STUDIES ON THE MICROSCOPIC MOTION OF A

DIATOMIC IN A MONATOMIC SOLVENT

Thesis by

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ABSTRACT

The microscopic motion of a diatomic in a monatomic solvent has been studied using the molecular dynamics method and a model of Lennard-Jones spheres for the monatomics and two such spheres joined by a rigid bond for the diatomic. Data were generated by computer for three systems, each at the same density but varying in temperature. From these data autocorrelation functions were calculated for the following random quantities of the motion of the diatomic: orientation of the diatomic, velocity of its center of mass, angular velocity and momentum, mean square displacement of its center of mass, and the forces on the diatomic bond. Infrared and Raman band shapes and NMR relaxation times were determined from the above correlation functions.

The decay times of the correlation functions were found to be in the range of 0.25 to 2.5×10^{-12} sec. The band shapes were symmetrical and their bandwidth change reflects the change in inhomogeneous broadening with respect to temperature. The NMR relaxation times also behave correctly with respect to temperature and indicate which of the relaxation mechanisms studied is dominant.

Further studies are proposed to determine the reason for the discrepancies between the above calculated quantities and those quantities obtained from experimental data.

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1. INTRODUCTION

Many properties of molecules in solution are affected by their microscopic thermal motions. These properties can be divided into two general groups--spectral and transport properties. Spectral band shapes have been found to depend on thermal fluctuations of the rotational motion of the solute molecules; this applies to IR,[1,2,3] Raman,[1,2,4] and NMR[1-13] spectroscopy. Relaxation times for NMR[1-13] and rotation relaxation[1,2,4,5,14] times also depend on these fluctuations. The transport properties of 'singlet' and 'pair' diffusion[15,16] depend on thermal effects on the translational motion. Evaluation of these somewhat random motions can then lead to functional relationships for the above.

Zwanzig,[17] Abragam,[18] Gordon[2,4,5,19] and others have shown that correlation functions of variables of the thermal motion (described later) do yield measures of the fluctuations and can give the desired relationships. Unfortunately, these correlation functions involve interactions of the solute molecules with their environment on the microscopic level and, as a result, are incalculable at the moment. But theorists, hating a void, have developed many models and theories. Each of these involve approximations, of one degree or another, to determine the shape or functionality of the correlation function. Often an exponential form is assumed in order to obtain comparable results.

One of these models is molecular dynamics. Using a simple interaction potential and periodic boundary conditions, the motion of the solute and solvent can be followed by employing Newtonian mechanics and the predictor-corrector technique of Rahman[20, 21] or Verlet.[22] This model has the advantage of being precise within the potential chosen--no further approximations need be made. Its disadvantage lies in that the potential may not be completely real. Yet this model should mirror a real system within a small percentage error and, as such, should yield results that are in the right range and that change correctly (with respect to temperature and density). Anyway, using this model, time-dependent position, velocities, and acceleration data can be obtained and evaluated to determine the form and functionality of the above mentioned correlation functions.

2. THEORY

a) Correlation Functions

The time correlation function $c(t)$ of a dynamical variable $\underset{\sim}{A}$ is defined as the ensemble average $\langle\ \rangle$ of the scalar product of $\underset{\sim}{A}(t)$ and $\underset{\sim}{A}(t'+t)$,[17] i.e.,

$$c(t) = \langle \underset{\sim}{A}(t') \cdot \underset{\sim}{A}(t'+t) \rangle . \tag{1}$$

This function measures the decay of the average 'memory' of the system with time. The above expression involves only one variable and is called an autocorrelation function. Similarly a correlation function of two variables $c_1(t)$ can be defined;[17]

$$c_1(t) = \langle \underset{\sim}{A}(t') \cdot \underset{\sim}{B}(t'+t) \rangle \tag{2}$$

it would measure the average interaction 'memory'.

These correlation functions play the same role in transport processes as do the partition function in equilibrium statistical mechanics. The analogy breaks down in that for each transport process a different correlation function may be needed. For these processes there are two categories into which the correlation functions may be divided: those processes driven by external forces and those driven by internal (thermodynamics) forces. The first category can be described by a Kubo method,[23] the latter by a

number of more complex formulations.[17] This work is involved with
the thermodynamic forces.

These thermodynamic forces produce somewhat random thermal
motion (in the system being studied). Variables of this motion would
also be somewhat random. Then autocorrelation functions of these
variables would measure how that variable is randomized (the form
of the autocorrelation function) by this motion and how long it takes
for $\underset{\sim}{A}(t'+t)$ to become independent of the known initial condition $\underset{\sim}{A}(t')$.
That is, at some time τ

$$\langle \underset{\sim}{A}(t') \cdot \underset{\sim}{A}(t' + \tau) \rangle = \langle \underset{\sim}{A}(t') \rangle \langle \underset{\sim}{A}(t' + \tau) \rangle . \tag{3}$$

At this time the correlation function has decayed to zero, for the
first-order average of a random variable $\langle \underset{\sim}{A} \rangle$ is zero.

Although both the form of the correlation function and the time
τ give a measure of the randomizing character of the thermal motions,
only τ has to be considered to obtain a simple picture of what is
happening in the system. The size of τ is directly related to the
degree of fluctuations of the thermal motion. A large τ indicates that
$\underset{\sim}{A}$ is randomized slowly; this implies the fluctuations are slow and
small (on the average). A small τ indicates large and rapid fluctu-
ations.

If the system is a solution where $\underset{\sim}{A}$ is a variable of the motion
of the solute, $\underset{\sim}{A}$ can be considered as changing because of the inter-
actions of the solute with the solvent. These interactions can be

considered from two approaches; the first is the collisions between the solvent and the solute (assuming no solute-solute interactions) producing random motion on the part of the solute. The second is that the solute molecules exist in a number of types of local environments due to the inhomogeneity of the solvent. Changes in a local environment cause random motion in the solute molecule. Since these changes cause $\underset{\sim}{A}$ to undergo random motion, the autocorrelation function of $\underset{\sim}{A}$ should reflect a measure of their effect on the solute. These factors are responsible for various phenomena: inhomogeneous or collisional broadening of vibration-rotation spectral bands and pure rotational and NMR lines; spin relaxation in NMR; rotational and vibrational relaxation. And, as such, relationships should exist that will relate the above to appropriate correlation functions.

Before these relationships are developed (in the succeeding sections), the properties of correlation functions must be presented, for they are used to calculate these functions. They are given below:

1) Although the correlation function can be described as $\langle \underset{\sim}{A}(t') \cdot \underset{\sim}{A}(t'+t) \rangle$ it is dependent only on the variable t.

$$\langle \underset{\sim}{A}(t') \cdot \underset{\sim}{A}(t'+t) \rangle = \langle \underset{\sim}{A}(0) \cdot \underset{\sim}{A}(t) \rangle . \tag{4}$$

In other words, the starting point can be arbitrarily chosen.

2) The correlation functions exhibit time reversal properties;

$$C(t) = \langle \underset{\sim}{A}(0) \cdot \underset{\sim}{A}(t) \rangle$$

$$= \langle \underset{\sim}{A}(-t) \cdot \underset{\sim}{A}(0) \rangle$$

$$= \langle \underset{\sim}{A}(0) \cdot \underset{\sim}{A}(-t) \rangle$$

$$= C(-t) \tag{5}$$

The function $C(t)$ is symmetric about the $t = 0$ axis.

3) If the data from which the correlation function is calculated is equilibrium data and if, in a sufficiently long time, the variable $\underset{\sim}{A}$ for each system of the ensemble will pass through all values accessible to it, then time averaging can replace ensemble averaging.[32] For example, take $\underset{\sim}{A}^{(K)}$ for the Kth system of the ensemble and measure it over a long time. Divide this time into large intervals such that the behavior of $\underset{\sim}{A}^{(K)}$ in one interval is independent of its behavior in another. A large collection of such intervals should be as good a representative ensemble of the statistical behavior of $\underset{\wedge}{A}$ as the original ensemble. For this work, time averaging will replace ensemble averaging in the calculation of the correlation functions.

b) Wiener-Khintchine Theorem

It was shown in section (a) that there should exist relations between various phenomena and appropriate correlation functions. Such a relation has been developed for classical systems; it is called the Wiener-Khintchine theorem.[33] Using an electrical system as an example, where the random variable is the electric current through a resistor, the relationship between the power spectrum $G(\omega)$ (the average power dissipated per unit resistance per unit frequency band width) and the correlation function of the random current $C(t)$ is known to be

$$G(\omega) \;=\; \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} C(t)\, e^{-i\omega t}\, dt. \tag{6}$$

Since all spectroscopy involves energy being absorbed or emitted per unit time per unit 'resistance' term per unit frequency band width, there exists a power spectrum for each kind of spectroscopy. (The 'resistance' term can be, for a solution, the concentration per unit volume.) And since these power spectra depend on random variables of the solute (fluctuating thermal motions), there should exist a similar relationship as given above. Unfortunately, the mathematics and manipulations are more complicated for these quantum systems. They will be carried out in the next sections.

c) Vibration-Rotational and Pure Rotational IR Spectra

This relationship between the power spectrum and the correlation function can be generated in the Heisenberg approach to quantum mechanics.[2] The usual expression for an absorption band shape, in terms of transitions between quantum states (Schrödinger approach) where, for simplicity, the coupling between internal vibrations and the other degrees of freedom is neglected, is (Gordon's derivation)

$$I(\omega) \;=\; \frac{h\,c\,\sigma(\omega + \omega_0)}{4\pi^2(\omega + \omega_0)\left\{1 - \exp\left[-\hbar(\omega + \omega_0)/kT\right]\right\}}$$

$$I(\omega) \;=\; \sum_{if} \xi_i \left|\langle i|\underset{\sim}{\epsilon}\cdot M^{\nu}|f\rangle\right|^2 \delta\left[(E_f - E_i)/\hbar - \omega)\right], \tag{7}$$

where σ is the absorption cross section per molecule, ω_0 is the vibrational band center, ω is the frequency displacement from ω_0, $|i\rangle$ and $|f\rangle$ are initial and final quantum states for the (coupled) rotation-translational motion of the solute molecules with energy eigenvalues E_i and E_f, respectively. ζ_i is the Boltzmann factor for the initial rotation-translational state $|i\rangle$, assuming the sample is in thermal equilibrium. $\underset{\sim}{\epsilon}$ is the unit vector along the electric vector of the incident radiation. $\underset{\sim}{M}^\nu$ is the transition dipole moment vector for the particular vibration band ν. The first step in transforming to the Heisenburg approach is to represent the δ function by its Fourier integral,

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(i\omega t)\, dt. \tag{8}$$

Then

$$I(\omega) = \frac{1}{2\pi} \sum_{if} \zeta_i \langle i | \underset{\sim}{\epsilon} \cdot \underset{\sim}{M}^\nu | f \rangle \langle f | \underset{\sim}{\epsilon} \cdot \underset{\sim}{M}^\nu | i \rangle$$

$$\times \int_{-\infty}^{\infty} \exp\left[i(E_f - E_i)t/\hbar\right] e^{-i\omega t}\, dt. \tag{9}$$

The energy eigenvalues E_f and E_i are now expressed in terms of the Hamiltonian operator H for the rotational-translational motion, giving

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_{if} \zeta_i \langle i | \underset{\sim}{\epsilon} \cdot \underset{\sim}{M}^\nu | f \rangle$$

$$\times \langle f | e^{iHt/\hbar} \underset{\sim}{\epsilon} \cdot \underset{\sim}{M}^\nu e^{-iHt/\hbar} | i \rangle\, dt, \tag{10}$$

Now the sum over the complete set of final states may be performed:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_i \zeta_i$$

$$\times \langle i | \hat{\epsilon} \cdot \underset{\sim}{M}^{\nu} (e^{iHt/\hbar} \hat{\epsilon} \cdot \underset{\sim}{M}^{\nu} e^{-iHt/\hbar}) | i \rangle \, dt. \qquad (11)$$

Since $(e^{iHt/\hbar} \hat{\epsilon} \cdot \underset{\sim}{M}^{\nu} e^{-iHt/\hbar})$ is the Heisenberg operator for the direction of the transition dipole moment at time t, Eq. (11) may be expressed more concisely,

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle [\hat{\epsilon} \cdot \underset{\sim}{M}^{\nu}(0)][\hat{\epsilon} \cdot \underset{\sim}{M}^{\nu}(t)] \rangle \, dt. \qquad (12)$$

Where the brackets $\langle \ \rangle$ represent an equilibrium statistical average,

$$\langle Op \rangle = \sum_i \zeta_i \langle i | Op | i \rangle.$$

For an isotropic sample, the same result is obtained if we average over the polarization directions $\hat{\epsilon}$ of the radiation giving

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \frac{1}{3} \langle \underset{\sim}{M}^{\nu}(0) \cdot \underset{\sim}{M}^{\nu}(t) \rangle \, dt. \qquad (13)$$

Finally to convert to a spectrum normalized to unit area,

$$\hat{I}(\omega) = I(\omega) / \int_{Band} I(\omega) \, d\omega \qquad (14)$$

and to a vector $\hat{u} = M^{\nu} / \langle (M^{\nu})^2 \rangle^{\frac{1}{2}}$ along the direction of the transition dipole moment, Eq. (13) then becomes

$$\hat{I}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \hat{u}(0) \cdot \hat{u}(t) \rangle \, dt. \tag{15}$$

(Using a normalized spectrum largely eliminates dielectric effects on the local electric field due to the radiation. Only fluctuations about the average local field will effect the normalized spectrum.) This equation expresses the Heisenberg-type description of the infrared band shape: The distribution of absorption frequencies about the vibration frequency is the Fourier transform of the average motion of the transition dipole moment. Note that for a diatomic molecule, $\hat{u}$ is the unit vector along the bond, the symmetry axis.

Analogously, for a pure rotational spectrum[2] we obtain (in the Heisenberg picture)

$$\frac{3 \hbar \sigma(\omega)}{4\pi^2 \omega \left[1 - \exp(-\hbar\omega/kT) \right]} = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t}$$

$$\times \left[\langle \underset{\sim}{\mu}_1(0) \cdot \underset{\sim}{\mu}_1(t) \rangle + \sum_{i \neq 1} \langle \underset{\sim}{\mu}_1(0) \cdot \underset{\sim}{\mu}_i(t) \rangle \right] dt, \tag{16}$$

where $\underset{\sim}{\mu}_i$ is the permanent dipole moment of the ith molecule. Using the unit vector $\hat{u} = \underset{\sim}{\mu} / |\underset{\sim}{\mu}|$ and very dilute solutions

Eq. (16) becomes

$$\frac{3\hbar\sigma(\omega)}{4\pi^2\omega[1-\exp(\hbar\omega/kT)]} = \frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}\langle \underset{\sim}{u}_1(0)\cdot \underset{\sim}{u}_1(t)\rangle dt. \qquad (17)$$

Where it is assumed that there is no correlation between the dipole moments of the different solute molecules (the solvent is monatomic) and thus

$$\sum_{i=1}\langle \underset{\sim}{u}_1(0)\cdot \underset{\sim}{u}_i(t)\rangle = 0. \qquad (18)$$

Again for a diatomic molecule $\underset{\wedge}{u}$ is the unit vector along the bond.

The correlation function $\langle \underset{\wedge}{u}(0)\cdot \underset{\wedge}{u}(t)\rangle$ applies to both vibration-rotational and pure rotational band shapes. For pure rotational spectroscopy this is valid, for the above correlation function measures the fluctuations in the rotational motion of the solute molecule. For vibration-rotational spectra the inhomogeneity of the solvent affects both the rotations and the vibrations of the solute molecule. Gordon has assumed that the solvent has no effect on the vibrations. As a result of this, the frequency ω in $\exp(-i\omega t)$ is taken to be measured relative to the shifted vibration frequency. The shift is due to the effect of the solvent on the vibrational motion. By this the oscillations of the vibrational transition dipole moment are taken into account. These then may be considered to change with time only as the rotational motion changes the direction of the molecule.

d) Vibration-Rotational Raman Spectroscopy

A similar derivation can be performed for Raman scattering.[15] Starting with the polarizability formula for non-resonant Raman scattering, one obtains (Gordon's derivation)

$$\lambdabar^4 (d\sigma/d\Omega) = \sum_i \zeta_i \sum_f \left| \langle i | \hat{\epsilon} \cdot \hat{\alpha}^\nu \cdot \hat{\epsilon}^S | f \rangle \right|^2 \delta(\omega^S - \omega^I + \omega_\nu + \omega_f - \omega_i),$$

(19)

where $2\pi\lambdabar$ is the scattered wave length, $d\sigma/d\Omega$ is the differential light-scattering cross section per molecule, for the transition from the ground vibrational state to a vibrational state ν with vibrational energy $\hbar\omega_\nu$. $\hat{\alpha}^\nu$ is the off-diagonal matrix element of the electric polarizability tensor between the ground vibrational state of the molecule and vibrational state ν. We assume $\hat{\alpha}^\nu$ is constant in a coordinate system rotating with the molecule. ω^I is the frequency of the incident photon, whose electric vector is polarized along the unit vector $\hat{\epsilon}^I$; ω^S and $\hat{\epsilon}^S$ are the analogous quantities for the scattered photon.

Performing the same derivation as before (Section c) yields the following equation

$$\lambdabar^4 (d\sigma/d\Omega) =$$

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \langle [\hat{\epsilon}^I \cdot \hat{\alpha}^\nu(0) \cdot \hat{\epsilon}^S][\hat{\epsilon}^I \cdot \hat{\alpha}^\nu(t) \cdot \hat{\epsilon}^S] \rangle \exp(-i\omega t) \, dt$$

(20)

where $\underset{\sim}{\alpha}(t) = \exp(iHt/\hbar) \, \underset{\sim}{\alpha}(0) \, \exp(-iHt/\hbar)$ and $\omega = \omega^O - \omega^S - \omega_\nu$.

For spatially isotropic systems (liquids and gases) and for scattering in which the incident and scattered electric vectors are perpendicular, Eq. (20) can be expressed as[26]

$$\lambdabar^4 \frac{d\sigma}{d\Omega} = \frac{1}{60\pi} \int_{-\infty}^{\infty} \langle 3 \, \mathrm{Tr} \, \underset{\sim}{\alpha}^\nu(0) \cdot \underset{\sim}{\alpha}^\nu(t)$$

$$- [\mathrm{Tr} \, \underset{\sim}{\alpha}^\nu(0)][\mathrm{Tr} \, \underset{\sim}{\alpha}^\nu(t)] \rangle \, \exp(-i\omega t) \, dt \qquad (21)$$

where the traces are taken over the spatial indices of $\underset{\sim}{\alpha}^\nu$. This simplifies if we decompose the transition polarizability $\underset{\sim}{\alpha}^\nu$ into its spherical $(\underset{\sim}{\alpha}^\nu)$ and traceless $(\underset{\sim}{\beta}^\nu)$ parts:

$$\underset{\sim}{\alpha}^\nu = \underset{\sim}{\alpha}^\nu + \underset{\sim}{\beta}^\nu \qquad\qquad \mathrm{Tr} \, \underset{\sim}{\beta}^\nu = 0$$

$$\lambdabar^4 \frac{d\sigma}{d\Omega}\bigg|_\perp = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{1}{10} \langle \mathrm{Tr} \underset{\sim}{\beta}^\nu(0) \cdot \underset{\sim}{\beta}^\nu(t) \rangle \, \exp(-i\omega t) \, dt. \qquad (22)$$

Then the normalized intensity distribution is

$$\hat{I}(\omega) = \lambdabar^4 \frac{d\sigma}{d\Omega}\bigg|_\perp \bigg/ \int_{\mathrm{Band}} \lambdabar^4 \frac{d\sigma}{d\Omega}\bigg|_\perp d\omega$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{c}(t) \, \exp(-i\omega t) \, dt \qquad (23)$$

where

$$\hat{c}(t) = \frac{\langle \mathrm{Tr} \, \underset{\sim}{\beta}^\nu(0) \cdot \underset{\sim}{\beta}^\nu(t) \rangle}{\langle \mathrm{Tr} \, \underset{\sim}{\beta}^\nu(0) \cdot \underset{\sim}{\beta}^\nu(0) \rangle}. \qquad (24)$$

Now we consider the form of $\hat{c}(t)$ for a specific case of a totally symmetric vibration in a linear molecule. These vibrations (by definition) maintain the symmetric-top form of the molecule so that the anisotropic part of the transition polarizability has the form

$$B_{ij} = \text{constant} \times (u_i^z \, u_j^z - \tfrac{1}{3} \delta_{ij}) \tag{25}$$

where u_i^z is the ith component of a unit vector fixed along the symmetry axis (z) of the molecule and δ_{ij} is the Kronecker delta. Thus

$$\text{Tr}\,\beta(0) \cdot \beta(t) \propto \sum_{i,\,j=1}^{3} [u_i^z(0)\,u_j^z(0) - \tfrac{1}{3}\delta_{ij}][u_i^z(t)\,u_j^z(t) - \tfrac{1}{3}\delta_{ij}]$$

$$= \sum_{i,\,j=1}^{3} [u_i^z(0)\,u_j^z(0)\,u_i^z(t)\,u_j^z(t)] - \tfrac{1}{3} \tag{26}$$

and the normalized correlation function Eq. (24) is

$$\hat{c}(t) = \tfrac{1}{2} \langle 3 \sum_{i,\,j=1}^{3} u_i^z(0)\,u_j^z(0)\,u_i^z(t)\,u_j^z(t) - 1 \rangle. \tag{27}$$

In the classical limit $\underset{\sim}{u}(0)$ and $\underset{\sim}{u}(t)$ commute so, in this case, the correlation function reduces to

$$\hat{c}(t) = \langle P_2[\underset{\sim}{u}^z(0) \cdot \underset{\sim}{u}^z(t)] \rangle \tag{28}$$

where $P_2(x) = \tfrac{1}{2}(3x^2 - 1)$. This is the classical form. For a diatomic molecule $\underset{\sim}{u}^z = \underset{\sim}{u}$, the unit vector along the bond. Therefore,

for diatomic molecules,

$$\hat{I}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle P_2[\underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t)] \rangle \exp(-i\omega t)\, dt \tag{29}$$

Here, the correlation function measures the same thing as does $\langle \underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t) \rangle$ --the inhomogeneity of the solvent and how it changes with time. The difference between these two cases lies in the random variable (dipole moment vs. the polarizability tensor) and the method of measuring the absorption or emission experimentally.

e) NMR Spectroscopy

NMR spectroscopy has two points significantly different from IR and Raman spectroscopy. Firstly the resonance condition is described by a classical equation, $\omega = \gamma H_0$, where γ is the gyromagnetic ratio and H_0 the static field. Secondly the motional narrowing limit exists. The effect of the former makes the correlation function formulism somewhat classical in nature. This can be seen in the random operators involved in the correlation function. They are the fluctuating local fields (which effect the resonance condition) exerted on a nuclear spin by (1) a neighboring spin through magnetic dipole-dipole coupling, (2) the spin itself due to the rotational motion of the molecule, or (3) by fluctuating electric field gradients when the spin has a quadrupole moment. Each of these randomly change the resonance frequency and thus cause broadening. The local fields are also responsible for transferring energy to the lattice and allowing the spin system to relax to its equilibrium magnetism along the static field direction (this is spin-lattice relaxation, described by a time T_1).

They are also responsible for the relaxation of the magnetism that can appear in a plane perpendicular to the static field due to a '90 degree' pulse (this sets up a phase relationship between the spins). The couplings gradually destroy the phase relationship causing the magnetism to average to zero (spin-spin relaxation, described by a time T_2).

While the above couplings result in broadened bands, motional narrowing causes the bands to become very narrow. This is also a result of the classical nature of the calculation. In quantum systems the random operator does not change unless the local environments change. But in the NMR calculations the local fields change with any change in thermal motion relative to the direction of the static field. When this motion is sufficiently rapid the spin senses an average local field, not a time dependent one. Therefore, since all spins would feel the same average local field, the resonance is narrowed, as is the absorption band. In extreme narrowing where the band is very narrow, T_1 is equal to T_2.

Using this limit, which applies in liquids and dense gases, and employing Abragam's formalisms,[18] Gordon[5] has shown that the correlation function associated with Raman spectroscopy is also involved in the magnetic dipole-dipole and quadrupole spin relaxation processes. For magnetic dipole, spin-spin relaxation the formula (assuming $T_1 = T_2$) is[5,19]

$$T_1^{-1} = T_2^{-1} = \gamma^4 \hbar^2 I(I+1) \langle r^{-3} \rangle^2 \int_{-\infty}^{\infty} \langle P_2[\underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t)] \rangle \, dt , \qquad (30)$$

where γ is the magnetogyric ratio for the nuclei, r is the distance between the nuclei, and I is the nuclear spin.

When the nuclei have a spin of one or more, its charge distribution has a quadrupole moment, which interacts with intramolecular electric field gradients. When it is present this interaction usually provides the dominant mechanism for spin relaxation. The formula for this type of relaxation is [5, 19]

$$T_1^{-1} = T_2^{-1} = \frac{3(2I-1)}{40\,I^2(2I-1)} \left(\frac{e^2 qQ}{\hbar}\right)^2 \int_{-\infty}^{\infty} \langle P_2[\underset{\sim}{u}(0)\cdot\underset{\sim}{u}(t)]\rangle \, dt \qquad (31)$$

where $e^2 qQ/\hbar$ is the quadrupole coupling constant. These two formulae are valid in the extreme narrowing limit, which applies to liquids, except for very viscous ones.

Spin-rotational coupling, where the spins are weakly coupled to the rotational and translational motion, also causes spin relaxation. This coupling is an important relaxation process for nuclei of spin $\frac{1}{2}$. For a linear molecule, this interaction Hamiltonian is of the form

$$\mathcal{H} = -c\,\underset{\sim}{I}\cdot\underset{\sim}{J} \qquad (32)$$

where c is a spin-rotation constant, $\underset{\sim}{I}$ and $\underset{\sim}{J}$ are angular momenta of the nuclear spin and the molecular rotation, respectively. Using $\mathcal{H}$ of Eq.(32), Gordon gives for the relaxation time [4, 6]

$$T_1^{-1} = \frac{2\,c^2}{3\,\hbar^2} \int_0^{\infty} \langle \underset{\sim}{J}(0)\cdot\underset{\sim}{J}(t)\rangle \, dt$$

$$= \frac{2\,c^2}{3\,\hbar^2} \langle \underset{\sim}{J}(0)^2 \rangle \int_0^\infty \frac{\langle \underset{\sim}{J}(0) \cdot \underset{\sim}{J}(t) \rangle}{\langle \underset{\sim}{J}(0)^2 \rangle}\, dt$$

$$= \frac{2\,c^2}{3\,\hbar^2} \langle \underset{\sim}{J}(0)^2 \rangle \int_0^\infty \frac{\langle \underset{\sim}{\omega}(0) \cdot \underset{\sim}{\omega}(t) \rangle}{\langle \underset{\sim}{\omega}(0)^2 \rangle}\, dt. \tag{33}$$

(See the section on transport mechanisms under angular velocity for this transformation.)

f) Transport Mechanisms

i) Angular velocity

For the solute molecule, the rotational diffusion constant D_i about the ith principle axes depends on the angular velocity correlation function. The normalized angular velocity correlation function is

$$\langle \underset{\sim}{\omega}(0) \cdot \underset{\sim}{\omega}(t) \rangle / \langle \underset{\sim}{\omega}(0)^2 \rangle. \tag{34}$$

This is also the same correlation function for $\underset{\sim}{J}$ the angular momentum, for $\underset{\sim}{J} = I'\underset{\sim}{\omega}$ where I' is constant for a diatomic molecule;

$$\frac{\langle \underset{\sim}{J}(0) \cdot \underset{\sim}{J}(t) \rangle}{\langle \underset{\sim}{J}(0)^2 \rangle} = \frac{\langle \underset{\sim}{\omega}(0) \cdot \underset{\sim}{\omega}(t) \rangle}{\langle \underset{\sim}{\omega}(0)^2 \rangle}. \tag{35}$$

This correlation function is used to calculate the diffusion constant for i^{th} principal axis of rotation;[8]

$$D_i = \int_0^{\Delta t} \langle \omega_i(0) \cdot \omega_i(t) \rangle\, dt. \tag{36}$$

The rotational diffusion tensor principal axis system coincides with the principal symmetry axis of the molecule as does the principal inertial system. For a diatomic the axes of interest are perpendicular to the bond. Since the diffusion constant $D_i = kT/\xi_i$, the friction constant ξ_i can also be determined,[14]

$$kT/\xi_i = \int_0^\infty \langle \omega_i(t) \cdot \omega_i(0) \rangle \, dt. \tag{37}$$

ii) Diatomic center of mass motion

Fehder et al.[16] have calculated diffusion constants for a two-dimentional liquid. The diffusion constant for singlet diffusion D_S is related to the mean square displacement (MSD) correlation function

$$\Sigma(t) = \langle [\underset{\sim}{r}(t) - \underset{\sim}{r}(0)]^2 \rangle \tag{38}$$

and the velocity autocorrelation function

$$A_v(t) = \langle \underset{\sim}{v}(0) \cdot \underset{\sim}{v}(t) \rangle \tag{39}$$

by the following relations

$$D_S = \frac{1}{4} \dot{\Sigma}(t)$$

$$D_S = \frac{1}{2} \int_0^\infty A_v(t) \, dt. \tag{40}$$

They found that there was poor agreement between the two values of D_S. These equations should apply to the diatomic center of mass

displacement and velocity.

Note that the velocity and momentum correlation functions are related. The normalized translational momentum correlation function $c_p(t)$ is

$$c_p(t) = \langle \underset{\sim}{P}(0) \cdot \underset{\sim}{P}(t) \rangle / \langle \underset{\sim}{P}(0)^2 \rangle . \tag{41}$$

Therefore

$$\frac{\langle \underset{\sim}{P}_c(0) \cdot \underset{\sim}{P}_c(t) \rangle}{\langle \underset{\sim}{P}_c(0)^2 \rangle} = \frac{\langle \underset{\sim}{v}_c(0) \cdot \underset{\sim}{v}_c(t) \rangle}{\langle \underset{\sim}{v}_c(0)^2 \rangle} , \tag{42}$$

where c refers to the center of mass.

iii) Solvent transport mechanisms

The question of what effect the diatomic has on the solvent structure can be determined by the MSD and velocity auto correlation functions [20, 21, 15, 27] for the system. These functions are the same as the ones described in the previous section, except the vectors $\underset{\sim}{r}$ and $\underset{\sim}{v}$ refer to the solvent molecules now. Also, the relationship between the momentum and the velocity is the same.

These correlation functions can also be used to determine if the whole system is behaving approximately correctly. Further information of this type can be obtained from the velocities and speed distributions. The most accurate determination, of course, comes from the thermodynamic data (i.e., total energy, potential, kinetic energy, and pressure vs. time).

g) Total Force on the Bond

Berne, Jortner and Gordon[24,25] have developed a correlation function for vibrational relaxation for the high frequency components of the power spectrum of the rotational kinetic energy. The coupling between the diatomic and its environment (necessary to produce vibrational relaxation) requires the system and the diatomic to vibrate at similar frequencies. The frequencies of the diatomic are the vibrational frequencies, which are usually very high. The system frequencies can be determined in terms of phonons and they occur at lower values on the frequency scale. The high frequency components of the system frequencies are almost non-existent. Therefore, their formulation[24,25] must be restricted to diatomics with low frequencies of vibrations (i.e., a classical vibrator or oscillator). Keeping this in mind, the rate of radiationless decay (dependent on vibrational relaxation) is

$$W_{\nu_0 \to \nu_0 - 1} = \hbar^{-2} |q_{\nu_0, \nu_0 - 1}| \int_{-\infty}^{\infty} dt \, \exp(-i\omega_0 t) \langle f(0) \cdot t(t) \rangle \qquad (43)$$

where q is the deviation of the internuclear separation from its equilibrium value, and

$$f(t) = f_{int}(t) + f_{cent}(t) \qquad (44)$$

$f_{int}(t)$ is the force on the bond due to the solvent and $f_{cent}(t)$ is the centrifugal force. Then

$$f_{int}(t) = [\underset{\sim}{u}_1(t) \cdot \underset{\sim}{F}_1(t) + \underset{\sim}{u}_2(t) \cdot \underset{\sim}{F}_2(t)]/2$$

$$f_{cent}(t) = 2 E_r(t)/R_0 \tag{45}$$

where $\underset{\sim}{u}_i$ is the unit vector from the center of mass of the diatomic to the ith atom of the diatomic, $\underset{\sim}{F}_i$ is the force on that atom due to the solvent, E_r is the rotational kinetic energy and R_0 the equilibrium interatomic distance. Therefore

$$f(t) = [\{\underset{\sim}{u}_1(t) \cdot \underset{\sim}{F}_1(t) + \underset{\sim}{u}_2(t) \cdot \underset{\sim}{F}_2(t)\}/2 + 2E_r(t)/R_0]. \tag{46}$$

Since $\underset{\sim}{u}_1(t) = -\underset{\sim}{u}_2(t)$, Eq. (46) can be expressed as

$$f(t) = \left[\frac{\underset{\sim}{u}_1(t) \cdot \{\underset{\sim}{F}_1(t) - \underset{\sim}{F}_2(t)\}}{2} + 2 E_r(t)/R_0 \right]. \tag{47}$$

This can be simplified if the unit vector $\underset{\sim}{u}_1$ is replaced by $\underset{\sim}{u}$ which is the unit vector along the diatomic bond running from atom 2 to atom 1; then

$$f(t) = \left[\frac{\underset{\sim}{u} \cdot \{\underset{\sim}{F}_1(t) - \underset{\sim}{F}_2(t)\}}{2} + 2 E_r(t)/R_0 \right]. \tag{48}$$

The vibration relaxation time can be found from the correlation function $\langle f(0) f(t) \rangle$.

3. METHOD OF CALCULATION

a) Reduced Units

In order to obtain some generality in this model reduced units were used. The following is a list of those units:[15, 20]

Distance:

$$\underset{\sim}{r}^* = \frac{r}{\sigma} \qquad\qquad \sigma, \epsilon = \text{Lennard-Jones parameters} \qquad (49)$$

Velocity:

$$\underset{\sim}{v}^* = \underset{\sim}{v}/(\epsilon/m)^{\frac{1}{2}} \qquad\qquad m = \text{mass of an argon atom} \qquad (50)$$

Time:

$$\Delta\tau = \Delta t(\epsilon/m)^{\frac{1}{2}} \left(\frac{1}{\sigma}\right) \qquad\qquad (51)$$

Potential:

$$\underset{\sim}{\phi}(\underset{\sim}{r}_{ij}) = 4\epsilon\left\{\left(\frac{\sigma}{\underset{\sim}{r}_{ij}}\right)^{12} - \left(\frac{\sigma}{\underset{\sim}{r}_{ij}}\right)^{6}\right\}$$

$$\underset{\sim}{\phi}^*(\underset{\sim}{r}_{ij}) = 4\left\{\left(\frac{1}{\underset{\sim}{r}^*_{ij}}\right)^{12} - \left(\frac{1}{\underset{\sim}{r}^*_{ij}}\right)^{6}\right\} \qquad\qquad (52)$$

Acceleration:

$$\underset{\sim}{A}^*_i = \frac{\underset{\sim}{F}^*_i}{m^*} = \underset{\sim}{F}^*_i \qquad\qquad m^* = 1$$

$$A^*_{\underset{\sim}{i}} = -\sum_{j=1}^{NN} \frac{\partial \phi^*_{\underset{\sim}{j}}}{\partial r} \qquad NN = \text{nearest neighbor}$$

$$= 24 \sum_{j=1}^{NN} \left\{ \frac{2.0}{(r^*_{ij})^{13}} - \frac{1.0}{(r^*_{\underset{\sim}{ij}})^7} \right\}$$

$$= 24 \sum_{j=1}^{NN} \frac{1}{r^*_{\underset{\sim}{ij}}} \left\{ \frac{2.0}{(r^*_{\underset{\sim}{ij}})^{12}} - \frac{1.0}{(r^*_{\underset{\sim}{ij}})^6} \right\} \qquad (53)$$

$$Ax^*_i = \frac{\Delta x^*_{ij}}{r^*_{\underset{\sim}{ij}}} A^*_{\underset{\sim}{i}}$$

$$Ax^*_i = 24 \sum \frac{x^*_i - x^*_j}{r^*_{\underset{\sim}{ij}}{}^2} \left\{ \frac{2.0}{(r^*_{\underset{\sim}{ij}})^{12}} - \frac{1.0}{(r^*_{\underset{\sim}{ij}})^6} \right\} \qquad (54)$$

(similar for $A\overset{*}{y}_i$ and $A\overset{*}{z}_i$)

Temperature:

$$T^* = T/(\epsilon/k) \qquad (55)$$

$$3/2\,kT = \tfrac{1}{2}m\,v^2$$

$$T = \tfrac{1}{3}\left(\frac{m\,v^2}{k}\right)$$

$$T^* = \tfrac{1}{3}\frac{m\,v^2}{k} \cdot \frac{k}{\epsilon}$$

$$= \tfrac{1}{3}v^2/(\epsilon/m)$$

$$T^* = \tfrac{1}{3} v^{*2} = \tfrac{2}{3} (K.E.)^*. \tag{56}$$

This system loses some generality when the parameters ϵ, σ are chosen for some substance. This potential function is applicable for argon[20,21] and ϵ and σ are the argon parameters:

$$\sigma = 3.407 \,\text{Å}$$

$$\epsilon = 1.656 \times 10^{-14} \text{ ergs}$$

$$m = 6.6321 \times 10^{-23} \text{ g}$$

$$\epsilon/k = 119.8°K$$

$$(\epsilon/m)^{\frac{1}{2}} = 1.5804 \times 10^4 \text{ cm/sec}$$

$$\Delta\tau = 4.6386842 \times 10^{-3} \qquad \text{for } \Delta t = 10^{-14}.$$

Above, the potential function for the argon solvent is presented. The diatomic solute has to be represented by a more complicated function. We shall employ a two-center Lennard-Jones (6-12) potential. Choosing N_2 as the diatomic and using the data of Sweet and Steele[28] with an intercenter separation of $0.3\sigma_{N_2}$, the potential function for two interacting N_2 molecules is

$$\phi_{N_2-N_2}(\underset{\sim}{r}_{ij}) = \sum_{\substack{i=1 \\ j=1}}^{4} \epsilon_{N_2} \left[\left(\frac{\sigma_{N_2}}{\underset{\sim}{r}_{ij}} \right)^{12} - \left(\frac{\sigma_{N_2}}{\underset{\sim}{r}_{ij}} \right)^{6} \right]. \tag{57}$$

For N_2-A interactions the combining laws

$$\sigma_{AB} = \tfrac{1}{2}(\sigma_A + \sigma_B) \qquad \epsilon_{AB} = (\epsilon_A \epsilon_B)^{\frac{1}{2}} \tag{58}$$

must be used. Also there will be only two interaction distances not four as was the case for N_2-N_2.
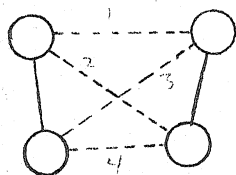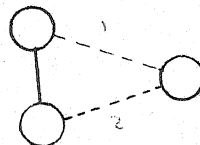
$$N_2-N_2 \qquad\qquad N_2-A$$

Then

$$\phi_{N_2\text{-}A}(\underset{\sim}{r}_{ij}) = 2 \sum_{i=1}^{2} \epsilon_{N_2A} \left[\left(\frac{\sigma_{N_2A}}{\underset{\sim}{r}_{ij}} \right)^{12} - \left(\frac{\sigma_{N_2A}}{\underset{\sim}{r}_{ij}} \right)^{6} \right] \qquad (59)$$

where $\sigma_{N_2} = 3.382\text{Å}$, $\epsilon_{N_2} = 138.9°K$. To express these quantities in reduced units, σ_{N_2A} and ϵ_{N_2A} are expressed in units of σ_A and ϵ_A, giving

$$\epsilon_{N_2A}/\epsilon_A = 1.0768$$

$$\sigma_{N_2A}/\sigma_A = 0.9965.$$

The only other quantity that needs to be re-expressed is the mass term in the acceleration formula,

$$\text{reduced } N_2 \text{ mass} = \frac{\text{mass of N}}{\text{mass of A}}$$

$$= 2.8518 .$$

Then

$$\phi^*_{N_2-A}(\underset{\sim}{r}_{ij}) = 2.1536 \sum_{i=1}^{2} \left[\left(\frac{0.9965}{\underset{\sim}{r}^*_{ij}} \right)^{12} - \left(\frac{0.9965}{\underset{\sim}{r}^*_{ij}} \right)^{6} \right] \tag{60}$$

$$A\overset{*}{x}_{N_2-A_i} = \sum_{i=1}^{2} 12 \times 2.8518 \sum_{j=1}^{NN} \frac{x^*_i - x^*_s}{\underset{\sim}{r}^{*2}_{ij}}$$

$$\times \left\{ 2.0 \left(\frac{0.9965}{\underset{\sim}{r}^*_{ij}} \right)^{12} - \left(\frac{0.9965}{\underset{\sim}{r}^*_{ij}} \right)^{6} \right\} . \tag{61}$$

This slight loss of generality isn't severe. The system can still be considered as having other constituents if they aren't much different from the N_2-A system (i.e., NO-A, CO-A, etc.).

b) Calculation Algorithm

The method of calculating the positions, velocities and the accelerations for every $\Delta\tau$ is a modified version of Rahman's[20] predictor-corrector technique. This algorithm is equationally summarized below (where N - 1, N, N + 1 refer to three consecutive $\Delta\tau$'s; Vx is the velocity in the x direction, etc.; Ax is the acceleration in the x direction, etc.; and x is the x position, etc.):

i) Predict the velocities

$$Vx^*_i(N+1) = Vx^*_i(N-1) + 2(\Delta\tau) Vx^*_i(N) \tag{62}$$

ii) Determine the positions

$$x^*_i(N+1) = x^*_i(N) + \tfrac{1}{2}(\Delta\tau)\left\{ Vx^*_i(N) + Vx^*_i(N+1) \right\} \tag{63}$$

iii) Calculate the accelerations

$$Ax_i^*(N+1) = 24 \sum_{j=1}^{NN} \frac{x_i^*(N+1) - x_j^*(N+1)}{r_{\sim ij}^{*\,2}} \left\{ \frac{2.0}{r_{\sim ij}^{*\,12}} - \frac{1.0}{r_{\sim ij}^{*\,6}} \right\}$$

(64)

iv) Calculate the velocities

$$Vx_i^*(N+1) = Vx_i^*(N) + \tfrac{1}{2}(\Delta\tau)\left\{Ax_i^*(N) + Ax_i^*(N+1)\right\}$$ (65)

v) Redetermine the positions

$$x_i^*(N+1) = x_i^*(N) + \tfrac{1}{2}(\Delta\tau)\left\{Vx_i^*(N) + Vx_i^*(N+1)\right\}$$

At this point the velocities have been predicted and their first corrections made. To insure that successive values of x_i differ only by some small number, iterations (as shown) can be performed. The number of iterations necessary to achieve this is very small (one or two). The above also applies for those quantities in the y and z directions.

The potential function $\phi^*(r^*)$, which determines the accelerations, has a cut-off distance of $r^* = 2.5$. This introduces a small error $[\phi^*(r^* > 2.5) < 0.01]$ but this has been shown to be small.[15] This cut-off also necessitates neighbor searching to find those neighbors within a sphere of radius 2.5 centered at the particle for which the potential is being calculated. This neighbor search is done as follows: all particles with $\Delta x^* > 2.5$ are ignored. Of the rest, all

those with $\Delta y^* > 2.5$ are deleted from the list. Then the remaining
are tested for $\Delta z^* > 2.5$. At this point there exists a cube of particle
neighbors with an edge of 5 units. These are then tested to see if the
distance between them and the central particle is greater than 2.5.
Those whose distance is less than 2.5 are the nearest neighbors over
which the potential on the central particle is determined.

The above equation for determining the accelerations apply only
to the monatomic solvent. For the diatomic a different approach must
also be taken in order to describe the diatomic rotational and trans-
lational motion. Since the diatomic is a rigid rotor, the complicated
and expensive inertial tensor analysis is not necessary.

Analysis of the angular momenta and the torques yields an
equation for the angular accelerations. The angular momentum $\underset{\sim}{L}$ is
given by
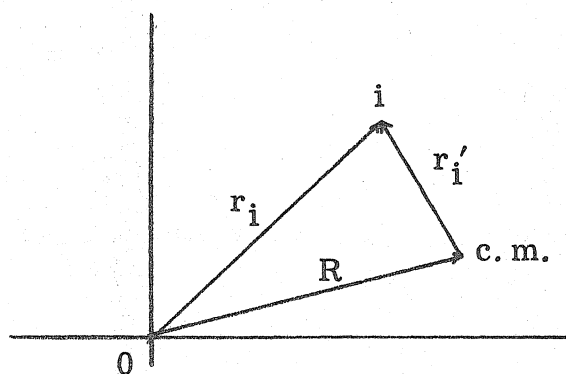
$$\underset{\sim}{r}_i = \underset{\sim}{r}_i' + \underset{\sim}{R}$$

$$\underset{\sim}{v}_i = \underset{\sim}{v}_i' + \underset{\sim}{V}$$

$$\underset{\sim}{V} = \frac{d\underset{\sim}{R}}{dt} \qquad \underset{\sim}{v}_i' = \frac{d\underset{\sim}{r}_i'}{dt}$$

$$\underset{\sim}{L} = \sum_i \underset{\sim}{r}_i \times \underset{\sim}{P}_i$$

Substituting for r_i and $P_i = m_i v_i$

$$\underset{\sim}{L} = \sum_i \underset{\sim}{R} \times m_i \underset{\sim}{V} + \sum_i \underset{\sim}{r}'_i \times m_i \underset{\sim}{v}'_i + \sum_i (m_i \underset{\sim}{r}'_i) \times \underset{\sim}{V} + \underset{\sim}{R}$$

$$\times \frac{d}{dt} \sum_i (m_i \underset{\sim}{r}'_i). \tag{67}$$

The last two terms disappear when the center of mass of the diatomic is taken as the origin. This origin is all that is needed to determine the angular accelerations.

$$\underset{\sim}{L} = \sum_i \underset{\sim}{R} \times m_i \underset{\sim}{V} + \sum_i \underset{\sim}{r}'_i \times \underset{\sim}{P}'_i \qquad \underset{\sim}{P}'_i = m_i v'_i \tag{68}$$

$$\underset{\sim}{L} = \underset{\sim}{R} \times M \underset{\sim}{V} + \sum_i \underset{\sim}{r}'_i \times \underset{\sim}{P}'_i. \qquad M = \sum_i m_i \tag{69}$$

The angular momentum L can then be divided into two parts: $R \times MV$ is the angular momentum of the diatomic about the origin 0 where the total mass M of the diatomic is concentrated at the center of mass of the diatomic. $\sum_i \underset{\sim}{r}'_i \times P'_i$ is the angular momentum of the diatomic about its center of mass. Then labelling the former as $L^{(e)}$ and the latter as $L^{(I)}$,

$$\underset{\sim}{L} = \underset{\sim}{L}^{(e)} + \underset{\sim}{L}^{(I)}$$

$$\underset{\sim}{L}^{(I)} = \underset{\sim}{L} - \underset{\sim}{L}^{(e)}$$

$$\dot{\underset{\sim}{L}}^{(I)} = \dot{\underset{\sim}{L}} - \dot{\underset{\sim}{L}}^{(e)}$$

By definition the torque N is related to $\dot{L}$

$$\dot{\underset{\sim}{L}} = \underset{\sim}{N}^{(e)} + \underset{\sim}{N}^{(I)} = \underset{\sim}{N}^{(e)}.$$

The internal torque $N^{(I)}$ is due to internuclear effects, which are not present for this problem. Therefore

$$\dot{\underset{\sim}{L}}^{(I)} = \underset{\sim}{N}^{(e)} - \underset{\sim}{L}^{(e)}$$

$$\dot{\underset{\sim}{L}}^{(I)} = \sum \underset{\sim i}{r} \times \underset{\sim i}{F} - \frac{d}{dt}(\underset{\sim}{R} \times M\underset{\sim}{V}) \tag{71}$$

where $\underset{\sim}{N}^{(e)} = \sum \underset{\sim i}{r} \times \underset{\sim i}{F}$; $\underset{\sim i}{F}$ is the force on the diatomic atom i. Then

$$\dot{\underset{\sim}{L}}^{(I)} = \sum_i \underset{\sim i}{r} \times \underset{\sim i}{F} - \{\frac{d\underset{\sim}{R}}{dt} \times M\underset{\sim}{V} + \underset{\sim}{R} \times \frac{d}{dt}(M\underset{\sim}{V})\}$$

$$\dot{\underset{\sim}{L}}^{(I)} = \sum_i \underset{\sim i}{r} \times \underset{\sim i}{F} - \underset{\sim}{V} \times M\underset{\sim}{V} - \underset{\sim}{R} \times \underset{\sim cm}{F}. \tag{72}$$

The second term on the right vanishes. But $\dot{\underset{\sim}{L}}^{(I)}$ = torque about the diatomic center of mass,

$$\dot{\underset{\sim}{L}}^{(I)} = I'\underset{\sim cm}{\alpha} \tag{73}$$

where $\underset{\sim cm}{\alpha}$ is the angular acceleration about the diatomic center of mass and $I' = 2 m_i r_i'^2$ is the moment of inertia. Therefore

$$\underset{\sim cm}{\alpha} = \dot{\underset{\sim}{L}}^{(I)}/I'$$

$$\alpha_{cm} = \left(\sum_i r_i \times F_i - R \times F_{cm} \right) / 2\, m_i r_i^2 . \tag{74}$$

For an homonuclear diatomic $m = m_1 = m_2$ and $r' = r_1' = r_2' =$ (bond length B/2).

$$\alpha_{cm} = \left(\sum_i r_i \times F_i - R \times F_{cm} \right) / \left(\frac{mB^2}{2} \right) . \tag{75}$$

In reduced units

$$\alpha_{cm}{}^* = \left(\sum_i r_i{}^* \times F_i{}^* - R^* \times F_{cm}{}^* \right) / \left(\frac{B^{*2}}{2} \right) , \tag{76}$$

or

$$\alpha_{cm}^* = \left(\sum_i r_i{}^* \times a_i{}^* - R^* \times a_{cm}{}^* \right) / \left(\frac{B^{*2}}{2} \right) . \tag{77}$$

Using this acceleration, the predictor-corrector technique can be applied to the angular velocities ω.

$$\omega_{cm}{}^*(N+1) = \omega_{cm}{}^*(N) + \tfrac{1}{2}(\Delta\tau)\left\{ \alpha_{cm}{}^*(N) + \alpha_{cm}{}^*(N+1) \right\} . \tag{78}$$

Then the linear rotational velocity can be determined

$$V_{rot}^* = \omega_{cm}{}^* \times r'$$

and the velocity on the ends of the diatomic calculated

$$V_i^* = V^* + V_{rot}^*$$

$$\underset{\sim}{V}_2{}^* = \underset{\sim}{V}{}^* - \underset{\sim}{V}_{rot}{}^* . \qquad (79)$$

From these velocities the positions of the diatomic can be determined by the technique described before. The iterative process is the same, except for the diatomic, $\underset{\sim}{\alpha}_{cm}{}^*$, $\underset{\sim}{\omega}_{cm}{}^*$, $\underset{\sim}{V}_{rot}{}^*$, $\underset{\sim}{V}{}^*$ are the vectors involved.

To apply this algorithm, it is necessary to retain two sets of data corresponding to the two previous time intervals in order to calculate the next one. Initially these do not exist and therefore must be supplied. The first set can be generated by uniformly placing the particles in a box with periodic boundary conditions and randomly assigning the velocities. The second cycle is produced by a less accurate algorithm. Instead of Eq. (62) the following was used;

$$V x_i{}^*(N+1) = V x_i{}^*(N) + (\Delta\tau)\, V x_i{}^*(N) . \qquad (80)$$

After the first two cycles have been calculated the reguar algorithm is applied. Then for every successive calculation the two preceding sets of data are retained.

This method of calculation will be applied to a system of 156 Lennard-Jones spheres (argon parameters) and a rigid diatomic (N_2 parameters) molecule. The box has dimensions of approximately six units of distance to an edge. This distance may vary slightly to produce different densities.

c) Correlation Functions

Since the correlation functions are independent of the initial times t' (Eq. (4)) and since for the range over which the correlation functions are calculated the system is in equilibrium, ensemble averaging can be replaced by time averaging.[15, 21-23] Then the function $\hat{A}(t') \cdot \hat{A}(t'+t)$ is calculated for many initial times t' and averaged for each value of t to give $\langle \hat{A}(0) \cdot \hat{A}(t) \rangle$. Normalization is determined by the average over the initial times $\hat{A}(t')^2$, giving $\langle \hat{A}(0)^2 \rangle$.

Since the correlation functions have the time reversal property, they are also calculated in reverse to yield a better statistical average. But since this system has only one diatomic, a great number of calculations have to be done (110 for some and 168 for others). Although these numbers are large, there should still exist some statistical fluctuation.

4. DATA

a) Systems Calculated

Three systems have been calculated: The first involves an A_2 diatomic in an argon solvent. (The potential function for this system is very simple for $\sigma_{A_2-A} = \sigma_A$ and $\epsilon_{A_2-A} = \epsilon_A$ and the masses are the same.) The last two systems involve a N_2-A solution. The thermodyanmic data for these systems are presented in Table 1. Plots of these data are presented for the first system (Figs. 1-4). There is much instantaneous fluctuation but the average kinetic energy, potential energy, and pressure are essentially constant. The total energy shows a slight increase with time but this increase involves a change of 0.0038 over 3000 intervals of calculation for an energy of approximately -2.0 units per particle. This is 0.19 per cent change--well within the error limit of the algorithm (1%).[15] Therefore this system is stable.

These same data were calculated and plotted for the N_2-A systems. As for the A_2-A system there were instantaneous fluctuations about some constant value. And again the change in the total energy over the 3000 intervals of calculation was within the 1% limit. These plots aren't presented in this thesis for they add nothing different from the A_2-A plots.

b) Solvent Calculations

As another check on the system stability the solvent data were analyzed to determine their mean square displacement (MSD) and velocity autocorrelation functions. Assuming that the diatomic doesn't effect these functions significantly, they should be similar to the argon calculations[15, 16, 21, 22]--the MSD function should become linear rapidly and the velocity autocorrelation function should die within 50 cycles. These functions are presented (for A_2-A) in Figs. 5 and 6 and do show the above characteristics.

The speed and velocity distributions were also calculated (for A_2-A) and compared to the theoretical Gaussian distributions. These distributions are presented in Figs. 7-10 and show that, in this respect, the solvent behaves correctly.

Although no data are presented for the N_2-A systems for the above functions, their results are the same; the MSD and the velocity correlation functions behave correctly and the velocity and speed distributions are Gaussian within statistical fluctuations.

A previous calculation[29] on a diatomic and one monatomic showed that the diatomic behaves correctly with respect to rotation and constant total energy. Therefore it is concluded that this system is stable and behaves correctly within its error limits.

c) Diatomic Calculations

i) Correlation functions

Presented in Table 2 are the correlation times (where the correlation function has an effective value of zero) for each of the six correlation functions mentioned before for each calculation. The data for the A_2-A system are different from the others because of its large bond distance (3.4Å) and its higher temperature (Table 1).

The first five correlation functions for the A_2-A system are presented (Figs. 11-13, 16, 19), but for the N_2-A systems only the first three of Table 2 are. The last three for these systems were excluded, except the bond forces correlation functions of calculation 2.

The angular velocity correlation functions are shown in Figs. 13-15. The A_2-A function is ignored for further calculations. For the N_2-A systems the relaxation times are almost identical. This is probably a statistical fluctuation problem. Both are at the same liquid densities and they are only separated by 30°K in temperature. This may cause their decay times to be close together.

The bond vector correlation functions $\langle \underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t) \rangle$ are presented in Figs. 16-18. The A_2-A system has a large correlation time because of the large moment of inertia that results from the long bond distance; this causes the diatomic to reorientate slower and increases the randomizing time. The $\langle P_2[\underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t)] \rangle$ correlation functions are shown in Figs. 19-21. Here also the A_2-A has a large correlation time. Since the A_2-A systems are so unreal they will not enter into any

further calculations; they are included for comparison only.

The N_2-A systems show a strong temperature dependence in the $\langle \underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t) \rangle$ and $\langle P_2[\underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t)] \rangle$ correlation functions. At $T^* = 0.9396$ (112°K) the correlation (or decay) times are over twice as large as these times at $T^* = 1.19$ (143°K). This strong dependence does not appear in the other correlation functions. This is probably due to the fact that at the higher temperature more collisions result in greater interaction with the repulsive part of the potential. Since the repulsive part of the Lennard-Jones (6-12) potential goes as the 12th power it has a stronger reorientational effect on the diatomic, causing the orientation to be randomized quicker. Therefore the correlation function will decay to zero in a smaller time. The only effect on the other correlation functions (those that don't involve the orientation of the diatomic) would be due to the increase in temperature only; they should charge slightly as the thermal motions are increased.

An interesting result appears in the bond forces correlation function. This function is presented for calculation 2 system in Fig. 22. It can be seen that the correlation function does not reach zero, except in some fluctuations. This is so because the function expressed in Eq. (48) does not take into account the average forces on the bond due to the solvent or the rotations (see Table 3). Only fluctuations about the average are important in this relaxation process; the average forces merely cause a change in the force constant. Then Eq. (48) has to be corrected to include this constant

$$f(t) = \left[\frac{u}{2} \cdot \{ F_1(t) - F_2(t) \} + 2\,Er/R_0 - F_{constant} \right]. \quad (81)$$

Then the correlation function will decay to zero as is shown for the corrected version in Fig. 23. The same occurs for the other systems.

In all the correlation functions there exist statistical fluctuations. These results from the small number of time intervals into which the whole calculation can be divided. Because of these fluctuations it is difficult to judge where the correlation function has reached zero. Fortunately, in those areas where comparisons are to be made (IR and Raman band shapes and NMR relaxation times) the correlation times are very different (by a factor of 2); therefore approximations to the forms and the decay times of the correlation functions should not invalidate these comparisons for these approximations are within 10% of the real situation for this model (molecular dynamics).

ii) Band shapes

According to Eq. (15) and Eq. (29) the appropriate correlation function can be Fourier transformed to produce IR and Raman band shapes. This was done for the N_2-A systems using smoothed functions for $\langle u(0) \cdot u(t) \rangle$ and $\langle P_2[u(0) \cdot u(t)] \rangle$ (Figs. 24-27); the resulting bands are presented in Figs. 28-31. These bands represent IR and Raman transitions that have been broadened by the motions of the solvent. Therefore the frequency ω in $I(\omega)$ represents the displacement frequency.

Although the calculations were performed for N_2-A systems,
they should apply (within a small error)to a CO–A system. The change
in the moment of inertia (important for the calculation of angular
accelerations) is small and the effect of the dipole-induced dipole
potential is small ($<1\%$) compared to the Lennard-Jones (6-12) potential
for such a system (the dipole moment of CO is very small $\approx .1$ Debye).
Making the above assumption, the $\langle \underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t) \rangle$ and $\langle P_2[\underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t)] \rangle$
functions are applied to CO and considered as data for CO in Argon.

There are two points to note about the band shapes. First, they
are symmetrical about $\omega = 0$. This is a consequence of the classical
nature of the calculation. The CO-A system is a quantum mechanical
one, with a complex $e^{-i\omega t}$ such that

$$\int_{-\infty}^{\infty} C(t)\, e^{-i\omega t}\, dt \;\neq\; 2 \int_{0}^{\infty} C(t)\, \cos \omega t\, dt. \tag{82}$$

This allows asymmetric band shapes. Therefore this analysis is
restricted to the symmetrical portion of such a band. The more
symmetrical the experimental band is, the more applicable is the
above analysis.

The second is to note that the change in the bandwidths mirrors
the change in the decay times of the appropriate correlation functions.
More will be said on this later.

iii) Relaxation times

The relaxation times for the three types of spin-lattice coupling
mentioned before were also calculated. Using a spin-rotation

constant for N^{15} of 1.38×10^5 radians/sec [30] and a value of 3.35×10^7 radians/sec for $e^2qQ/\hbar$, [31] these times were determined and are presented in Table 5 for the N_2-A systems. The quadrupole coupling is by far the strongest and the dominant relaxation mechanism for N^{14} at these temperatures and densities. The spin-rotational coupling yields relaxation times two orders of magnitude smaller than the dipole-dipole coupling under these conditions. The long time for the dipole-dipole coupling results from the fact that a nuclear spin experiences a somewhat average local field (extreme narrowing limit) rather than a fluctuating local field which allows energy to be transferred to the lattice. Then at higher temperatures (at the same density), where the above limit is even more applicable, the relaxations times should be even longer for those couplings that don't directly depend on the thermal motion of N_2 (dipole-dipole and quadrupolar couplings). This effect occurs in the N_2-A systems calculated as is shown in Table 5. Note that the spin-rotation coupling undergoes an opposite effect with respect to temperature.

5. DISCUSSION AND POSSIBLE ANALYSIS

a) IR and Raman Spectroscopy

The above data were obtained for systems of liquid densities and low temperatures. It indicates a strong temperature dependence in the decay times of the correlation functions for IR and Raman spectroscopy. Then at higher temperatures (still liquid densities) the decay times should become very small. Yet Gordon has calculated from experimental data these times for CO dissolved in liquid $CHCl_3$, CCl_4, $N-C_7H_{16}$, and argon gas and obtained values for these times of approximately 3×10^{-13} to 7×10^{-13}.[2,19] This would seem to indicate that increasing the temperature beyond 141°K has less effect on the decay times than decreasing it below 141°K. A room temperature calculation for N_2-A at liquid densities would show whether this phenomena actually occurs.

Furthermore, the correlation functions ($\langle u(0) \cdot u(t) \rangle$) calculated by Gordon have rather interesting but somewhat unexplainable forms.[2,17] For liquid CCl_4 and $CHCl_3$ a shoulder appears, while for CO in dilute gas the correlation function dips below zero significantly. These forms can be checked by the above calculation and by another one at a gas density but at the same temperature.

The same inconsistencies between this calculated data and Gordon's exist for his $\langle P_2[u(0) \cdot u(t)] \rangle$ calculated for liquid N_2. There exists a shoulder in the correlation function[2,4] that doesn't appear in these calculations even though the temperature-density conditions are

similar. The above analysis as applied to Raman spectroscopy should throw some light on this problem.

Gordon's correlation function times and forms are derived from Fourier transforms of experimental lines and bands. If these experimental data involve any factor that is not included in Gordon's formulism, the times and forms of the correlation functions will be incorrect. If the vibrational transition is affected by the solvent inhomogeneities, the band is further broadened and the decay times become shorter. A multiple peaked band shape causes the correlation function to have shoulders or dips. Then calculation of the correlation functions by molecular dynamics would yield an evaluation of Gordon's formulism, his correlation functions, and the systems in which his formulism is applicable.

b) NMR Spectroscopy

The above analysis can also be applied in this area to give the temperature dependence of the relaxation times. Also the dominant mechanism for relaxation can be determined. Further data on the magnetic dipole-dipole relaxation process should result in a clearer picture of the effect of the thermal motion of the diatomic on the relaxation time.

c) Decay Times and Potential Functions

It was postulated that the temperature dependence of the decay times of the IR and Raman correlation functions depended on what part of the potential function applied most on the average. The effect

of the repulsive wall of the potential function can be determined by trying potential functions other than the Lennard-Jones (6-12). One possibility would be the hard sphere potential

$$
\begin{aligned}
\phi &= 0 \qquad \underset{\sim}{r} \geq a \\
&= \frac{c}{\underset{\sim}{r}^{-6}} \qquad \underset{\sim}{r} > a .
\end{aligned}
$$
(83)

This analysis should give the dependence of the correlation function on potential functions and an evaluation of the potential functions used.

d) Functionality of the Correlation Function

In working with formulisms similar to Gordon's many authors have had to assume various functional forms for the correlation functions. These functions involve mainly exponentials[8, 11, 14] such as

$$
e^{-t/\tau}; \quad e^{-(t/\tau)^2}; \quad [1-t/\tau]e^{-t/\tau}
$$
(84)

where τ is the decay time. Gordon has postulated polynomial forms for $\langle \underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t) \rangle$ and $\langle P_2[\underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t)] \rangle$;[2, 19]

$$
\langle \underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t) \rangle = 1 - (\frac{kT}{I})t^2 + \left[\frac{1}{3}(\frac{kT}{I})^2 + (\frac{1}{24I})^2 \langle (OV)^2 \rangle\right]t^4 + O(t^6)
$$
(85)

$$
\langle P_2[\underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t)] \rangle = 1 - (\frac{3kT}{I})t^2 + \left[4(\frac{kT}{I})^2 + \frac{1}{8I^2} \langle (OV)^2 \rangle\right]t^4 + O(t^6)
$$
(86)

where T is the temperature, I the molecular moment of inertia, and OV the torque on a molecule due to its neighbors.

All these forms can be analyzed to check their validity and their effects if they are used. These effects could be quite striking in the band shapes they give for IR and Raman spectroscopy. Since in NMR spectroscopy only the rate of relaxation is sought, these effects should be much smaller.

This analysis allows one to calculate the correlation functions that others have had to approximate. This leads to analyses in the opposite direction, from the correlation functions back to the quantity that depends on it. Thus many formulisms or their applications can be checked. This is the advantage of the molecular dynamics approach.

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Table 1

Calcuation	System	δ^*	T^*	P. E.*	E^*	P^*
1	A_2-A	0.7341	1.533	-4.32	-2.02	1.20
2	N_2-A	0.7341	1.190	-4.93	-3.16	0.895
3	N_2-A	0.7341	0.9396	-5.14	-3.73	0.679

δ^* is the reduced density, T^* the reduced temperature, P. E. * the reduced potential energy, E^* the reduced total energy, and P^* the reduced pressure.

Table 2

Correlation Function	Calculation System	Correlation Times (10^{-13} sec)		
		1 A_2-A	2 N_2-A	3 N_2-A
$\langle \underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t) \rangle$		84.0	10.63	21.25
$\langle P_2[\underset{\sim}{u}(0) \cdot \underset{\sim}{u}(t)] \rangle$		80.0	3.45	8.50
$\langle \underset{\sim}{\omega}(0) \cdot \underset{\sim}{\omega}(t) \rangle$		4.0	2.40	2.50
$\langle [\underset{\sim}{r}(0) - \underset{\sim}{r}(t)]^2 \rangle$		4.59×10^{12} cm^2/sec	1.52×10^{12} cm^2/sec	1.86×10^{12} cm^2/sec
$\langle \underset{\sim}{v}_c(0) \cdot \underset{\sim}{v}_c(t) \rangle$		4.6	3.50	5.7
$\langle f(0)\, f(t) \rangle$		2.0	1.80	2.1

Table 3

Calculation	System	Average Value of Forces on the Bond		
		f_{int}	f_{cent}	$f_{int} + f_{cent}$
1	A_2-A	-4.68	3.05	-1.63
2	N_2-A	-15.44	21.46	6.02
3	N_2-A	-13.84	13.89	0.046

Table 4

Calculation	Bandwidths ($\Delta\omega \times 10^{-13}$)	
	IR Band	Raman Band
2	0.7735	2.0995
3	0.3808	1.222

Table 5

Calculation	Relaxation Times for Spin-Lattice Couplings		
	Spin-rotation	Magnetic dipole-dipole	Quadrupolar
2	7.46×10^2 sec (N_2^{15})	4.62×10^4 sec (N_2^{15}) 6.70×10^4 sec (N_2^{14})	8.61 msec (N_2^{14})
3	9.64×10^2 sec (N_2^{15})	2.84×10^4 sec (N_2^{15}) 4.12×10^4 sec (N_2^{14})	5.29 msec (N_2^{14})

ANGULAR VELOCITY AUTOCORRELATION
FUNCTION (DIATOMIC)
CALCULATION #1

TIME

Figure 13

ANGULAR VELOCITY AUTOCORRELATION
FUNCTION (DIATOMIC)

CALCULATION #2

Figure 14

ANGULAR VELOCITY AUTOCORRELATION FUNCTION (DIATOMIC)

CALCULATION #3

TIME

Figure 15

BOND VECTOR AUTOCORRELATION
FUNCTION (DIATOMIC)

CALCULATION #1

$\langle \vec{u}(o) \cdot \vec{u}(t) \rangle$

TIME

Figure 16

BOND VECTOR AUTOCORRELATION FUNCTION (DIATOMIC)

$\langle \vec{u}(o) \cdot \vec{u}(t) \rangle$

CALCULATION #2

TIME

Figure 17

BOND VECTOR AUTOCORRELATION
FUNCTION (DIATOMIC)

CALCULATION #3

$\langle \vec{u}(o) \cdot \vec{u}(t) \rangle$

TIME

255×10^{-14}

Figure 18

$\langle P_2 [\vec{u}(o) \cdot \vec{u}(t)] \rangle$

CALCULATION #1

P_2 = SECOND LEGENDRE
POLYNOMIAL

Figure 19

Figure 20

$$\langle P_2 [\vec{u}(o) \cdot \vec{u}(t)] \rangle$$

CALCULATION #3

P_2 = SECOND LEGENDRE
POLYNOMIAL

TIME

Figure 21

BOND FORCES AUTOCORRELATION
FUNCTION (DIATOMIC)
CORRECTED

CALCULATION #2

Figure 22

BOND FORCES AUTOCORRELATION
FUNCTION (DIATOMIC)
UNCORRECTED

CALCULATION #2

TIME

Figure 23

BOND VECTOR AUTOCORRELATION
FUNCTION (DIATOMIC)
SMOOTHED
$\langle \vec{u}(o) \cdot \vec{u}(t) \rangle$

CALCULATION #2

TIME

16×10^{-14}

Figure 24

BOND VECTOR AUTOCORRELATION
FUNCTION (DIATOMIC)
SMOOTHED
$\langle \bar{u}(o) \cdot \bar{u}(t) \rangle$

CALCULATION #3

TIME

Figure 25

$$\langle P_2 [\vec{u}(o) \cdot \vec{u}(t)] \rangle \text{ SMOOTHED}$$

CALCULATION #2

P_2 = SECOND LEGENDRE POLYNOMIAL

TIME

Figure 26

$$\langle P_2 \left[\vec{u}(o) \cdot \vec{u}(t) \right] \rangle$$ SMOOTHED

CALCULATION #3

P_2 = SECOND LEGENDRE POLYNOMIAL

TIME

Figure 27

IR BAND $I(\omega)$
NORMALIZED
CALCULATION #2

I(ω)

FREQUENCY ($\omega \times 10^{-13}$)

Figure 28

IR BAND $I(\omega)$
NORMALIZED
CALCULATION #3

$I(\omega)$

1.0

0.0

-6.5   -5.2   -3.9   -2.6   -1.3   0.0   1.3   2.6   3.9   5.2   6.5

FREQUENCY ($\omega \times 10^{-13}$)

Figure 29

RAMAN BAND I(ω)
NORMALIZED
CALCULATION #2

I(ω)

FREQUENCY ($\omega \times 10^{-13}$)

Figure 30

RAMAN BAND I(ω)
NORMALIZED
CALCULATION #3

I(ω)

1.0

0.0

FREQUENCY ($\omega \times 10^{-13}$)

-6.5 -5.2 -3.9 -2.6 -1.3 0.0 1.3 2.6 3.9 5.2 6.5

Figure 31