A MONTE CARLO PROCEDURE FOR THE STUDY OF SOLVENT EFFECTS ON QUANTUM MOLECULAR DEGREES OF FREEDOM

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A Monte Carlo method is devised for the study of systems which have a few quantum degrees of freedom coupled to many essentially classical coordinates The density dependence of the solvent-induced shifts in the vibrational spectrum is investigated for a diatomic (Br_2) dissolved in a monatomic fluid (Ar).

1. Introduction

The Monte Carlo method has been used to great advantage to study the thermal and mechanical properties of classical condensed systems [1]. Recently, considerable effort has been expended on developing Monte Carlo techniques for fully quantized systems [2,3]. Unfortunately, this effort has not yet progressed to the point where finite temperature fully ab initio simulations of even simple many-body systems can be carried out. In this note we address the problem of solvent effects on molecular internal degrees of freedom. Past simulations have been done only on purely classical systems We have in mind systems where the solvent consists of "classical particles" whereas the solute has one (or more) quantum mechanical internal degrees of freedom. A Monte Carlo technique based on the Born–Oppenheimer approximation [4], is described to determine the thermal properties of the system. The method is then used to determine how "liquid argon" perturbs the vibrational properties of a dissolved Br_2 molecule.

2. Theory

The system of interest consists of one "fast" degree of freedom, r, and $f-1$ slow degrees of freedom, X $(= X_1, .., X_{f-1})$. The hamiltonian can be expressed as

$$H = T_s + T_f + V(r, X) = T_s + H_v \,, \tag{1}$$

where T_s, T_f and $V(r, X)$ are respectively the kinetic energy of the slow (s) set of variables, X, the kinetic energy of the fast variable, r, and the total potential energy. The latter depends on the instantaneous configuration of the system. H_v can be regarded as the energy of the fast degree of freedom given the configuration of the solvent. H_v can be used to generate the adiabatic states $\{\psi_n(r|X)\}$,

$$H_v \psi_n(r|X) = E_n(X)\psi_n(r|X) \,. \tag{2}$$

The Born–Oppenheimer approximation [5] to the states of the full system is

$$\psi_{nm}(r, X) = \psi_n(r|X)\,\Phi_{nm}(X) \,, \tag{3}$$

where

$$[T_s + E_n(X)]\,\Phi_{nm}(X) = E_{nm}\Phi_{nm}(X) \tag{4}$$

The density matrix in the canonical ensemble can thus be expressed as

$$\rho(r, X; r', X', \beta) = \sum_n \psi_n^*(r'|X')\psi_n(r|X)\rho_n(X, X', \beta) \,, \tag{5}$$

where

$$\rho_n(X, X', \beta) \equiv \sum_m \Phi_{nm}^*(X')\,\Phi_{nm}(X)\exp(-\beta E_{nm}) \,. \tag{6}$$

When all the slow variables are translational, when $\hbar^2/2M$ is small, and when $E_n(X)$ varies slowly over the de Broglie wavelength of the slow degrees of freedom, it is a simple matter to show that

$$\rho_n(X, X'; \beta) = (2\pi MkT/h^2)^{(f-1)/2} \times \exp\{-[M(X-X')^2/2\hbar^2\beta + \beta E_n(X)]\} \tag{7}$$

Here M is the mass of the classical particles. Thus for $\hbar^2/2M \to 0$, the density matrix is to a very good approximation diagonal in X. Similarly, when the slow degrees of freedom are not only translational, it can be shown that

$$\rho(r, X, r', X, \beta) = Q_c \sum_n \psi_n^*(r'|X)\psi_n(r|X)\exp[-\beta E_n(X)] \tag{8}$$

where the prefactor, Q_c, is simply the exact classical kinetic partition function

$$Q_c = (1/h^{f-1}) \int \mathrm{d}P \exp[-\beta T_s(P)] \tag{9}$$

and P represents the momenta conjugate to the slow variables, X.

At this point it is worth noting that the normalized diagonal component of the density matrix

$$\bar{\rho}(r, X, \beta) = \frac{\Sigma_n \psi_n^*(r|X)\,\psi_n(r|X)\exp[-\beta E_n(X)]}{\Sigma_n \exp[-\beta E_n(X)]} \tag{10}$$

can be sampled using a straightforward variation of the Metropolis Monte Carlo algorithm [6]. In the algorithm a move $r, X \to r', X'$ is accepted with probability

$$A(r', X'|r, X) = \mathrm{Min}\left[1, \frac{\Sigma_n \psi_n^*(r'|X')\psi_n(r'|X')\exp[-\beta E_n(X')]}{\Sigma_n \psi_n^*(r|X)\,\psi_n(r|X)\exp[-\beta E_n(X)]}\right]. \tag{11}$$

To implement this procedure one must compute the eigenfunctions and eigenvalues $\{\psi_n(r|X), E_n(X)\}$ and $\{\psi_n(r'|X'), E_n(X')\}$ in the old and new configurations respectively. The algorithm starts with selection of an initial configuration (r_0, X_0). A move is then attempted for one of the classical variables by sampling uniformly in some domain. This move is then accepted or rejected with probability $A(r, X'|r, X)$. This is repeated in sequence for the next classical variable, and the next until all $f-1$ classical variables have been tried. A move is then attempted for the quantum position, $r \to r'$. This move is also sampled uniformly in some domain. The move is either accepted or rejected according to $A(r', X|r, X)$. One cycle through these f degrees of freedom is called a pass. A full simulation consists of many passes. Obviously many variations are possible. For example, since r is the fast variable, one can attempt a move in it after each attempted classical move. This procedure generates the equilibrium distribution of configurations, and with it one can compute many interesting properties of the system.

3. Solvent effects on diatomic molecules

Consider a diatomic molecule dissolved in a monatomic host liquid. If its mass, m, and moment of inertia, I, is sufficiently large, the diatomic's center of mass (c.m.) coordinate, $\boldsymbol{R}$, and rotational coordinates, (θ, ϕ) are to a good approximation classical whereas its vibrational degree of freedom, r, is highly quantized. Thus the set of coordinates $X = (\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N, \boldsymbol{R}, \theta, \phi)$ are taken as classical coordinates and r is the single fast or quantized coordinate. Here $\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N$ are the positions of the solvent atoms (whose mass is M). In this case, Q_c in eq. (9) becomes

$$Q_c = (2\pi MkT/h^2)^{3N/2}(2\pi mkT/h^2)^{3/2}2\pi IkT/h^2, \tag{12}$$

where we have assumed that the centrifugal energy $L^2/2\mu r^2 \to L^2/2I$ and have thus ignored translation rotation coupling.

The eigenstates $\psi_n(r|X) = R_n(r|X)/r$ are found by solving the radial wave equation

$$[-(\hbar^2/2\mu)\,\mathrm{d}^2/\mathrm{d}r^2 + V(r|X)]R_n(r|X) = E_n(X)R_n(r|X). \tag{13}$$

Clearly the most time-consuming procedure in the algorithm is the computation of $E_n(X)$ and $R_n(r|X)$ for every configuration X generated by the MC algorithm. In principle, any technique for solving the Schrödinger equation could be employed. However, it is important to find an efficient procedure for accomplishing this. In a longer paper [7], we provide details of a fast perturbation method for obtaining the $E_n(X)$ and $R_n(r|X)$ for the diatomic-in-a-solvent problem. Since the point of this letter is to provide a simple, clear description of our overall program for this mixed quantum-classical problem and present preliminary results, it suffices to present only the barest outline of the details of the specific method employed in obtaining $E_n(X)$ and $R_n(r|X)$.

In the solution of (13), we expand $V(r|X)$ in a Taylor series in r about its minimum, r_m, for fixed values of the slow variables. The harmonic oscillator, whose frequency, ω, is fit to the curvature of $V(r|X)$ at r_m, is used as our reference system. A scaled length variable, $y = (\mu\omega/\hbar)^{1/2}(r - r_e)$ and a scaled energy variable, $\epsilon = E/\hbar\omega$ are employed. All the integrals needed for the perturbation theory are of the form $y^k_{mn} \equiv \langle\psi^{(0)}_n|y^k|\psi^{(0)}_m\rangle$, where $\psi^{(0)}_n$ and $\psi^{(0)}_m$ are harmonic oscillator wavefunctions. In scaled variables the matrix elements are independent of solvent configuration, therefore, they need not be recalculated at every Monte Carlo step. Likewise, every term in the perturbation series can be arranged as a product of configuration-dependent and configuration-independent factors. The configuration-dependent factors are just products of the Taylor series expansion coefficients of the potential in terms of the scaled variables. The configuration-independent factors contain products of scaled matrix elements divided by differences in zeroth-order scaled energies, summed over intermediate states. By arranging the perturbation series in this way, the matrix elements and summations over intermediate states (i.e., the hard work) need be performed only once and stored. Thus, for each configuration of the slow variables, we need only locate r_m, evaluate the first few Taylor coefficients of the potential at r_m, and then perform some simple multiplications of these with the precalculated configuration independent factors. The details of the perturbation series, how we truncate it, and evidence of its accuracy will be given elsewhere [7].

In this paper we present results for a model of Br_2 dissolved in liquid argon. We choose this model because it has already been studied classically [8]. In this model the internal potential of the Br_2 is taken as a Morse potential with parameters $D_0 = 23100$ K, $\alpha = 1.94$ Å^{-1} and $r_c = 2.28$ Å with a harmonic frequency of $\omega_0 = 60.15$ ps^{-1}. The argon atoms interact pairwise with each other through a Lennard-Jones 12–6 potential with $\sigma_{ArAr} = 3.42$ Å, $\epsilon_{ArAr} = 120$ K. The interaction of a Br_2 molecule with an Ar atom is modeled by a site–site potential. It is important to note that because the electron distribution in a diatomic molecule changes with bond length, the interaction energy between Ar and Br_2 should depend on r [9]. Here each Br atom is assumed to interact with a given Ar atom through a L-J 12–6 potential with $\sigma_{ArBr} = 3.51$ Å. Two models for ϵ_{ArBr} are considered. In the first, ϵ_{ArBr} is set to the constant value 143 K, while in the second

$$\epsilon_{ArBr}(r) = a - A \exp[-\gamma(r - b)^2] , \qquad (14)$$

with $b = r_c - 0.5 = 1.78$ Å, and the values of a, A and γ are fitted so that $\epsilon_{ArBr}(r_e) = 143$ K, $(d\epsilon/dr)_{r_e} = 143$ K/Å and $(d^2\epsilon/dr^2)_{r_e} = 0$ [‡1].

The coordinates of this system are divided into two sets, one set consisting of the positions of the solvent atoms and the c.m. position of the diatomic, and the other set consisting of the internal coordinates (the orientational angles and the vibrational coordinate) of the diatomic molecule. In the MC algorithm each translational coordinate (set 1) is moved with a maximum step size of Δ_1. The internal coordinates are sampled by moving the relative x, y and z components of the Br–Br vector (with a maximum step size of Δ_2), and then finding the angles θ, ϕ and the vibrational displacement r from the cartesian coordinates. In order to improve the statistics for quantities related to the vibrational coordinate, it was thought best to sample the internal coordinates more frequently. Thus the algorithm adopted is one in which the internal coordinates are moved following each single molecule translational move. Thus a pass consists of $N+1$ translational moves and $N+1$ samplings of the internal coordinate. The moves are accepted or rejected according to eq. (11).

Each simulation includes a Br_2 molecule and 107 Ar atoms. Periodic boundary conditions are employed. The box length, L, is adjusted so that the effective excluded volume, χ, is 0.3 for the lower density case and 0.6 in the higher density case, where χ is defined by

$$\chi = (\pi/6L^3)(n_{Ar}\sigma^3_{ArAr} + n_{Br}\sigma^3_{ArBr})$$

and $n_{Ar} = 107$ and $n_{Br} = 2$. Spherical cut-offs are utilized for Ar–Ar and Ar–Br potentials. The cut-offs are chosen at distances for which the potentials would be 1 K. (For the Ar–Br potential this cut-off is defined using a value of $\epsilon_{ArBr}(r_e) = 143$ K in the Lennard-Jones potential.)

Each simulation consists of 250 passes, each pass containing 216 moves. The maximum step size, Δ_1

[‡1] These values of ϵ_{ArBr}, $d\epsilon/dr$ and $d^2\epsilon/dr^2$ at r_e are chosen to agree with the values used by Pratt and Chandler [9] in the attractive part of V_{ArBr}. We choose this functional form because it is simple, analytic, approximately linear [9] near $r = r_e$ ($d^2\epsilon/dr^2 = 0$ at r_e) and goes to finite asymptotic limits. It differs from the model used by Pratt and Chandler in the repulsive region.

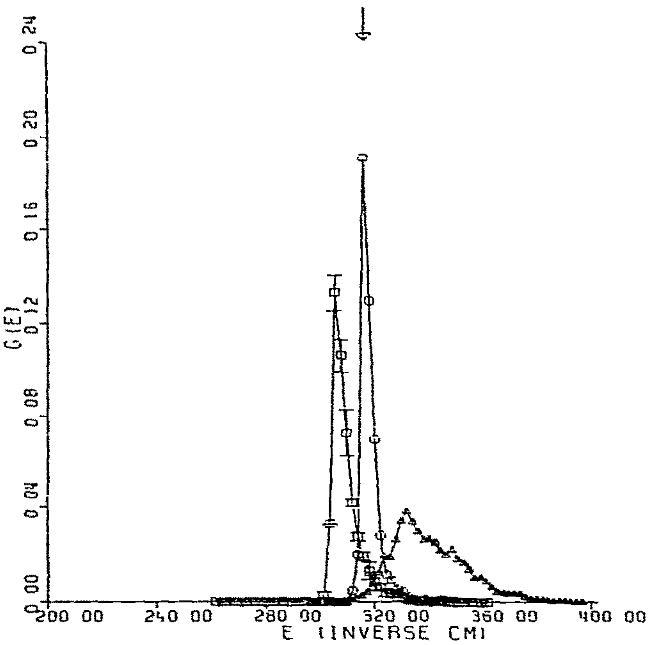

Fig. 1. Distribution of transition energies for the 0 → 1 vibrational excitation from simulations of Br_2 in Ar. □ represents the $\chi = 0.3$ simulation (lower density) with ϵ_{ArBr} given by eq. (14). ○ represents $\chi = 0.3$ simulation with constant ϵ_{ArBr}, △ represents $\chi = 0.6$ simulation (higher density) with ϵ_{ArBr} given by eq. (14). □ is the average of two independent simulations. Error bars give $\pm\sigma$ as estimated from the two independent simulations.

of the x, y and z components for each move of a translational coordinate is 1.0 Å for the lower density case and 0.35 Å for the higher density run. Maximum step sizes of $\Delta_2 = 0.2$ Å and 0.175 Å are employed for the internal coordinates in the $\chi = 0.3$ and $\chi = 0.6$ simulations, respectively.

In fig. 1, we present the distribution of transition frequencies $\omega_{0\to1}$ vibrational excitation of Br_2. The distribution is very sensitive to density and to the form of the potential function. When the density is moderate ($\chi = 0.3$), and ϵ_{ArBr} is independent of bond length, the $\omega_{0\to1}$ distribution is quite narrow and centered very close to the gas-phase value. However, inclusion of the r dependence in ϵ_{ArBr} [eq. (14)] results in a significant red-shift in the transition frequency and some broadening of the distribution. Two independent runs have been performed for this latter case with $\chi = 0.3$ and a bond-length dependent ϵ_{ArBr}. These two runs give a rough estimate of the error arising from the finite run length. Fig. 1 shows that statistical errors are small, so that the results may be regarded as statistically significant. When the density is high, $\chi = 0.6$, the distribution of transition energies are shifted to the blue, even though the bond-length dependent ϵ_{ArBr} is employed. The distribution is also broadened considerably. In each of the three cases considered, the distribution functions are noticeably asymmetric, being skewed to the high-frequency side. A similar asymmetry was noted by Dijkman and van der Maas [10] in their model calculation of infrared line shapes of a number of molecules in inert solvents. Detailed analysis of these shifts and distribution shapes will be presented elsewhere [7].

These results show that the inhomogeneous spectrum is very sensitive to the nature of the solvent–molecule interactions. Levesque et al. [11] have made a similar observation in relation to the calculation of vibrational dephasing times. Raman scattering indicates that the polarizability, $\alpha(r)$ of Br_2 increases linearly with bond length for $r \to r_e$. The potential models specified by eq. (14) mimics this observed linearity and leads to the qualitative expectation that in a dilute system, where attractive forces are important, the solute–solvent forces should oppose the intramolecular restoring force and give rise to a red-shift. The results reported here show that this is indeed the case. This study further shows that despite the dependence of ϵ on r, the solvent effect at high density leads to a substantial blue-shift.

The sensitivity of the results to the exact nature of the solvent–solute potential emphasizes the importance of a reliable simulation procedure for studying these systems numerically. To the best of our knowledge, these results represent the first successful liquid simulation that actually takes into direct account the quantum nature of vibrations. An approximate treatment of the vibrational motion that has been employed in other calculations [10,11] treats the molecular bond as rigid but estimates the shifts in the transition frequencies by low-order perturbation theory based upon an expansion (up to quadratic terms) of the solvent–solute interaction potential about the free molecule geometry. This approximation should be very reasonable for very stiff bonds and ordinary temperatures for which it has been applied, but is more questionable for weaker bonds. An investigation of the validity of this simplifying approximation for various systems is presently under way. To our knowledge, the only other simulations of these effects are based entirely on classical mechanics.

In summary, in this letter we have outlined a straightforward and efficient Monte Carlo procedure for directly studying solvent effects on molecular vibrations. This method is based upon the Born–Oppenheimer approximation and treats the rotations and translations classically, while taking the quantum nature of the vibrations into account. It is applicable to pure state vibrational distributions as well as thermal distributions, and should be useful in exploring other properties than those focused on here.

We have applied this method to the problem of inhomogeneous broadening of the distribution for lowest vibrational transition frequency. We have found the results to be very sensitive to the density and also to the interaction potential employed.

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