MOLECULAR DYNAMICS AND INTERACTIONS
IN LIQUIDS

Dissertation

Presented to the Graduate Council of the North Texas State University in Partial Fulfillment of the Requirements

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DOCTOR OF PHILOSOPHY

By

Jen Hui Chen, B.S.
Denton, Texas
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Various modern spectroscopies have been utilized with considerable success in recent years to probe the dynamics of vibrational and reorientational relaxation of molecules in condensed phases. We have studied the temperature dependence of the polarized and depolarized Raman spectra of various $A_1$ modes in the following dihalomethanes: dibromomethane, dichloromethane, dichloromethane-$d_2$, and bromochloromethane. Among other observed trends, we have found the following: Vibrational dephasing times calculated from the $\nu_2$ (CH$_2$ bend) and $\nu_3$ (C-Br stretch) lineshapes are of the same magnitude in CH$_2$Br$_2$. The vibrational dephasing time of $\nu_1$ [C-D(H) stretch] is twice as long in CD$_2$Cl$_2$ as in CH$_2$Cl$_2$, and the relaxation time of $\nu_3$ (C-Cl stretch) is greater in CH$_2$Cl$_2$ than in CD$_2$Cl$_2$. Isotropic relaxation times for all three stretching vibrations are significantly shorter in CH$_2$BrCl than in CH$_2$Cl$_2$ or CH$_2$Br$_2$. Application of the Kubo model revealed that derived modulation times are close to equal for equivalent vibrations in the various dihalomethanes. Thus, the more efficient relaxation of the $A_1$ modes in CH$_2$BrCl can be attributed almost entirely to the broader mean squared frequency perturbation of the vibrations in this molecule.
The frequency shifts and vibrational relaxation times of the $v_1$ mode of CH$_2$Cl$_2$ and CD$_2$Cl$_2$ were measured in a number of the mixtures. It was observed that displacements of the band center were not correlated to electron donating capability, but rather to dispersion energy variations among the solutions. It was found, though, that relaxation times decreased dramatically in Lewis basic solvents. The same results were reported in an earlier study on chloroform. Therefore, this latter property of the $v_1$ band provides a more sensitive measure of hydrogen bond interactions involving CH bonds.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>List</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>v</td>
</tr>
</tbody>
</table>

**Chapter**

I. MOLECULAR DYNAMICS IN LIQUIDS BY RAMAN LINESHAPEs  
   Parameters of Vibrational Bands  
   Relaxation Processes  
   Theoretical Models  

II. RAMAN LINESHAPE STUDIES OF DIHALOMETHANES  
   Molecular Reorientation and Vibrational Relaxation in CH$_2$Br$_2$  
   Vibrational Relaxation in CH$_2$Cl$_2$ and CD$_2$Cl$_2$  
   Vibrational Relaxation in CH$_2$BrCl. A Comparison with Dibromo and Dichloromethane  

III. SOLVENT DEPENDENCE OF VIBRATIONAL FREQUENCIES AND RELAXATION TIMES IN DICHLOROMETHANE  
   Experimental Results and Discussion  

APPENDIX  

BIBLIOGRAPHY  

111
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>Rotational and Vibrational Dephasing Parameters in CH₂Br₂</td>
<td>26</td>
</tr>
<tr>
<td>II.</td>
<td>Vibrational and Rotational Relaxation Parameters in CH₂Cl₂</td>
<td>40</td>
</tr>
<tr>
<td>III.</td>
<td>Vibrational and Rotational Relaxation Parameters in CD₂Cl₂</td>
<td>41</td>
</tr>
<tr>
<td>IV.</td>
<td>Summary of Vibrational Relaxation Parameters in the Dihalomethanes</td>
<td>48</td>
</tr>
<tr>
<td>V.</td>
<td>Frequency Shifts and Vibrational Relaxation Times of Dichloromethane in Solution</td>
<td>63</td>
</tr>
</tbody>
</table>
## LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Comparison of Lorentzian and Gaussian Lineshapes</td>
<td>6</td>
</tr>
<tr>
<td>2.</td>
<td>Correlation Function of Lorentzian and Gaussian Peaks</td>
<td>8</td>
</tr>
<tr>
<td>3.</td>
<td>Comparison of the Isotropic, Anisotropic, and Reorientational Correlation Functions of a Given Vibrational Mode</td>
<td>12</td>
</tr>
<tr>
<td>4.</td>
<td>Temperature Dependence of Reorientational Correlation Times</td>
<td>28</td>
</tr>
<tr>
<td>5.</td>
<td>Temperature Dependence of Vibrational Correlation Times and Fischer-Laubereau Dephasing Times</td>
<td>32</td>
</tr>
<tr>
<td>6.</td>
<td>Temperature Dependence of Modulation and Collision Times</td>
<td>37</td>
</tr>
<tr>
<td>7.</td>
<td>Temperature Dependence of Experimental Relaxation Times (1/e Values)</td>
<td>50</td>
</tr>
<tr>
<td>8.</td>
<td>Dependence of the Gas-Solution Frequency Shifts on Solvent Polarizability</td>
<td>65</td>
</tr>
<tr>
<td>9.</td>
<td>Experimental Vibrational Relaxation Times Versus Theoretical Times Calculated from the IBC Model</td>
<td>69</td>
</tr>
</tbody>
</table>
Parameters of Vibrational Bands

In vibrational spectroscopy, one encounters two extremes in the experimental lineshape, which are termed Lorentzian and Gaussian bands.

For Lorentzian bands, the spectral lineshape is given by:

\[ I_L(\omega) = A \left\{ 1 + \frac{(\omega - \omega_0)^2}{\Delta^2} \right\}^{-1} \]

where \( A \) is the intensity at the peak frequency \( \omega_0 \) (i.e. the peak height), \( \omega_0 \) is the frequency at the peak center, and \( \Delta \) is the half-width at half the peak maximum (HWHM).

For Gaussian peaks, the intensity as a function of frequency is given by the equation:

\[ I_G(\omega) = A \exp \left\{ -\ln 2 \cdot \frac{(\omega - \omega_0)^2}{\Delta^2} \right\} \]

with the same parameters as for a Lorentzian peak.

It is of interest to compare relative intensities of these two lineshapes at various displacements from the peak center.

For \( \omega - \omega_0 = \Delta \), \( I_L = A/2 \) and \( I_G = A/2 \)

For \( \omega - \omega_0 = 2\Delta \), \( I_L = A/5 \) and \( I_G = A/16 \)
One sees that Gaussian peaks decrease more rapidly than Lorentzian peaks in the wings, and approach triangular functions.

**Spectral Moments**

The spectral moment is an important property of the vibrational lineshape. The general equation for the $n^{\text{th}}$ moment is:

$$M_n = \int (\omega')^n \hat{I}(\omega') \, d(\omega')$$

where $\omega'$ is the displacement from the peak center and $\hat{I}(\omega')$ is the normalized intensity.

As defined, the zeroth moment is equal to one. If, instead we use non-normalized intensities, $M_0$ is simply the area of the peak.

$$M_0 = \int (\omega')^0 I(\omega') \, d(\omega')$$

$$= \int I(\omega') \, d(\omega')$$

The first moment is defined by:

$$M_1 = \int (\omega')^1 \hat{I}(\omega') \, d(\omega')$$

Since both Lorentzian and Gaussian lineshapes are symmetric around their peak centers, the integrand is an odd function of frequency, and the first moment becomes zero.

The second moment is given by:

$$M_2 = \int (\omega')^2 \hat{I}(\omega') \, d(\omega')$$

The physical meaning of the spectral second moment is the average squared frequency displacement from the peak center.
Peak Area and Second Moment of a Lorentzian Peak

\[ M^L_O = \int I_L(\omega') \, d\omega' \]
= \[ \int A \left[ 1 + \left( \omega' / \Delta \right)^2 \right]^{-1} \, d\omega' \]
= \[ \pi A \Delta \]
= \[ 3.14 A \Delta \]

\[ M^L_2 = \int (\omega')^2 \hat{I}_L(\omega') \, d\omega' \]
= \[ \int (\omega')^2 I_L(\omega') \, d\omega' / \int I_L(\omega') \, d\omega' \]
= \[ \int (\omega')^2 A \cdot [1 + (\omega' / \Delta)^2]^{-1} \, d\omega' / M^L_O \]
= \[ 2A \Delta^2 \int \{ (\omega')^2 / [\Delta^2 + (\omega')^2] \} \, d\omega' / M^L_O \]
+ \[ 2A \Delta^2 \int \{ (\omega')^2 / (\omega')^2 \} \, d\omega' / M^L_O \]
+ \[ \infty \]

Peak Area and Second Moment of a Gaussian Peak

\[ M^G_O = \int I_G(\omega') \, d\omega' \]
= \[ \int A \cdot \exp[-\ln2(\omega' / \Delta)^2] \, d\omega' \]
= \[ (\pi/\ln2)^{1/2} \cdot A \Delta \]
= \[ 2.13 A \Delta \]

One sees that the area of a Gaussian peak is almost the same as that of a triangle, \( 2A \Delta \), and is smaller than the area of a Lorentzian peak with the same height, \( A \), and width, \( \Delta \).

\[ M^G_2 = \int (\omega')^2 \hat{I}_G(\omega') \, d\omega' \]
= \[ \int (\omega')^2 I_G(\omega') \, d\omega' / \int I_G(\omega') \, d\omega' \]
One observes that the second moment of a Gaussian peak is finite, whereas the spectral second moment of a Lorentzian peak diverges. Experimental peaks are actually a mixture of the Lorentzian and Gaussian lineshapes. Therefore, the value of $0.72\Delta^2$ represents a lower limit on experimental spectral second moments.

**Fourier Transforms**

The correlation function $G(t)$, which is in the time domain, can be obtained by mathematical Fourier transformation of the frequency domain spectral intensity function $I(\omega)$. The definition of a Fourier transformation and its inverse is given by the following equations:

$$G(t) = \int I(\omega) e^{i\omega t} d\omega$$

$$I(\omega) = (2\pi)^{-1} \int G(t) e^{-i\omega t} dt$$

When Fourier transformation is performed on a Lorentzian peak one obtains:

$$G(t) = \int A \left[1 + \left(\frac{\omega}{\Delta}\right)^2\right]^{-1} e^{i\omega t} d\omega$$

$$= A\Delta\pi \cdot \exp(-\Delta|t|)$$

$$= C \cdot \exp(-\Delta|t|) \text{ where } C = A\Delta\pi$$
\[ C \cdot \exp(-t/\tau) \text{ where } \tau = 1/\Delta \]

C is a normalization constant which equals unity if the Lorentzian function is normalized. Thus, one can see that a larger half width at half maximum corresponds to a faster decay of \( G(t) \). Note that the units of \( \Delta \) are radians/sec, so the width in cm\(^{-1}\) must be multiplied by \( 2\pi c \) to convert it into the correct units.

On the other hand, after Fourier transformation of a Gaussian peak, the result is as follows:

\[
G(t) = \int A \cdot \exp[-\ln2(\omega/\Delta)^2] \; e^{i\omega t} \; d\omega \\
= (\pi/\ln2)^{1/2} A \Delta \cdot \exp[-\Delta^2 t^2/(4\ln2)] \\
= C \cdot \exp[-\Delta^2 t^2/(4\ln2)] \text{ where } C = (\pi/\ln2)^{1/2} A \Delta \\
= C \cdot \exp[-(4\ln2)^{-1} \cdot (t/\tau)^2] \\
= 2.13 A \Delta \cdot \exp[-(4\ln2)^{-1} \cdot (t/\tau)^2]
\]

One sees that the Fourier transformation of a Gaussian peak is a Gaussian function of time. And again, C is equal to unity if the Gaussian peak is normalized. A large value of \( \Delta \) (i.e., a broad peak) leads to a fast decay (short \( \tau \)).

Figure 1 shows Lorentzian and Gaussian lineshapes with identical heights and half-widths and Figure 2 displays the Fourier transformation of these bands.

In vibrational lineshape studies, one objective is to determine the relaxation time \( \tau \). Three general methods to calculate the value of \( \tau \) are as follows:
FIGURE 1

COMPARISON OF LORENTZIAN AND GAUSSIAN LINESHAPES

The height and width are identical. The solid curve represents the Lorentzian and the dotted curve represents the Gaussian.
FIGURE 2

CORRELATION FUNCTION OF LORENTZIAN AND GAUSSIAN PEAKS

This is plotted as $\ln G(t)$ vs. time. The straight line is the transformation of the Lorentzian and the non-linear curve is the transformation of the Gaussian. In both cases the half-width at half-maximum is 5 cm$^{-1}$. 
(A) measure the half-width; \( \tau = \delta^{-1} = (2\pi c \Delta)^{-1} \)
(B) evaluate \( t \) for \( G(t) = e^{-t} \)
(C) evaluate the area under \( G(t) \)

Relaxation Processes

Generally, the broadening of vibrational spectral lines in condensed phases results from a combination of rotational and vibrational relaxation. There are two major differences between these processes. First, rotational transition energies are smaller than vibrational excitation energies encountered in the mid- or near-infrared and the Raman spectra. This requires ensemble averaging over a Boltzmann distribution of rotational energies. Second, it is useful to include the rotational kinetic energy in the description of rotational relaxation. This requires that theoretical models of rotational relaxation be constructed in terms of orientational and kinetic coordinates.

Rotational and vibrational relaxation contribute differently to the depolarized and polarized components of the Raman scattered light; this allows the two relaxation processes to be studied. In the early 1970's, Bratos and Marechal (1) pointed out that Raman spectroscopy is well suited to studying the molecular dynamics of diatomic molecules in inert solvent systems. Bartoli and others then extended this idea to polyatomic symmetric-top molecules (2-4).

With a Raman experiment, which records both the
polarized and depolarized bands, the rotational and vibrational correlation functions can be separated from each other by the following procedure. Fourier transformation of the isotropic Raman peak will lead to the vibrational (i.e. isotropic) correlation function:

\[ G_V(t) = \text{FT} \left[ I_{iso}(\omega) \right] = \text{FT} \left[ I_{pol}(\omega) - 4/3 I_{dep}(\omega) \right] \]

where \( I_{iso}(\omega) \) is identified with that part of the scattered intensity resulting from non-reorientational (i.e. vibrational) relaxation.

On the other hand, Fourier transformation of the anisotropic (i.e. depolarized) Raman band will result in the anisotropic correlation function:

\[ G_A(t) = G_V(t) \cdot G_R(t) = \text{FT} \left[ I_{aniso}(\omega) \right] = \text{FT} \left[ I_{dep}(\omega) \right] \]

In this expression, \( I_{aniso}(\omega) \) is identified with a convolution of rotational and vibrational relaxation.

Therefore, one can obtain the rotational correlation function, \( G_R(t) \), by the relationship:

\[ G_R(t) = G_A(t)/G_V(t) \]

Figure 3 illustrates the comparison of anisotropic, vibrational, and rotational correlation functions. One can see the anisotropic curve decays most rapidly since it encompasses both relaxation mechanisms. The curve which decays least sharply is due to the less effective of the two relax-
FIGURE 3

COMPARISON OF THE ISOTROPIC, ANISOTROPIC, AND REORIENTATIONAL CORRELATION FUNCTIONS OF A GIVEN VIBRATIONAL MODE

The solid curve represents the anisotropic function since it has the most rapid decay. The other two represent the two relaxation mechanisms with the triangles showing the dominate one and the circles showing the less effective one. In this case, the half-widths at half-maximum are 5 cm⁻¹, 3 cm⁻¹, and 2 cm⁻¹, respectively.
ation mechanisms. Thus, one can compare the vibrational and rotational contributions to linebroadening.

From various studies of molecular vibrational relaxation (5-10), it has been found that there are four different vibrational relaxation processes which may induce broadening of the vibrational spectrum.

(A) Vibrational Dephasing. The observed peak shape and its associated correlation function arise from a quasi-continuous distribution of vibrational energies about a mean. The distribution is induced by the effect of locally different environment-oscillator perturbations which shift the oscillator energy level. Motional narrowing plays an important role in this process. It permits us to elucidate the time scale of collisions that scramble the molecular environment. Therefore, the dephasing process probes local static and dynamic properties.

(B) Vibrational Resonance Energy Transfer. The phonon population loss of an upper oscillator level is the subsequent phonon population gain in the same oscillator level but on an adjacent molecule.

(C) Vibrational Energy Dissipation. The phonons of the excited vibrational level of an intramolecular vibrational mode return to ground level by dissipating the energy difference into lattice phonons.

(D) Intramolecular Vibrational Energy Transfer. In this process, vibrational energy is redistributed from originally
excited mode to a different mode or modes in the same molecule.

Picosecond spectroscopy experiments have shown that the lifetimes of excited vibrational levels that lose their excess energy by way of dissipation to the heat motions of the bath are relatively long. From isotope dilution experiments, it is found that vibrational resonance energy transfer is usually not an effective mechanism of vibrational relaxation since molecular motion always takes place at a faster rate than the resonance energy transfer. The process of intramolecular vibrational energy transfer requires that two vibrational modes have nearly equal energy levels and the same vibrational symmetry, which is relatively unusual. In conclusion, the vibrational dephasing process usually predominates vibrational relaxation.

Theoretical Models

There are various theories that are currently used to explain the isotropic (vibrational) contribution to the width of Raman spectral bands in condensed phases. The concept of vibrational dephasing is one which has been proven successful in a number of systems.

One theory, which applies Kubo's NMR lineshape formalism (11) to the vibrational relaxation process, was developed by Bratos (12), and extended by Rothschild (13), Döge (14), and Van Woerkom (15). This model assumes that the vibrational
relaxation is due primarily to the loss of phase coherence caused by different molecular environments in the liquids. There are two parameters to characterize the efficiency of the vibrational dephasing process (16-19). The first is the spectral second moment, $M_2$, which measures the mean squared frequency deviation from $\omega_0$ (the band center). Its magnitude is determined by the strength of the coupling between the oscillator and its environment. The second parameter which affects the efficiency of relaxation by vibrational dephasing is the modulation time, $\tau_m$, which in a strict sense denotes the time constant characterizing decay of the stochastic perturbation arising from intermolecular interactions. However, in a more qualitative sense, it may be pictured roughly as the structural, or environmental relaxation time. For short-range, repulsive interactions, it represents the time between collisions in the liquid. The faster the modulation (i.e. short $\tau_m$), the longer the phase memory of the system.

The derived expression (13-15) for the vibrational (isotropic) correlation function, in terms of the above two quantities is:

$$G_V(t) = \exp\{-M_2[\tau_m^2(e^{-t/\tau_m} - 1) + \tau_m t]\}$$

Rothschild (13,20) showed that there are two limiting types of behavior, depending upon the value of the product $M_2 \tau_m^2$. 
When $M_2^2 \ll 1$ (termed fast modulation), the isotropic correlation function exhibits exponential behavior. In the fast modulation (or motional narrowing) limit, the short duration of the perturbative collisions lowers their effectiveness, and therefore a relatively large number of these collisions may be required to achieve significant vibrational dephasing. In this situation, the general expression for the correlation function reduces to a simple exponential:

$$G_v(t) = \exp(-t/\tau_v) \text{ where } \tau_v = (M_2^2 \tau_m)^{-1}$$

In this limit, the spectral lineshape is Lorentzian in form.

At the other extreme, $M_2^2 \gg 1$ (termed the rigid lattice limit). In this case, the mean squared frequency displacement, $M_2$, is far greater than the modulation rate, $\tau_m^{-1}$, and one has a relatively static system. When the modulation is slow, the effects of a perturbation on an oscillator are significant over a long time. This type of linebroadening, considered in an earlier work by Bratos (12), may be likened to an inhomogeneous solvent shift. In this situation, $G_v(t)$ becomes Gaussian in form and the general expression for the correlation function becomes:

$$G_v(t) = \exp(-M_2 t^2/2)$$

As noted earlier, a Gaussian correlation function corresponds to a Gaussian spectral lineshape.

A second recent theoretical approach to vibrational
dephasing is the Isolated Binary Collision (IBC) model, developed by Fischer and Laubereau (21) for diatomic molecules. This model has been applied to explain the temperature and density behavior of the vibrational broadening. Their derived expression for the relaxation time is:

\[ \tau_V = \frac{2}{9} \frac{L^2}{kT} \frac{M^2}{\mu \gamma^2} \omega_0^2 T \]

In this expression, \( k \) is Boltzmann's constant; \( T \) is the temperature; \( L \) is the interaction length (22); \( M \) is the reduced mass of the atom pair; \( \mu \) is the reduced mass of the combined oscillator and its collision partner; \( \gamma = M_A/(M_A + M_B) \), where molecule AB is the oscillator; \( \omega_0 \) is the frequency of the oscillator and \( \tau_C \) is the collision time.

At the present time, the Enskog model (23) is the preferred way to obtain hard-sphere collision times for use with the IBC model. This model assumes that the behavior of a liquid is similar to that of a dilute gas and is corrected to compensate for the excluded volume by the factor of \( \chi(\sigma) \), which is defined as (24):

\[ \chi(\sigma) = \frac{(Z - 1)}{\eta} \]

where \( Z \) is the compressibility and \( \eta \) is the packing fraction.

Therefore, the collision time may be calculated using the Enskog model of hard-sphere collisions. The expression for \( \tau_C \) is (18):
\[ \tau_C = \left[ 4 \left( \frac{kT}{\pi m} \right)^{1/2} \pi \rho \sigma^2 \chi(\sigma) \right]^{-1} \]

In this expression, \( m \) is the molecular mass, \( \rho \) is the number density, and \( \sigma \) is the molecular diameter.
REFERENCES


CHAPTER II

RAMAN LINESHAPE STUDIES OF DIHALOMETHANES

Following the development of new procedures for the analysis of vibrational lineshapes (1-3), there have been numerous studies of vibrational relaxation and molecular reorientation in liquids utilizing Raman spectroscopy (4-6). However, with relatively few exceptions (7-17), these studies have been performed on symmetric-top molecules such as methyl iodide, chloroform and benzene (4-6).

In order to provide further information on the reorientational behavior of asymmetric-top molecules as deduced from different vibrational modes and to test the applicability of current theories of vibrational relaxation (18-21), we have undertaken several spectral investigations of liquid phase dihalomethanes.

First, the polarized and depolarized Raman spectra of the $\nu_2$ (CH$_2$ bend) and $\nu_3$ (C-Br stretch) vibrational modes of dibromomethane have been studied at various temperatures between 235 K and 350 K. The lineshape of the $\nu_1$ (C-H stretching mode) was not studied since it appears as a doublet due to Fermi resonance with the first overtone of the symmetric methylene deformation (22).
Then, in order to provide additional information on the relaxation parameters of similar modes in structurally analogous molecules, we have extended the above study to various symmetric vibrations in dichloromethane and dichloromethane-d$_2$. The polarized and depolarized Raman spectra of the following $A_1$ bands were analyzed at various temperatures (from 193 K to 298 K) in the liquid phase: CD$_2$Cl$_2$ - $v_1$ (C-D stretch), $v_2$ (CD$_2$ bend), and $v_3$ (C-Cl stretching mode); CH$_2$Cl$_2$ - $v_1$ and $v_3$ vibrations. Spectra were also acquired for the $v_2$ band in the latter compound. However, attempts to analyze this mode proved unsuccessful, due both to its inherently weak intensity and very high depolarization ratio ($\rho = 0.6$).

As part of our continuing investigation of vibrational relaxation in liquids, we felt it would be of interest to compare the results of the above studies with those obtained for the structurally analogous molecule, bromochloromethane. We have analyzed the polarized and depolarized Raman spectra of the following $A_1$ stretching modes in CH$_2$BrCl at a number of temperatures in the liquid (from 203 K to 318 K): $v_1$ (CH$_2$), $v_4$ (C-Cl), and $v_5$ (C-Br). The derived vibrational relaxation parameters have been compared with those obtained from the analogous vibrations in CH$_2$Cl$_2$ ($v_1$; CH$_2$ stretch and $v_3$; C-Cl stretch) and in CH$_2$Br$_2$ ($v_3$; C-Br stretch).
Experimental

All four compounds were available commercially. Dibromomethane, dichloromethane, dichloromethane-d$_2$ (99.6%), and bromochloromethane were purchased from Aldrich Chemical Company. All liquids were purified by fractional distillation except the CD$_2$Cl$_2$, which was used as received.

The sample was contained in a sealed melting-point capillary tube which was inserted into a Harney-Miller cell. Temperature regulation was accomplished via liquid nitrogen boil-off or heated air flow, and measured with an iron-constantan thermocouple adjacent to the sample. Light from an Ar$^+$ laser (Coherent Radiation Model CR-3) (4880 Å) was focused into the sample and the scattered radiation was directed into a SPEX 14018 double monochromator, followed by photon counting electronics. The spectrometer drive was stepped in increments of 0.5 cm$^{-1}$ by an interfaced microprocessor (Apple II+). Photon counts were accumulated over a 1 second interval at each frequency and stored in the computer (on floppy disk) for further processing. The monochromator slit width (full width at half maximum intensity) for each vibrational mode was set as follows: (A) 1.7 cm$^{-1}$ for the $v_1$ and $v_3$ modes, and 3.7 cm$^{-1}$ for $v_2$ of both dibromo- and dichloro-methane; (B) 1.6 cm$^{-1}$ for $v_1$ and $v_5$, and 4.4 cm$^{-1}$ for the $v_4$ mode of bromochloromethane. To avoid interference from other vibrations in the band wings, spectra
were recorded on the low frequency side of the \( \nu_1 \) and \( \nu_3 \) modes, and on the high frequency side of \( \nu_2 \) of both dibromo- and dichloro-methane. The low frequency sides of the \( \nu_1 \) and \( \nu_5 \) modes and the high frequency side of \( \nu_4 \) were used in bromochloromethane. Polarized and depolarized spectra were obtained over a range of at least 100 cm\(^{-1}\) from the band center. This ensured accurate determination of the spectral second moments.

Following baseline subtraction, the isotropic spectra were obtained via the relation:

\[
I_{iso}(\omega) = I_{pol}(\omega) - (4/3) I_{dep}(\omega)
\]

Calculation of the isotropic spectra and second moments, the isotropic and reorientational correlation functions and the associated correlation times was accomplished utilizing standard equations and computer programs, these have been presented in detail elsewhere (23). The isotropic correlation functions were corrected for finite slit-width via numerical division by the slit correlation function, assuming a Gaussian instrumental lineshape.

Molecular reorientation and vibrational relaxation in \( \text{CH}_2\text{Br}_2 \)

Table I summarizes the experimentally derived isotropic second moments and correlation times (at 25 °C), together with their associated activation energies. Although not given in the table, it was found via linear regression that the
<table>
<thead>
<tr>
<th>Mode</th>
<th>$\tau_R$</th>
<th>$E_a(\tau_R)$</th>
<th>$M_2$</th>
<th>$\tau_V$</th>
<th>$E_a(\tau_V)$</th>
<th>$\tau_m$</th>
<th>$E_a(\tau_m)$</th>
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<tbody>
<tr>
<td>CH$_2$ bend</td>
<td>4.0$^e$</td>
<td>-0.8$^e$</td>
<td>56</td>
<td>2.5$^e$</td>
<td>+0.1$^e$</td>
<td>0.16</td>
<td>-0.26</td>
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<tr>
<td>($\nu_2$)</td>
<td>1.5$^f$</td>
<td>($\pm$0.07)</td>
<td></td>
<td>3.0$^f$</td>
<td>($\pm$0.13)</td>
<td>(±0.20)</td>
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<td>2.3$^g$</td>
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<td>1.8$^g$</td>
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<td>C-Br stretch</td>
<td>4.4$^e$</td>
<td>-0.7$^e$</td>
<td>36</td>
<td>1.9$^e$</td>
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<td>($\nu_3$)</td>
<td>2.5$^f$</td>
<td>($\pm$0.07)</td>
<td></td>
<td>2.2$^f$</td>
<td>($\pm$0.16)</td>
<td>(±0.17)</td>
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<tr>
<td></td>
<td>2.7$^g$</td>
<td></td>
<td></td>
<td>2.3$^g$</td>
<td></td>
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<tr>
<td></td>
<td>5.3$^i$</td>
<td></td>
<td></td>
<td>2.7$^h$</td>
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<tr>
<td></td>
<td>5.1$^j$</td>
<td></td>
<td></td>
<td>1.8$^i$</td>
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<tr>
<td></td>
<td>5.9$^k$</td>
<td></td>
<td></td>
<td>2.5$^j$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) These represent room temperature values interpolated via linear regression.
b) ps.  c) Kcal/mol.  d) cm$^{-2}$.
e) This work. Zeroth moment of the correlation function.
f) This work. Time for correlation function to decay to e$^{-1}$.
g) Ref. 12. Calculated directly from band half-widths.
h) Ref. 11. Calculated from slope of a straight-line portion of correlation function.
i) Ref. 13. Calculated directly from band half-widths.
j) Ref. 13. Calculated from slope of a straight-line portion of correlation function.
k) Ref. 11. Calculated directly from band half-widths.
second moments tend to increase with increasing temperature (by approximately 20 and 15 cm$^{-2}$ over 115 °C range for $v_2$ and $v_3$, respectively, see Appendix). This behavior seems contrary to intuitive expectations (18-20, 24-26), but has also been observed in several other systems (2, 14).

Molecular Reorientation in CH$_2$Br$_2$

As can be seen from Table I, we calculated rotational correlation times both from the zeroth moment of the correlation function and from the decay time ($1/e$) of the function. There is a considerable discrepancy between the results derived from the two methods (by almost a factor of three for the CH$_2$ bending mode). One sees similar deviation in correlation times obtained directly from lineshapes (11-13) and from the long-time slope of the correlation function (11-13). This large variation in reported values indicates clearly that caution must be exercised when comparing data obtained by different methods of analysis.

It can be seen from both Table I and Figure 4 that the rotational correlation times calculated from the $v_2$ and $v_3$ modes are similar in both magnitude and dependence on temperature. Indeed, the activation energies for the two modes are virtually identical, to within experimental error. Moreover, they are in good agreement with the value reported by Wang and coworkers (11) for the CH$_2$ bending mode. This result is at first surprising since apparent correlation times from
FIGURE 4

TEMPERATURE DEPENDENCE OF REORIENTATIONAL CORRELATION TIMES

◆, ν₂; ◇, ν₃; broken line, theoretical times from rotational diffusion model.
The graph depicts a plot of $T_R$ (in ps) versus $1000/T$ (in K$^{-1}$). The data points are represented by different symbols, with the solid line indicating one trend and the dashed line another. The $T_R$ values range from approximately 3.5 to 6.0 ps, while the $1000/T$ values range from approximately 2.75 to 4.00 K$^{-1}$. The graph suggests a linear relationship between the two variables.
different modes in asymmetric-tops are expected to depend in varying fashion on all three components of the rotational diffusion tensor. This is unlike symmetric-top molecules, where times measured for all \( A_1 \) modes represent the tumbling time of the top axis (1-5). However, one finds from the literature that the moments of inertia about the two axes perpendicular to \( C_2 \) are almost identical (27). Further, the polarizability tensor appears to possess nearly cylindrical symmetry (28). Therefore, one is led to conclude that the rotational dynamics of liquid dibromomethane appears to exhibit quasi symmetric-top behavior. This is corroborated by Rayleigh-scattering measurements (13), in both the neat liquid and solution; one would normally expect a superposition of Lorentzians for asymmetric-top molecules.

Similar behavior has been reported in a review on liquid dichloromethane (29). The authors stated that "there is some experimental evidence to suggest that the reorientational motion of \( \text{CH}_2\text{Cl}_2 \) in the liquid has symmetric-top character" (30).

Also shown in Figure 4 (dashed line) are correlation times calculated from the extended microviscosity model (31) of reorientational diffusion (4,32). It is evident that the temperature dependence of rotational times calculated from this theory is far greater (\( E_a = -2.47 \text{ Kcal/mol} \)) than that observed experimentally. This comparison suggests, although by no means proves, that the reorientational motion
in $\text{CH}_2\text{Br}_2$ is at least somewhat inertial in character. The same behavior has also been suggested for the reorientation of liquid $\text{CH}_2\text{Cl}_2$ (30). Thus, the results obtained in this study provide evidence that the rotational dynamics of both dibromo- and dichloro-methane are similar in nature.

**Vibrational Relaxation in $\text{CH}_2\text{Br}_2$**

Table I and Figure 5 give the experimentally derived isotropic (i.e. vibrational relaxation) correlation times for both the $\nu_2$ and $\nu_3$ modes in dibromomethane. As found earlier for the reorientational times, the calculated values of $\tau_V$ are somewhat dependent on the method of analysis, although the variation is less than for the former quantity.

The correlation times are similar in magnitude for both vibrations, although they are greater for the $\text{CH}_2$ bending mode, particularly at the higher temperatures studied. In addition, $\tau_V$ for the carbon-halogen stretching vibration exhibits a modest negative dependence on temperature whereas the correlation time for the $\text{CH}_2$ bend remains almost constant. With few exceptions (33), these same trends have been found in most systems studied to date (6).

For comparative purposes we have applied the Isolated Binary Collision (IBC) model, originally developed by Fischer and Laubereau (21), to predict vibrational relaxation (i.e. dephasing) times in diatomic molecules. Their derived expression is:
FIGURE 5

TEMPERATURE DEPENDENCE OF VIBRATIONAL CORRELATION TIMES
AND FISCHER–LAUBÈREAU DEPHASING TIMES

\( \Delta, \tau_V(\nu_2); \Delta, \tau_V(\nu_3); \)

\( \blacksquare, \tau_{ph}(\nu_2); \blacksquare, \tau_{ph}(\nu_3). \)
\[ \frac{1000}{T} (K^{-1}) \]

Graph showing data points and trend lines for \( T_V, T_{ph} \) (PS) versus \( \frac{1000}{T} (K^{-1}) \).
\[ \tau_{ph} = \frac{2}{9} \frac{L^2}{kT} \frac{M^2}{\mu \gamma^2} \omega_0^2 \tau_C \]

Utilizing the various approximations suggested by Jonas and coworkers (34,35) to adapt the above equation to polyatomic systems, we have calculated values of \( \tau_{ph} \) for both modes as a function of temperature. The results are shown in Figure 5. Although the IBC model provides correct order of magnitude estimates of the relaxation times, there is no quantitative agreement between theory and experiment. Specifically, the calculated values of \( \tau_{ph} \) are greater than the experimental correlation times for the C-Br stretch and significantly shorter than the measured results for the CH\(_2\) bend. Further, this equation fails to predict the observed negative temperature dependence of \( \tau_V \) for the former vibration. This lack of close agreement is not unexpected considering the extremely simplified nature of the model.

In many of the previous studies on vibrational relaxation, it has been found that the correlation times can vary markedly between dissimilar vibrations in a given molecule (7,33,34,36). Therefore, the similar values of \( \tau_V \) for the \( \nu_2 \) and \( \nu_3 \) modes in CH\(_2\)Br\(_2\) raises the question of whether the mechanism of vibrational dephasing is the same for the bending and stretching modes in this molecule. In order to test this possibility we employed the Kubo general line-shape formalism (37) as adapted to vibrational dephasing (18-20).
The theoretical expression for the vibrational (isotropic) correlation function is (18-20):

$$G_v(t) = \exp\{-M_2 [(e^{-t/\tau_m} - 1) + \tau_m t]\}$$

where $M_2$, the experimental second moment of the isotropic spectrum, is a measure of the breadth of the frequency distribution of molecular subenvironments in the liquid. The modulation time, $\tau_m$, is strictly the stochastic decay time of the frequency perturbation, but may be thought of roughly as the structural, or environmental, relaxation time in the neighborhood of the oscillator.

One limiting form of this equation, when $M_2 \cdot \tau_m^2 \ll 1$, corresponds to motionally narrowed homogeneous dephasing (20). In this case, the lineshape is close to Lorentzian and the equation reduces to a simple exponential:

$$G_v(t) = e^{-t/\tau_V}; \quad \tau_V = (M_2 \cdot \tau_m)^{-1}$$

The other extreme, when $M_2 \cdot \tau_m^2 \gg 1$, corresponds to purely inhomogeneous dephasing by comparatively static interactions. In this case, both the lineshape and correlation function are Gaussian in form (20).

In order to obtain a qualitative measure of the importance of inhomogeneous dephasing in these systems and to determine whether the theory can provide an explanation for the more efficient vibrational relaxation of both the $v_2$ and $v_3$ modes in CH$_2$Br$_2$, we have applied the Kubo model to
the symmetric vibrations in dibromomrthane. The equation has been fitted to the isotropic correlation function, using the experimentally measured second moments, to obtain values for the modulation times of each of the modes as a function of temperature. As shown in Figure 6, the values of $\tau_m$ for the methylene bending mode are of the same magnitude (although with opposite temperature dependence) as collision times calculated using the Enskog model (16,26,38). Modulation times for the carbon-halogen stretch, on the other hand, are significantly longer, by as much as a factor of three, compared with the CH$_2$ bend. This disparity between the two sets of results appears to indicate that the forces influencing vibrational relaxation differ for the two modes and that the relative closeness of the measured correlation times is probably fortuitous.

Based on a comparative isotropic linewidth study of various dihalomethanes, it has been suggested that vibrational dephasing of the CH$_2$ deformation modes may be caused by dipole-dipole interactions (12). If this were indeed the mechanism of relaxation, one would expect to obtain modulation times on the order of half the dipolar reorientational time ($\tau_D \gg 1$ ps) (29). The much shorter values of calculated here (0.1–0.2 ps) suggest, rather, that relaxation may be caused by short-range repulsive forces between molecules in the liquid (20).
FIGURE 6

TEMPERATURE DEPENDENCE OF MODULATION AND COLLISION TIMES

●, $\tau_m(\nu_2)$; ○, $\tau_m(\nu_3)$; ◊, $\tau_c$(Enskog).
Vibrational Relaxation in CH₂Cl₂ and CD₂Cl₂

Presented in Tables II and III are the various derived vibrational relaxation parameters for the bands studied in CH₂Cl₂ and CD₂Cl₂, respectively. We note first that the isotropic second moment of the C-D stretching mode is significantly smaller, by a factor of two, than that of the corresponding vibration in CH₂Cl₂. A similar reduction of M₂ upon deuteration has also been observed in studies of the carbon-hydrogen valence mode in chloroform (23) and acetonitrile (39).

In contrast to the above result, second moments of the carbon-chlorine stretching vibration (ν3) are of the same magnitude in both isotopic species. The values obtained here are greater than that reported for the C-Br stretch (M2 = 36 cm⁻² at 25 °C) in our previous study of dibromo-methane. It is perhaps significant that the same trend in second moments was observed in an earlier investigation of the isopropyl and t-butylchlorides and bromides (16). Further studies would be of interest to determine whether this trend in relative M₂'s is common to other structurally similar haloalkanes.

Although not presented in the tables, it was determined from linear regression that vibrational second moments for ν₁ in both molecules and for ν₂ in CD₂Cl₂ are approximately independent of temperature to within experimental error.
### TABLE II

VIBRATIONAL AND ROTATIONAL RELAXATION PARAMETERS IN CH₂Cl₂

<table>
<thead>
<tr>
<th>Mode</th>
<th>M₂</th>
<th>τᵥ</th>
<th>Eₐ(τᵥ)</th>
<th>τₚʰ</th>
<th>τₘ</th>
<th>Eₐ(τₘ)</th>
<th>$\sqrt{M_2 \cdot \tau_m}$</th>
<th>τᵣ</th>
<th>Eₐ(τᵣ)</th>
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<tr>
<td>C-H stretch</td>
<td>68</td>
<td>2.0e</td>
<td>-0.2e</td>
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<tr>
<td>C-Cl stretch</td>
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</tr>
</tbody>
</table>

a) These represent room temperature values interpolated via linear regression.
b) cm⁻².  c) ps.  d) Kcal/mol.
e) This work. Time for correlation function to decay to e⁻¹.
f) This work. Zeroth moment of the correlation function.
g) Ref. 41. Calculated directly from linewdths.
h) Ref. 47. Calculated directly from linewidths.
i) Ref. 48. Determined from depolarized Rayleigh scattering.
\begin{table}
\centering
\caption{Vibrational and Rotational Relaxation Parameters in CD$_2$Cl$_2$\textsuperscript{a}}
\begin{tabular}{llllllllllll}
\hline
\multicolumn{1}{l}{Mode} & \multicolumn{1}{c}{M$_2$\textsuperscript{b}} & \multicolumn{1}{c}{\(\tau_{V}\)\textsuperscript{c}} & \multicolumn{1}{c}{\(E_a(\tau_V)\)\textsuperscript{d}} & \multicolumn{1}{c}{\(\tau_{ph}\)\textsuperscript{c}} & \multicolumn{1}{c}{\(\tau_{m}\)\textsuperscript{c}} & \multicolumn{1}{c}{\(E_a(\tau_m)\)\textsuperscript{d}} & \multicolumn{1}{c}{\(\sqrt{M_2 \cdot \tau_m}\)} & \multicolumn{1}{c}{\(\tau_{R}\)\textsuperscript{c}} & \multicolumn{1}{c}{\(E_a(\tau_R)\)\textsuperscript{d}} \\
\hline
C-D stretch & 33 & 4.4\textsuperscript{e} & +0.19\textsuperscript{e} & 1.4 & 0.21 & +0.2\textsuperscript{g} & 0.23 \\
\((\nu_1)\) & & (\pm 0.2) & & & & (\pm 0.2) \\
& & 3.7\textsuperscript{f} & +0.14\textsuperscript{f} & & & & & \\
& & 3.9\textsuperscript{g} & & & & & & \\
CD$_2$ bend & 53 & 6.0\textsuperscript{e} & +0.38\textsuperscript{e} & 1.2 & 0.07 & -0.6\textsuperscript{f} & 0.10 & 1.0\textsuperscript{e} & -1.2\textsuperscript{e} \\
\((\nu_2)\) & & (\pm 0.2) & & & & (\pm 0.2) & & 1.1\textsuperscript{g} & & \\
& & 4.2\textsuperscript{f} & -0.62\textsuperscript{f} & & & & & & & \\
& & 4.1\textsuperscript{g} & & & & & & & & \\
C-Cl stretch & 76 & 1.3\textsuperscript{e} & -0.50\textsuperscript{e} & 3.8 & 0.30 & +0.12\textsuperscript{f} & 0.49 & 0.9\textsuperscript{e} & -1.79\textsuperscript{e} \\
\((\nu_3)\) & & (\pm 0.14) & & & & (\pm 0.09) & & 1.0\textsuperscript{g} & & \\
& & 1.2\textsuperscript{f} & -0.48\textsuperscript{f} & & & & & & & \\
& & 1.3\textsuperscript{g} & & & & & & & & \\
\hline
\end{tabular}
\textsuperscript{a}See footnotes for TABLE II
\end{table}
On the other hand, $M_2$ was found to increase modestly with rising temperature (by 20 cm$^{-2}$ over a 100 °C range) for $\nu_3$. Although opposite to theoretical expectations, this behavior has been observed in other systems (14), including the C-Br stretch in dibromomethane.

Vibrational relaxation times ($\tau_v$) were calculated from both the decay (1/e) times and the zeroth moments of the isotropic correlation function. The agreement, in general, is quite reasonable although, as noted above and in earlier studies from this laboratory (40), there is some deviation in correlation times calculated by different methods. This is particularly true for $\nu_1$ and $\nu_2$ of CD$_2$Cl$_2$, which have rather long relaxation times. As shown in the tables, the results obtained here also compare well with earlier reported values (41).

From calculated activation energies (column 3 in Tables II and III) it was found that the correlation times do not show any systematic temperature dependence for $\nu_1$ and $\nu_2$ of either species. $\tau_v$ does appear to exhibit a modest decrease with rising temperature for $\nu_3$ in both molecules. This behavior, although by no means general, has been observed in the majority of systems investigated to date (6).

As found earlier for second moments, deuteration also has a striking effect on the vibrational relaxation time of the carbon-hydrogen mode, which is seen to be longer, by a factor of two, in CD$_2$Cl$_2$. Again, this feature has been
observed in lineshape studies of various other systems including chloroform (26), acetonitrile (39,42) and methyl iodide (41).

Perhaps more surprising are the results for \( v_3 \). One would at first expect that the isotropic correlation times for the C-Cl stretching vibration should be roughly equal for the two species. However, it was observed that \( \tau_v \) is noticeably longer in CH\(_2\)Cl\(_2\); this was found to be true at all eight temperatures studied.

The Isolated Binary Collision model of vibrational dephasing developed by Fischer and Laubereau (21) has been employed successfully to interpret trends in vibrational relaxation times in a number of systems. Utilizing approximation for the mass factors (M, \( \mu \), and \( \gamma \)) introduced to adapt the IBC model to polyatomic systems (34), and the Enskog model (26,43) for collision times, \( \tau_C \), we have calculated values of \( \tau_{\text{ph}} \) for each of the five vibrations.

It may be seen from the tables that although the calculated dephasing times for both the C-H and C-D stretching modes are shorter than the experimental results, this simplified theory does indeed predict the more efficient relaxation of the former vibration. We note that the IBC model was first utilized by Jonas and coworkers (26) to explain the same phenomenon in chloroform.

One expects, in general, for carbon-hydrogen stretching vibrations that
since the other factors in IBC model are virtually unchanged upon deuteration. Given that \((M_{CD}/M_{CH}) \approx 2\) and \((\omega_0,CD/\omega_0,CH) \approx 2^{-1/2}\), the IBC model predicts that relaxation times of carbon-hydrogen stretching vibrations should be roughly twice as long in all deuterated compounds. At the present time, the only experimentally observed exception has been in benzene (34,44), where relaxation times of the two species are approximately equal.

It is also interesting to see that, in agreement with the experimental results, the calculated dephasing time of the C-Cl stretching mode is greater in CH₂Cl₂, due almost entirely to the greater peak frequency, \(\omega_0\), in the former compound (705 cm⁻¹ vs. 679 cm⁻¹). However, it must be pointed out that an alternative, or perhaps auxiliary, explanation lies in the fact that force constant calculations reveal that the Potential Energy Distribution (PED) for this mode contains a secondary contribution from the H(D)-C-Cl bending coordinates (45).

A second model which has been employed in earlier studies is the Kubo lineshape theory (34) adapted by several researchers (20-22) to vibrational dephasing. We have fitted this model to the experimental correlation functions to obtain values of \(\tau_m\) for each of the modes. It is satisfying
to see that the calculated modulation times are quite similar for both the $\nu_1$ and $\nu_3$ vibrations in the two molecules indicating, as one might expect, that the mechanism of dephasing is independent of isotopic substitution. Further, we note that the values of the modulation times are all of the same magnitude as the Enskog collision times (0.13 ps at 25 °C), and far shorter than the dipolar reorientation time (approximately 2-3 ps) (29). This latter result would appear to indicate that dephasing in the liquid results from repulsive collisional interactions. However, this conclusion must be stated with a degree of caution since the Enskog model predicts a positive dependence on temperature (i.e. an activation energy of +0.4 Kcal/mol). Yet, as seen in the tables, $E_a(\tau_m)$ varies somewhat erratically between modes, due probably to uncertainties in the calculation of this quantity.

We wish now to discuss, briefly, the rotational correlation times derived from the Raman lineshapes. We have obtained the reorientational correlation functions via the standard relation given earlier:

$$G_R(t) = G_A(t)/G_V(t)$$

The functions were observed to exhibit oscillatory behavior at longer times (resulting from errors in the division of two small numbers), introducing large errors in the area of $G_R(t)$. Therefore, the rotational times in the tables represent decay times of the correlation functions (46).
Unlike symmetric-top molecules, where values of $\tau_R$ from $A_1$ vibrations measure the tumbling times of the unique axis, the effective reorientational times in asymmetric-tops represent different linear combinations of the three components of the rotational diffusion tensor (2,3). Therefore, one does not expect $\tau_R$ to be the same for the various $A_1$ vibrations. Hacura, et al. (47) and Fukushi and Kimura (41) have also studied $v_1$ and $v_3$ in CH$_2$Cl$_2$. As displayed in Table II, their room temperature correlation times are in quite reasonable agreement with those obtained here. This is particularly satisfying since their values were obtained directly from linewidths and, as noted above, there are often significant discrepancies in results derived by different methods of analysis.

We also see from the table that their activation energy for $\tau_R$ of $v_1$ (calculated from Table III of ref. 47) compares quite well with our result. Unfortunately there is no agreement in this quantity for $v_3$. We would tend to believe that their result is more likely to be accurate, since our value of -0.4 Kcal/mol is far lower than $E_a$ for any of the other modes in either species.

In summary, we have studied the vibrational relaxation of various $A_1$ modes in CH$_2$Cl$_2$ and CD$_2$Cl$_2$. Similar to results reported in several other systems, it was determined that second moments were smaller and relaxation times longer for $v_1$ in the deuterated species. The Isolated Binary Collision
model successfully predicted the above trend in $\tau_v$, and could also be used to rationalize the longer observed relaxation times of the $\nu_3$ mode in $\text{CH}_2\text{Cl}_2$. Modulation times calculated from the Kubo lineshape theory were close to equal for both $\nu_1$ and $\nu_3$ in the two molecules. The values of $\tau_m$ were of the same order of magnitude as collision times calculated from the Enskog model, providing evidence that vibrational dephasing of the $A_1$ modes in dichloromethane results from short range repulsive interactions in the liquid.

Vibrational Relaxation in $\text{CH}_2\text{BrCl}$

Contained in Table IV is a summary of the relaxation parameters derived from three symmetric stretching (i.e. C-H, C-Br, and C-Cl) modes in bromochloromethane. Also include in Table IV are the results obtained for the equivalent vibrational modes in $\text{CH}_2\text{Cl}_2$ and $\text{CH}_2\text{Br}_2$. We note first that the isotropic (vibrational) second moments determined here for $\text{CH}_2\text{BrCl}$ are significantly larger, by greater than a factor of two, than those obtained earlier for any of the three vibrations in the other dihalomethanes. This was found to be the case at all temperatures studied. As noted in the experimental section, the method of data acquisition here was the same as before, with the exception of the C-Cl stretch, for which the low frequency side was utilized in the previous work. However, one would expect possible hot bands or isotope effects to broaden the low side of the peak. Therefore,
<table>
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<td>$M_2^c$</td>
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<tr>
<td>CH$_2$BrCl ($\nu_1^c$)</td>
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<td>0.14</td>
<td>0.33</td>
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<td>CH$_2$Cl$_2$ ($\nu_1^c$)</td>
<td>68</td>
<td>2.0</td>
<td>1.9</td>
<td>0.8</td>
<td>0.24</td>
<td>0.37</td>
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</tr>
<tr>
<td>CH$_2$BrCl ($\nu_5^c$)</td>
<td>76</td>
<td>1.3</td>
<td>1.3</td>
<td>3.1</td>
<td>0.38</td>
<td>0.62</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>CH$_2$Br$_2$ ($\nu_3^c$)</td>
<td>36</td>
<td>2.2</td>
<td>1.9</td>
<td>3.7</td>
<td>0.43</td>
<td>0.49</td>
<td>1.8</td>
<td></td>
</tr>
</tbody>
</table>

a) These represent room temperature values interpolated via linear regression. Values in parentheses are "activation energies" (Kcal/mol).

b) Ref. 55. c) cm$^{-2}$. d) ps.
the much larger values of $M_2$ obtained here can not attribute to either of these factors.

Vibrational relaxation times have been calculated both from exponential decay times ($\tau_V^{1/2}$) and zeroth moments of the isotropic correlation functions ($\tau_V^{\text{area}}$). As shown in the table, values of $\tau_V$ determined by the two methods are in very good agreement.

One may observe from Table IV and, more strikingly, from Figure 7, that the relaxation times for all three symmetric stretching vibrations are significantly shorter in $\text{CH}_2\text{BrCl}$ than for the analogous modes in $\text{CH}_2\text{Cl}_2$ and $\text{CH}_2\text{Br}_2$. One also notes from the table that $\tau_V$ for the C-Cl stretch is somewhat shorter than for the C-Br stretching mode in $\text{CH}_2\text{BrCl}$.

It may be seen from Figure 7 and from calculated "activation energies" in Table IV that relaxation times for all of the vibrations exhibit only a modest temperature dependence, with $\tau_V$ either decreasing slightly or remaining approximately constant with rising temperature.

In order to determine whether the Fischer-Laubereau model (23) could explain the experimental trends in relaxation times observed here, we have utilized this model to calculate dephasing times, $\tau_V^{\text{cal}}$, for the stretching modes in the dihalomethanes. As seen from the table, the model meets with only mixed success. While it does correctly predict the shorter relaxation times of the C-H and C-Br vibrations in $\text{CH}_2\text{BrCl}$, it fails to explain the same trend for the C-Cl.
FIGURE 7

TEMPERATURE DEPENDENCE OF EXPERIMENTAL RELAXATION TIMES
(1/\epsilon \text{ values})

(A) CH$_2$ stretch. △, CH$_2$BrCl; Δ, CH$_2$Cl$_2$.

(B) C-Cl stretch. ◆, CH$_2$BrCl; ◊, CH$_2$Cl$_2$.

(C) C-Br stretch. ●, CH$_2$BrCl; ○, CH$_2$Br$_2$.
stretching mode. It predicts that the C-Cl relaxation time should be longer than that of the C-Br stretch, whereas the reverse trend is observed. In addition, it does not replicate the observed temperature dependence of $\tau_v$ for many of the modes. In particular, it predicts a relatively large negative temperature dependence for all relaxation times in CH$_2$BrCl, which is not found experimentally.

It is not surprising that the IBC model does not provide a satisfactory interpretation of many of the observed trends. As noted above, the derived equation is strictly valid only for diatomic molecules and, in its simplest form, neglects vibrational anharmonicity (6). More fundamentally, however, the theory was developed assuming that vibrational relaxation results entirely from homogeneous dephasing via rapidly modulated collisional interactions. Yet, recent theoretical (49) and experimental (50-52) studies indicate that inhomogeneous dephasing processes arising from slowly varying long range attractive forces may often contribute significantly to vibrational relaxation in condensed phases.

The derived Kubo expression has been fitted to the isotropic correlation functions, using the experimentally measured second moments, to obtain values for the modulation times of each of the modes as a function of temperature. The results are summarized in Table IV.

One sees first that the modulation times are comparable in magnitude for the two carbon-halogen stretches in CH$_2$BrCl
and roughly twice as long as $\tau_m$ for the CH$_2$ valence mode. Variation of this quantity between bands in a given molecule has been observed in other systems (34,41,54), and indicates that different intermolecular forces influence vibrational relaxation of the various modes. We note also from the table that modulation times for each of the C-X stretches are quite close to the values derived for the equivalent vibrations in CH$_2$Cl$_2$ and CH$_2$Br$_2$.

In the next column of the table, we see that values for the quantity $M_2^2 \cdot \tau_m^2$ are quite close for the two C-X vibrations in bromochloromethane, much larger than for the C-H stretch. On this basis we can conclude, at least qualitatively, that the former vibrations are closer to the intermediate regime, in which rapidly modulated repulsive interactions and quasi-static long range attractive forces both contribute significantly to the overall rate of vibrational relaxation.

In order to ascertain whether the Kubo model provides an explanation for the enhanced relaxation efficiency of the three modes in CH$_2$BrCl compared to the same vibrations in CH$_2$Cl$_2$ and CH$_2$Br$_2$, we refer to the derived expression. It is seen that, at least in the motional narrowing regime, the relaxation time is inversely proportional to both $M_2$ and $\tau_m$. This is intuitively quite reasonable, signifying that a broad distribution of vibrational frequencies and/or a slowly varying perturbation (reduced motional narrowing) enhances the relaxation rate.
Presented in the table are values of \((M_2 \cdot \tau_m)^{-1}\) for each of the modes. This quantity is somewhat lower than the experimental relaxation times in all cases. That is to be expected since the simplified equation is strictly valid only when \(M_2 \cdot \tau_m^2 \ll 1\). It is seen, however, that use of this approximate relation does indeed predict shorter relaxation times of the vibrations in bromochloromethane. As noted above, modulation times for the C-Cl and C-Br stretches are very close to each other in the different compounds. Thus, the shorter relaxation times in \(\text{CH}_2\text{BrCl}\) is due virtually entirely to the broader distribution of molecular environments (larger \(M_2\)'s) in liquid bromochloromethane. For the C-H stretch, \(\tau_m\) is longer in \(\text{CH}_2\text{Cl}_2\), but this is more than compensated for by the much larger moments in \(\text{CH}_2\text{BrCl}\).

Current theories lack the sophistication to predict spectral moments and modulation times in complex liquids. However, it is hoped that these and future experiments to characterize experimental trends in these parameters will spur further theoretical developments and lead ultimately to a better understanding of interactions in condensed phases.
REFERENCES


46. During analysis, the presence of a very weak plasma line was noted in the depolarized band wing of $v_1$ in CD$_2$Cl$_2$. Therefore, the derived rotational relaxation times from this mode are believed to be unreliable and are not presented in Table III.


CHAPTER III

SOLVENT DEPENDENCE OF VIBRATIONAL FREQUENCIES AND RELAXATION TIMES IN DICHLOROMETHANE

There have been numerous investigations of the Raman lineshapes of the $v_1$ mode of chloroform in the liquid phase and in solution (1). It has been demonstrated that the hydrogen bonding interaction of this molecule is manifested both by a shortened vibrational relaxation time and by longer reorientational times in Lewis basic solvents (2-3).

Like chloroform, there is much spectroscopic evidence that dichloromethane and other methylene halides form weak hydrogen bonded complexes with suitable electron donors (4-6). In conjunction with a previous study on the temperature dependence of vibrational relaxation of various $A_1$ modes in liquid dichloromethane, we have investigated the vibrational relaxation of this molecule in solution. The isotropic line-widths and frequency shifts of the $v_1$ mode in CD$_2$Cl$_2$ [$v_0$(liq) = 2199 cm$^{-1}$] have been measured in a number of mixtures. The same mode in CH$_2$Cl$_2$ [$v_0$(liq) = 2989 cm$^{-1}$] has been studied in the corresponding deuterated solvents.

The results of this investigation and a comparison with earlier published data on chloroform (2) is presented below.
Experimental

Mixtures of dichloromethane and dichloromethane-d$_2$ were prepared in the various solvents (see Table V) at a solute mole fraction of 0.05, and were contained in sealed melting point capillaries. Details of the spectrometer operation and digital data acquisition have been presented earlier in this work and will not be repeated here (see Chapter II, Experimental).

The polarized Raman spectra of the $v_1$ mode in the two compounds were recorded three times in each of the solutions, and the results in Table V represent the average of the three runs. Due to the relatively low depolarization ratios [$\rho = 0.05$ in CH$_2$Cl$_2$; $\rho = 0.06$ in CD$_2$Cl$_2$ (7)], it was assumed that $I_{iso}(\omega) = I_{pol}(\omega)$. Following digital baseline subtraction, the spectra were plotted on graph paper and linewidths ($\Delta_{iso} = \text{HWHM}$) were determined directly. The measured values were corrected for the monochromator slitwidth [$S = 0.85 \text{ cm}^{-1}$ (HWHM)], using the equation presented by Tanabe and Hiraishi (8). Vibrational relaxation times were calculated from standard relation, $\tau_V = (2\pi \Delta_{iso})^{-1}$. Standard deviations for the three runs were typically 0.02-0.03 cm$^{-1}$. However, considering possible systematic errors resulting from the slitwidth correction and the assumption of equality of the isotropic and polarized spectra, a reasonable error estimate for the relaxation times presented in the table is $\pm 0.1$ ps.
Peak frequencies were interpolated to the nearest 0.1 cm\(^{-1}\) by a linear regression algorithm (9) using nine points in the vicinity of the maximum. The band centers in the solutions were referenced to values obtained here for the neat liquids. Gas-solution frequency shifts, \(\Delta \nu_{g-s}\), were then determined from earlier published values of the gas-liquid shifts (10). The precision of the measured peak positions was \(\pm 0.1-0.2 \text{ cm}^{-1}\), based on the deviation between runs. However, the absolute accuracy of the frequency shifts are, of course, dependent upon the earlier results (10).

Results and Discussion

It is well known that the vibrational band centers of vapor phase molecules are displaced, usually to lower frequency upon liquification or dilution in a solvent. The magnitude of this shift is determined by a competition of short range repulsive interactions and longer range attractive forces (11,12), the latter including dispersion, induction and dipolar attractions. In molecules involved in hydrogen bonding, there is an additional displacement of the XH stretching mode to lower frequencies as a result of decreased force constant and increased anharmonicity in the potential surface (15). The red shift due to this association usually predominates over all other interactions and is often considered the principal diagnostic of hydrogen bond formation (16).
As seen in Table V, the gas-solution frequency shifts, $\Delta \nu_{g-s}$, in dichloromethane are all found to be negative, in the range from $-4$ to $-20$ cm$^{-1}$ in CH$_2$Cl$_2$, but somewhat diminished in magnitude for the deuterated species.

The molecules acetone, pyridine and DMSO (solvents 5-7) are all known to be excellent electron donors for hydrogen bonding and, indeed, mixtures in the latter two solvents show relatively large frequency shifts. However, the band centers in acetone exhibit quite small displacements from the vapor phase values, less even than in the neat liquid. Further, the greatest red shifts of the CH (CD) stretching modes are found in the relatively inert solvent carbon disulfide. Thus, we are forced to conclude that our results are inconsistent with the classic Badger-Bauer rule (16), which relates the magnitude of $\Delta \nu$ to the strength of the hydrogen bonding interaction within a given series.

In order to explain the observed data, we note first that the uniformly negative shifts indicate that the attractive forces exert the dominant influence on $\Delta \nu_{g-s}$ in the liquid mixtures. In addition, it has been found that London dispersion interactions are usually the most important of these attractions (13,14). A simplified expression for the frequency shifts due to dispersion forces, given by Drickamer and coworkers (11,12), is of the form:

$$-\Delta \nu_{g-s} \propto (\nu \nu_0)^{-1/2} \sigma^6 \propto \nu_0 \alpha_2 \sigma_1^6$$
<table>
<thead>
<tr>
<th>No.</th>
<th>Solvent</th>
<th>( d^a )</th>
<th>( \frac{n^2-1}{n^2+2} )</th>
<th>( \Delta V_{g-s} ) ( \frac{b}{\text{Exp}^C \text{Cal}^C} )</th>
<th>( \Delta V_{g-s} ) ( \frac{b}{\text{Exp}^C \text{Cal}^C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.</td>
<td>neat liquid</td>
<td>4.75</td>
<td>0.255</td>
<td>9.7</td>
<td>1.8</td>
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<tr>
<td>1.</td>
<td>benzene</td>
<td>5.46</td>
<td>0.295</td>
<td>12.7</td>
<td>1.9</td>
</tr>
<tr>
<td>2.</td>
<td>carbon tetrachloride</td>
<td>5.61</td>
<td>0.274</td>
<td>11.6</td>
<td>1.8</td>
</tr>
<tr>
<td>3.</td>
<td>carbon disulfide</td>
<td>4.58</td>
<td>0.357</td>
<td>19.4</td>
<td>2.4</td>
</tr>
<tr>
<td>4.</td>
<td>chloroform</td>
<td>5.18</td>
<td>0.267</td>
<td>10.0</td>
<td>1.9</td>
</tr>
<tr>
<td>5.</td>
<td>acetone</td>
<td>4.60</td>
<td>0.220</td>
<td>3.9</td>
<td>1.0</td>
</tr>
<tr>
<td>6.</td>
<td>pyridine</td>
<td>4.92</td>
<td>0.299</td>
<td>15.7</td>
<td>0.7</td>
</tr>
<tr>
<td>7.</td>
<td>dimethylsulfoxide</td>
<td>4.94</td>
<td>0.283</td>
<td>18.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

a) \( d \), hard-sphere diameters taken from Ref. 29.

b) \( \text{cm}^{-1} \)

c) ps.
In this equation, $\sigma_{12}$ is the mean diameter of the solute and solvent molecules and $\alpha_2$ is the solvent's polarizability. $\mu$ and $\nu_0$ represent the oscillator's reduced mass and vapor phase peak frequency, respectively. We note briefly that it is the factor $(\mu \nu_0)^{-1}$ which explains the smaller shifts observed for the deuterated compound here and in other systems. $\alpha_2$ is related to the solvent's refractive index by $\alpha_2 \propto (n^2-1)/(n^2+2)$ (17). Therefore, one would expect an approximately linear relationship between $-\Delta \nu_{\text{g-s}}/\nu_0$ and $(n^2-1)/(n^2+2)$ (18). As seen in Figure 8, with the exception of solutions in DMSO, this is indeed the case, and furnishes a simple explanation of the otherwise 'anomalous' values of $\Delta \nu_{\text{g-s}}$ observed in such solvents as acetone and carbon disulfide.

Thus, we may conclude that the solution behavior of the band maxima of $\nu_1$ in dichloromethane can be interpreted in terms of solvent variation of the dispersion energy. This same trend and conclusion was presented recently by Yarwood et al. (19) in an investigation of acetonitrile. Also, Tanabe and Hiraishi (2) have reported peak frequencies for $\nu_1$ of CDCl$_3$ in a number of solvents. From Table I of their paper, it may be seen that frequency displacements, also with the exception of DMSO, are not correlated to hydrogen bond strength, but rather to dispersion energy variations among solvents.

Displayed also in the table are the experimental
FIGURE 8

DEPENDENCE OF THE GAS-SOLUTION FREQUENCY SHIFTS ON SOLVENT POLARIZABILITY

Open circles-CH$_2$Cl$_2$.
Filled circles-CD$_2$Cl$_2$.
See TABLE V for solvent numbers.
vibrational relaxation times of dichloromethane in solution. One notes that, with one exception (CD$_2$Cl$_2$ in C$_6$H$_6$), $\tau^\text{Exp}_V$ is either roughly constant or shows a modest increase (in CS$_2$) in the non-polar solvents and in chloroform. On the other hand, the dephasing times exhibit a drastic decrease in solution with the three Lewis bases (nos. 5-7), by as much as a factor of six for CD$_2$Cl$_2$ in DMSO.

It is well established that the hydrogen bonding interaction enhances the relaxation efficiency, $\tau_V^{-1}$, of XH valence modes (15). However, there have also been investigations of the solution dependence of vibrational dephasing times in non-hydrogen bonded systems (13, 20-22), which demonstrate that relaxation times are also sensitive to varying solvent properties including number density, diameter and molecular weight. In order to interpret the effects of these properties on $\tau_V$ in solution, several investigators have employed the simplified Isolated Binary Collision model of Fischer and Laubereau (23).

The basic expression for the relaxation time, modified for binary mixtures, (21) is:

$$\tau^\text{Cal}_V = 2\alpha \tau^\text{ph} = 2\alpha[(\tau^\text{11,ph})^{-1} + (\tau^\text{12,ph})^{-1}]^{-1}$$

$(\tau^\text{11,ph})^{-1}$ and $(\tau^\text{12,ph})^{-1}$ represent dephasing rates from solute-solute and solute-solvent collisions and may be determined from (20, 21, 24):
\[ \tau_{ph}^{ij} = \frac{1}{2} \frac{M_{ij}^2}{\mu_{ij} \gamma^k} \frac{\omega_{ij}^2}{kT} \tau^{ij}_C \]

The meanings of the various terms have been given elsewhere. \( \tau_{ph}^{ij} \) is the hard-sphere collision time and may be calculated from the Enskog model (20,21). The quantity, \( \alpha \), is an empirical factor introduced by various authors (20-22) to account for vibrational anharmonicity and for the approximations required to apply a theory developed for diatomic molecules to polyatomic systems. We have chosen values for this quantity in CH\(_2\)Cl\(_2\) (\( \alpha = 1.09 \)) and CD\(_2\)Cl\(_2\) (\( \alpha = 1.76 \)) to obtain agreement between \( \tau_{Cal}^V \) and \( \tau_{Exp}^V \) in the neat liquids (25), and have used the same values in the mixtures.

The calculated dephasing times are given in the table. More informative, though, is a correlation plot of \( \tau_{Exp}^V \) versus \( \tau_{Cal}^V \), displayed in Figure 9. We observe that for the first four solvents, with one exception, the agreement between the experimental and calculated relaxation times is quite good. For the three Lewis bases, however, the experimental dephasing times are far shorter than predicted by the Fischer-Laubereau (i.e. IBC) model (23). This demonstrates unambiguously that the enhanced relaxation efficiencies result from hydrogen bonding, rather than from variation in other properties of these solvents. For the results on dichloromethane in benzene, the results remain inconclusive. There is some evidence that the \( \pi \)-system in this molecule can hydrogen bond to acidic protons (6). We
FIGURE 9

EXPERIMENTAL VIBRATIONAL RELAXATION TIMES VERSUS THEORETICAL TIMES CALCULATED FROM THE IBC MODEL

Open circles—CH$_2$Cl$_2$.
Filled circles—CD$_2$Cl$_2$.
Box in upper right is a four-fold expansion of a portion of the graph.
See TABLE V for solvent numbers.
see from Table V and from Figure 9 that the experimental relaxation time is below the predicted value for CD₂Cl₂ in C₆H₆. However, this behavior is not replicated for CH₂Cl₂ in C₆D₆. Therefore, we can make no firm conclusions concerning molecular association in this system.

Finally, we note that Tanabe and Hiraishi (2) compared theoretical and experimental relaxation times for CDCl₃ in solution. As here, they found substantial agreement in most solvents, with the exception of Lewis bases, where experimental dephasing times were well below values calculated from the IBC model.

A brief note is in order on the nature of the relaxation process in these systems. The Fischer-Laubereau model assumes homogeneous dephasing via short range collisional interactions. Yet there is recent theoretical (14,26) and experimental (27,28) evidence that long range, slowly varying attractive forces often produce inhomogeneous vibrational dephasing in liquids. Considering that the gas-solution frequency shifts observed here could be interpreted on the basis of dispersion interactions, it appears likely that the latter mechanism contributes to relaxation in these solutions. It may well account for the drastic decrease in relaxation times of dichloromethane in basic solvents since inhomogeneous dephasing has been found to be particularly important in hydrogen bonding liquids (27).

In conclusion, we have found that the hydrogen bonding
interaction of dichloromethane in solution is quite similar to that observed earlier in chloroform. It was seen that the frequency shifts are not correlated to the hydrogen bonding ability of the solvent, but that molecular association dramatically increases the relaxation efficiency of the carbon-hydrogen valence mode. Thus, for weak CH hydrogen bonds, variations in the vibrational linewidth provide a more sensitive measure of interactions in solution.
REFERENCES


18. We also plotted \(-\Delta \nu_{g-s}/\nu_0\) versus \(\sigma_2/\sigma_{ij}^6\). The trends were the same, but there was significantly greater scatter due to the sensitivity of \(\sigma_{ij}^6\) to errors in the hard-sphere diameters.


25. The more common procedure is to choose \(\alpha\) to match experimental and calculated dephasing times in isotopically dilute solutions to remove possible contributions from resonant energy transfer. However, we found that \(\tau_\text{exp}^P\) of both CH\(_2\)Cl\(_2\) and CD\(_2\)Cl\(_2\) decreased when dissolved in the other species, indicating an additional relaxation mechanism, possibly intermolecular non-resonant transfer.


APPENDIX A

In Chapter II only room temperature values of the derived lineshape parameters and their activation energies were presented. The following tables list the complete set of parameters at temperatures throughout the liquid range for dibromomethane, dichloromethane, dichloromethane-\textsubscript{d}\textsubscript{2}, and bromochloromethane.
TABLE A-I

DERIVED LINESHAPE PARAMETERS OF DIBROMOMETHANE;
C-H BEND ($v_2$)

<table>
<thead>
<tr>
<th>Temp $^a$</th>
<th>$M_2$ $^b$</th>
<th>$\tau_m$ $^c$</th>
<th>$\tau_{R,d}$ $^c$</th>
<th>$\tau_{R,e}$ $^c$</th>
<th>$\tau_{V,d}$ $^c$</th>
<th>$\tau_{V,e}$ $^c$</th>
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</thead>
<tbody>
<tr>
<td>-36</td>
<td>46</td>
<td>0.24</td>
<td>2.5</td>
<td>4.5</td>
<td>2.6</td>
<td>2.3</td>
</tr>
<tr>
<td>-24</td>
<td>58</td>
<td>0.25</td>
<td>2.5</td>
<td>5.3</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td>-11</td>
<td>43</td>
<td>0.16</td>
<td>2.2</td>
<td>4.7</td>
<td>3.6</td>
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<td>+04</td>
<td>60</td>
<td>0.18</td>
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<td>2.8</td>
<td>2.7</td>
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<tr>
<td>+21</td>
<td>38</td>
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<tr>
<td>+59</td>
<td>104</td>
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<td>3.5</td>
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<td>+78</td>
<td>79</td>
<td>0.14</td>
<td>0.9</td>
<td>3.4</td>
<td>3.1</td>
<td>2.4</td>
</tr>
</tbody>
</table>

a) degrees Celsius  
b) cm$^{-2}$  
c) ps  
d) Time for correlation function to decay to $e^{-1}$  
e) Correlation time determined from zeroth moment
TABLE A-II

DERIVED LINESHAPE PARAMETERS OF DIBROMOMETHANE; C-Br STRETCH ($v_3$)

<table>
<thead>
<tr>
<th>Temp ( ^\circ \text{C} )</th>
<th>( M_2 )</th>
<th>( \tau_c )</th>
<th>( \tau_c,d )</th>
<th>( \tau_c,e )</th>
<th>( \tau_v )</th>
<th>( \tau_v )</th>
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<tr>
<td>-36</td>
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<td>0.34</td>
<td>6.0</td>
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<td>2.7</td>
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<td>0.42</td>
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<td>2.1</td>
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<tr>
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<td>29</td>
<td>0.42</td>
<td>2.4</td>
<td>4.9</td>
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<td>2.0</td>
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<td>2.1</td>
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<td>2.5</td>
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<tr>
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<td>0.41</td>
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<td>2.0</td>
<td>1.8</td>
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f) See footnotes for TABLE A-I
### TABLE A-III

DERIVED LINESHAPE PARAMETERS OF DICHLOROMETHANE; C-H STRETCH ($v_1$)

<table>
<thead>
<tr>
<th>Temp $^a$</th>
<th>$M_2$ $^b$</th>
<th>$\tau_m$ $^c$</th>
<th>$\tau_{c,d}$</th>
<th>$\tau_{c,d}$</th>
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<td>58</td>
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<td>2.0</td>
</tr>
<tr>
<td>+25</td>
<td>66</td>
<td>0.25</td>
<td>0.8$^f$</td>
<td>1.9</td>
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</tr>
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</table>

$^f$ See footnotes for TABLE A-I
**TABLE A-IV**

DERIVED LINESHAPE PARAMETERS OF DICHLOROMETHANE;
C-Cl STRETCH ($v_3$)

<table>
<thead>
<tr>
<th>Temp</th>
<th>$M_2$</th>
<th>$\tau_c$</th>
<th>$\tau_R$</th>
<th>$\tau_{c,d}$</th>
<th>$\tau_{c,e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-80</td>
<td>40</td>
<td>0.37</td>
<td>2.7</td>
<td>2.5</td>
<td>2.0</td>
</tr>
<tr>
<td>-70</td>
<td>34</td>
<td>0.38</td>
<td>2.0</td>
<td>2.3</td>
<td>1.8</td>
</tr>
<tr>
<td>-58</td>
<td>43</td>
<td>0.60</td>
<td>1.8</td>
<td>1.8</td>
<td>1.5</td>
</tr>
<tr>
<td>-46</td>
<td>41</td>
<td>0.34</td>
<td>2.8</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>-32</td>
<td>41</td>
<td>0.35</td>
<td>2.6</td>
<td>2.1</td>
<td>1.9</td>
</tr>
<tr>
<td>-15</td>
<td>48</td>
<td>0.52</td>
<td>1.4</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td>+03</td>
<td>51</td>
<td>0.34</td>
<td>2.5</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>+25</td>
<td>57</td>
<td>0.35</td>
<td>1.5</td>
<td>1.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

f) See footnotes for TABLE A-I
TABLE A-V

DERIVED LINESHAPE PARAMETERS OF DICHROMETHANE-D$_2$; C-D STRETCH ($v_1$)

<table>
<thead>
<tr>
<th>Temp $^a$</th>
<th>$M_2^b$</th>
<th>$\tau_c^c$</th>
<th>$\tau_{c,d}^d$</th>
<th>$\tau_{c,d}^e$</th>
<th>$\tau_{v,c}^c$</th>
<th>$\tau_{v,c}^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-80</td>
<td>52</td>
<td>0.16</td>
<td>0.63</td>
<td>3.7</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>-70</td>
<td>47</td>
<td>0.16</td>
<td>0.70</td>
<td>3.9</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>-58</td>
<td>46</td>
<td>0.17</td>
<td>0.66</td>
<td>3.8</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>-32</td>
<td>35</td>
<td>0.18</td>
<td>0.63</td>
<td>4.1</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>-15</td>
<td>39</td>
<td>0.21</td>
<td>0.63</td>
<td>3.7</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>+03</td>
<td>31</td>
<td>0.20</td>
<td>0.56</td>
<td>4.3</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>+25</td>
<td>40</td>
<td>0.38</td>
<td>0.56</td>
<td>2.7</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

f) See footnotes for TABLE A-I
TABLE A-VI

DERIVED LINESHAPE PARAMETERS OF DICHLOROMETHANE-D₂;
C-D BEND (ν₂)

<table>
<thead>
<tr>
<th>Temp a</th>
<th>M₂ b</th>
<th>τₘ c</th>
<th>τₗ c,d</th>
<th>τᵥ c,d</th>
<th>τᵥ c,e</th>
</tr>
</thead>
<tbody>
<tr>
<td>-80</td>
<td>61</td>
<td>0.16</td>
<td>2.9</td>
<td>4.3</td>
<td>3.4</td>
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<td>39</td>
<td>0.10</td>
<td>2.2</td>
<td>4.4</td>
<td>7.0</td>
</tr>
<tr>
<td>-58</td>
<td>27</td>
<td>0.09</td>
<td>2.0</td>
<td>7.1</td>
<td>6.0</td>
</tr>
<tr>
<td>-46</td>
<td>43</td>
<td>0.13</td>
<td>1.9</td>
<td>4.5</td>
<td>3.4</td>
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<td>29</td>
<td>0.08</td>
<td>1.7</td>
<td>5.8</td>
<td>6.0</td>
</tr>
<tr>
<td>-15</td>
<td>37</td>
<td>0.09</td>
<td>1.3</td>
<td>5.3</td>
<td>4.0</td>
</tr>
<tr>
<td>+03</td>
<td>68</td>
<td>0.05</td>
<td>1.2</td>
<td>6.0</td>
<td>7.5</td>
</tr>
<tr>
<td>+25</td>
<td>57</td>
<td>0.07</td>
<td>0.9</td>
<td>5.8</td>
<td>4.4</td>
</tr>
</tbody>
</table>

f) See footnotes for TABLE A-I
TABLE A-VII

DERIVED LINESHAPE PARAMETERS OF DICHLOROMETHANE-D₂;
C-Cl STRETCH (ν₃)

<table>
<thead>
<tr>
<th>Temp</th>
<th>M₂</th>
<th>τₘ</th>
<th>τᵣ</th>
<th>τᵥ</th>
<th>τᵥ</th>
</tr>
</thead>
<tbody>
<tr>
<td>-80</td>
<td>55</td>
<td>0.25</td>
<td>4.5</td>
<td>2.4</td>
<td>2.0</td>
</tr>
<tr>
<td>-58</td>
<td>53</td>
<td>0.30</td>
<td>3.2</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>-46</td>
<td>64</td>
<td>0.42</td>
<td>1.4</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>-32</td>
<td>61</td>
<td>0.31</td>
<td>1.4</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>-15</td>
<td>74</td>
<td>0.43</td>
<td>1.2</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>+03</td>
<td>68</td>
<td>0.27</td>
<td>1.1</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>+25</td>
<td>76</td>
<td>0.31</td>
<td>1.0</td>
<td>1.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

f) See footnotes for TABLE A-I
TABLE A-VIII

DERIVED LINESHAPE PARAMETERS OF BROMOCHLOROMETHANE;
C-H STRETCH ($\nu_1$)

<table>
<thead>
<tr>
<th>Temp $^a$</th>
<th>$M_2^b$</th>
<th>$\tau_c^c$</th>
<th>$\tau_{V}^{c, d}$</th>
<th>$\tau_{V}^{c, e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-70</td>
<td>143</td>
<td>0.13</td>
<td>1.59</td>
<td>1.33</td>
</tr>
<tr>
<td>-57</td>
<td>180</td>
<td>0.14</td>
<td>1.62</td>
<td>1.35</td>
</tr>
<tr>
<td>-48</td>
<td>92</td>
<td>0.10</td>
<td>1.74</td>
<td>1.63</td>
</tr>
<tr>
<td>-31</td>
<td>155</td>
<td>0.13</td>
<td>1.65</td>
<td>1.29</td>
</tr>
<tr>
<td>-13</td>
<td>158</td>
<td>0.13</td>
<td>1.95</td>
<td>1.73</td>
</tr>
<tr>
<td>+06</td>
<td>149</td>
<td>0.09</td>
<td>1.97</td>
<td>1.65</td>
</tr>
<tr>
<td>+24</td>
<td>111</td>
<td>0.15</td>
<td>1.40</td>
<td>1.28</td>
</tr>
<tr>
<td>+45</td>
<td>201</td>
<td>0.16</td>
<td>1.42</td>
<td>1.23</td>
</tr>
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</table>

f) See footnotes for TABLE A-I
<table>
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<th>Temp $^a$</th>
<th>$M_2$ $^b$</th>
<th>$\tau_m$ $^c$</th>
<th>$\tau_v$ $^{c,d}$</th>
<th>$\tau_v$ $^{c,e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-70</td>
<td>147</td>
<td>0.42</td>
<td>0.89</td>
<td>0.84</td>
</tr>
<tr>
<td>-57</td>
<td>105</td>
<td>0.34</td>
<td>0.89</td>
<td>1.56</td>
</tr>
<tr>
<td>-48</td>
<td>104</td>
<td>0.42</td>
<td>0.85</td>
<td>0.84</td>
</tr>
<tr>
<td>-31</td>
<td>94</td>
<td>0.30</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td>-13</td>
<td>156</td>
<td>0.77</td>
<td>0.78</td>
<td>0.81</td>
</tr>
<tr>
<td>+06</td>
<td>173</td>
<td>0.38</td>
<td>0.88</td>
<td>0.76</td>
</tr>
<tr>
<td>+24</td>
<td>105</td>
<td>0.25</td>
<td>1.03</td>
<td>1.26</td>
</tr>
<tr>
<td>+45</td>
<td>158</td>
<td>0.31</td>
<td>0.99</td>
<td>0.82</td>
</tr>
</tbody>
</table>

$^a$ See footnotes for TABLE A-I
### TABLE A-X

**DERIVED LINESHAPE PARAMETERS OF BROMOCHLOROMETHANE; C-Br STRETCH ($\nu_5$)**

<table>
<thead>
<tr>
<th>Temp$^a$</th>
<th>$M_2^b$</th>
<th>$\tau_c^c$</th>
<th>$\tau_{c,d}^c$</th>
<th>$\tau_{c,e}^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-70</td>
<td>100</td>
<td>0.32</td>
<td>1.45</td>
<td>1.39</td>
</tr>
<tr>
<td>-57</td>
<td>73</td>
<td>0.30</td>
<td>1.45</td>
<td>1.25</td>
</tr>
<tr>
<td>-48</td>
<td>60</td>
<td>0.25</td>
<td>1.60</td>
<td>1.51</td>
</tr>
<tr>
<td>-31</td>
<td>76</td>
<td>0.28</td>
<td>1.53</td>
<td>1.33</td>
</tr>
<tr>
<td>-13</td>
<td>96</td>
<td>0.38</td>
<td>1.32</td>
<td>1.26</td>
</tr>
<tr>
<td>+06</td>
<td>70</td>
<td>0.28</td>
<td>1.57</td>
<td>1.45</td>
</tr>
<tr>
<td>+24</td>
<td>71</td>
<td>0.39</td>
<td>1.29</td>
<td>1.30</td>
</tr>
<tr>
<td>+45</td>
<td>81</td>
<td>0.49</td>
<td>1.21</td>
<td>1.32</td>
</tr>
</tbody>
</table>

*f) See footnotes for TABLE A-I*
APPENDIX B

The following figures are the representive spectrum and correlation functions of the $v_3$ mode of dichloromethane at 25 °C.
FIGURE B-1

RAMAN SPECTRA OF CH₂Cl₂ AT 25 °C

Polarized and depolarized spectra of the ν₃ mode.
Upper scale represents in peak vicinity.
Lower scale represents baseline frequency.
FIGURE B-2

CORRELATION FUNCTIONS OF CH₂Cl₂ AT 25 °C

Correlation functions derived from the ν₃ mode.

-----, vibrational correlation function.

-.--., Rotational correlation function.

____, Anisotropic correlation function.
APPENDIX C

In Chapter III only the final values of the experimental vibrational relaxation times and the theoretical vibrational dephasing times are presented. The following tables list the complete set of experimental data and of calculated parameters.
TABLE C-I

EXPERIMENTAL VIBRATIONAL RELAXATION TIMES
OF CH₂Cl₂ IN SOLUTION

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Half-Width at Half-Maximum&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Exp&lt;sup&gt;b&lt;/sup&gt;ν&lt;sub&gt;TV&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Neat liquid</td>
<td>3.45</td>
<td>3.44</td>
</tr>
<tr>
<td>C₆D₆</td>
<td>3.36</td>
<td>3.38</td>
</tr>
<tr>
<td>CCl₄</td>
<td>3.41</td>
<td>3.41</td>
</tr>
<tr>
<td>CS₂</td>
<td>2.90</td>
<td>2.88</td>
</tr>
<tr>
<td>CDCl₃</td>
<td>3.40</td>
<td>3.38</td>
</tr>
<tr>
<td>CD₃COCDC₃</td>
<td>5.83</td>
<td>5.86</td>
</tr>
<tr>
<td>C₅D₅N</td>
<td>8.27</td>
<td>8.30</td>
</tr>
<tr>
<td>CD₃SOCD₃</td>
<td>9.14</td>
<td>9.18</td>
</tr>
</tbody>
</table>

<sup>a</sup> cm⁻¹

<sup>b</sup> ps
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Half-Width at Half-Maximum (^a)</th>
<th>(^b) (t_V^{Exp})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Neat liquid</td>
<td>1.90</td>
<td>1.89</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_6)</td>
<td>2.17</td>
<td>2.14</td>
</tr>
<tr>
<td>(\text{CCl}_4)</td>
<td>1.86</td>
<td>1.84</td>
</tr>
<tr>
<td>(\text{CS}_2)</td>
<td>1.77</td>
<td>1.81</td>
</tr>
<tr>
<td>(\text{CHCl}_3)</td>
<td>1.77</td>
<td>1.86</td>
</tr>
<tr>
<td>(\text{CH}_3\text{COCH}_3)</td>
<td>3.12</td>
<td>3.14</td>
</tr>
<tr>
<td>(\text{C}_5\text{H}_5\text{N})</td>
<td>4.97</td>
<td>4.96</td>
</tr>
<tr>
<td>(\text{CH}_3\text{SOCH}_3)</td>
<td>6.11</td>
<td>6.15</td>
</tr>
</tbody>
</table>

\(^{c}\) See footnotes for TABLE C-I
TABLE C-III
CALCULATED VIBRATIONAL DEPHASING TIMES
OF CH$_2$Cl$_2$ IN SOLUTION

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$m_2$</th>
<th>$d_2$</th>
<th>$\omega$</th>
<th>$\sigma$</th>
<th>$\tau_{ph}$</th>
<th>$\tau_{v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat liquid</td>
<td>84.9</td>
<td>1.327</td>
<td>2988.8</td>
<td>4.75</td>
<td>0.37</td>
<td>1.81</td>
</tr>
<tr>
<td>C$_6$D$_6$</td>
<td>84.2</td>
<td>0.940</td>
<td>2985.8</td>
<td>5.46</td>
<td>0.44</td>
<td>1.86</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>153.8</td>
<td>1.584</td>
<td>2986.9</td>
<td>5.61</td>
<td>0.42</td>
<td>1.83</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>76.1</td>
<td>1.255</td>
<td>2979.1</td>
<td>4.58</td>
<td>0.41</td>
<td>2.35</td>
</tr>
<tr>
<td>CDC$_3$</td>
<td>120.4</td>
<td>1.492</td>
<td>2988.5</td>
<td>5.18</td>
<td>0.42</td>
<td>1.86</td>
</tr>
<tr>
<td>CD$_3$COCD$_3$</td>
<td>64.1</td>
<td>0.865</td>
<td>2994.6</td>
<td>4.60</td>
<td>0.79</td>
<td>0.95</td>
</tr>
<tr>
<td>C$_5$D$_5$N</td>
<td>84.1</td>
<td>1.595</td>
<td>2982.8</td>
<td>4.92</td>
<td>0.09</td>
<td>0.66</td>
</tr>
<tr>
<td>CD$_3$SOCD$_3$</td>
<td>84.2</td>
<td>1.582</td>
<td>2979.6</td>
<td>4.94</td>
<td>0.09</td>
<td>0.59</td>
</tr>
</tbody>
</table>

a) g/mol
b) g/cm$^3$
c) cm$^{-1}$
d) $\AA$
e) ps
TABLE C-IV
CALCULATED VIBRATIONAL DEPHASING TIMES OF CD$_2$Cl$_2$ IN SOLUTION

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$m_2^a$</th>
<th>$d_2^b$</th>
<th>$\omega^c_o$</th>
<th>$\sigma_2^d$</th>
<th>$\tau_{ph}^e$</th>
<th>$\tau_V^{Cal^e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat liquid</td>
<td>86.9</td>
<td>1.358</td>
<td>2198.4</td>
<td>4.75</td>
<td>0.69</td>
<td>5.47</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>78.2</td>
<td>0.873</td>
<td>2195.8</td>
<td>5.46</td>
<td>0.83</td>
<td>3.93</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>153.8</td>
<td>1.584</td>
<td>2197.5</td>
<td>5.61</td>
<td>0.78</td>
<td>5.90</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>76.1</td>
<td>1.255</td>
<td>2192.0</td>
<td>4.58</td>
<td>0.76</td>
<td>6.64</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>119.4</td>
<td>1.480</td>
<td>2198.3</td>
<td>5.18</td>
<td>0.78</td>
<td>6.26</td>
</tr>
<tr>
<td>CH$_3$COCH$_3$</td>
<td>58.1</td>
<td>0.784</td>
<td>2202.5</td>
<td>4.60</td>
<td>1.50</td>
<td>2.06</td>
</tr>
<tr>
<td>C$_5$H$_5$N</td>
<td>79.1</td>
<td>1.500</td>
<td>2194.8</td>
<td>4.92</td>
<td>0.33</td>
<td>1.20</td>
</tr>
<tr>
<td>CH$_3$SOCH$_3$</td>
<td>78.1</td>
<td>1.468</td>
<td>2193.3</td>
<td>4.94</td>
<td>0.17</td>
<td>0.91</td>
</tr>
</tbody>
</table>

f) See footnotes for TABLE C-III
APPENDIX D

In Chapter III, the polarized Raman spectra of the $v_1$ mode in $\text{CH}_2\text{Cl}_2$ and $\text{CD}_2\text{Cl}_2$ were recorded three times in each of the solutions, and the results in the Table V represent the average of the three runs. Representative spectra are displayed in Figure D-1.
FIGURE D-1

POLARIZED RAMAN SPECTRA OF THE $v_1$ BAND
OF DICHLOROMETHANE IN ACETONE

(A) CD$_2$Cl$_2$ in (CH$_3$)$_2$CO; (B) CH$_2$Cl$_2$ in (CD$_3$)$_2$CO.
The frequencies in the figure correspond to the
Vicinity of the band centers. The frequency ranges
for the baselines (plotted below each peak) are:
(A) 2260-2270 cm$^{-1}$; (B) 2920-2930 cm$^{-1}$. 
APPENDIX E

The following tables list the complete set of experimental lineshape parameters of isotope dilution studies in dichloromethane.
<table>
<thead>
<tr>
<th>Conc. a</th>
<th>M₂ b</th>
<th>τₐ c,d</th>
<th>τₑ c,e</th>
<th>τᵥ c,d</th>
<th>τᵥ c,e</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 %</td>
<td>112</td>
<td>0.67</td>
<td>2.66</td>
<td>1.81</td>
<td>1.69</td>
</tr>
<tr>
<td>40 %</td>
<td>66</td>
<td>0.57</td>
<td>2.31</td>
<td>1.90</td>
<td>1.72</td>
</tr>
<tr>
<td>60 %</td>
<td>50</td>
<td>1.96</td>
<td>3.61</td>
<td>1.86</td>
<td>1.75</td>
</tr>
<tr>
<td>80 %</td>
<td>47</td>
<td>3.79</td>
<td>4.96</td>
<td>1.77</td>
<td>1.66</td>
</tr>
<tr>
<td>Neat CH₂Cl₂</td>
<td>46</td>
<td>0.96</td>
<td>2.21</td>
<td>1.95</td>
<td>1.82</td>
</tr>
</tbody>
</table>

a) solute mole fraction  
b) cm⁻²  
c) ps  
d) Time for correlation function to decay to e⁻¹  
e) Correlation time determined from zeroth moment
<table>
<thead>
<tr>
<th>Conc. (^a)</th>
<th>(M_2) (^b)</th>
<th>(\tau_{R}^{c,d})</th>
<th>(\tau_{R}^{c,e})</th>
<th>(\tau_{V}^{c,d})</th>
<th>(\tau_{V}^{c,e})</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 %</td>
<td>818</td>
<td>0.38</td>
<td>2.39</td>
<td>0.24</td>
<td>0.77</td>
</tr>
<tr>
<td>40 %</td>
<td>491</td>
<td>1.17</td>
<td>1.93</td>
<td>0.68</td>
<td>1.77</td>
</tr>
<tr>
<td>60 %</td>
<td>410</td>
<td>1.23</td>
<td>2.45</td>
<td>0.54</td>
<td>0.98</td>
</tr>
<tr>
<td>80 %</td>
<td>548</td>
<td>1.49</td>
<td>3.77</td>
<td>0.32</td>
<td>0.87</td>
</tr>
<tr>
<td>Neat (\text{CH}_2\text{Cl}_2)</td>
<td>285</td>
<td>1.54</td>
<td>2.10</td>
<td>0.80</td>
<td>1.69</td>
</tr>
</tbody>
</table>

f) See footnotes for TABLE E-I
<table>
<thead>
<tr>
<th>Conc. a</th>
<th>( M_2^b )</th>
<th>( \tau_{c,d}^c )</th>
<th>( \tau_{c,e}^d )</th>
<th>( \tau_V^e )</th>
<th>( \tau_{V}^e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 %</td>
<td>58</td>
<td>0.34</td>
<td>1.63</td>
<td>3.92</td>
<td>3.37</td>
</tr>
<tr>
<td>40 %</td>
<td>35</td>
<td>1.05</td>
<td>1.89</td>
<td>4.37</td>
<td>3.51</td>
</tr>
<tr>
<td>60 %</td>
<td>45</td>
<td>3.11</td>
<td>4.41</td>
<td>4.16</td>
<td>3.46</td>
</tr>
<tr>
<td>80 %</td>
<td>36</td>
<td>4.70</td>
<td>5.85</td>
<td>4.05</td>
<td>3.39</td>
</tr>
<tr>
<td>Neat ( \text{CD}_2\text{Cl}_2 )</td>
<td>31</td>
<td>0.58</td>
<td>2.57</td>
<td>4.58</td>
<td>3.52</td>
</tr>
</tbody>
</table>

f) See footnotes for TABLE E-I
TABLE E-IV

DERIVED LINESHAPE PARAMETERS OF CD$_2$ BEND (v$_2$)
OF CD$_2$Cl$_2$ IN CH$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Conc. $^a$</th>
<th>$M_2$ $^b$</th>
<th>$\tau_{c,d}^{c,d}$</th>
<th>$\tau_{c,e}^{c,d}$</th>
<th>$\tau_{V}^{c,d}$</th>
<th>$\tau_{V}^{c,e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 %</td>
<td>191</td>
<td>0.90</td>
<td>1.72</td>
<td>5.69</td>
<td>3.62</td>
</tr>
<tr>
<td>40 %</td>
<td>84</td>
<td>1.10</td>
<td>2.05</td>
<td>3.08</td>
<td>2.22</td>
</tr>
<tr>
<td>60 %</td>
<td>69</td>
<td>0.84</td>
<td>2.36</td>
<td>3.11</td>
<td>2.44</td>
</tr>
<tr>
<td>80 %</td>
<td>44</td>
<td>1.00</td>
<td>2.23</td>
<td>3.31</td>
<td>2.49</td>
</tr>
<tr>
<td>Neat CD$_2$Cl$_2$</td>
<td>42</td>
<td>1.11</td>
<td>1.13</td>
<td>5.79</td>
<td>4.38</td>
</tr>
</tbody>
</table>

f) See footnotes for TABLE E-I
BIBLIOGRAPHY

Books


Debye, P., Polar Molecules, (Chemical Catalog Co., 1929).


Articles


