3$ case. The skewing of these distributions is interesting since Gaussian approximations are sometimes employed for $g(\omega)$ [and $g(\omega, t, \omega_0, t_2)$ the two time distribution function] on the basis of a central limit argument.$^{33}$ A similar skewing has been noted by Dijkmam and van der Maas$^{34}$ in their model calculations of inhomogeneous broadening of infrared line shapes by inert solvents.

Figure 2 is a plot of the shift in the average frequency (relative to the value for the isolated Morse potential) versus density. All points correspond to simulations with bond length dependent $\epsilon_{\text{br}}(r)$. The red shift at low frequencies which turns into a blue shift at higher frequencies is very reminiscent of similar trends seen in experimental studies on the density dependence of infrared frequencies.$^{14}$ For $\chi = 0.3$ ($\rho^2 \sim 6$) and fixed $\epsilon_{\text{br}}$ (cf. Fig. 1), there is no shift suggesting that the red shift would be lost if the $\epsilon_{\text{br}}(r)$ were not treated as a function of bond length as it has been in these simulations. Comparison of the results of two identical simulations at $\chi = 0.3$ suggests that the statistics of these runs are rather good. The difference in the average
mann factor

\[ g(\omega') = Q^{-1} \int dx \exp\left\{ -\beta \left[ \frac{1}{2} \hbar \omega(x) + V_{g}(x) \right] \right\} \times \delta(\omega' - \omega(x)) , \]  

(3.4)

where \( V_{g}(x) = V(\gamma(x), x) \), \( \omega(x) \) is the bond length for which \( V(\gamma, x) \) is a minimum for constant \( x \). In Eq. (3.4) it has been assumed only that the ground vibrational state is significantly populated and that the harmonic approximation for the state energy is reasonable. Clearly for \( \omega' < \omega_{y} \), \( g(\omega') = 0 \). Close to \( \omega_{y} \) Eq. (3.3) provides the relationship between \( x \) and \( \omega \). Since

\[ dx = d\omega \left( \frac{dx}{d\omega} \right) = \frac{d\omega}{2(\omega - \omega_{y}/A)^{1/2}} \]  

(3.5)

the integral over \( x \) in Eq. (3.4) can be converted into two integrals over \( \omega \) [one for each branch of \( \pm (\omega - \omega_{y}/A)^{1/2} \)] which are easily performed yielding

\[ g(\omega') = \frac{1}{[(\omega' - \omega_{y})/A]^{1/2}} \exp\left\{ -\beta \left[ \frac{1}{2} \hbar \omega' + V(x(\omega')) \right] \right\} \]  

(3.6)

for \( \omega' \) slightly greater than \( \omega_{y} \), and \( x(\omega') \) is found by inverting Eq. (3.3). Therefore, the dominant behavior near \( \omega_{y} \) is a jump from zero to \( \infty \) at \( \omega_{y} \) and then a subsequent decay as \( (\omega - \omega_{y})^{-1/2} \). Thus, the case of one perturber yields a skewed distribution.

When many solvent molecules are present, the integral over \( x \) in Eq. (3.4) is replaced by a multidimensional integral over the entire solvent configuration space. The harmonic frequency still has an absolute minimum as a function of all solvent coordinates. Below this value \( \omega_{y} \), \( g(\omega) = 0 \). The \( \delta \) function in the integrand of the integral over solvent configurations picks out the volume of configuration space corresponding to a given \( \omega \). Since \( \omega_{y} \) corresponds to a single point in configuration space (actually a number of equivalent points related by interchange of solvent particles), it has zero volume and the singular behavior of the one-dimensional example does not appear. However, if the most probable frequency lies near \( \omega_{y} \), the low frequency wing must necessarily be truncated. This is the case at low and moderate densities since the nearest solvent particles tend to be located at distances from the diatomic at which the solvent–solute interaction is attractive.

At higher densities, the repulsive portions of the inter-

frequencies of the two runs is only 0.082 ps⁻¹.

As a test of the convergence of the perturbation expansion for the vibrational state energies, Table II presents results of the zeroth, second, and fourth order calculations of the internal vibrational state energies \( \epsilon_{n}(\chi) \) for \( n = 0 \) through 7 for a particular solvent configuration (taken from \( \chi = 0.3 \)) for a variable \( \epsilon_{B} \) simulation. This indicates that the fourth order perturbation calculations should provide highly accurate results.

It has been suggested that the frequency distribution should be Gaussian since the instantaneous frequency is the superposition of numerous more or less random perturbations due to the interactions of the solute with the solvent particles. To understand why this central limit argument does not predict the correct result, first consider the case of one solvent particle interacting with the diatomic. For simplicity we assume a collinear geometry. As the particles are brought closer from an infinite separation, the long range attractive solvent solute interaction causes a slight decrease of the effective harmonic frequency of the diatomic. At some separation of the diatomic and perturber the frequency goes through a minimum and for shorter separations shifts to higher frequencies as the repulsive portion of the solvent–solute interaction squeezes the vibrational coordinate. Near the minimum frequency \( \omega_{y} \) the frequency can be expanded as a function of the solvent–solute separation variable \( x \):

\[ \omega = \omega_{y} + A(x - x_{y})^{2} , \]  

(3.3)

where \( x_{y} \) is the value of \( x \) which corresponds to \( \omega_{y} \). The distribution of frequencies \( g(\omega') \) is defined as the integral over all \( x \) of \( \delta(\omega' - \omega) \) weighted by the Boltz-
TABLE III. Morse parameters for two electronic states.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_e$</td>
<td>23 100 K (1.99 eV)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1.94 Å$^{-1}$</td>
</tr>
<tr>
<td>$r_e$</td>
<td>2.28 Å</td>
</tr>
<tr>
<td>$V_0$ (r)</td>
<td>0</td>
</tr>
<tr>
<td>$\omega_{\text{HO}}$</td>
<td>6.016 x 10$^{13}$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>319 cm$^{-1}$</td>
</tr>
<tr>
<td>$\omega_{\text{NO}}$</td>
<td>9.57 x 10$^{12}$ Hz</td>
</tr>
</tbody>
</table>

action dominate. The most probable frequency lies far above $\omega_{\text{HO}}$ and the low frequency cutoff is obscured since it is far out in the wings of the distribution. Therefore, $g(\omega)$ for high densities appears less skewed.

B. Solvent effects on electronic spectra

The methods outlined in Sec. II can be used to study how the solvent perturbs the electronic absorption and fluorescence spectra of diatomic molecules. In this section, we consider a fictitious diatomic molecule $X_2$ dissolved in various simple solvents. In its ground electronic state, labeled $A$, $X_2$ is identical to the Br$_2$ molecule studied in Sec. II A; however, in the excited state studied here (labeled the $B$ state), $X_2$ bears no relationship to any of the excited states of Br$_2$. The $B$ state intramolecular potential is also taken to be a Morse potential. The parameters used in the Morse potentials for the $A$ and $B$ states are given in Table III. The minimum of the $B$ state potential is 6950.3 cm$^{-1}$ above the minimum of the $A$ state potential so that in the absence of solvent, and in the harmonic approximation, the $A$ O-BO transition is at 6925.9 cm$^{-1}$.

In Fig. 3(a) we show the exact absorption and emission spectrum for isolated $X_2$. This was computed using the exact states of the Morse oscillator. In Fig. 3(b) we show the spectrum determined by the perturbation treatment outlined in Sec. II B together with the numerically determined Franck-Condon factors. Comparison of Figs. 3(a) and 3(b) shows that the numerical techniques introduced here are quite good.

How does solvent perturb the electronic spectrum? This depends sensitively on the intermolecular potential between solvent and solute. It is expected that the molecule $X_2$ in the $B$ state interacts differently with solvent molecules than $X_2$ in the $A$ state. Because little is known about the interaction potential, we will study several simple models.

In all of the systems studied, the temperature is 85 K, and the density is $\chi = 0.4$ with one $X_2$ molecule and 107 solvent atoms. The potentials are spherically truncated and shifted, and periodic boundary conditions are used. Each run consists of 250 passes after initial aging. For each system separate simulations were performed with configurations sampled from the $A$ state and from the $B$ state. The transition energies and Franck-Condon weighting factors are evaluated for the transitions from the ground vibrational state of the initial electronic state ($A$ or $B$) to the first eight vibrational states of the final surface ($B$ or $A$). Hot bands are thus ignored. The weighted transition energies are binned. For the case where $A$ is the initial surface, the weighted distribution of transition energies gives the absorption spectrum, whereas when $B$ is the initial state, a similar procedure gives the emission spectrum. In the latter case, the assumption is made that the lifetime of the $B$ state is sufficiently long that the vibrations in that state have relaxed to the ground vibrational state, and furthermore, the solvent has fully relaxed around the $B$ state. In two cases (the first and last below) the emission spectrum has also been computed, assuming that the solvent does not have time to relax at all.

In all of the systems studied, each X center in $X_2$ interacts with each solvent atom through a Lennard-Jones potential with parameters $\epsilon_{x}, \sigma_{x}$ which depend on whether $X_2$ is in the $A$ or $B$ state. Thus for each system we must choose $[\epsilon_{x}(A), \sigma_{x}(A)]$ and $[\epsilon_{x}(B), \sigma_{x}(B)]$ where the $A$ and $B$ define the state. The solvent atoms Ar interact with each other through a LJ potential with $\epsilon_{Ar} = 120$ K and $\sigma_{Ar} = 3.42$ Å as before. In one of the simulations, $X_2$ is treated like a heteronuclear molecule in that it is given a bond length dependent dipole molecule and the solvent atoms are given point dipole moments of magnitude 0.5 D. The dipole moment of the diatomic is modeled as a point dipole located at the center of the bond. These latter cases will be discussed shortly.

The potential parameters are defined in Table IV.

In system IV, the $B$ state has a bond length dependent...
TABLE IV. A summary of the potential parameters used in the systems studied in this section.

<table>
<thead>
<tr>
<th>System</th>
<th>$\epsilon_x$ (K)</th>
<th>$\sigma_x$ (Å)</th>
<th>$\epsilon_y$ (K)</th>
<th>$\sigma_y$ (Å)</th>
<th>$\mu_x^2$ (D)</th>
<th>$\mu_y^2$ (D)</th>
<th>Solvent $\mu$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>143</td>
<td>3.51</td>
<td>143</td>
<td>3.51</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>II</td>
<td>143</td>
<td>3.51</td>
<td>71.5</td>
<td>3.51</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>III</td>
<td>143</td>
<td>3.51</td>
<td>143</td>
<td>3.69</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>IV</td>
<td>143</td>
<td>3.51</td>
<td>143</td>
<td>3.51</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The dipole moment

$$\mu(r) = 0.5 \left[ 1 + \tanh(r - 2.40) \right]$$

such that at $r_0(B)$, the dipole is 0.5 D. This dipole has a linear dependence on $r$ in the neighborhood of $r_0(B)$.

The absorption and emission spectra for these four systems are presented in Figs. 4-7. The high frequency side gives the absorption spectrum and the low frequency side gives emissions. Several comments are in order:

(i) System I has a spectrum that is very similar to the isolated molecule spectrum, except that the individual lines are inhomogeneously broadened because of solute potential. The lines are slightly shifted; the shifts are smaller than the inhomogeneous line widths.

(ii) In system II [$\epsilon_x(B) = 1/2 \epsilon_x(A)$], the peak positions shift ~1000 cm$^{-1}$ to the blue compared with system I [$\epsilon_x(B) = \epsilon_x(A)$], and the peaks are much broader. This is entirely expected from the fact that in the $B$ state, the solute solvent energy is 50% smaller than in the $A$ state. If we assume that only the nearest neighbor solvent atoms contribute, and that there are $\varepsilon$ of these atoms, we estimate a decrease of $2\varepsilon (\epsilon_x(A) - \epsilon_x(B)) = 2\epsilon_x(A)$ in the cohesive energy of the $B$ state relative to the $A$ state. To account for the observed blue shift of 1440 K, all we require is on the order of ten “nearest neighbor” solvent atoms. We have somewhat more than this number, but they do not all sit at the potential minimum. In the case where $\epsilon_x(B) = 2\epsilon_x(A)$, we expect a substantial red shift in the spectrum.

(iii) In system III, $\sigma_x(B) = 1.05 \sigma_x(A)$, the emission peaks shift 150 cm$^{-1}$ to the red and the absorption peaks shift to the blue compared to system I where $\sigma_x(B) = \sigma_x(A)$. The spectral lines are much broader. The broadening clearly follows from the fact that in the $B$ state, the molecule experiences stronger repulsions with the solvent with concomitant broadening of the individual vibrational states. Interestingly, the 00 lines for the absorptions and emissions are shifted to the blue and red, respectively. They no longer overlap. The blue shift of the absorption band can be explained by the observation that in absorption the solvent configura-

---

FIG. 4. Normalized vibronic absorption and emission Franck-Condon intensities for a model diatomic in a monatomic solvent system corresponding to system I of Table IV. The solvent is not allowed to relax in the evaluation of the emission spectra.
FIG. 5. Same as Fig. 4 but corresponding to system II of Table IV and the solvent is allowed to relax in the evaluation of the emission intensities.

FIG. 6. Same as Fig. 4 but corresponding to system III of Table IV and the solvent is allowed to relax in the evaluation of the emission intensities.
tion is in equilibrium with the $A$ state. For the solvent atoms near the solute, the transition to the $B$ state is accompanied by an increase in $\sigma_{x-x}$ and with a concomitant increase in potential energy. Hence, the $B$ surface shifts up from the $A$ surface and rises more steeply on the repulsive side. This gives a blue shift. The red shift of the emission lines can be understood as follows. The solvent is allowed to relax around the $B$ state. Because $\sigma_{x-x}$ is larger, there will now be more solvent atoms in the coordination shell with a concomitant increase in attractive energy with the $B$ state. This lowers the energy of the $A$ state relative to the $B$ state.

(iv) In all cases, the absorption lines are somewhat broader than the emission lines. This is presumably because the electronically excited diatomic is slightly larger than the ground state molecule ($r_e = 2.4 \ \text{Å}$ in the excited state versus $2.28 \ \text{Å}$ for the ground electronic state). Therefore, similar arguments to those invoked in (iii) apply. In case (III) the diatomic-solvent interaction radius $\sigma_{x-x}$ is larger for the upper electronic surface than for the lower surface, causing the observed effects. However, even when $\sigma_{x-x}(B) = \sigma_{x-x}(A)$ there is still a slight effect due to the increased equilibrium bond length for the isolated diatomic for state $B$ compared with state $A$.

(v) In system IV, a dipolar interaction is included; nevertheless we see very little change in the spectrum from what it was without the dipole. The spectral shifts are very small and there is only a very slight broadening. At first, this may appear surprising, but further reflection shows that at contact the dipolar interaction with one solvent is $\sim 40 \ \text{K}$. The solvent dipoles in the nearest neighbor solvent shell at 85 K will thus not be terribly ordered. Small increases in dipole moment may have profound effects on the spectra.

To better understand how the solvent perturbs the electronic absorption and emission spectra, we adopt the following simple model in which the potential curves for the $A$ and $B$ states are merely shifted by the solvent but are otherwise unchanged. Moreover, we assume that the potentials are harmonic. For the average frequencies of absorption we have

$$\hbar \omega_{AB}^{\text{abs}} = \frac{1}{2} \hbar (\omega_B - \omega_A) + \eta_B \hbar \omega_B + \rho \int d^3 R \int d \Omega \rho_A(R, \Omega) \{ V_B - V_A \} , \quad (3.8)$$

where $V_A$ and $V_B$ are, respectively, the solute-solvent interaction potential in the $A$ and $B$ state, and $\rho_A(R, \Omega)$ is the pair correlation function giving the density of solvent molecules at a distance $R$ from the COM of the $Br_2$ molecule which is oriented in space with angles $\Omega$. The subscript $A$ denotes the fact that the solvent is in equilibrium with the electronic state $A$. Similarly, $\rho_B$ describes the distribution of solvent around $Br_2$ in equilibrium with the $B$ state.

Likewise, the average emission frequencies are

$$\hbar \omega_{AB}^{\text{emt}} = \frac{1}{2} \hbar (\omega_B - \omega_A) - \eta_A \hbar \omega_A + \rho \int d^3 R \int d \Omega \rho_B(R, \Omega) \{ V_B - V_A \} . \quad (3.9)$$

For simplicity, let us assume that the solute is a spherical molecule. From these expressions, we see that if $\epsilon$, $\sigma$ are the same in the $A$ and $B$ state $V_B - V_A = 0$ and there are no solvent shifts in this model. Taking $V_B(R)$
null
shifting of the vibrational frequency distributions in the ground electronic state that were observed when the Lennard-Jones potential for the Br₂–Ar interaction is such that $\kappa_{\text{Br}}(\text{Ar})$ depends on the Br₂ bond length is an example of this type of investigation. The interaction between the solvent particles and electronically excited states of the diatomic is apt to be more complicated than the ground state interaction, due to the open shell nature of most excited electronic states. Moreover, less is generally known about excited molecule–solvent interactions, both theoretically and experimentally. Nevertheless (or maybe because of this), it is of interest to study the consequences of various model solvent interactions with excited electronic states molecules. We have undertaken such a study, with the various potentials outlined in Tables III and IV. This results in the various absorption and emissions spectra given in Figs. 4–7 and we easily understand these on the basis of the potential models used.

We have mentioned previously that this work rests upon the adiabatic separation of the vibrational motion from the translational and rotational motions. Non-adiabatic effects which are neglected result in solvent-induced relaxation of the vibrational populations. To test the consequences of this neglect of vibrational relaxation, the behavior of the solvent-induced nonadiabatic coupling must be studied. This coupling has the form $\text{IP}_{\text{Br}} = \langle \psi | \nabla_2 | \psi \rangle$ where $\psi$ is the vibrational wave function for the system, $\nabla_2$ is the multidimensional gradient with respect to all translational and rotational coordinates, and $\text{IP}_{\text{Br}}$ is the multidimensional vector composed of the conjugate momenta to these coordinates. One approach to this problem would be to run the dynamics and calculate the rate at which the first excited vibrational state is produced according to first order perturbation theory. The evaluation of the $\nabla_2 \Phi$ factor in the coupling would proceed very similarly to the evaluation of $\nabla_2 E_\text{e}(\mathbf{R})$ described in Sec. II C, where $E_\text{e}(\mathbf{X})$ is the $n$th vibrational state energy.

Recently a number of workers have considered problems concerning quantum degrees of freedom in the condensed phase. One notable approach has been to study approximations to the quantum distribution function based upon the discretized representation of the path integral. Applying the techniques of classical liquid state statistical mechanics to the path integral, quantum problems as the hard sphere model for He above the $\lambda$ transition and solvation effects on a very simple model of tunneling have been analyzed. This approach may well be useful for simulating certain properties, but as matters now stand, it does not appear to offer a practical alternative to the simulations of spectra discussed here.

Wilson and co-workers have analyzed the classical limit of infrared and Raman spectra calculated from quantum mechanical linear response theory and present quantum corrections which can be applied to rotational and vibrational spectra calculated from classical molecular dynamics. Calculations are presented for the IR spectrum of CO in Ar and the Raman spectrum of N₂ in Ar. The vibrational quantum corrections are more significant than the rotational corrections. The vibrational corrections arise from the anharmonicity of the potential and, therefore, are expected to be relatively small for such harmonic bonds N₂ and CO₂, as compared with the vibrations of weaker bonds. It would be interesting to test these corrections on more anharmonic systems.

To summarize, in this work we describe how the solvent induced perturbations upon vibrational modes of different electronic excited states can be studied in gases and liquids. The model is based on an adiabatic separation of vibrational and rotational/translational motions and a classical limit approximation for the latter types of motions. The key to the simulation methods discussed is the availability of a highly efficient procedure for the repeated solution of the vibrational Schrödinger equation. A perturbative method which has been found to be accurate for the low lying vibrational states is presented.

A series of Monte Carlo calculations are presented which model the Br₂ in Ar system in a high density fluid state at 300 K. In the Monte Carlo work, particular attention is paid to the distribution of harmonic frequencies for the vibrational coordinates. This distribution function is found to be a sensitive function of density. The average frequency shows a red shift at moderate densities and is blue shifted at high densities. The shift is also found to be sensitive to the form of the potential employed. In particular, the red shift is enhanced if the Ar–Br interaction is taken to be an increasing function of Br₂ bond length, in agreement with the qualitative prediction of Pratt and Chandler, and the detailed studies of Schweitzer and Chandler. The frequency distributions are skewed, tailing off more slowly on the high frequency side. This conclusion, which corroborates the finding of Dijkman and van der Mass, raises questions about the validity of the Gaussian distribution function approximation, which is sometimes invoked on the basis of a central limit theorem argument. The skewing is less significant at higher densities.

A second electronic state on the diatomic is included in a number of simulations in order to study the distribution of vibrionic transition frequencies between the ground and excited electronic levels. The well depth and interaction radius between the solvent and the electronically excited solute are varied. We find that decreasing the well depth blue shifts both the excitation (absorption) and deexcitation (emission) vibrionic bands. Increasing the excited state interaction radius results in higher absorption frequencies and low emission frequencies. In each of these cases the frequency distributions are much broader than when the same solvent–solute potential is employed for the ground and excited states of the solute. This broadening is especially pronounced when the interaction radius is increased. The addition of 0.5 D dipoles to the solvent and to the electronically excited solute results in only minor changes to the vibrionic frequency distributions. This indicates only partial orientational ordering of the dipoles at the temperature (85 K) considered.
M. F. Herman and B. J. Berne: Solvent effects on spectra

15L. R. Pratt and D. Chandler, J. Chem. Phys. 72, 4045 (1980). This was based on a suggestion made by D. W. Oxtoby.
18P. Morse, Phys. Rev. 34, 57 (1929).