MOLECULAR DYNAMICS IN THE LIQUID PHASE BY
FT-NMR, FT-IR, AND LASER RAMAN
LINESHAPE ANALYSIS

DISSERTATION

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By

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Nuclear magnetic resonance (NMR) provides a convenient probe for the study of molecular reorientation in liquids because nuclear spin-lattice relaxation times are dependent upon the details of molecular motion. The combined application of Raman and Infrared (IR) lineshape analysis can furnish more complete information to characterize the anisotropic rotation of molecules.

Presented here are the studies of NMR relaxation times, together with Raman/IR lineshape analysis of the solvent and temperature dependence of rotational diffusion in 1,3,5-tribromobenzene and 1,3,5-trifluorobenzene. In these experiments, it was found that the rotational diffusion constants calculated from Perrin's stick model were two to three times smaller than the measured values of \( D_i \) and \( D_n \). Similarly, rotational diffusion constants predicted by the Hu-Zwanzig slip model were too large by a factor of 2. Application of the newer Hynes-Kapral-Weinberg model furnished rotational diffusion constants that were in reasonable agreement with the experimental results.
The vibrational peak frequencies and relaxation times of the isotropic Raman spectra of the $\nu_1$ modes of CD$_2$Br$_2$ and CHBr$_3$ were studied in solution. The frequency shifts in non-interactive solvents were explained well on the basis of solution variations in the dispersion energy. In Lewis bases, the displacements were in some, but not all, cases greater than predicted. On the other hand, it was found that the vibrational relaxation times of the C-H/C-D modes decreased dramatically in all Lewis base solvents. Therefore, it was concluded that relaxation times of the $\nu_1$ modes, rather than frequency shifts, furnish a more reliable measure of hydrogen bonding interactions of halomethanes in solution.
PREFACE

The rotation of molecules in the gas phase is well understood and may be described completely by classical mechanics. In liquids, however, the molecular reorientation is strongly influenced by the intermolecular forces.

The early theories do not provide a good characterization of rotation of small- to medium-sized molecules. More recent theories appear to offer better predictions of molecular rotation diffusion constants. However, the extent of the general capability of these new modes has not yet been explored comprehensively.

This research uses the techniques of the NMR relaxation times combined with Raman infrared linewidth analysis to determine the rotation diffusion constants in a number of systems. The results are compared with the various theories to determine which theories are closest in agreement with the experimental results.
TABLE OF CONTENTS

PREFACE ........................................ iii
LIST OF TABLES .................................. vii
LIST OF ILLUSTRATIONS ......................... viii

Chapter

I. THEORY OF ROTATIONAL DIFFUSION ........ 1

   Fundamental Concepts
   Theoretical Rotational Diffusion Models
      The Stokes-Einstein-Debye (SED) Model
      The Stick (Perrin) Model
      The Microviscosity (MV) Model
      The Free Rotor (FR) Model
      The Slip (HZ) Model
      The Hynes-Kapral-Weinberg (HKW) Model

II. NUCLEAR MAGNETIC RESONANCE RELAXATION .... 11

   Introduction
   Basic Theory
   Relaxation Mechanisms
      Dipole-Dipole (DD) Relaxation
      Quadrupolar Relaxation (QR)
      Spin-Rotation (SR) Relaxation
      Chemical Shift Anisotropy (CSA) Relaxation
      Scalar Coupling (SC) Relaxation
   Separation of Mechanisms
   The Relationship between Dipole-Dipole Relaxation Correlation Times and Diffusion Constants

III. RAMAN AND IR LINESHAPE ANALYSIS ........ 36

   Basic Concepts
      Raman Spectroscopy
      Infrared Spectroscopy
      Vibrational Lineshapes
      Fourier Transformations
Relaxation Processes
Determination of Rotational Diffusion
Constants by Raman and IR
Lineshape Analysis

IV. SOLVENT AND TEMPERATURE DEPENDENCE OF
$^{13}$C RELAXATION TIMES AND REORIENTATIONAL DYNAMICS IN TRIBROMOBENZENE

Introduction
Experimental Method
Results and Discussion
  Experiment 1: Solvent Dependence of $^{13}$C Relaxation Times and Reorientational Dynamics in Tribromobenzene
  Experiment 2: Temperature Dependence of Rotational Correlation Times in Tribromobenzene

V. RAMAN AND INFRARED STUDY OF REORIENTATIONAL DYNAMICS IN TRIFLUOROBENZENE AND TRIBROMOBENZENE

Introduction
Experimental Method
  Raman Spectroscopy
  Infrared Spectroscopy
Experiment 1: Raman/Infrared Study of Reorientational Dynamics in Trifluorobenzene
  Introduction
  Experimental Method
  Results and Discussion
    Determination of Rotational Diffusion Constants
    Temperature Dependence of the Perpendicular Diffusion Constant in TFB
    Reorientational Dynamics of TFB in Solution
Experiment 2: Rotational Diffusion of Tribromobenzene in Solution
  Introduction
  Experimental Method
  Results and Discussion
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>VI. THE EFFECTS OF HYDROGEN BONDING ON VIBRATIONAL FREQUENCIES AND RELAXATION TIMES IN HALO-METHANES</td>
<td>106</td>
</tr>
<tr>
<td>Introduction</td>
<td></td>
</tr>
<tr>
<td>Experimental Method</td>
<td></td>
</tr>
<tr>
<td>Results and Discussion</td>
<td></td>
</tr>
<tr>
<td>Peak Frequencies</td>
<td></td>
</tr>
<tr>
<td>Vibrational Relaxation</td>
<td></td>
</tr>
<tr>
<td><strong>BIBLIOGRAPHY</strong></td>
<td>126</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>Microviscosity Factor Dependence upon Solvent/Solute Radius Ratio</td>
<td>5</td>
</tr>
<tr>
<td>II.</td>
<td>Solvent Properties, Relaxation Times, and Correlation Times of Tribromobenzene in Solution</td>
<td>60</td>
</tr>
<tr>
<td>III.</td>
<td>Relaxation and Correlation Times</td>
<td>61</td>
</tr>
<tr>
<td>IV.</td>
<td>Rotational Diffusion Constants and Correlation Times Calculated with the Hynes-Kapral-Weinberg Model</td>
<td>68</td>
</tr>
<tr>
<td>V.</td>
<td>Temperature Dependence of Raman Linewidths in Neat Trifluorobenzene</td>
<td>82</td>
</tr>
<tr>
<td>VI.</td>
<td>Solvent Dependence of Raman and Infrared Linewidths in Trifluorobenzene</td>
<td>84</td>
</tr>
<tr>
<td>VII.</td>
<td>Temperature Dependence of D\textsubscript{1} in Neat Trifluorobenzene</td>
<td>88</td>
</tr>
<tr>
<td>VIII.</td>
<td>Solvent Dependence of D\textsubscript{1} in Trifluorobenzene</td>
<td>91</td>
</tr>
<tr>
<td>IX.</td>
<td>Raman and Infrared Linewidths of Trifluorobenzene in Solution</td>
<td>96</td>
</tr>
<tr>
<td>X.</td>
<td>Experimental and Calculated Diffusion Constants of Tribromobenzene in Solution</td>
<td>97</td>
</tr>
<tr>
<td>XI.</td>
<td>Experimental and Calculated Correlation Times of Tribromobenzene in Solution</td>
<td>100</td>
</tr>
<tr>
<td>XII.</td>
<td>Frequency Shifts and Vibrational Relaxation Times of Dihalomethanes in Solution</td>
<td>109</td>
</tr>
<tr>
<td>XIII.</td>
<td>Frequency Shifts and Vibrational Relaxation Times of Trihalomethanes in Solution</td>
<td>110</td>
</tr>
</tbody>
</table>
**LIST OF ILLUSTRATIONS**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (A) Precession of ( \mu ) about ( H_0 ); (B) Precession of an ensemble of nuclei with ( I = 1/2 )</td>
<td>16</td>
</tr>
<tr>
<td>2. Diagram showing the positions of the two nuclei ( I ) and ( S ) and the angle ( \theta_{IS} ) between their internuclear vector ( r_{IS} ) and the magnetic field ( H_0 )</td>
<td>20</td>
</tr>
<tr>
<td>3. Energy level diagram illustrating the fundamental processes of Raman scattering</td>
<td>39</td>
</tr>
<tr>
<td>4. Comparison of Gaussian and Lorentzian bandshapes</td>
<td>43</td>
</tr>
<tr>
<td>5. Correlation function of Gaussian and Lorentzian</td>
<td>46</td>
</tr>
<tr>
<td>6. Viscosity dependence of reorientational correlation times in tribromo-benzene</td>
<td>63</td>
</tr>
<tr>
<td>7. Temperature dependence of experimental and calculated rotational correlation times</td>
<td>73</td>
</tr>
<tr>
<td>8. Basic components of the Laser Raman spectrometer</td>
<td>80</td>
</tr>
<tr>
<td>9. Dependence of the gas-solution frequency shifts on solvent polarizability in the dihalomethanes</td>
<td>114</td>
</tr>
<tr>
<td>10. Dependence of the gas-solution frequency shifts on solvent polarizability in the haloforms</td>
<td>115</td>
</tr>
</tbody>
</table>
CHAPTER I

THEORY OF ROTATIONAL DIFFUSION

Fundamental Concepts

The diffusion concept describes the spontaneous motion of small particles and carries with it implications of continuous motion and a retarding force. The rotational diffusion of a liquid view is seen as the reorientational motion of a molecule which is hindered by a fractional viscous force operating at the molecule's surface. The rotational diffusion constant is given by (4)

\[ D = \frac{kT}{\epsilon} \]  

where \( k \) is Boltzmann's constant, \( T \) is the temperature, and \( \epsilon \) is the rotational friction coefficient.

In the hydrodynamical view of molecules rotating within a continuous fluid, it is assumed that the molecule undergoes small, random jumps about its three axis, each of which is characterized by rotational diffusion constants \( (D_i, i = x, y, z) \).

The r.m.s. angle of rotation during an interval, \( \Delta t \), is given by (14,15):

\[ \langle \Delta \theta \rangle_{\text{rms}} = (2D_i \Delta t)^{1/2} \]
The value of $\Delta t$ required for $\langle \Delta \theta \rangle_{\text{rms}}$ to reach one rad is defined as $\tau_\theta$. For spherical molecules, in which motion is isotropic in nature, only a single diffusion constant is needed to describe the reorientational motion.

For totally asymmetrical molecules there are three different diffusion constants; however for symmetric-top molecules, which experience anisotropic motion, only two diffusion constants are required to characterize the reorientation motion ($D_\parallel$ and $D_\perp$, which represent rotation parallel to the symmetry axis and the axis perpendicular to the top axis, respectively).

Several techniques can be utilized to measure the diffusion constants. For example, NMR measures a correlation time, $\tau_C$, which depends upon both $D_\parallel$ and $D_\perp$. Similarly, the rotational linewidths of Raman and IR bands depend upon both. Separation to acquire the individual diffusion constants is discussed in later chapters.

Theoretical Rotational Diffusion Models

In past years, several rotational diffusion models have been developed in an attempt to describe liquid-phase molecular reorientation. All treat the motion as being a diffusional process, characterized by one or more diffusion constants.
The Stokes-Einstein-Debye (SED) Model

The first model which attempted to describe the resistance to rotation of a macroscopic sphere rotating in a viscous liquid was introduced by Stokes (11) in 1856. He showed that the friction constant is given by

$$\tau = \frac{\text{torque}}{\text{angular momentum}} = 8\pi a^3 \eta$$  \[3\]

where \(a\) is the radius of the molecule and \(\eta\) is the viscosity of that medium.

Einstein and Debye extended its application. In the case of spherical molecules, the rotational diffusion constant \(D_0\) was given by (4)

$$D_0 = \frac{kT}{\tau}$$  \[4\]

The resulting expression is

$$D_0 = \frac{kT}{8\pi a^3 \eta}$$  \[5\]

However, experimental evidences from many NMR relaxation studies reveal faster-than-predicted actual rates of rotation, using this model. Such results indicate that the frictional restraint must be lower than that represented by the Stokes coefficient. All this suggests that the bulk
viscosity \( \eta \) does not adequately represent the viscosity at the surface of the molecule.

**The Stick (Perrin) Model**

The earliest hydrodynamic theory of anisotropic reorientation was developed by Perrin (1) who extended the Stokes-Einstein-Debye (SED) "stick" theory of reorientation of spheres in a viscous, continuous medium. This model assumes that the solvent sticks to the surface of the molecule, thus creating a viscous drag which retards its rotation. Perrin solved the Navier-Stokes equation (11) to obtain diffusion constants, given by:

\[
D_i = \frac{1}{f_i} D_0 = \frac{1}{f_i} \frac{kT}{8 \pi r^3 \eta}
\]  

[6]

In this equation, \( D_i = D_\perp \) or \( D_\parallel \), \( f_\perp \) or \( f_\parallel \), \( D_0 \) is the original SED isotropic diffusion constant, \( k \) is Boltzmann's constant, \( T \) is the temperature, \( \eta \) is the viscosity, and \( r = \sigma/2 \), is the mean radius of the particle, \( r = (ab^2)^{1/3} \) (16). The correlation factors, \( f_\perp \) and \( f_\parallel \), are dependent on the axial ratio, \( \rho = b/a \), and on whether the rotor is prolate or oblate in shape. Unfortunately, the Perrin treatment has proven to be inadequate for small-to-medium size molecules and predicts rotational diffusion constants that are an order of magnitude smaller than the experimentally measured values (9).
The Microviscosity (MV) Model

To alleviate the discrepancy encountered with the Perrin treatments, Gierer and Wirtz (GW) (5) modified the SED model by introducing a rotational microviscosity correction factor $f_{GW}$, given by

$$f_{GW} = \left[6(a_s/a) + (1 + a_s/a)^3\right]^{-1}$$  \[7\]

where $a_s/a$ is the ratio of solvent to solute radius (see Table I).

<table>
<thead>
<tr>
<th>$a_s/a$</th>
<th>$f$</th>
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<tr>
<td>0.01</td>
<td>0.97</td>
</tr>
<tr>
<td>0.1</td>
<td>0.74</td>
</tr>
<tr>
<td>0.5</td>
<td>0.30</td>
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<tr>
<td>0.7</td>
<td>0.23</td>
</tr>
<tr>
<td>1.0</td>
<td>0.16</td>
</tr>
<tr>
<td>2.0</td>
<td>0.08</td>
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<tr>
<td>10.0</td>
<td>0.02</td>
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One limiting case, $a_s/a \gg 1$, corresponds to the "slip" boundary condition in which the rotating molecule slips through the solvent without retarding forces ($\varepsilon = 0$). The other limit, $a_s/a \ll 1$, corresponds to the "stick" boundary condition, in which the rotating molecule experiences a retarding force ($\varepsilon = 8\pi a^3 \eta$). In pure liquid, $a_s/a = 1$, which corresponds to a microviscosity factor, $f = 0.16$, represents a friction coefficient with 16% of the stick value.
The Free Rotor (FR) Model

The free rotor model assumes that the surrounding solvent does not stick at all to the rotating molecule. Thus, for spherical molecules, there is no retarding friction and the molecule rotates freely (as in the gas phase) at a rate controlled by its moment of inertia. The diffusion constant is given by

\[ (D)_{FR} = \left[ 6 \tau_{FR} \right]^{-1} \]  

where

\[ \tau_{FR} = 2\pi \left( \frac{41}{360} \right) \left( \frac{I}{kT} \right)^{1/2} \]

\( \tau_{FR} \) is the time for a "free rotor" (2) to travel 41°, I is the molecular moment of inertia, k is Boltzmann's constant, and T is the temperature.

The Slip (HZ) Model

Hu and Zwanzig (6) pointed out that the discrepancies arise from application of the "stick" boundary condition in solving the Navier-Stokes equation to determine the friction coefficient. They noted that a "slip" boundary condition (zero tangential stress) is probably more realistic for rotation on a molecular scale. Of course, for rotation of a sphere or parallel to the unique axis of a symmetric top (\(D_n\)), this condition implies vanishing friction and, therefore, the molecule can be treated as a "free rotor". However, rotation perpendicular to the top axis (\(D_\perp\)) is
retarded since it requires displacement of solvent molecules. Hu and Zwanzig solved the equation numerically, using the slip boundary condition and the perpendicular diffusion constant given by

\[ D_\perp = \frac{1}{f_{HZ}} \frac{kT}{8\pi b^3 \eta} \]  

where \( b \) is the largest semi-axis length, \( f_{HZ} \) is a numerical factor dependent on the axial ratio and on whether the molecule is prolate or oblate. The Hu-Zwanzig factor, \( f_{HZ} \), may be obtained from the reduced friction coefficients \( (f_{HZ} = \xi^* / \theta) \) in Table I of their paper (6).

The Hynes-Kapral-Weinberg (HKW) Model

One of the latest models describing molecular reorientation has been proposed by Hynes, Kapral, and Weinberg (7,8). The HKW model provides a general description for the reorientational behavior of molecules in liquids and the theory allows for the fact that rotation, in general, lies somewhere between the "stick" and "slip" limits. These researchers introduced a slip coefficient, \( \beta \), into a modified boundary condition and re-solved the Navier-Stokes equation. The magnitude of \( \beta \) indicates the degree of coupling between the particle's rotation and the solvent continuum. \( \beta = 0 \) corresponds to the slip boundary condition, whereas the hydrodynamic stick limit is approached as \( \beta \to \infty \). The authors developed an expression for the
rotational diffusion constant and also employed the Enskog collision theory (8) to obtain an equation for the approximate calculation of $\beta$.

Although the above model was formulated assuming isotropic reorientation, Tanabe (12,13) suggested an intuitive extension of the HKW equations in order to calculate the diffusion constants ($D_{\perp}$ and $D_{\|}$) of symmetric-top molecules. His modified HKW equations may be written:

$$D_{\perp} = \frac{1}{f_{\perp}}D_{0}[1 + \frac{3n}{8 + a_{\perp}n}]$$  \hspace{1cm} [11]$$

and

$$D_{\|} = \frac{1}{f_{\|}}D_{0}[1 + \frac{3n}{8}]$$  \hspace{1cm} [12]$$

In these equations, $f_{\perp}$ and $f_{\|}$ are the Perrin coefficients (10) and $D_{0}$ is the SED diffusion constant [$D_{0} = kT/(8\pi\eta r^{3})$]. Thus, in the stick limit ($\beta \to \infty$), they reduce to the Perrin results for $D_{\perp}$ and $D_{\|}$. One sees, also, that $D_{\|}$ diverges in the slip limit ($\beta = 0$), as expected (see above). The quantity $\alpha$ in eq 11 may be calculated via the relation

$$\frac{\rho^{2}}{f_{HZ}} = \frac{1}{f_{\perp}}[1 + \frac{3\alpha_{\perp}}{a_{\perp}}]$$  \hspace{1cm} [13]$$. 
This ensures that eq 12 reduces to the Hu-Zwanzig expression (1) in the slip limit ($\beta \to 0$). The slip coefficient, $\beta$, may be estimated from the Enskog theory as:

$$\beta = \frac{2\kappa}{\kappa + \frac{1}{\pi} \frac{2\mu_{12} kT}{\pi}} \rho_2 g_{12}(\sigma_{12})$$  \[14\]

$\mu_{12}$ is the reduced mass of the solute-solvent pair; $\sigma_{12}$ is the mean diameter, $(\sigma_1 + \sigma_2)/2$ and $\rho_2$ are the solvent's number density. The radial distribution function, $g_{12}(\sigma_{12})$, may be calculated in the manner presented elsewhere (12). Finally, $\kappa = I_{\text{avg}}/mr^2$, where $I_{\text{avg}} = (2I_x + I_z)/3$ and "m" is the molecular mass.

The modified HKW model demonstrates considerable promise in narrowing the gap between calculated and experimental rotational diffusion constants.
CHAPTER NOTES


16. In a symmetric top molecule, the semi-axis lengths of the volume ellipsoid are given by \( a \), \( b \), and \( c \), where \( b \) and \( c \) are equal.
CHAPTER II

NUCLEAR MAGNETIC RESONANCE RELAXATION

Introduction

In recent years, considerable interest has been directed toward the study of molecular reorientation in liquids (26). Several spectroscopic techniques have been used, including Raman and IR lineshape analysis (18,19,21,39-41), Rayleigh scattering (27,45), dielectric relaxation (34), and magnetic relaxation (8,17,26,34,35). As used in the past, however, these techniques do not furnish the total picture of molecular behavior in the liquid phase. With the advent of modern pulsed Fourier transform Nuclear Magnetic Resonance (NMR) Spectrometers (8,17,26,34,35), the measurement of NMR spin-lattice relaxation times ($T_1$) has become routine (9,15,16,46,47) and can furnish valuable information for the study of rotational diffusion constants.

For most molecules in the liquid phase, the rotation rate depends upon the viscosity and is independent of the moment of inertia, indicating that intermolecular frictional forces, rather than inertial factors, are paramount. NMR provides a convenient probe for the study of molecular reorientation in liquids, since nuclear spin relaxation times are dependent on the details of the molecular motion.
The nuclear relaxation process is subject to a variety of contributing relaxation mechanisms, which include dipole-dipole, spin-rotation, chemical shift anisotropy, and scalar-coupling. Moreover, quadrupolar relaxation may occur if the nuclear spin number \( I \) is greater than 1/2. Any combination of these mechanisms can operate in a given liquid.

One important dynamic parameter obtained from NMR relaxation studies is \( \tau_c \), the molecular reorientation correlation time, which is roughly a measure of the time taken by a molecule to reorient itself by one radian. Its measurement can be utilized to calculate rotational diffusion constants \( (D_i) \) and to characterize molecular behavior in liquids. Therefore, NMR spectroscopy has become the most powerful method for investigating the intimate details of reorientational dynamics.

**Basic Theory**

The concept of NMR was originally developed in the classic investigations of Purcell, Torrey, and Pound (37) and Bloch, Hansen, and Packard (5), who independently observed the first NMR signals. Since then, the theory has been considerably modified and extended by a number of authors (1,11,26,36,38).

NMR spectroscopy is concerned with the atomic nuclei in a molecule. Most nuclei have a spin angular momentum which is expressed in terms of the maximum observable component of
the nuclear spin (i.e., the spin quantum number $I$). This can have the values $0$, $1/2$, $1$, $-1$, $-1/2$, $...$ etc. The nuclear magnetic moment, $\mu$, which is proportional to $I$, is given by (11)

$$\mu = \gamma \hbar$$  \[15\]

where $\gamma$ is the magnetogyratic ratio, which is a constant for a given nucleus, and $\hbar = \hbar/2\pi$; here $\hbar$ is Planck's constant.

Consider the consequences of placing a nucleus in a magnetic field. A nucleus is a magnetic dipole, and when placed in a static field $H_0$ (traditionally assumed to be in the $z$ direction), an interaction will take place, and the spin will acquire energy given by the following equation:

$$E = -\mu_z H_0$$  \[16\]

where $\mu_z$ is the component of the nuclear magnetic moment in the $z$ direction. $\mu_z$ is quantized in the magnetic field and has $2I + 1$ different values (i.e., $\mu_z = \gamma M_I \hbar$, where $M_I = -I$, $-I + 1$, $...$ to $+I$). Combining this with eqs 15 and 16 gives the energy of each spin state of the nucleus in the magnetic field as

$$E_M = -\gamma \hbar M_I H_0$$  \[17\]

From the Bohr relation, the frequency of radiation that can induct transitions between the different spin states giving rise to a net absorption of energy is
\[ h\nu = \Delta E = \gamma \hbar H_0 \]  \hspace{1cm} \text{[18]}

where \(\nu\) is the Larmor frequency, given by

\[ \nu = \frac{\gamma}{2\pi} H_0 \quad (Hz) \quad \text{[19]} \]

or

\[ \omega = 2\pi \nu = \gamma H_0 \quad (rad\cdot sec^{-1}) \quad \text{[20]} \]

As given by the Boltzmann distribution, there is an excess of nuclei in the lower energy state at equilibrium, which is established by means of specific relaxation processes. If an rf magnetic field, \(H_1\), is applied after equilibrium is attained, the nuclei absorb energy, and the populations of the two spin states tend to equalize. Finally, when \(H_1\) is removed, the system returns to the former equilibrium distribution appropriate to \(H_0\) through the same energy relaxation phenomena. The excess nuclear population is then restored to the lower energy level, and the energy previously acquired by the spin system is transferred to the "lattice" (its surroundings) by a first-order relaxation process, giving rise to what is called spin-lattice relaxation (12,22), which is discussed later in this study.

From classical mechanics, it is known that a torque is exerted on the magnetic moment which tends to align it parallel to the field. However, since this torque can only
alter the component of angular momentum perpendicular to $H_0$ and $\mu$, the net result corresponds to a rotation of the direction of $\mu$ in a cone with its axis along $H_0$. Such movement is known as Larmor precession and is shown in Figure 1(a). For spin $I = 1/2$ nuclei, the two spin states are shown in Figure 1(b).

When a large number of nuclei are placed in a magnetic field, there will result, after a sufficient amount of time, a net magnetization $M_0$ in the field direction, given by Curie's law (1)

$$M_0 = \frac{N \gamma^2 h I(I + 1) H_0}{3 k T} \tag{21}$$

where $N$ is the nuclei number density. This magnetization is due to the preferential population of the lower energy levels according to a Boltzmann distribution.

Suppose, now, that the magnetization is perturbed from its equilibrium value $M_0$ by application of an rf magnetic field $H_1$ perpendicular to $H_0$. It can be shown (42) that the equation of motion of this nonequilibrium magnetization in the absence of interactions between the spins or with their surroundings is simply

$$\frac{dM}{dt} = \gamma (M \times H_0) \tag{22}$$
Figure 1. Precession of nuclei in a magnetic field.
(A) Precession of $\mu$ about $H_0$; (B) Precession of an ensemble of nuclei with $I=1/2$. 
Equation 22 describes the nuclear precession about $H_0$ with Larmor frequency, $\omega = \gamma H_0$. In order to simplify the characterization of the nuclear motion, it is a common practice to view $M$ from a reference frame rotating at the Larmor frequency. In this case, the magnetization appears to be a constant vector with components both parallel ($M_z$) and perpendicular ($M_x, M_y$) to the applied field. In the equilibrium state, the average value of the magnetization in the $x$ and $y$ direction is zero (i.e., $M_x = M_y = 0$). If an exciting field $H_1$ is applied precisely at the Larmor frequencies of the nuclei, then resonance occurs. After removing $H_1$, $M_z$ returns to its original value $M_0$ by a spin-lattice relaxation process

$$\frac{dM_z}{dt} = -\frac{1}{T_1}(M_z - M_0)$$  \[23\]

The above process can be explained in this way: the spin-lattice relaxation occurs via transitions which are stimulated by components of the local magnetic field of a particular nucleus which fluctuates at its Larmor frequency. Fluctuations in the local magnetic field are generated from Brownian motion. Other possible sources of fluctuating magnetic fields are discussed below in the section on relaxation mechanisms.

The nonequilibrium component of magnetization, $M_x$ or $M_y$, which is perpendicular to the applied field, is also
subject to relaxation by its environment and is zero at equilibrium. This relaxation is also characterized by a first-order rate with exponential decay time $T_2$. This $T_2$ represents the amount of time for the magnetization, $M_x$, to decay to $1/e$ of its initial value. The relaxation time $T_2$ is known as the spin-spin relaxation time and can be expressed by

$$\frac{dM_x}{dt} = -\frac{1}{T_2}M_x$$ \[24\]

When molecular motions are very fast, as in nonviscous liquids and gases, $T_1 = T_2$ for most interactions, and $T_2$ offers no additional information. However, this is not true in general, and typically in solids $T_1 \gg T_2$, and $T_2$ does provide additional information.

As many as five independent mechanisms may contribute to the total relaxation process. The relaxation rate for a particular nucleus in a specific chemical environment will depend upon which mechanisms contribute and the effectiveness of each. In the following sections of this chapter, a brief review of these mechanisms is discussed.

**Relaxation Mechanisms**

As mentioned above, when the nuclei have absorbed radiation and have been excited to the upper energy level, there are ways to return them to the lower state by exchanging
energy with their environment, called spin-lattice relaxation. The efficiency of this process is characterized by the relaxation time $T_1$, or alternatively, the relaxation rate, $R_1 = \frac{1}{T_1}$. The spin-lattice relaxation time $T_1$ is required for a perturbed system of nuclei to reach an equilibrium condition. A large value of $T_1$ indicates an inefficient relaxation process. The different types of interactions which cause relaxation are (a) magnetic dipole-dipole interaction ($R_{1DD}$), (b) quadrupole interaction ($R_{1QR}$), (c) spin-rotation interaction ($R_{1SR}$), (d) chemical shift anisotropy interaction ($R_{1CSA}$), and (e) scalar-coupling interaction ($R_{1SC}$).

In fact, each of the foregoing interactions may be contained in the overall relaxation process, where the relaxation rate is usually considered as a summation of the specific rates of all the mechanisms:

$$R_{1ALL} = R_{1DD} + R_{1QR} + R_{1SR} + R_{1CSA} + R_{1SC} \quad [25]$$

Fortunately, in many cases only one of the numerous possible mechanisms predominates, so a quantitative interpretation can be done easily.

Dipole-Dipole (DD) Relaxation

The principal source of nuclear relaxation for spin 1/2 nuclei is via magnetic dipole-dipole interactions. Consider the relaxation of a nucleus $I$ by another nucleus $S$. The
local field \( H_{\text{loc}}^{\text{DD}} \) generated at \( I \) by \( S \) is given by the classical equation (44)

\[
H_{\text{loc}}^{\text{DD}} = \pm \mu_s (3\cos^2 \theta - 1) \gamma_{IS}^3
\]

[26]

where \( \mu_s \) is the magnetic moment, \( \theta \) is the angle between the static field and the axis through \( I \) and \( S \), and \( \gamma_{IS} \) is the distance between \( I \) and \( S \) (44), as shown in Figure 2.

![Diagram showing the positions of the two nuclei and the angle \( \theta_{IS} \) between their internuclear vector \( \gamma_{IS} \) and the magnetic field \( H_0 \).](image)

Figure 2. Diagram showing the positions of the two nuclei \( I \) and \( S \) and the angle \( \theta_{IS} \) between their internuclear vector \( \gamma_{IS} \) and the magnetic field \( H_0 \).

The above equation tells us two things: First, because the local field depends on \( \mu_s \), the nucleus with the largest nuclear magnetic moment (such as a proton) will be the most powerful source of internuclear dipolar relaxation. Second, due to inverse sixth power dependence on the interdipole distance, dipole-dipole relaxation is a very short-range effect.
Just as a precessing nuclear moment can interact with a coherent applied rf magnetic field, so can it interact with the component at the Larmor frequency of the randomly fluctuating local magnetic field.

A detailed derivation of the full equations for dipolar relaxation can be found in Tsang and Farrar (44). Assuming rotational motion for the case of n spins of type S relaxing a spin I, the result is

\[ R_{1DD} = \frac{1}{T_{1DD}} = \frac{2\gamma_i^2\gamma_j^2\hbar^2 S(S + 1)}{15r_{ij}^6} \left[ \frac{3\tau_c}{1 + \tau_c^2\omega_I^2} + \frac{\tau_c}{1 + \tau_c^2(\omega_I - \omega_S)^2} + \frac{6\tau_c}{1 + \tau_c^2(\omega_I + \omega_S)^2} \right] \]

[27]

For mobile liquids, where molecular reorientation is fast, and thus \( \tau_c \) is short enough (i.e., \( \tau_c \ll 1 \)), the above equation can be simplified to

\[ R_{1DD} = \frac{1}{T_{1DD}} = \frac{4}{3n} \frac{\gamma_i^2\gamma_j^2\hbar^2 S(S + 1)}{r_{ij}^6} \tau_c \]

[28]

where \( \gamma_i \) and \( \gamma_j \) are the magnetogyric ratios of nuclei i and j, respectively; \( \tau_c \) is the reorientational correlation time; and \( n_S \) is the number of nuclei of spin S. According to the above equation, dipole-dipole relaxation is temperature...
dependent. At high temperatures, $\tau_c$ is shorter (fast motion), and the efficiency of dipole-dipole interactions is lowered. Thus, this $T_{1DD}$ is lengthened.

It is necessary to point out that the relaxation of the spin dipole is caused both by other spins on the same molecule (intramolecular) and on different molecules (intermolecular). When the nuclear spin is located on the interior of the molecule (such as carbon-13 in CH$_2$Cl$_2$), intermolecular relaxation is negligible. In fact, when studying relaxation times, intermolecular contribution is usually eliminated by dissolving the solute in a solvent which does not have significant nuclear magnetic moment (for example, deuterated solvents).

Once the relaxation times have been determined by experimentation, they can furnish information about the correlation times of spin-spin vectors in the molecule, which can be used to characterize the molecular reorientation. Frequently, they are compared with those theoretical models discussed in Chapter I to establish a relationship between the relaxation time and the parameters of the model.

### Quadrupolar Relaxation (QR)

Nuclei with a spin quantum number greater than 1/2 (e.g., $^{17}$O, $I = 5/2$) will undergo a relaxation process through interactions with a fluctuating electric field opposed to a magnetic field. A spin $I = 1/2$ nucleus has a
spherical nuclear charge distribution; but for a nucleus with a higher spin quantum number, the charge distribution is nonspherical and has a quadrupole moment $Q$ (23). If such a nucleus is in a molecule where it is surrounded by an asymmetric electronic charge distribution, it can be relaxed quite efficiently by electric quadrupole interaction. In the liquid phase, the quadrupole mechanism is four or five orders of magnitude more effective than any other mechanism in promoting relaxation, and where present, accounts for essentially all of the relaxation.

In the simplified case of extreme narrowing conditions, the quadrupole relaxation rate can be given by (3)

$$R_{1QR} = \frac{1}{T_{1QR}} = \frac{3}{125} \left( \frac{\epsilon^2 gQ}{\mathcal{H}} \right)^2 (1 + \frac{n^2}{3}) \tau_c$$

[29]

where $\frac{\epsilon^2 gQ}{\mathcal{H}}$ is the electric Quadrupolar Coupling Constant (QCC), which is made up of the nuclear quadrupole moment $Q$, the electric field gradient $g$, and the fundamental constants $\epsilon$ and $\mathcal{H}$. $\tau_c$ is the correlation time for molecular reorientation, and $n$ is the asymmetry factor. By measuring $T_{1QR}$, one can obtain the QCC, which measures the asymmetry of electronic charge distribution around the nucleus. Since $T_{1QR}$ depends upon the rotational correlation time, its relation to temperature is the same as that for $T_{1DD}$. 
Spin-Rotation (SR) Relaxation

When a molecule rotates in a liquid, fields associated with this mechanism are generated by the motion of the molecular magnetic moment arising from the electronic distribution within the molecule. Consider a rotating molecule with a moment of inertia $I$. Any electron in the molecule undergoing such rotation will generate a local magnetic field at the nucleus because it behaves like a circulating electric current. Molecular collisions causing changes in both directions and rotation will modulate this field and provide a relaxation process. It can be shown that for molecules undergoing diffusional reorientation, the relaxation rate for a symmetric top molecule (4) is given by

$$R_{1SR} = \frac{1}{T_{1SR}} = \frac{2kT}{3\hbar^2} [I_n C_n^2 (\tau_j)_\| + 2I_\perp C_\perp^2 (\tau_j)_\perp]$$

where $I_n$ and $I_\perp$ are components of inertia tensors and $C_n$ and $C_\perp$ are components of the spin-rotation tensors with respect to the symmetry axis. The terms $(\tau_j)_n$ and $(\tau_j)_\perp$ are the angular momentum correlation times.

For spherical molecules, $I_n = I_\perp = I$, $(\tau_j)_n = (\tau_j)_\perp = \tau_j$, and the above equation can be written as

$$R_{1SR} = \frac{1}{T_{1SR}} = \frac{2kT}{\hbar^2} [C_n^2 + 2C_\perp^2] = \frac{2kT}{\hbar^2} C^2 \tau_j$$

[31]
where $c^2 = \frac{1}{3}[C_n^2 + 2C_1^2]$ is called the spin-rotation coupling constant, and $\tau_j$ is the angular momentum correlation time. Hubbard (25) has shown that $\tau_j$ is related to the molecular reorientation correlation time used in the dipole-dipole mechanism by the following equation;

$$\tau_i \cdot \tau_j = \frac{1}{6kT} \quad [32]$$

From eqs 31 and 32, it can be seen that the spin-rotation relaxation rate, $R_{1\text{SR}}$, is proportional to $\tau_j$ which, in turn, is inversely proportional to $\tau_C$. Therefore, as the temperature increases, $\tau_j$ also increases, causing an increase in the $R_{1\text{SR}}$. Therefore, the spin-rotation relaxation rate is most efficient for small symmetrical molecules at high temperatures.

Spin-rotation is also a more important relaxation mechanism for small molecules which have short $\tau_C$ and, therefore, a longer $\tau_j$. At low temperatures, $R_{1\text{SR}}$ is inefficient and $R_{1\text{DD}}$ is efficient because of the slow molecular motion. As the temperature increases, $R_{1\text{DD}}$, in general, decreases slowly (within the extreme narrowing limit) due to decreasing $\tau_C$ until $R_{1\text{DD}}$ becomes negligible. At high temperature, $T_1$ begins to decrease with temperature, due to spin-rotation relaxation.
If the relaxation mechanism were pure spin rotation, $T_1$ would decrease monotonically with temperature ($\ln T_1$ is linear with $1/T$), which is totally opposite to other mechanisms. Nuclei relaxed partially by spin rotation, therefore, in $T_1$, show a nonlinear behavior as a function of temperature. This enables spin rotation to be detected in the presence of other relaxation mechanisms.

Chemical Shift Anisotropy (CSA) Relaxation

As is well known, the local magnetic field, $H_{loc}$, experienced by a nucleus in a magnetic field is determined by the shielding tensor, according to the equation (3)

$$H_{loc} = H_0 - \sigma H_0 = H_0 (1 - \sigma)$$

[33]

The shielding tensor is dependent upon the orientation of the molecule in the magnetic field. Rapid molecular motions in the liquid state average these values, yields an average chemical shift, given by (33,18)

$$\sigma_{avg} = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

[34]

For symmetric top molecules, the equation reduces to

$$\sigma_{avg} = \frac{1}{3} (2\sigma_1 + \sigma_u)$$

[35]
where \( \sigma_{xx} = \sigma_{yy} = \sigma_1 \) and \( \sigma_{zz} = \sigma_n \) refer, respectively, to the shielding perpendicular and parallel to the molecular symmetry axis. The rotation of the molecule will produce a fluctuating magnetic field which also provides a spin-lattice relaxation mechanism (i.e., chemical shift anisotropy). In the extreme narrowing case for axial symmetry, the equation for \( T_{1CSA} \) can be written as (3)

\[
R_{1CSA} = \frac{1}{T_{1CSA}} = \frac{2}{15} \gamma^2 H^2 \rho (\Delta \sigma)^2 \tau_c \tag{36}
\]

where

\[
\Delta \sigma = \sigma_n - \sigma_1 \tag{37}
\]

Chemical shift anisotropy is usually an inefficient mechanism and is rarely found to contribute significantly to spin relaxation, except in the following situations:

(a) Experiments performed at very high fields. However, even at 63 MHz, CSA relaxation still does not dominate relaxation for the nonprotonated carbon in toluene (29); and

(b) Heavy molecules with large shielding tensors (\( \sigma \)).

Scalar Coupling (SC) Relaxation

Suppose a nucleus (I) is spin-spin coupled with a second nucleus (S). It is possible for S to provide a fluctuating magnetic field and cause relaxation mechanisms,
called scalar relaxation. If the relaxation time of nucleus S is short enough (usually S is a quadrupolar nucleus), this mechanism would be efficient for spin-lattice relaxation. Equations for this type of scalar relaxation have been derived (3)

\[ R_{1SC}^I = \frac{1}{T_{1SC}^I} = \frac{8\pi^2}{3} S(S + 1)J_{IS}^2 \frac{T_S^I}{1 + (\omega_I - \omega_S)^2(T_1^S)^2} \]  \[ (38) \]

and

\[ R_{2SC}^I = \frac{1}{T_{2SC}^I} = \frac{4\pi^2}{3} S(S + 1)J_{IS}^2 \left[ \frac{T_S^I}{T_1^I} + \frac{T_S^I}{1 + (\omega_I - \omega_S)^2(T_1^S)^2} \right] \]  \[ (39) \]

where \( J_{IS} \) is the spin-spin coupling constant, S is the spin of the quadrupolar nucleus, \( \omega_I \) and \( \omega_S \) are the Larmor frequencies of the two nuclei, and \( T_1^S \) is the longitudinal relaxation time of nucleus S.

The above two equations show that this mechanism can have very different effects on \( T_1 \) and \( T_2 \) processes. For example, in the most common case \((\omega_I - \omega_S)^2(T_1^S)^2 \gg 1\), so

\[ \frac{1}{T_{1SC}^I} = \emptyset \quad \text{and} \quad T_{1SC}^I \to \infty \]  \[ (40) \]

then
\[
\frac{1}{T_2^{SC}} = \frac{4\pi^2}{3} S(S + 1) J_{1S}^2 \tau_S^C
\]

which means scalar coupling relaxation contributes only to \(T_2\). The exceptions occur when the Larmor frequencies are very close. For instance, \(^{13}\text{C} - ^{81}\text{Br}\) \((\gamma_{^{13}\text{C}} \approx \gamma_{^{81}\text{Br}})\), scalar coupling relaxation does contribute significantly to \(T_1\) (13,14,28,29,32).

**Separation of Mechanisms**

The observed relaxation rate is the sum of the relaxation rates of all the various mechanisms outlined in the previous section. Each mechanism gives different chemical information. Consequently, to gain the full knowledge from a study of relaxation data, it is important to resolve the contribution of each mechanism.

Several methods are available for differentiating the various relaxation mechanisms (3,31). First, if quadrupolar interaction is present (nucleus with \(I > 1/2\)), it is predominant over other spin-lattice relaxation mechanisms. Second, since relaxation by scalar coupling makes a significant contribution in only very special cases (e.g., in the case of a bromine-bearing carbon), it is normally considered to be absent.

The rest of mechanism (i.e., \(R_{1DD}, R_{1SR}, \) and \(R_{1CSA}\)) can be separated in the following manner. The dipolar
contribution to the overall relaxation process can be separated from all of the other relaxation mechanisms by measuring the nuclear Overhauser enhancements (NOE or \( \eta \)) (12).

The NOE is a property whose magnitude is directly proportional to the fraction of the total relaxation that occurs by the dipole-dipole mechanism. The theoretical maximum NOE for a nucleus can be observed when 100% of the relaxation is dipolar, and also can be calculated from magnetogyric ratios. For carbon-13 bonded to hydrogen atoms, the ratio \( \eta_{\text{max}} = \gamma_H^2 \gamma_{13}^C \). The experimentally observed NOE is defined as

\[
\eta_{\text{exp}} = \frac{I_E}{I_N} - 1
\]  

where \( I_E \) is the intensity of the enhanced signal, \( I_N \) is the intensity of the non-enhanced signal, and the contribution of the dipole-dipole mechanism can be obtained by

\[
T_{1DD} = T_{\text{obsed}} \times \frac{\eta_{\text{max}}}{\eta_{\text{exp}}}
\]  

where \( T_{\text{obsed}} \) is the measured spin-lattice relaxation time. If \( \eta_{\text{exp}} < \eta_{\text{max}} \), this indicates the presence of a nondipolar relaxation process. The contribution to the relaxation rate from other processes (\( T_{1\text{other}} \)) can be given as

\[
T_{\text{obsed}} = \frac{1}{T_{1DD}} + \frac{1}{T_{1\text{other}}}
\]
For $I = 1/2$ nuclei without scalar coupling relaxation,

$$\frac{1}{T_{\text{tother}}} = \frac{1}{T_{1\text{SR}}} + \frac{1}{T_{1\text{CSA}}}$$  \[45\]

Since $T_{1\text{CSA}}$ is field dependent, the above equation can be written as

$$\frac{1}{T_{\text{tother}}} = \frac{1}{T_{1\text{SR}}} + \frac{2\gamma^2H_0^2(\Delta \sigma)^2}{15\gamma_1 \gamma_2 \tau_C}$$  \[46\]

Thus, by measuring $T_1$ at two different field strengths, can be calculated. Then, by simply plugging $T_{1\text{SR}}$ into eq 45, $T_{1\text{CSA}}$ can be determined easily. Finally, $T_{1\text{SR}}$ can be obtained by means of eq 46. As mentioned before, the spin-rotation mechanism is dependent on temperature, which allows it to be distinguished from other mechanisms.

The Relationship between Dipole-Dipole Relaxation Correlation Times and Diffusion Constants

Since the dipole-dipole relaxation time can be isolated from $T_{1\text{obsed}}$, the rotational correlation times may be obtained directly from $T_{1\text{DD}}$ from eq 28. The experimental correlation times, $\tau_C$, can be calculated using standard values for $\gamma_1$, $\gamma_j$, $\tau$, and $r_{ij}$.

Several investigators (26,43) have considered the problem of anisotropic diffusion of symmetric top molecules,
and Woessner (48) has developed the following expression relating the correlation $\tau_c$ to its diffusion constants:

$$\tau_c = \frac{A}{6D_\perp} + \frac{B}{5D_\perp + D_\parallel} + \frac{C}{2D_\perp + 4D_\parallel}$$  \[47\]

where $A = (3\cos^2 \theta - 1)/4$, $B = 3\sin^2 \theta \cos^2$, and $C = (3\sin^4 \theta)/4$; $D_\perp$ and $D_\parallel$ are the diffusion constants for rotation perpendicular and parallel to the symmetry axis; and $\theta$ is the angle between the axis and the reorienting vector.

If one has measured $\tau_c$ from two vectors at different angles relative to the symmetry axis ($\theta$), then eq 47 may be used to obtain values for both $D_\perp$ and $D_\parallel$. Alternatively, the above equation can also be used to obtain predictions of the correlation times from theoretical models (see Chapter I) and to compare predictions with experimental results.
CHAPTER NOTES


CHAPTER III

RAMAN AND INFRARED LINESHAPE ANALYSIS

Basic Concepts

Two of the spectroscopic methods commonly used for the study of molecular vibrations and rotations are Raman and infrared spectroscopy \((2, 6, 11, 12, 21, 34)\). With the developments of the laser light source, direct recording signals from Raman and infrared (IR) spectrometers allow researchers to obtain a complete picture of the effects of specific intermolecular interactions on molecular dynamics in liquid.

Although both Raman and IR spectra supply complementary vibrational information, the two forms of spectroscopy arise from different physical processes.

Raman Spectroscopy

The Raman effect is named in honor of C. V. Raman, who developed the technique in 1928 \((22, 24)\). Although it had been theorized by Smekal \((31)\) and Landsberg and Mandelstam \((15)\), Raman was awarded a Nobel Prize in 1930 for his study of the Raman effect.

Let us consider a molecule placed in an electric field. In this situation, the electron cloud will be displaced relative to the nuclear framework. This distortion (or polarization) produces an induced dipole moment, regardless
of whether there is a permanent molecular dipole moment. This situation can be represented mathematically as

\[ P = \alpha E \]  

where \( P \) is the induced electric moment (i.e., dipole moment per unit volume, called polarization), \( E \) is the electric field, and \( \alpha \) is the polarizability of the material. Imagine an electric field \( E \) which is associated with an incident beam of frequency \( \nu_0 \). This electric field may be expressed (27) as

\[ E = E_0 \cos(2\pi \nu_0 t) \]  

where \( E_0 \) is the amplitude of the wave. In this case, the molecular polarizability will fluctuate as

\[ P = \alpha E_0 \cos(2\pi \nu_0 t) \]  

The Raman effect results from the interaction of the polarizability \( \alpha \) with the normal mode of vibration of the molecules. For the \( k \)th normal mode, \( \alpha \) can be expressed as

\[ \alpha = \alpha_0 + \Sigma \kappa \cos(2\pi \nu_k t) \]  

The first term, \( \alpha_0 \), expresses the static polarizability for the molecule with a fixed nuclear position. The second term expresses the polarizability changes which arise from the
time-dependent normal modes of the molecule, and \( k \) is the frequency of the \( k \)th vibration. Substituting the above equation into eq 51 for the induced dipole results in

\[
P = \alpha_0 E_0 \cos(2\pi \nu_0) + \frac{E_0}{2} \sum_k [\cos 2\pi (\nu_0 + \nu_k)t] + \cos 2\pi (\nu_0 - \nu_k)t]
\]

[52]

The first term describes a classically oscillating dipole radiating at frequency \( \nu_0 \), (i.e., Rayleigh scattering). The second term describes dipoles oscillating at frequencies \( \nu_0 - \nu_k \) and \( \nu_0 + \nu_k \) (called Stokes and anti-Stokes Raman scattering), and thus, also describe the radiation at the frequencies (see Figure 3). The scattering at these frequencies is known as Raman scattering.

**Infrared Spectroscopy**

In order to absorb infrared radiation, a molecule must undergo a net change in dipole moment as a consequence of its vibrational or rotational motion. Only under these circumstances can the alternating electrical field of the incident radiation interact with the molecule and cause changes in the amplitude of one of its motions. For example, when a hydrogen chloride molecule vibrates, a regular fluctuation in dipole moment occurs, and a field is established that can interact with the electrical field associated with the probing radiation. If the frequency of the radiation matches the natural vibrational frequency of the
Figure 3. Energy level diagram illustrating the fundamental processes of Raman scattering. The exciting line is of energy $\hbar \nu_0$. Raman bands appear at $\hbar (\nu_0 - \nu_1)$ and at $\hbar (\nu_0 + \nu_1)$. 
molecule, there occurs a net transfer of energy which results in a change in the amplitude of the molecular vibration; absorption of the radiation is the consequence. Similarly, the rotation of asymmetric molecules around their centers of mass results in a periodic dipole fluctuation. Again, interaction with incident radiation is possible. The predominant source of molecular radiation in the infrared is the result of vibration of the molecules in characteristic modes. Energy transitions between various states of molecular rotation also produce infrared absorption.

**Vibrational Lineshapes**

From normal vibrational spectra, three types of information can be obtained: peak frequency, peak intensity, and lineshape. Most investigations have been directed toward the study of peak frequencies and intensities.

In recent years, however, a significant number of studies have used Raman and infrared band contours to probe the dynamics of molecular reorientation processes in gases and liquids. Although it has long been known that the spectral lines can be broadened by both vibrational and molecular reorientational relaxation, Gordon (16) first introduced a quantitative theory relating lineshape to molecular motion. This theory has since been extended by Bartoli and Litovitz (11) and Nafie and Peticolas (18) and
is now used extensively in the analysis of Raman and infrared band contours (5, 7, 8, 13, 16, 24, 25, 26, 28-30, 36, 37).

A careful analysis of a vibration bandshape can provide information about molecular motion in neat liquids and in solution. In lineshape analysis, one encounters two extremes in the experimental lineshape. They are Lorentzian and Gaussian bands; both are symmetrical about their peak centers (27).

Theoretically, Lorentzian bands describe an exponential process in a rapidly changing environment. Consequently, we have a time-dependent distribution of line shifts about the unperturbed oscillator. The frequency distribution of band intensities, \( I(\omega)_L \) is

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

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

Theoretically, Gaussian band shapes describe static situations in a slowly changing environment. Therefore, the distribution about the center of the unperturbed oscillator is independent of time. Under these conditions, the frequency distribution of band intensities, \( I(\omega)_G \), can be expressed as

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

[54]
where all the parameters have the same meanings as for a Lorentzian peak.

There is a difference, however, between the above two band shapes which can best be illustrated by comparing their relative intensities at greater displacements from their band centers.

For \((\omega - \omega_0) = \Delta\)

\[ I(\omega)_L = \frac{A}{2} \quad \text{and} \quad I(\omega)_G = \frac{A}{2} \quad \text{[55]} \]

For \((\omega - \omega_0) = 2\Delta\)

\[ I(\omega)_L = \frac{A}{5} \quad \text{and} \quad I(\omega)_G = \frac{A}{16} \quad \text{[56]} \]

Obviously, the Gaussian peaks will decrease more rapidly than the Lorentzian peaks, which can be observed in the band wings (see Figure 4).

Experimentally, very few pure Gaussian or Lorentzian profiles are encountered, but a combination of both is almost always the case. For small- to medium-sized molecules in the liquid phase, the vibrational lineshape is closer to a Lorentzian band contour.
Figure 4. Comparison of Gaussian and Lorentzian bandshapes. Dotted line = Gaussian bandshapes; Solid line = Lorentzian bandshapes.
Fourier Transformations

In many experiments, it is useful to sort out what frequencies are present in a complex waveform and to determine the intensity at each of these frequencies. Fourier analysis is a mathematical technique for separating a complex waveform into its spectral components. A complex waveform, for example, measured as a function of time, is often called a function in the "time domain", whereas its corresponding frequency spectrum is said to be in the "frequency domain". By using the principles of Fourier analysis, it is possible to transform data from one domain into the other, which can be expressed as

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

where \( \omega \) is the angular frequency (i.e., \( \omega = 2\pi v \)), and \( i = \sqrt{-1} \). It has been shown that the inverse relation is also true (2,17), as illustrated in the following equation

\[
I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} G(t) e^{-i\omega t} dt
\]

This technique has been widely used in NMR, IR, and Raman spectroscopy.

Both Lorentzian and Gaussian peaks can be Fourier transformed. For the Lorentzian peak, the result is (27)
\[ G(t)_L = \int A \left[ 1 + \left( \frac{\omega}{\Delta} \right)^2 \right]^{-1} e^{i\omega t} d\omega \]

\[ = A\Delta^2 \int \frac{e^{i\omega t}}{\Delta^2 + \omega^2} d\omega \quad [59] \]

\[ = A\Delta \pi \cdot \exp(-\Delta t) = B \cdot \exp(-t/\tau) \]

where \( \tau = 1/\Delta \), \( B = A\Delta \pi \), \( \Delta \) is the half-width at half maximum, and \( B \) is a normalization constant which is equal to unity if the Lorentzian function were initially normalized. For the Gaussian peak, the result is (27)

\[ G(t)_G = \int_{-\infty}^{+\infty} A e^{-\ln 2 (\omega/\Delta)^2} e^{i\omega t} d\omega \]

\[ = 2A \int_{-\infty}^{+\infty} e^{-\ln 2 (\omega/\Delta)^2} \cos \omega t d\omega \quad [60] \]

\[ = A (\pi/\ln 2)^{1/2} \exp(-\Delta^2 t^2/4\ln 2) \]

\[ = B \cdot \exp[-(4\ln 2)^{-1}(t/\tau)^2] \]

where \( \tau = 1/\Delta \) and \( B = A (\pi/\ln 2)^{1/2} \). Again, in this case, \( B \) is unit, assuming an initially normalized peak. The unit of \( \Delta \) for both cases is radians/sec, so the width in cm\(^{-1}\) must be multiplied by 2\(\pi c\) to convert it to the correct units.

From the above Fourier transformation result, and from the semi-log plot in Figure 5, one can see that the Fourier
Figure 5. Correlation function of Gaussian and Lorentzian
in $G(t)$ versus time.
transformation of a Lorentzian peak is an exponential. On the other hand, Fourier transformation of a Gaussian peak results in a nonlinear, semi-logarithmic curve. In both cases, however, a large value of $\Delta$ (i.e., a broad peak) indicates a fast decay (i.e., short $\tau$ value).

**Relaxation Processes**

Both rotational and vibrational relaxation will cause broadening of the observed peak in the condensed phase. For example, in IR, the molecule can absorb radiation at the frequency of the oscillating dipole. However, the molecule itself will rotate and, in doing so, will reorient its dipole moment with respect to the direction of the incoming electric field. Then, the total dipole moment is given by

$$\mu = \mu_0 + \frac{1}{2}\mu_0'\left\{\cos(\omega_v + \omega_\tau)t + \cos(\omega_v - \omega_\tau)t\right\}$$

where $\mu_0$ is the equilibrium dipole moment, $\mu_0'$ is its first derivative with respect to the normal coordinate, $\omega_v$ is the vibrational frequency, and $\omega_\tau$ is the rotational frequency.

In the liquid phase, these rotational frequencies are arranged according to the Boltzmann distribution, which means that there is a greater population at smaller frequency displacements from the vibrational frequency than at larger displacements. Furthermore, an increase in temperature leads to higher average rotational frequencies. This
is manifested by a wider peak, which is, in turn, characterized by a shorter reorientation time.

In Raman spectroscopy, one must consider the polarizability, instead of the dipole moment. A Taylor series expansion of the polarizability in terms of vibrational normal coordinates allows the vibrational-rotational correlation function to be written as the product of an amplitude and an angle-dependent factor (35). The time-dependent development of the amplitude factor is assigned to vibrational relaxation, whereas the time development of the angle-dependent factor is assigned to rotational relaxation.

If we consider reorientational effects in IR, then the reorientational correlation function is given as

\[ G_1(t) = \langle P_1(\cos \theta) \rangle = e^{-2Dt} = e^{-t/\tau_1} \]  \[62\]

where \( \tau_1 = (2D)^{-1} \) and \( D \) is the diffusion constant.

A plot of \( \ln G_1(t) \) vs. \( t \) will produce a Gaussian function in the limit of zero time. At later times, the curve will decay exponentially. This relaxation time, \( \tau_1 \), can be obtained from the area under the curve.

On the other hand, in Raman spectroscopy, the reorientation correlation function is given as

\[ G_2(t) = \langle P_2(\cos \theta) \rangle = e^{-6Dt} = e^{-t/\tau_2} \]  \[63\]
An analogous plot of \( \ln G_2(t) \) vs. \( t \) will assume a Gaussian contour at short intervals of time and will become exponential at longer intervals. The area under the curve is equal to

\[
\tau_2 = (6D)^{-1}
\]

Thus, there is greater broadening due to reorientation in Raman than in IR, as shown in the following equation:

\[
\tau_{1,\text{IR}} = 3\tau_{2,\text{Raman}}
\]

### Determination of Rotational Diffusion Constants

By Raman and IR Lineshape Analysis

After Gordon's introduction analysis of reorientational relaxation from IR lineshapes, rotational relaxation times or diffusion constants for various molecules have been obtained on the assumption that the overall observed IR band width can be attributed entirely to reorientational relaxation. Bartoli and Litovitz showed that vibrational relaxation plays an important role in the broadening of vibrational lines. Thus, it is necessary to correct vibrational band widths before diffusion constants can be obtained. This correction can readily be done by utilizing isotropic Raman spectra (4,9,14).

In Raman spectroscopy, we are able to obtain both polarized (\( I_{\text{pol}} \)) and depolarized (\( I_{\text{dep}} \)) linewidths. The
observed Raman pure vibrational isotropic spectrum (6) is
given by

$$I(\omega)_{iso} = I(\omega)_{pol} - \frac{4}{3} I(\omega)_{dep}$$  \[66\]

where $I(\omega)_{iso}$ is that component of the scattered intensity
resulting only from vibrational relaxation (i.e.,
independent of molecular orientation). Thus, isotropic
linewidths are equal to vibrational relaxation linewidths

$$\Delta_{iso} = \Delta_{vib}$$  \[67\]

On the other hand, the depolarized (i.e., anisotropic)
Raman spectrum contains both vibrational and reorientational
components (i.e., dependent on both vibrational and reorienta-
tional motions). The linewidth term can be expressed as

$$\Delta_{aniso} = \Delta_{dep} = \Delta_{vib} + \Delta_{rot}$$  \[68\]

The substitution of eq 67 into eq 68 produces

$$\Delta_{rot} = \Delta_{aniso} - \Delta_{iso}$$  \[69\]

For non-totally symmetric modes, such as $E'$ modes,

$$I_{anis}(\omega) = \frac{3}{4} I_{pol}(\omega)$$  \[70\]
Introducing the above equation into eq 66 produces

\[ I_{iso}(\omega) = I_{pol}(\omega) - 4/3 I_{anis}(\omega) = 0 \quad [71] \]

and

\[ \Delta_{aniso} = \Delta_{vib} + \Delta_{rot} \quad [72] \]

The IR line profile is given by the Fourier transformation of both vibrational and reorientational correlation functions, and the linewidth can be expressed as (32)

\[ \Delta_{IR} = \Delta_{vib} + \Delta_{rot} \quad [73] \]

As mentioned in Chapter I, for symmetric-top molecules, two diffusion constants are required to characterize their reorientational motion (i.e., \( D_L \) and \( D_H \)). By using the small-step rotational diffusion model \((1, 33)\), the bandwidth \( \Delta_{rot} \) is related to the rotational diffusion constants by

\[ \Delta_{rot} = \frac{1}{2\pi c} \left[ n(n+1)D_L + m^2(D_H - D_L) \right] \quad [74] \]

where \( n \) is the rank of the tensor involved in the description of each spectroscopic process. \( n = 1 \) in IR, and \( n = 2 \)
in Raman spectroscopy, $m$ is an integer related to the symmetry of the individual vibrational modes, which can be $0$ or $\pm 1$ in IR and $0$, $\pm 1$ or $\pm 2$ in Raman spectroscopy, respectively.

For totally symmetrical Raman modes (i.e., $A'$ modes), $n = 2$ and $m = 0$; thus, eq 74 can be simplified to

$$\Delta_{\text{rot}}^{\text{RAMAN}} = \frac{1}{2\pi c} [6D_\perp]$$

By combining the above equation with eq 69, $D_\perp$ can be solved easily as

$$D_\perp = \frac{\pi c}{3} [\Delta_{\text{depol}}^{\text{RAMAN}} - \Delta_{\text{pol}}^{\text{RAMAN}}]$$

For nontotally symmetric modes (i.e., $E'$ modes), two situations are possible:

1. In Raman, $n = 2$ and $m = \pm 2$; thus, eq 74 can be written as

$$\Delta_{\text{rot}}^{\text{Raman}} = \frac{1}{2\pi c} [2D_\perp + 4D_n]$$

Combining the above equation with eq 72 produces

$$\Delta^{\text{RAMAN}} = \Delta^{\text{vib}} + \frac{1}{2\pi c} [2D_\perp + 4D_n]$$

where $\Delta^{\text{Raman}}$ is the HWHM of Raman band; and
(2) In IR, where $n = 1$ and $m = \pm 1$, eq 74 is then expressed as

$$\Delta_{\text{rot}}^{\text{IR}} = \frac{1}{2\pi c}(D_1 + D_n)$$  \hspace{1cm} [79]$$

Combining the above equation with eq 73 produces

$$\Delta^{\text{IR}} = \Delta^{\text{vib}} + \frac{1}{2\pi c}(D_1 + D_n)$$  \hspace{1cm} [80]$$

where $\Delta^{\text{IR}}$ is the HWHM of the IR band.

Theoretical (19,34) and experimental (32) evidence suggests that for a given mode, the vibrational linewidth ($\Delta^{\text{vib}}$) will be the same in both IR and Raman; therefore, by combining the Raman and IR results, one may use eqs 78 and 80 to solve for $D_n$, which is given by

$$D_n = \frac{1}{3}(2\pi c(\Delta^{\text{RAMAN}} - \Delta^{\text{IR}}) - D_1)$$  \hspace{1cm} [81]$$
CHAPTER NOTES


CHAPTER IV

SOLVENT AND TEMPERATURE DEPENDENCE OF $^{13}$C RELAXATION
TIMES AND REORIENTATIONAL DYNAMICS
IN TRIBROMOBENZENE

Introduction

As discussed earlier in Chapter II, NMR relaxation measurements have been found to be an important method in the study of molecular motion both in the neat liquid and in solution. NMR solvent- and temperature-dependent measurements can be utilized to study solute-solvent interactions. In some cases, these interactions can be monitored by observing the changes in the solute's spin-lattice relaxation time.

Benzene is an oblate symmetric top molecule of relatively high asphericity whose reorientational dynamics in the liquid phase and in solution have been well characterized by both NMR and vibrational spectroscopy (1-3,13,14,26, 27,29). Like the parent compound, the 1,3,5-trisubstituted benzenes are oblate tops whose asphericities are even greater than that of benzene. There have, however, been far fewer investigations of their rotational dynamics (8,18).

Presented in this chapter is an investigation of the carbon-13 spin-lattice relaxation times ($T_1$'s) of the protonated carbons in 1,3,5-tribromobenzene (TBB) in a
number of solvents of widely varying viscosity. Also pre-
presented is a study of the temperature-dependent carbon-13
relaxation times in tribromobenzene. The derived reorienta-
tional correlation times were compared with those of benzene
and with the predictions of various theories of rotational
diffusion.

Experimental Method

Tribromobenzene, a solid at room temperature, was puri-
fied by vacuum sublimation. CCl₄ and CS₂ were distilled
prior to use; deuterated solvents were used as received.
Samples were prepared gravimetrically at mole fractions
ranging from 0.02 to 0.05, depending on solubility. The
mixtures were placed in 10 mm NMR tubes, degassed by four
freeze-pump thaw cycles, and sealed under vacuum.

Experiments were performed on a Varian VXR-300 FT-NMR
spectrometer operating at 75.4 MHz. The ambient probe tem-
perature was 23 ± 1°C.

Spin-lattice relaxation times were determined using
the standard inversion recovery pulse sequence,
\[(\pi - \tau - \frac{\tau}{2} - t_d)_n (2\Omega)\]. Four or sixteen transients (depen-
ding on concentration) were acquired at each to ten \(\tau\)-values,
ranging from 0.1 to 1.5 times the estimated \(T_1\) (obtained in
a preliminary experiment). The delay time between repeti-
tions, \(t_d\), was at least 5\(T_1\). An initial estimate for \(M_0\) was
obtained by a measurement at \(\tau > 5T_1\).
The magnetization data were fit, using a nonlinear least-squares program, to the following three-parameter ($M_0$, $\cos \theta$, $T_1$) equation (24):

$$M(t) = M_0[1 - (1 - \cos \theta) e^{-t/T_1}]$$  \[82\]

Initial estimates for $T_1$ and $\cos \theta$ were obtained from the slope and intercept of a preliminary linear least-squares fit. Three or four measurements of $T_1$ were performed in each solution. The average values in each solution are shown in the fourth column of Tables II and III, together with standard deviations between runs.

Nuclear Overhauser enhancements, $n$, were obtained using standard decoupling procedures (19). Enhanced intensities ($I_E$) were measured by acquiring four or sixteen transients under continuous broadband proton decoupling. Non-enhanced intensities ($I_N$) were obtained by measuring four or sixteen transients with gated decoupling (decoupler on only during FID acquisition). Overhauser enhancements were calculated as $n = (I_E/I_N) - 1$. The delay time between repetitions was, in all cases, at least $10T_1$. Three or four measurements of $n$ were performed in each solution. The enhancements were found to be complete in all solvents (5); that is,

$$\text{NOE} = (I_E/I_N) - 1 = (1/2)(\gamma(1H)/\gamma(13C)) = 2.0$$  \[83\]
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\sigma$ [Å]</th>
<th>$\eta$ [cP]</th>
<th>$T_1^a$ [s]</th>
<th>$\tau_C(\text{exp})^a$ [ps]</th>
<th>$\tau_C(\text{P})$ [ps]</th>
<th>$\tau_C(\text{HZ})$ [ps]</th>
<th>$\tau_C(\text{MV/FR})$ [ps]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Acetone-d$_6$</td>
<td>4.60</td>
<td>0.313</td>
<td>5.9</td>
<td>7.5</td>
<td>15.4</td>
<td>3.6</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.7)</td>
<td>(0.9)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Carbon disulfide</td>
<td>4.58</td>
<td>0.359</td>
<td>7.0</td>
<td>6.3</td>
<td>17.6</td>
<td>3.8</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.2)</td>
<td>(0.2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Dichloromethane-d$_2$</td>
<td>4.75</td>
<td>0.423</td>
<td>5.6</td>
<td>7.9</td>
<td>20.7</td>
<td>4.2</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.2)</td>
<td>(0.3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Chloroform-d</td>
<td>5.18</td>
<td>0.552</td>
<td>4.7</td>
<td>9.5</td>
<td>27.1</td>
<td>4.8</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.3)</td>
<td>(0.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Benzene-d$_6$</td>
<td>5.46</td>
<td>0.621</td>
<td>4.0</td>
<td>11.0</td>
<td>30.5</td>
<td>5.1</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.2)</td>
<td>(0.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Pyridine-d$_5$</td>
<td>4.92</td>
<td>0.911</td>
<td>2.9</td>
<td>15.2</td>
<td>44.7</td>
<td>6.5</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.3)</td>
<td>(0.1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Carbon Tetrachloride</td>
<td>5.61</td>
<td>0.928</td>
<td>3.5</td>
<td>12.7</td>
<td>45.5</td>
<td>6.5</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.1)</td>
<td>(0.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Quantities in parentheses represent one standard deviation.
Table III.
Relaxation and Correlation Times\(^a\)

<table>
<thead>
<tr>
<th>(T(°C))</th>
<th>(T_1(s))</th>
<th>(\tau_C(\text{exp})) (ps)</th>
<th>(\tau_C(\text{HKW})) (ps)</th>
<th>(\tau_C(\text{HZ})) (ps)</th>
<th>(\tau_C(\text{MV/FR})) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>3.8 (0.2)</td>
<td>11.6 (0.6)</td>
<td>10.5</td>
<td>5.9</td>
<td>7.9</td>
</tr>
<tr>
<td>23</td>
<td>4.0 (0.2)</td>
<td>11.8 (0.5)</td>
<td>9.6</td>
<td>5.1</td>
<td>6.0</td>
</tr>
<tr>
<td>39</td>
<td>5.1 (0.6)</td>
<td>8.7 (1.0)</td>
<td>8.1</td>
<td>4.4</td>
<td>5.1</td>
</tr>
<tr>
<td>54</td>
<td>5.3 (0.9)</td>
<td>8.4 (1.4)</td>
<td>7.3</td>
<td>3.9</td>
<td>4.5</td>
</tr>
<tr>
<td>72</td>
<td>6.4 (0.4)</td>
<td>6.9 (0.4)</td>
<td>6.7</td>
<td>3.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>

\(E_a\) (kcal/mol) | 1.7 (0.2) | 1.5 | 1.7 | 1.7 | 1.7

\(^a\)Quantities in parentheses represent one standard deviation.
Results and Discussion

Experiment 1: Solvent Dependence of $^{13}$C Relaxation Times and Reorientational Dynamics in Tribromobenzene

Presented in Table II are the measured $^{13}$C longitudinal relaxation times ($T_1$'s) of TBB in solution. The solvents are ordered in the direction of increasing viscosity.

Because the measured Overhauser enhancements were at their maximum in all solvents, the sole significant contribution to relaxation is from $^{13}$C-$^1$H dipole-dipole interaction ($\gamma$). Thus, the rotational correlation times may be obtained directly from $T_1$ (4) via the expression given in eq 28. The numerical relation was calculated using standard values for $\gamma(^{13}$C) = $6.726 \times 10^3$ rad·s$^{-1}$·Gauss$^{-1}$, $\gamma(^1$H) = $2.675 \times 10^4$ rad·s$^{-1}$·Gauss$^{-1}$, $\hbar = 1.0545 \times 10^{-27}$ erg·s; and $r_{CH} = 1.08 \times 10^{-8}$ cm.

Shown in the fifth column of Table II are the experimental correlation times, $\tau_C(\text{exp})$, of TBB in the various solvents. As one might expect, the reorientational times are substantially greater than the values reported for benzene in solution, where $\tau_C = 1.2$ - 1.6 ps at room temperature [as determined from diffusion constants (29)]. It is seen, also, from Figure 6 that, as predicted by hydrodynamic theories of rotational diffusion (6), $\tau_C(\text{exp})$ exhibits an approximately linear increase with solvent viscosity.
Figure 6. Viscosity dependence of reorientational correlation times in tribromobenzene. See Tables II and III for solvent numbers. Filled circles = $\tau_c$(exp); Open circles = $\tau_c$(HKW).
Like benzene, TBB is an oblate spheroid (i.e., $a < b = c$, where $a$, $b$, and $c$ are the semi-axis lengths of the volume ellipsoid). From bond lengths and van der Waal's radii (7), the axis lengths are approximately: $a = 1.85 \, \text{Å}$ and $b = c = 4.43 \, \text{Å}$. The mean radius, therefore, is $r = c/2 = 3.31 \, \text{Å}$.

TBB's axial ratio, $\rho = b/a = 2.39$, indicates that the molecule is quite nonspherical, as do its moments of inertia, $I_a = 4.68 \times 10^{-37} \, \text{g} \cdot \text{cm}^2$ and $I_B = I_C = 2.34 \times 10^{-37} \, \text{g} \cdot \text{cm}^2$.

Based both upon its shape and inertia tensor, one would predict that TBB's reorientational behavior is highly anisotropic, characterized by two rotational diffusion constants, $D_1$ and $D_\infty$, which represent the tumbling of the unique ($C_3$) axis and spinning about this axis, respectively.

The C-H vector, whose reorientation modulates the $^{13}\text{C}-^{1}\text{H}$ dipolar coupling, lies at $90^\circ$ relative to the principal axis. Therefore, the classic Woessner equation for the rotational diffusion of a symmetric-top rotor (see eq 47) reduces to

$$\tau_C = (24D_1)^{-1} + (3/4)(2D_1 + 4D_\infty)^{-1}$$

This equation, together with values for $D_1$ and $D_\infty$ estimated from models of anisotropic reorientation, will be used to calculate theoretical correlation times to be compared with the experimental results.
The earliest model of anisotropic molecular reorientation was formulated by Perrin (22), who extended the Stokes-Einstein-Debye (SED) model of isotropic diffusion to asymmetric rotors. Assuming a solvent continuum and "stick" boundary conditions, he solved the Navier-Stokes equation (25) to obtain diffusion constants via the expression given in eq 6. Using eq 96 of Perrin's paper (22) and \( \rho = 2.39 \), one finds for TBB that \( f_L = 1.252 \) and \( f_H = 1.394 \). Application of eq 6 with \( r = 3.31 \text{ Å}, T = 296 \text{ K}, \) and solvent viscosities (\( \eta \) in Table II) permits calculation of \( D_L \) and \( D_H \), which together with eq 28, yield theoretical estimates of the reorientational correlation times using the Perrin model (\( \tau_C(P) \) in Table II). As seen from Table II, \( \tau_C \) s predicted with this model are uniformly greater than experimental times by a factor of 2-3. This is not surprising and has been generally found for the reorientation of small to moderate size molecules in solution (6).

Hu and Zwanzig (15) noted that the longer-than-observed correlation times predicted by the Perrin model result from use of the stick boundary condition and suggested that the alternative "slip" condition may furnish a more realistic description of reorientation on a molecular scale. In the slip limit, the perpendicular diffusion constant is given by eq 10. For TBB, \( f_{HZ} = 0.195 \). In the slip limit, "spinning" about the top axis is unhindered by frictional torques. Therefore, \( D_H \) may be obtained from the correlation time of a
Free Rotor via eqs 8 and 9. For TBB at 296 K, \((D_n)_{FR} = 68.9 \times 10^9\) s\(^{-1}\) = 68.9 ns\(^{-1}\). This value for \(D_n\), which is independent of solvent viscosity, and \(D_i\) from eq 84 permit calculation of correlation times, \(\tau_c(HZ)\), from the Hu-Zwanzig model, as shown in Table II.

One sees that, just as the stick limit correlation times, \(\tau_c(P)\), are too long, \(\tau_c\)'s calculated using the slip boundary condition are far shorter than the experimental results by approximately a factor of 2. Note, however, that in contrast to small molecules such as methyl iodide (6), acetonitrile (6), and dichloromethane (23), in which experimental \(\tau_c\)'s are closer to the slip limit, the observed reorientational dynamics of the larger TBB molecule is found to lie midway between the slip and stick extremes.

Although it has not been used widely, the model created by Gillen and Griffiths (13) provides a good description of rotation in liquid benzene. They assume that \(D_n\) is that of an inertially controlled Free Rotor (FR) and that \(D_i\) can be calculated from the microviscosity (MV) model of Gierer and Wirtz (see Chapter I) which was originally developed for isotropic diffusion. This study used the Gierer-Wirtz expressions for \(D_i\), replacing the radius of the sphere with \(B = 4.43\) Å, the larger semi-axis length, together with \((D_n)_{FR} = 68.9\) ns\(^{-1}\), to calculate correlation times predicted by the combined Microviscosity/Free Rotor (MV/FR) approach. As seen in the last column of Table II, the calculated
reorientational times, $\tau_C(MV/FR)$, are only marginally superior to those predicted by the slip model and are still almost a factor of 2 below $\tau_C(exp)$. Indeed, if one uses the mean radius, $r = 3.31$ Å, rather than $b$ in the Gierer-Wirtz equations, the calculated times are even lower than $\tau_C(HZ)$.

Hynes, Kapral, and Weinberg (HKW) (see Chapter I) noted the failure of the stick and slip models to provide a realistic general description of molecular rotation in fluids. They introduced a slip coefficient, $\beta$, into a modified boundary condition and re-solved the Navier-Stokes equation. The limiting values $\beta = 0$ and $\beta = +\infty$ correspond to purely slip and stick diffusion, respectively. Although their model was originally formulated assuming isotropic reorientation, Tanabe (27) has intuitively extended the HKW approach to calculate $D_1$ and $D_\infty$ of symmetric-top rotors. His modified HKW equations may be written as eqs 11 and 12; for TBB, $a_1 = 1.766$. The slip coefficient, $\beta$, may be calculated from Enskog collision theory using equations presented in Chapter I.

This study utilized the modified HKW model to calculate $D_1$ and $D_\infty$, and from these, $\tau_C(HKW)$ for TBB in the various solvents. The results are displayed in Table IV and plotted in Figure 6.

One observes immediately that this model predicts correlation times that are far superior to those of either of the limiting (slip or stick) theories of rotational
Table IV
Rotational Diffusion Constants and Correlation Times
Calculated with the Hynes-Kapral-Weinberg Model

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Theta^3 \beta$ [\si{\textdegree}]</th>
<th>$D_{\perp}$ [\si{\text{ns}^{-1}}]</th>
<th>$D_{\parallel}$ [\si{\text{ns}^{-1}}]</th>
<th>$\tau_C(\text{HKW})$ [\si{\text{ps}}]</th>
<th>$\tau_C(\text{exp})$</th>
<th>$\frac{\tau_C(\text{exp})}{\tau_C(\text{HKW})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Acetone-$d_6$</td>
<td>2.2</td>
<td>25.3</td>
<td>54.1</td>
<td>4.5</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>2. Carbon disulfide</td>
<td>4.41</td>
<td>29.0</td>
<td>30.8</td>
<td>6.7</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>3. Dichloromethane-$d_2$</td>
<td>5.20</td>
<td>16.9</td>
<td>26.2</td>
<td>7.9</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>4. Chloroform-$d$</td>
<td>5.25</td>
<td>13.7</td>
<td>24.2</td>
<td>9.1</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>5. Benzene-$d_6$</td>
<td>5.13</td>
<td>12.4</td>
<td>24.0</td>
<td>9.6</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>6. Pyridine-$d_5$</td>
<td>\begin{array}{l} A^a \ \text{2.95} \ \text{9.6} \ \text{36.2} \ \text{8.9}\ \text{1.71} \ \text{3}^b \ \text{5.21} \ \text{9.0} \ \text{22.1} \ \text{11.7} \ \text{1.30} \end{array} &amp;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Carbon Tetrachloride</td>
<td>5.61</td>
<td>8.7</td>
<td>29.7</td>
<td>12.3</td>
<td>1.03</td>
<td></td>
</tr>
</tbody>
</table>

\(^a^{\text{Calculation using } \sigma(\text{pyr}) = 4.92 \text{ \AA}, \text{ from reference 28.}}\)

\(^b^{\text{Calculation using } \sigma(\text{pyr}) = 5.24 \text{ \AA}, \text{ see text.}}\)
diffusion. Indeed, with the exception of the solvents acetone and pyridine, there is virtually quantitative agreement between theory and experiment.

Tanabe has studied the temperature, pressure, and solvent dependence of reorientation in benzene\(^\text{(26,27,29)}\). He, too, found that diffusion constants calculated with the HKW model were in far better agreement with experimental results than were values determined from any of the earlier models.

Finally, a brief discussion of the poorer agreement between \(\tau_c(\text{HKW})\) and \(\tau_c(\text{exp})\) found for solutions of TBB in acetone and pyridine (calculation A) is appropriate. One sees from the second column of Table IV that the slip coefficients calculated in these solvents are markedly below the values in the other five solutions. This leads directly to larger diffusion constants (particularly \(D_n\)) and, thus, shorter calculated correlation times. There is no apparent physical reason for a greater degree of slip (lower \(S\)) between TBB and either of these solvent molecules. Therefore, the disagreement appears to result from errors in the calculation of \(S\).

It is well established that parameters calculated using the Enskog model are critically sensitive to values chosen for the solute and solvent diameters. Therefore, for consistency both here and in earlier studies, the "recommended" values of Mourits and Rummens \(^{(21)}\), who performed a
critical review of different methods of estimating \( \sigma \), were adopted. There is no value for \( \sigma \)(pyr) in this (21) or most earlier references; the current research used \( \sigma \)(pyr) = 4.92 \AA, which was obtained by Tanabe and Hiraishi (29) from Raman linewidth measurements. However, this method yields generally lower \( \sigma \)'s. For example, \( \sigma \)(benz) = 5.12 \AA (29), versus the recommended value of 5.46 \AA (21). If, alternatively, one assumes that \( \sigma \)(pyr)/\( \sigma \)(benz) = 4.92/5.12 = 0.96, then, with \( \sigma \)(benz) = 5.46 \AA, one obtains \( \sigma \)(pyr) = 5.24 \AA. As seen in calculation B on pyridine using this diameter, one calculates a higher slip coefficient and, hence, a correlation time in much closer agreement with the experimental result.

Experiment 2: Temperature Dependence of Rotational Correlation Times In Tribromobenzene

In Experiment 1, the results of an investigation of \(^{13}\)C spin-lattice relaxation and carbon-hydrogen correlation times, \( \tau_c \)(C-H), of 1,3,5-tribromobenzene (TBB) in solution were reported. The experimental results were compared to the predictions of various theoretical models of rotational diffusion (6). It was observed that the relatively new Hynes-Kapral-Weinberg (HKW) model (see Chapter I) proved superior to earlier theories; correlation times calculated with this model were in excellent agreement with measured \( \tau_c \)'s in five of the seven solvents studied.
In a subsequent Raman/IR study of the rotational diffusion constants, $D_1$ and $D_\infty$, of the related molecule, 1,3,5-trifluorobenzene (TFB) (see Chapter V), it was observed that, again, the HKW model predicted diffusion coefficients that agreed closely with experimental values for TFB in solution. It was found, though, that the theory failed to describe accurately the temperature dependence of the perpendicular diffusion constant in neat TFB. The calculated activation energy for $D_1$ was 2.6 kcal/mol, substantially greater than the experimental value of $1.5 \pm 0.1$ kcal/mol. Other theories ($13,15$) yielded activation energies even further from experiment than did the HKW model.

In order to determine whether the incapacity to furnish accurate activation energies is specific to TFB or represents an inherent weakness of the HKW model, the temperature dependence of $\tau_C(C-H)$ in the structurally similar TBB was investigated. Because this compound is a solid at conveniently accessible temperatures ($T_{mp} = 121^\circ C$), the relaxation times and nuclear Overhauser enhancements of the protonated carbons of TBB as a function of temperature in the solvent benzene-$d_6$ ($X = 0.05$) were measured.

The spectrometer and experimental procedures were the same as in the earlier room temperature solution study outlined in this chapter (see page 58). The probe temperature was regulated by heated "boil-off" gas from a tank of
liquid-N$_2$. Temperatures were measured using an ethylene glycol "NMR thermometer" (30).

Shown in Table III are the $^{13}$C relaxation times of TBB in C$_6$D$_6$ as a function of temperature. These values represent the average of three measurements. The measured Overhauser enhancements were complete ($\eta = \eta_{\text{max}} = 2.8$) at all temperatures, which indicated that $^{13}$C-$^1$H dipolar interaction is the sole significant relaxation mechanism.

The standard equation (see eq 28) was used to calculate the carbon-hydrogen correlation times, $\tau_c(\text{exp})$, which are displayed in Table III and in Figure 7. Shown also are the theoretical reorientational correlation times calculated from the Hynes-Kapral-Weinberg (HKW), Hu-Zwanzig (HZ), and Microviscosity/Free Rotor (MV/FR) theories (see Chapter I). The times predicted by the HKW model are in quite acceptable agreement with the experimental results. Most importantly, unlike in TFB (see above), the calculated activation energy is close (within one standard deviation) to the experimental value.

One observes further from Table III that the MV/FR and HZ theories yield activation energies even closer to the measured value (within 0.1 kcal/mol). However, in contrast to the HKW model, the two models discussed earlier yield calculated correlation times that fall far below the measured values by as much as a factor of two.
Figure 7. Temperature dependence of experimental and calculated rotational correlation times. 

a = experiment; b = HKW; c = MV/FR; d = HZ.
The results observed here provide additional evidence that the Hynes-Kapral-Weinberg (HKW) theory of molecular reorientation furnishes rather accurate estimates of diffusion constants and correlation times in a number of systems (27-29). An assessment of its general utility must await the results of additional experimental investigations.
CHAPTER NOTES


CHAPTER V

RAMAN AND INFRARED STUDY OF REORIENTATIONAL DYNAMICS IN TRIFLUOROBENZENE AND TRIBROMOBENZENE

Introduction

As discussed in Chapter III, various spectroscopic techniques, such as IR, Raman, and NMR, have been widely used to study the vibrational and reorientational motions of liquid molecules. However, these techniques alone, as used in the past, do not furnish enough information to characterize the anisotropic rotation of molecules. Therefore, researchers often combine NMR with Raman spectroscopic results to evaluate the rotational diffusion constant for the tumbling ($D_t$) and spinning ($D_n$) motions.

Recently, a new technique has been developed by Lee and Kim (22). This process combines modern FT-IR with laser Raman linewidth measurements and can easily overcome the above-mentioned difficulties. In conjunction with the investigation of $^{13}$C NMR relaxation times and reorientational dynamics in tribromobenzene. Several $A_1'$ and $E'$ vibrations were measured for 1,3,5-trifluorobenzene and 1,3,5-tribromobenzene in a number of solvents. In addition, $2A_1'$ vibrations were measured in neat 1,3,5-trifluorobenzene as a function of temperature. Derived values of the two
rotational diffusion constants, $D_1$ and $D_m$, were compared with the predictions of several current theories.

**Experimental Method**

**Raman Spectroscopy**

The basic configuration of the laser Raman spectrometer used for all measurements is illustrated in Figure 8. The irradiation source ($2\theta$) of the Raman spectrometer is an argon-ion laser (coherent radiation model CR-3). The polarized and depolarized spectra were acquired at $90^\circ$ to the incident laser beam. The scattered light was collected through a polarization analyzer and polarization scrambler into the entrance slit of a Spex 14018 scanning double monochromator. Detection was accomplished using an RCA-C31034 photomultiplier tube and photon counting electronics. The resultant signals were recorded digitally via an interfaced microprocessor (Apple II+) and stored on floppy diskettes for further processing (16, 32).

**Infrared Spectroscopy**

Infrared spectra were recorded on a Nicolet 20-SXB Fourier transform infrared spectrometer, using a germanium-coated KBr beam splitter and a deuterated triglycine sulfate (DTGS) detector. The spectrometer was equipped with a Nicolet 1280 minicomputer. The sample was placed in the cell with NaCl window (the cell pathlength was 0.1 mm), was scanned 32 times, and the interferogram was converted to a
Figure 8. Basic components of the Laser Raman Spectrometer.
spectrum by a Fourier transform algorithm. Then, the spectrum was ratioed with a similar spectrum of the window without a sample, to produce the final spectrum.

**Experiment 1: Raman/Infrared Study of Reorientational Dynamics in Trifluorobenzene**

**Introduction**

There have been numerous spectroscopic investigations of the rotational behavior of benzene, both in the neat liquid and in solution (1-3, 12, 15-16, 19, 28-30, 33). Like benzene, its 1,3,5-trisubstituted derivatives (C₆H₃X₃) are oblate symmetric tops (a < b = c, where a, b, and c are the semi-axis lengths) with axial ratios, \( \rho = b/a > 1 \). There have, however, been comparatively few studies of their condensed phase reorientational dynamics.

In Experiment 1 of Chapter IV, the results of an NMR investigation of \( ^{13}C-{¹}H \) dipole-dipole relaxation times of 1,3,5-tribromobenzene in solution were reported. Several theories of molecular reorientation were employed to calculate the "tumbling" and "spinning" diffusion constants, \( D_t \) and \( D_n \), and hence, the rotational correlation times, \( \tau_C(C-H) \).

It was observed that the relatively new Hynes-Kapral-Weinberg model (see Chapter I) yielded the closest agreement to experimental correlation times derived from \( ^{13}C \) T₁'s. Unfortunately, \( \tau_C(C-H) \) is a nonlinear function of both \( D_t \) and \( D_n \) (32). A more stringent test of the relative merits of
current theories would be a direct comparison of the individual diffusion constants with predicted values.

With this goal in mind, an investigation of Raman/IR linewidth investigation of two $A'_1$ and two $E'$ vibrational modes of 1,3,5-trifluorobenzene (TFB) as a function of temperature in the neat liquid and at room temperature in the solvents $CH_2Cl_2$ and $CS_2$ has been undertaken. The derived diffusion constants, $D_z$ and $D_w$, are compared with the predictions of various theories of rotational diffusion.

**Experimental Method**

Trifluorobenzene and the solvents $CH_2Cl_2$ and $CS_2$ were obtained commercially and purified by fractional distillation prior to use. The sample was contained in a sealed melting-point capillary tube which was inserted into Harney-Miller cell. Temperature regulation was accomplished via liquid nitrogen boil-off or heated air flow and was measured with an iron-constantan thermocouple adjacent to the sample. Details of the Raman spectrometer, microprocessor controlled data acquisition and storage, and temperature regulation have been presented earlier in this chapter (see page 78).

The Raman spectra of $v_3(A'_1)$ at 1011 cm$^{-1}$ and $v_4(A'_1)$ at 579 cm$^{-1}$ (17) in neat TFB were acquired at various temperatures spanning the liquid range. Polarized and depolarized (anisotropic) spectra were measured three times
at each temperature. Following digital baseline subtraction, the isotropic spectrum for each of the runs was calculated via the relationship

\[ I_{\text{iso}}(\omega) = I_{\text{pol}}(\omega) - \frac{4}{3}I_{\text{anis}}(\omega) \]  

The isotropic and anisotropic spectra were plotted on graph paper to facilitate linewidth measurements. Both widths were corrected for the effect of finite monochromator slit-width \( s = 2.42 \text{ cm}^{-1} \) (FWHM), using the equation of Tanabe and Hiraishi (31). The temperature-dependent isotropic and anisotropic bandwidths of the two \( A_1' \) vibrations are presented in Table V. Values represent the average of the three runs at each temperature.

Table V
Temperature Dependence of Raman Linewidths
In Neat Trifluorobenzene

<table>
<thead>
<tr>
<th>T(k)</th>
<th>( \nu_3(A_1') - 1811 \text{ cm}^{-1} )</th>
<th>( \nu_4(A_1') - 579 \text{ cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta_{\text{iso}}(\text{Ram}) )</td>
<td>( \Delta_{\text{aniso}}(\text{Ram}) )</td>
</tr>
<tr>
<td>273</td>
<td>0.70</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>(0.05)</td>
<td>(0.02)</td>
</tr>
<tr>
<td>284</td>
<td>0.86</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>(0.03)</td>
<td>(0.20)</td>
</tr>
<tr>
<td>296</td>
<td>0.96</td>
<td>2.40</td>
</tr>
<tr>
<td></td>
<td>(0.02)</td>
<td>(0.10)</td>
</tr>
</tbody>
</table>
Table V—continued

<table>
<thead>
<tr>
<th>T(k)</th>
<th>$\nu_3(A_1^i) - 1\mu 11 \text{ cm}^{-1}$</th>
<th>$\nu_4(A_1^i) - 579 \text{ cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta_{\text{iso}}(\text{Ram})$</td>
<td>$\Delta_{\text{aniso}}(\text{Ram})$</td>
</tr>
<tr>
<td>316</td>
<td>1.12</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>(0.03)</td>
<td>(0.08)</td>
</tr>
<tr>
<td>338</td>
<td>1.24</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td>(0.04)</td>
<td>(0.10)</td>
</tr>
</tbody>
</table>

*aAll linewidths (FWHM) are given in cm$^{-1}$ and represent the average of the three runs.

*bQuantities in parentheses represent one standard deviation.

For TFB in CH$_2$Cl$_2$ and CS$_2$ solutions (X = 0.17), Raman spectra were acquired both from the $A_1^i$ modes, $\nu_3$ and $\nu_4$, and for the depolarized $E'$ vibrations, $\nu_{11}$ at 1124 cm$^{-1}$ and $\nu_{12}$ at 993 cm$^{-1}$ (17). The $A_1^i$ widths were analyzed in the same manner used for neat TFB. Widths of the $E'$ modes were corrected for monochromator slitwidth.

The infrared linewidths were also measured for both $E'$ bands ($A_1^i$ modes of D$_3h$ molecules are IR inactive) in the two solvents ($c = 0.05$ M), using a Nicolet 20-SXB Fourier transform infrared spectrometer. The cell pathlength was 0.1 mm. Widths were corrected for the finite instrumental resolution (1 cm$^{-1}$). All spectra were recorded three times at ambient temperature (23 ± 1°C) in each solvent. The average Raman and infrared linewidths for TFB in solution are presented in Table VI.
Table VI
Solvent Dependence of Raman and Infrared Linewidths in Trifluorobenzene$^a,b$

<table>
<thead>
<tr>
<th>Mode</th>
<th>$v_3(A_1^i)$</th>
<th>$v_4(A_1^i)$</th>
<th>$v_{11}(E')$</th>
<th>$v_{12}(E')$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta_{iso}$(Ram)</td>
<td>$\Delta_{aniso}$(Ram)</td>
<td>$\Delta$(IR)</td>
<td>$\Delta_{iso}$(Ram)</td>
</tr>
<tr>
<td>$\nu_3(A_1^i)$</td>
<td>0.79</td>
<td>2.58</td>
<td>---</td>
<td>0.70</td>
</tr>
<tr>
<td>1011 cm$^{-1}$</td>
<td>(0.01)</td>
<td>(0.03)</td>
<td>(0.02)</td>
<td>(0.08)</td>
</tr>
<tr>
<td>$\nu_4(A_1^i)$</td>
<td>2.80</td>
<td>3.77</td>
<td>---</td>
<td>2.32</td>
</tr>
<tr>
<td>579 cm$^{-1}$</td>
<td>(0.05)</td>
<td>(0.03)</td>
<td>(0.03)</td>
<td>(0.06)</td>
</tr>
<tr>
<td>$\nu_{11}(E')$</td>
<td>---</td>
<td>7.24</td>
<td>4.73</td>
<td>---</td>
</tr>
<tr>
<td>1124 cm$^{-1}$</td>
<td>(0.08)</td>
<td>(0.04)</td>
<td>(0.10)</td>
<td>(0.06)</td>
</tr>
<tr>
<td>$\nu_{12}(E')$</td>
<td>---</td>
<td>5.22</td>
<td>3.94</td>
<td>---</td>
</tr>
<tr>
<td>993 cm$^{-1}$</td>
<td>(0.04)</td>
<td>(0.03)</td>
<td>(0.05)</td>
<td>(0.02)</td>
</tr>
</tbody>
</table>

$^a$All linewidths (FWHM) are given in cm$^{-1}$ and represent the average of the three runs.

$^b$Quantities in parentheses represent one standard deviation.
The viscosity of neat TFB was measured as a function of temperature, using a Cannon-Fenske viscometer. The data was fit by a quadratic equation (34), which was used to interpolate viscosities at the temperatures of the Raman measurements. Densities were determined using a standard variable volume pycnometer and were also interpolated numerically (35) at the experimental temperatures.

Results and Discussion

Determination of Rotational Diffusion Constants

For totally symmetric vibrations in symmetric top molecules, if one assumes statistically independent linebroadening mechanisms, the anisotropic Raman bandwidth is the sum of contributions due to vibrational relaxation ($\Delta v$) and the tumbling rotational motion ($D_\perp$) (1). The isotropic linewidths, on the other hand, arise solely from vibrational relaxation. Thus, one may write (1)

$$\Delta_{iso}(Ram) = \Delta v$$  \hspace{1cm} [86]$$

and

$$\Delta_{aniso}(Ram) = \Delta v + \left(\frac{\pi c}{n c}\right)^{-1}[6D_\perp]$$  \hspace{1cm} [87]$$
where $\Delta_{\text{iso}}$ and $\Delta_{\text{aniso}}$ are full width full maximum (FWFM).

Thus, it is straightforward to extract $D_{\perp}$ from the isotropic and anisotropic bandwidths of the $A_i'$ modes in TFB.

For nontotally symmetric vibrations, the anisotropic Raman width is a linear function of $\Delta V$, $D_{\perp}$, and $D_{\|}$. Unlike symmetric modes, however, the isotropic scattering vanishes. Therefore, it is not possible to eliminate $\Delta V$ using Raman data alone. Fortunately, it has been shown that one may utilize Raman and infrared linewidths together to determine $D_n$ \cite{11,22,28}. The method is based on the theoretical \cite{23} and experimental \cite{31} evidence that vibrational relaxation contributes equally to the IR and Raman linewidths of a given vibration, whereas the rotational widths depend differently on $D_{\perp}$ and $D_{\|}$. For degenerate $E'$ vibrations in $D_{3h}$ molecules, one may write \cite{22}

\[
\Delta_{\text{aniso}}^{\text{(Raman)}} = \Delta V + \frac{1}{\pi C} [2D_{\perp} + 4D_{\|}] \tag{88}
\]

and

\[
\Delta^{\text{(IR)}} = \Delta V + \frac{1}{\pi C} [D_{\perp} + D_{\|}] \tag{89}
\]

where $\Delta_{\text{aniso}}^{\text{(Raman)}}$, $\Delta V$, and $\Delta^{\text{(IR)}}$ are FWFM.

The vibrational width, $\Delta V$, may be eliminated easily from these equations. Then, with $D_{\perp}$ calculated from the $A_i'$
widths, $D_w$ can be determined from the difference of the Raman and IR bandwidths via the relation

$$D_w = \left[ \Delta \text{anis} \left( \text{Ram} \right) - \Delta \text{IR} \right] / 3$$

Temperature Dependence of the Perpendicular Diffusion Constant in TFB

In the second and third columns of Table VII are shown the tumbling diffusion constants in neat TFB as a function of temperature, as determined from bandwidths of the $A_1$ vibrations (via eqs 86 and 87). The experimental values of $D_w$ calculated from $\nu_3$ and $\nu_4$ are in quite satisfactory agreement, as are their respective activation energies. This provides additional support for the statistical independence of vibrational relaxation and reorientational line broadening, implicit in the assumption of additive linewidths.

As in the earlier investigation of $^{13}$C NMR relaxation and C-H correlation times in tribromobenzene (see Chapter IV), it is informative to compare the experimental results to diffusion constants predicted by the various theories which have been employed to characterize molecular reorientation in benzene (4). Application of these models requires knowledge of the molecular dimensions and moments of inertia. Using standard bond lengths and van der Wall's radii (5), one obtains $a = 1.47$ Å and $b = c = 3.78$ Å for the semi-axis lengths in TFB; the inertia tensor components are
Table VII
Temperature Dependence of $D_1$ in Neat
Trifluorobenzene$^a, b$

<table>
<thead>
<tr>
<th>T(k)</th>
<th>$D_1$(exp)$^c$</th>
<th>$D_1$(exp)$^d$</th>
<th>$D_1$(MV/FR)</th>
<th>$D_1$(HZ)</th>
<th>$D_1$(HKW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>17</td>
<td>19</td>
<td>23</td>
<td>18</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>($\theta_1$)</td>
<td>($\theta_2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>284</td>
<td>20</td>
<td>20</td>
<td>28</td>
<td>21</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>($\theta_3$)</td>
<td>($\theta_1$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>296</td>
<td>22</td>
<td>25</td>
<td>34</td>
<td>26</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>($\theta_2$)</td>
<td>($\theta_2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316</td>
<td>25</td>
<td>26</td>
<td>47</td>
<td>35</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>($\theta_2$)</td>
<td>($\theta_2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>338</td>
<td>30</td>
<td>31</td>
<td>62</td>
<td>46</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>($\theta_2$)</td>
<td>($\theta_2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_a$(kcal/mol)</td>
<td>1.5</td>
<td>1.4</td>
<td>2.7</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>($\theta_1$)</td>
<td>($\theta_2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Diffusion constants are given in ns$^{-1}$.

$^b$Quantities in parentheses represent one standard deviation.

$^c$Calculated from $v_3(A_1^\prime)$ at 1011 cm$^{-1}$.

$^d$Calculated from $v_4(A_1^\prime)$ at 579 cm$^{-1}$.
I_\perp = 4.88 \times 10^{-38} \text{ g-cm}^2 \text{ and } I_\parallel = 9.76 \times 10^{-38} \text{ g-cm}^2. \text{ The appropriate equations and calculational procedures required for utilization of the theories have been presented in Chapter IV.}

Gillen and Griffiths (15) demonstrated that the tumbling diffusion constant, D_\perp, in liquid benzene can be reasonably well reproduced by the Gierer-Wirtz Microviscosity equation (see Chapter I), whereas the spinning rate, D_\parallel, is close to the gas phase Free Rotor limit (1). Application of the Microviscosity/Free Rotor (MV/FR) model yields perpendicular diffusion constants, D_\perp(MV/FR), that range from 25% to 100% greater than the experimental values as the temperature is increased.

The Hu-Zwanzig (HZ) "slip" model of reorientation predicts diffusion constants, D_\perp(HZ), which are virtually identical to D_\perp(exp) up to 296 K but are approximately 50% greater than experimental results at the highest temperature studies.

As seen in the last column of Table VII, the newer Hynes-Kapral-Weinberg (HKW) theory of rotational diffusion with a microscopic boundary layer also yields values, D_\perp(HKW), that are in excellent agreement with the experimental results at the lower temperatures but increases more rapidly than does D_\perp(exp).

From these results, one concludes that the HZ and HKW models are superior to the earlier MV/FR formalism in
describing the tumbling motion in liquid TFB. All three theories, however, predict a greater temperature dependence (larger $E_a$) than was found from the experiment.

Reorientational Dynamics of TFB
In Solution

In addition to studying the temperature dependence of $D_1$ in neat TFB, the diffusion constants, $D_1$ and $D_2$, of TFB in CH$_2$Cl$_2$ and CS$_2$ has been determined using the procedures outlined above. These solvents were chosen because they are transparent in the regions of all four $A_1^′$ and $E^′$ TFB vibrations.

As can be seen in Table VIII, perpendicular diffusion constants calculated from $v_3$ and $v_4$ are equal in both solvents. Values of $D_2$ from $v_1^1$ and $v_1^2$ are also in reasonable agreement, considering the greater degree of error in determining this quantity. One notes that $D_1$ in CH$_2$Cl$_2$ is substantially larger than in the neat liquid (Table VII) at room temperature and is greater still in CS$_2$. This trend in tumbling rates follows the order that one would expect on the basis of relative viscosities; at 23°C, $\eta$(TFB) = 0.529 cP (18), $\eta$(CH$_2$Cl$_2$) = 0.419 cP (25), and $\eta$(CS$_2$) = 0.359 cP (25).

One sees from Table VIII that values of $D_1$ calculated from the MV/FR model are close to the experimental results in both solvents, whereas predictions of the HZ model are too high. This is opposite to the relative accuracy
Table VIII

Solvent Dependence of $D_L$ and $D_n$ in Trifluorobenzene$^a, b$

<table>
<thead>
<tr>
<th></th>
<th>$D_L$(CS$_2$)</th>
<th>$D_L$(CH$_2$Cl$_2$)</th>
<th>$D_n$(CS$_2$)</th>
<th>$D_n$(CH$_2$Cl$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>31$^c$</td>
<td>28$^c$</td>
<td>89.5$^e$</td>
<td>69.5$^e$</td>
</tr>
<tr>
<td>($\beta_2$)</td>
<td>((\beta_1))</td>
<td></td>
<td>(3.7)</td>
<td>(2.8)</td>
</tr>
<tr>
<td>31$^d$</td>
<td>28$^d$</td>
<td></td>
<td>82.3$^f$</td>
<td>62.2$^f$</td>
</tr>
<tr>
<td>($\beta_2$)</td>
<td>((\beta_1))</td>
<td></td>
<td>(1.8)</td>
<td>(1.6)</td>
</tr>
<tr>
<td>MV/FR</td>
<td>33</td>
<td>29</td>
<td>151</td>
<td>151</td>
</tr>
<tr>
<td>HZ</td>
<td>39</td>
<td>33</td>
<td>151</td>
<td>151</td>
</tr>
<tr>
<td>HKW</td>
<td>33</td>
<td>29</td>
<td>75</td>
<td>66</td>
</tr>
</tbody>
</table>

$^a$Diffusion constants (at 296 K) are given in ns$^{-1}$.

$^b$Quantities in parentheses represent one standard deviation.

$^c$Calculated from $\nu_3$ ($A_1'$) at 1011 cm$^{-1}$.

$^d$Calculated from $\nu_4$($A_1'$) at 579 cm$^{-1}$.

$^e$Calculated from $\nu_{11}$($E'$) at 1124 cm$^{-1}$.

$^f$Calculated from $\nu_{12}$($E'$) at 993 cm$^{-1}$.
exhibited by the two models for neat TFB. As before, perpendicular diffusion constants calculated using the HKW theory are in quite good agreement with experimental results, both in CH$_2$Cl$_2$ and in CS$_2$.

As the last two columns of Table VIII show, the spinning diffusion constant is somewhat greater in CS$_2$ than in CH$_2$Cl$_2$. Again, this order may be attributed to the lower viscosity of the latter solvent. Like the MV/FR model, the Hu-Zwanzig theory of slip diffusion predicts that rotation parallel to the symmetry axis is unhindered by solution viscosity because this motion does not require the displacement of the solvent. Thus, in both cases, the parallel diffusion constant is predicted to be dependent only on temperature and I, and may be calculated from the Free Rotor expression (see Chapter I). D$_n$ calculated in this manner exceeds the measured values by approximately a factor of two in both solvents. In contrast, D$_n$(HKW), calculated using the HKW model, is in quite satisfactory agreement with the experimental results, as was also found above for D$_t$(HKW) in the two solvents.

On the basis of these results, the HKW theory clearly provides the best description of reorientational diffusion in TFB. The same conclusion was reached by Tanabe (29,31) and Hiraishi (30,31) in investigations of the rotational dynamics of benzene in the liquid phase (2) and in solution.
(33) and in the study of the solvent dependence of $^{13}$C NMR relaxation times in tribromobenzene reported in Chapter IV.

Finally, it is informative to compare the rotational diffusion constants of TFB with those of benzene in solution. For C$_6$H$_6$ in CD$_2$Cl$_2$, it has been reported that $D_1^{(exp)} = 102$ ns$^{-1}$ and $D_\perp^{(exp)} = 177$ ns$^{-1}$ at ambient temperature (33). Each diffusion constant is roughly three times larger than the corresponding quantity measured for TFB in CH$_2$Cl$_2$ (Table VIII). The greater rotational rates result from benzene's smaller dimensions and moments of inertia and are predicted semiquantitatively by the HKW model. For C$_6$H$_6$ in CD$_2$Cl$_2$ (33), one obtains $D_1^{(HKW)} = 90$ ns$^{-1}$ and $D_\perp^{(HKW)} = 197$ ns$^{-1}$, which, in each case, is three times greater than the calculated values for TFB in CH$_2$Cl$_2$ (Table VIII).

**Experiment 2: Rotational Diffusion of Tribromobenzene in Solution**

**Introduction**

In Chapter IV, the results of a carbon-13 NMR relaxation time study of the reorientational dynamics of 1,3,5-tribromobenzene (TBB) in a number of solvents of widely varying viscosity were reported. The derived correlation times, $\tau_C(C-H)$, were compared with the predictions of various theories of rotational diffusion (see Chapter I). It was observed that the relatively new Hynes-Kapral-Weinberg (HKW) model yielded predictions in agreement with the
experimental results in five of the seven solvents, which proves this model superior to the other models tested.

As noted earlier in this chapter, a more rigorous test of the relative merits of the models tested would be furnished by a comparison of the individual diffusion constants with values calculated theoretically.

In order to test the capability of current models to furnish accurate a priori predictions of reorientational diffusion constants, the Raman and IR bandwidths of two vibrations of TBB in several solvents have been measured. The results are compared with theoretical predictions and with the results of the NMR relaxation time experiments (see Chapter IV).

Experimental Method

Details of the Raman spectrometer, digital data acquisition and storage, and sample preparation have been presented earlier in this chapter (see page 78). All experiments were performed at ambient temperature (23 ± 1°C). The solvents CCl₄, CH₂Cl₂, and CS₂ were chosen because they are transparent in the regions of ν₃(A₁') at 985 cm⁻¹ and ν₁₁(E') at 1085 cm⁻¹ in the vibrational spectra of TBB (17). All Raman and IR spectra were recorded three times.

The polarized and depolarized (anisotropic) Raman spectra of ν₃ were acquired in each of the solutions
Following baseline subtraction, the isotropic spectrum was calculated via the relation,
\[ I_{iso}(\omega) = I_{pol}(\omega) - (4/3)I_{anis}(\omega) \].
Spectra were plotted on graph paper and the bandwidths, \( \Delta_{iso} \) and \( \Delta_{anis} \), were determined manually. Widths were corrected for the finite monochromator slit width \( (S = 2.42 \, \text{cm}^{-1}) \) (FWHM) using the equation of Tanabe and Hiraishi (30,31).

Anisotropic Raman spectra of \( \nu_{11}(E') \) were recorded in each solution. The bandwidths were measured and corrected for spectrometer broadening. Infrared linewidths of \( \nu_{11} \) in each solution \( (c = 0.3 \, \text{M}) \) were determined using a Nicolet 20-SXB Fourier transform infrared spectrometer. The cell pathlength was 0.1 mm. The measured widths were corrected for the finite instrument resolution \( (1.0 \, \text{cm}^{-1}) \). The Raman and IR bandwidths (average of the three runs) of the \( \nu_3 \) and \( \nu_{11} \) modes of TBB in solution are displayed in Table IX. The procedure followed for the calculation of the rotational diffusion constants was the same as that used in Experiment 1.

Results and Discussion

Shown in the first row of Table X are the experimental tumbling and spinning diffusion constants, \( D_t \) and \( D_n \), calculated using eqs 86, 87, and 90 above. One observes that, in general, both diffusion constants are substantially greater in \( \text{CH}_2\text{Cl}_2 \) and \( \text{CS}_2 \) than in \( \text{CCl}_4 \), as would be expected on the
Table IX
Raman and Infrared Linewidths of Tribromobenzene in Solution\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \nu_3(A'_1) - 99) cm(^{-1} )</th>
<th>( \nu_{11}(E') - 1085 ) cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta_{iso}^{(\text{Ram})} )</td>
<td>( \Delta_{anis}^{(\text{Ram})} )</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>0.66 (0.01)</td>
<td>1.19 (0.03)</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>0.98 (0.01)</td>
<td>2.05 (0.09)</td>
</tr>
<tr>
<td>CS(_2)</td>
<td>0.91 (0.01)</td>
<td>2.21 (0.15)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Linewidths (FWHM) are in cm\(^{-1}\) and represent the average of the three runs.

\textsuperscript{b}Quantities in parentheses represent one standard deviation.
Table X
Experimental and Calculated Diffusion Constants
Of Tribromobenzene in Solution\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>$D_t$(CCL\textsubscript{4})</th>
<th>$D_l$(CH\textsubscript{2}Cl\textsubscript{2})</th>
<th>$D_l$(CS\textsubscript{2})</th>
<th>$D_n$(CCL\textsubscript{4})</th>
<th>$D_n$(CH\textsubscript{2}Cl\textsubscript{2})</th>
<th>$D_n$(CS\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental\textsuperscript{b}</td>
<td>8.4</td>
<td>16.8</td>
<td>20.4</td>
<td>27.2</td>
<td>33.9</td>
<td>33.5</td>
</tr>
<tr>
<td></td>
<td>(0.5)</td>
<td>(1.3)</td>
<td>(2.3)</td>
<td>(3.1)</td>
<td>(2.6)</td>
<td>(2.5)</td>
</tr>
<tr>
<td>Perrin &quot;stick&quot;</td>
<td>3.9</td>
<td>8.0</td>
<td>10.0</td>
<td>3.5</td>
<td>7.7</td>
<td>9.0</td>
</tr>
<tr>
<td>HZ &quot;slip&quot;</td>
<td>10.4</td>
<td>23.1</td>
<td>26.9</td>
<td>68.9</td>
<td>68.9</td>
<td>68.9</td>
</tr>
<tr>
<td>MV/FR</td>
<td>8.1</td>
<td>15.6</td>
<td>17.7</td>
<td>68.9</td>
<td>68.9</td>
<td>68.9</td>
</tr>
<tr>
<td>HKW</td>
<td>8.7</td>
<td>17.2</td>
<td>20.0</td>
<td>20.7</td>
<td>27.0</td>
<td>30.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a}All diffusion constants are given in ns\textsuperscript{-1}.

\textsuperscript{b}Quantities in parentheses represent one standard deviation.
basis of relative solvent viscosities; at 23°C, (CCl₄) = 0.928 cP, (CH₂Cl₂) = 0.419 cP, and (CS₂) = 0.359 cP (25). It is not surprising, either, that the diffusion constants for TBB are significantly below those of 1,3,5-trifluorobenzene (TFB) in the same solvents; for example, for TFB in CS₂, D₁ = 31 ns⁻¹ and Dₙ = 82 ns⁻¹ (7). The slowed reorientation of TBB results from its greater dimensions and moments of inertia. The equations and methods of calculation necessary for application of the various theoretical models have been presented in Chapter IV. Similarly, TBB's dimensions and moments of inertia and the requisite solvent properties are taken from the NMR study reported in Chapter IV.

As shown in Table X, diffusion constants calculated with Perrin's "stick" model of anisotropic reorientation (see Chapter I) range from two to six times smaller than the experimental results. This is commonly observed (4) and results from overestimation of the frictional torque in systems where solute and solvent are of similar size. Significantly, this model predicts that D₁ > Dₙ in oblate spheroids, contrary to the observed behavior here in TFB (7) and in benzene (8,30).

It is generally found that the Hu-Zwanzig (HZ) model, which employs "slip" boundary conditions, yields perpendicular diffusion constants in much closer agreement with experimental results than does Perrin's "stick" model.
This is, in fact, observed for TBB in all three solvents, as shown in the third row of Table X. According to the slip model, rotation about the axis of symmetry does involve displacement of the solvent. Hence, the frictional hindrance vanishes, and the spinning motion is that of a freely rotating gas-phase molecule. However, one finds that values of \( D_m \) calculated from the Free Rotor expression are approximately three times greater than the experimentally measured diffusion coefficients (Table X). Thus, the parallel rotation of TBB is far from the slip limit.

The Microviscosity/Free Rotor (MV/FR) approach was introduced by Gillen and Griffiths to characterize the reorientational behavior in liquid benzene (see Chapter I). One can see from Table X that perpendicular diffusion constants calculated from the Microviscosity equations approximate the experimental results. As with the HZ model, however, the Free Rotor parallel diffusion constants are far too large.

In contrast to the three models discussed above, the Hynes-Kapral-Weinberg (HKW) model, as extended by Tanabe, yields far superior estimates of both \( D_p \) and \( D_m \). The capability of the HKW model to provide accurate predictions of rotational diffusion constants has also been reported for benzene (8, 10) and for TFB (see Experiment 1 in this chapter) in the neat liquid and in solution.
It is informative to compare carbon-hydrogen rotational correlation times, $\tau_c(C-H)$, determined directly from $^{13}$C NMR relaxation studies, with the results of this investigation. For reorientation of a vector $90^\circ$ relative to the axis of symmetry, the correlation time is related to the diffusion coefficients by the expression given in eq 84.

As shown in Table XI, correlation times calculated using $D_1$ and $D_\infty$ from Raman/IR linewidths are equal to those determined from NMR relaxation studies to within experimental limits of error in the solvent CS$_2$. The disagreement between the values in CCl$_4$ and CH$_2$Cl$_2$ would appear to be slightly outside the measured limits of error. However, the deviations are small, and the author hesitates to ascribe it to a real effect, rather than to an experimental artifact.

<table>
<thead>
<tr>
<th>Table XI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental and Calculated Correlation Times of Tribromobenzene in Solution $^a,b$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>NMRC $^c$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Raman/IR $^e$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Perrin &quot;stick&quot;</td>
</tr>
<tr>
<td>HZ &quot;slip&quot;</td>
</tr>
</tbody>
</table>
Table XI--continued

<table>
<thead>
<tr>
<th></th>
<th>$\tau_c$ (CCl$_4$)</th>
<th>$\tau_c$ (CH$_2$Cl$_2$)</th>
<th>$\tau_c$ (CS$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MV/FR</td>
<td>7.7</td>
<td>5.1</td>
<td>4.4</td>
</tr>
<tr>
<td>HKW</td>
<td>12.3</td>
<td>7.7</td>
<td>6.7</td>
</tr>
</tbody>
</table>

*aAll correlation times are given in ps.

Quantities in parentheses represent one standard deviation.

Chen, Wang, and Schwartz (6).

NMR experiment was run in CD$_2$Cl$_2$.

This work.

One may also employ eq 84 to determine correlation times from diffusion constants calculated by the various theories. As reported in numerous systems (4), $\tau_c$'s from the stick model are well above the measured values. Conversely, correlation times calculated from the HZ and MV/FR theories are as much as a factor of two lower than the experimental results, as reported in the NMR study in Chapter IV. The large deviation results almost entirely from the overestimation of $D_m$ by a factor of three (see above), which characterizes the HZ and MV/FR theories.

As found above for the individual diffusion constants, rotational correlation times predicted by the HKW model agree well with the experimental results. On the basis of
this investigation, one can conclude that the close agree-
ment reported in Chapter IV does not result from a fortui-
tous cancellation of errors in $D_1(\text{HKW})$ and $D_n(\text{HKW})$. Rather,
it reflects the superior capabilities of the HKW model to
furnish accurate estimations of both reorientational
diffusion constants in these systems.
CHAPTER NOTES


34. The temperature dependent viscosities were fit by the equation: 
\[ (\eta P) = 0.737 - 9.81 \times 10^{-3}t + 5.94 \times 10^{-5}t^2, \] 
where \( t \) is in °C. The standard deviation was ± 0.006 cP.
35. The temperature dependent densities were fit by the equation: 
\[ d(\text{g/cm}^2) = 1.2783 - 1.68 \times 10^{-3}t - 4.86 \times 10^{-6}t^2, \] 
where \( t \) is in °C. The standard deviation was ± 0.0007 g/cm².
CHAPTER VI

THE EFFECTS OF HYDROGEN BONDING ON VIBRATIONAL FREQUENCIES AND RELAXATION TIMES IN HALOMETHANES

Introduction

There is a substantial body of spectroscopic and thermodynamic evidence that the protons in di- and trihalomethanes are relatively acidic and participate in the formation of hydrogen-bonded complexes with Lewis bases in solution (1,13,15,16,18-20,24,25). However, it has been noted (1,16) that the carbon-hydrogen vibrational frequency displacements are not consistent with the classic Badger-Bauer rule, which correlates the magnitude of the frequency shift with the hydrogen bound strength within a given class of compounds (3,26).

It was observed in a recent study of the isotropic Raman spectra of the $\nu_1$ (C-H/C-D stretching) modes of CH$_2$Cl$_2$ and CD$_2$Cl$_2$ in solution (7) that peak frequency displacements were not at all correlated with the solvent's basicity but could be explained solely on the basis of solution variation in the dispersion energy. On the other hand, it was found that vibrational relaxation times ($\tau_v$) exhibited a dramatic decrease in Lewis base solvents. It was noted that the same
trend in $\tau_\nu$ upon hydrogen bond formation had been observed in an earlier investigation of CDCl$_3$ in solution (34). In an effort to obtain a more complete characterization of the effects of intermolecular complexation on the band parameters of the C-H/C-D stretching modes in halomethanes an analogous investigation of vibrational frequency displacements and relaxation times of the $\nu_1$ bands of dibromomethane-d$_2$ and bromoform in solution was undertaken.

**Experimental Method**

All chemicals were obtained commercially. Bromoform and nondeuterated solvents were distilled prior to use. Solutions were prepared gravimetrically with a solute mole fraction of 0.05. To avoid spectral interference, CHBr$_3$ solutions were prepared in deuterated solvents. Nondeuterated dibromomethane (CH$_2$Br$_2$) could not be studied because of Fermi resonance, which causes splitting of the $\nu_1$ mode (39). Attempts to obtain spectra of CDBr$_3$ were unsuccessful due to sample decomposition at various laser frequencies and after repeated distillation.

The basic details of the spectrometer operation and digital data acquisition and storage have been presented in Chapter V (see page 78). The spectra of CD$_2$Br$_2$ were obtained using light at 4880 Å with a monochromator slitwidth of 0.8 cm$^{-1}$ (HWHM). In order to eliminate sample decomposition, spectra of CHBr$_3$ were acquired using
radiation at 5145 Å. The monochromator slitwidth was 1.4 cm⁻¹ (HWHM).

The polarized Raman spectra of the $v_1$ bands of the two compounds were measured four times in each solution. Due to the low depolarization ratios of these modes in halomethanes (11), it was assumed that $I_{iso}(\omega) = I_{pol}(\omega)$. It is expected that this assumption may cause some error in the numerical values of the linewdths and relaxation times, but it should not have a significant effect on the variation of these quantities in the different solvents.

Following digital baseline subtraction, the spectra were plotted on graph paper. The bands were determined to be symmetric to within experimental error. Therefore, full-widths were measured directly. Following correction for the monochromator slitwidth, using the equation of Tanabe and Hiraishi (35), vibrational relaxation times were calculated from the relation, $\tau_v = (\pi c \Delta)^{-1}$, where $\Delta$ is the corrected bandwidth (FWHM).

Values of $\tau_v$ for CD₂Br₂ and CHBr₃ in Tables XII and XIII represent the average of the four measurements in each solvent. Standard deviations between runs were generally less than 0.05 ps. However, due to possible systematic errors from the use of polarized widths, it is felt that a more realistic error estimate for the relaxation times is 0.2 ps.
Table XII

Frequency Shifts and Vibrational Relaxation Times
Of Dihalomethanes in Solution

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\frac{n-1}{n+2})</th>
<th>(v_0) (cm(^{-1}))</th>
<th>(-(\Delta v_{g-e}/v_0) \times 10^3)</th>
<th>(\tau^{exp}) (ps)</th>
<th>(\tau^{cal}) (ps)</th>
<th>(\tau^{cal}/\tau^{exp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ø Neat Liquid</td>
<td>0.313*</td>
<td>2195</td>
<td>7.3</td>
<td>3.9</td>
<td>3.9</td>
<td>1.0</td>
</tr>
<tr>
<td>1 Carbon Tetrachloride</td>
<td>0.274</td>
<td>2199</td>
<td>5.4</td>
<td>4.3</td>
<td>4.4</td>
<td>1.3</td>
</tr>
<tr>
<td>2 Carbon Disulfide</td>
<td>0.357</td>
<td>2193</td>
<td>8.1</td>
<td>6.7</td>
<td>6.5</td>
<td>0.8</td>
</tr>
<tr>
<td>3 Cyclohexane</td>
<td>0.257</td>
<td>2199</td>
<td>5.7</td>
<td>---</td>
<td>4.3</td>
<td>0.9</td>
</tr>
<tr>
<td>4 Chloroform</td>
<td>0.267</td>
<td>2200</td>
<td>5.0</td>
<td>3.9</td>
<td>4.4</td>
<td>1.1</td>
</tr>
<tr>
<td>5 Benzene</td>
<td>0.295</td>
<td>2197</td>
<td>6.5</td>
<td>5.0</td>
<td>3.0</td>
<td>1.6</td>
</tr>
<tr>
<td>6 Acetone</td>
<td>0.220</td>
<td>2201</td>
<td>4.5</td>
<td>2.2</td>
<td>1.7</td>
<td>0.9</td>
</tr>
<tr>
<td>7 Pyridine</td>
<td>0.299</td>
<td>2193</td>
<td>8.1</td>
<td>5.5</td>
<td>5.0</td>
<td>7.2</td>
</tr>
<tr>
<td>8 Dimethylsulfoxide</td>
<td>0.283</td>
<td>2189</td>
<td>10.1</td>
<td>6.3</td>
<td>2.7</td>
<td>4.5</td>
</tr>
</tbody>
</table>

*CD\(_2\)Br\(_2\).*
Table XIII

Frequency Shifts and Vibrational Relaxation Times
Of Trihalomethanes in Solution

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\frac{n-1}{n^2+2}$</th>
<th>$\nu_0^{-1}$ (cm$^{-1}$)</th>
<th>$\frac{-(\Delta \nu_{g-s}/\nu_0)x10^3}{\nu_0}$</th>
<th>$\tau_{\text{exp}}$ (ps)</th>
<th>$\tau_{\text{cal}}$ (ps)</th>
<th>$\frac{\tau_{\text{cal}}}{\tau_{\text{exp}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Liquid</td>
<td>0.340</td>
<td>3919</td>
<td>10.4</td>
<td>1.1</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>0.274</td>
<td>3928</td>
<td>7.3</td>
<td>5.5</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Carbon Disulfide</td>
<td>0.357</td>
<td>3918</td>
<td>10.7</td>
<td>8.6</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.257</td>
<td>3929</td>
<td>7.1</td>
<td>6.0</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.267</td>
<td>3929</td>
<td>6.9</td>
<td>5.1</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.295</td>
<td>3921</td>
<td>9.4</td>
<td>7.3</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.220</td>
<td>3928</td>
<td>7.4</td>
<td>4.6</td>
<td>0.6</td>
<td>1.9</td>
</tr>
<tr>
<td>Pyridine</td>
<td>0.299</td>
<td>2970</td>
<td>26.6</td>
<td>---</td>
<td>0.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Dimethylsulfoxide</td>
<td>0.283</td>
<td>2980</td>
<td>23.3</td>
<td>16.6</td>
<td>0.2</td>
<td>5.0</td>
</tr>
</tbody>
</table>

*CHBr$_3$.  

110
Peak centers were determined manually by the method of bisection and were referenced to the band maxima in the neat liquids ($\nu_1 = 3019$ cm$^{-1}$ in CHBr$_3$; $\nu_1 = 2195$ cm$^{-1}$ in CD$_2$Br$_2$). Gas-solution frequency displacements, $\Delta\nu_{g-s}$, were then obtained from reported gas-liquid shifts in dibromomethane (17) and bromoform (37). The values of $-\left(\frac{\Delta\nu_{g-s}}{\nu_0}\right) \times 1000$ ($\nu_0$ is the vapor phase peak maximum) in Tables XII and XIII represent the average of the four runs. Standard deviations in the band maxima were generally less than $0.2$ cm$^{-1}$, but increased to $0.7$-$3.0$ cm$^{-1}$ for CHBr$_3$ in acetone, pyridine, and DMSO, due to the very large bandwidths. The absolute accuracy of the frequency displacements depend, of course, on the earlier reported gas-liquid shifts (12,27). Gas-liquid shifts for CD$_2$Br$_2$ were not available. Therefore, in accordance with the theory of Benson and Drickamer (4), the value of 22 cm$^{-1}$ for the shift in CH$_2$Br$_2$ was multiplied by the ratio, $\nu_0$(CD$_2$Br$_2$)/$\nu_0$(CH$_2$Br$_2$), to obtain an estimated shift of 16 cm$^{-1}$ in the deuterated compound.

Results and Discussion

Peak Frequencies

Drickamer and co-workers (4,38) developed a theory of vibrational frequency displacements in liquids and solution. In the absence of specific molecular association (e.g., hydrogen bonding), the net gas-solution shift is the result of competition between short-range repulsive energies and
longer range intermolecular attractions. It has been shown that the dispersion energy generally predominates these interactions, producing a net low frequency peak displacement in condensed phases (31,32).

A simplified expression for the gas-solution shift, \( \Delta \nu_{g-s} \), due to dispersion interaction is of the form

\[
-\frac{\Delta \nu_{g-s}}{\nu_0} = \frac{\alpha'_1 \alpha_2}{\sigma_{ij}^6}
\]

\( \nu_0 \) is the vapor phase frequency, \( \alpha'_1 \) and \( \alpha_2 \) are the solute polarizability derivative and solvent polarizability, respectively, and \( \sigma_{ij} \) is the mean solute-solvent collision diameter. It is noted that one expects the fractional frequency shift, \( \Delta \sigma_{g-s}/\nu_0 \), to be approximately equal for C-H and C-D vibrations. The solvent’s polarizability may be related to its refractive index by \( \alpha_2 (n^2 - 1)/(n^2 + 2) \) (5). Therefore, neglecting variations in \( \sigma_{ij} \) and in repulsive energies in different solvents, one expects a linear relationship between \( \Delta \sigma_{g-s}/\nu_0 \) and \( (n^2 - 1)/(n^2 + 2) \).

A very good linear correlation between these quantities has been observed in studies of acetonitrile (39) and 1,1,1-trichloroethane (28) in solution. Furthermore, in a recent investigation of hydrogen bonding of \( \text{CH}_2\text{Cl}_2 \) and \( \text{CD}_2\text{Cl}_2 \) (7), an excellent correlation between the fractional frequency shift and polarizability was observed in all
solvents except dimethylsulfoxide. Since measurements in the Lewis bases, acetone and pyridine, also fell on the line defined by the nonhydrogen bonding solvents, it was concluded that hydrogen bond formation does not appear to significantly affect the C-H/C-D vibrational frequencies in halomethanes.

In order to test this further, the peak frequencies of CD₂Br₂ and CHBr₃ in both basic and non-interacting solvents have been measured. Their fractional frequency displacements are shown in Tables XII and XIII, respectively, together with data from the earlier investigations of CD₂Cl₂ (7) and CDCl₃ (34).

The results for the dihalomethanes and the haloforms are plotted in Figures 9 and 10, respectively. The straight lines in these graphs represent least-squares fits to data in the neat liquids and in nonbasic solvents (Nos. 1-5). One notes first from these graphs that the fractional shifts in both bromomethanes are generally greater than the corresponding displacements in the chloromethanes. This could result either from larger polarizability derivatives in the bromomethanes (which would increase the slope) or from diminished repulsive interactions in these compounds (which would raise the intercept). The author does not believe that these data possess sufficient accuracy to ascertain the relative importance of the two effects.
Figure 9. Dependence of the gas-solution frequency shifts on solvent polarizability in the dihalomethanes. Closed circles = CD₂Br₂; Open circles = CD₂Cl₂. See Table XII for solvent numbers.
Figure 10. Dependence of the gas-solution frequency shifts on solvent polarizability in the haloforms. Closed circles = CHBr₃; Open Circles = CDCl₃. See Table XIII for solvent numbers. The data in dimethylsulfoxide and pyridine did not fall within the scale of the figure and are not displayed.
One sees from Figures 9 and 10 that, as found in earlier studies (7,28,29), the halomethanes' fractional frequency shifts in nonbonding solutions (Nos. 0-5) are well correlated with \((n^2 - 1)/(n^2 + 2)\), with all points falling within experimental error of the lines defined by the dispersion interaction. One sees, too, that as in the earlier study of CD₂Cl₂ (Fig. 9) and CH₂Cl₂ (7), the frequency displacements of CD₂Br₂ (Fig. 9) and CDCI₃ (Fig. 10) in acetone are explained well on the basis of dispersion energy; the frequency shift of CHBr₃ in this solvent is, however, somewhat greater than expected (Fig. 10).

In dimethylsulfoxide, the frequency shifts of CD₂Br₂ and CD₂Cl₂ are significantly greater than predicted (Fig. 9). From Table XIII, it may be seen that the frequency displacements of both haloform vibrations increase dramatically in this strongly basic solvent. From the same table, one also observes an extremely large shift of the CDCI₃ vibration in pyridine. As Figure 9 shows, unlike CD₂Cl₂, CD₂Br₂ exhibits a larger-than-expected frequency displacement in this solvent.

There is much spectroscopic (12,23) and thermodynamic (2,14) data which indicates that hydrogen bonds of Lewis acids with pyridine and dimethylsulfoxide are, in general, significantly stronger than those formed with acetone. Therefore, in view of the new results obtained in the current study, the earlier tentative conclusion (see above)
(7) must be modified. It does appear that in solution with strong Lewis bases, the C-H/C-D stretching vibrations in di- and trihalomethanes often exhibit increased negative frequency shifts resulting from hydrogen bond formation. However, the results are erratic. Therefore, unlike for alcohols and amines, vibrational peak frequencies in the halomethanes cannot be utilized as a general diagnostic tool to determine the presence or strength of hydrogen bond interactions.

Vibrational Relaxation

It is well established that in the IR spectra of hydrogen-bonded alcohols and amines, one observes, in addition to a large frequency displacement and intensity enhancement, a significant increase in the vibrational bandwidth of the O-H (or N-H) stretching mode with hydrogen bond formation (26). Linebroadening has also been observed in the IR spectra of the C-H mode of haloforms in Lewis base solvents (16,25). However, the effect is much less pronounced than in the above systems, and it has not received the same attention as have the vibrational frequency shifts and intensities.

It is actually more suitable to analyze the isotropic Raman bandwidth or, alternatively, the vibrational relaxation times of the C-H modes. This is because the IR width contains a reorientational component which diminishes upon
hydrogen bond formation, thus partially cancelling the increased width due to vibrational relaxation. On the other hand, the isotropic Raman spectra are unaffected by molecular reorientation.

As discussed in Chapter III, in Raman lineshape analysis, vibrational relaxation processes are characterized by the relaxation time $\tau_{iso}$. If one assumes a nearly Lorentzian lineshape (34), the following relationship can be used to obtain vibrational relaxation times (29):

$$\tau_{iso} = \frac{1}{\pi \Delta_{iso}}$$

[92]

where $\Delta_{iso}$ is the vibrational full-width at half-maximum.

Previous investigations of the isotropic Raman spectra of the $\nu_1$ modes in chloroform (21,34) and dichloromethane (7) show that the relaxation times of these bands decrease markedly (corresponding to an increasing bandwidth) in hydrogen bonding solvents. In order to determine the relative magnitude of this effect in bromomethanes, vibrational relaxation times ($\tau_v$) of the C-H/C-D stretching mode of CD$_2$Br$_2$ and CHBr$_3$ in various solvents were determined. The results ($\tau_v^{exp}$) are displayed in the two tables. As in the analogous chloromethanes, one observes a significant decrease of $\tau_v^{exp}$ in the basic solvents (Nos. 6-8).

It is not appropriate to use a decreased relaxation time by itself as an indicator of molecular association,
because other solvent properties, including molecular weight, collision diameter, and number density, have been shown to have a large effect on $\tau_\nu$ (28,33,36).

However, it has been demonstrated in solvent-dependent Raman studies of the $\nu_1$ vibrations of benzene (36), acetonitrile (33), and 1,1,1-trichloroethane (28) that the Isolated Binary Collision (IBC) model of Fisher and Laubereau (10) furnishes a surprisingly good prediction of variations in $\tau_C$ arising from non-associative interactions in different solvents.

The IBC model can be applied to explain the effects of temperature and density on the vibrational bandwidth. The expression for isotropic correlation times of an oscillator, A-B, as derived by Fisher and Laubereau (10), is

$$\tau_{iso} = \frac{2 L^2}{9 kT} \left( \frac{M^2}{\mu \gamma^4} \right) \omega_0^2 \tau_C$$

[93]

where $k$ is Boltzmann's constant, $T$ is the absolute temperature, $L$ is the interaction length (which is often taken to be proportional to the molecular hard-sphere diameter (usually $L = a/17.5$) (10)), $M$ is the reduced mass of the oscillator, $\mu$ is the reduced mass of the oscillator and its collision partner, and $\gamma = M_A/(M_A + M_B)$ indicates the relative amplitude of the motion of the colliding atoms of the oscillator. The value of $\gamma$ is normally taken to be $0.5$ and
0.25 for stretching and bending vibration, respectively \(^{(37)}\). \(v_0\) is the vibrational frequency of the oscillator, and \(\tau_c\) is the time between molecular collisions in the liquid.

In the past few years, it has been shown that the Enskog model \(^{(6)}\) provides the most realistic hard-sphere collision times. This model assumes that the collisional properties of a molecule in a liquid are similar to that of a dilute gas, but it must be corrected to compensate for the excluded volume by the factor of \(g(\sigma)\), that is, \(\tau_c = \tau_g/g(\sigma)\), where \(\tau_g\) is the collision time in a dilute gas and \(g(\sigma)\) is related to the compressibility factor \(Z\) by

\[
g(\sigma) = \frac{(Z - 1)}{\eta} \tag{94}
\]

where \(\eta\) is the packing faction equal to \(n_0^3/6\). The resulting correction of the collision time using the Enskog model is given as

\[
\tau_c = \left[4(kT/m)\pi \rho \sigma^2 g(\sigma) \right]^{-1} \tag{95}
\]

where \(m\) is the molecular mass, \(\rho\) is the number density, \(\sigma\) is the molecular diameter, and the remaining symbols have their previously assigned meanings.
As in the earlier investigation of dichloromethane (7), the relaxation times ($\tau_v^{\text{cal}}$) for CD$_2$Br$_2$ (Table XII) and CHBr$_3$ (Table XIII) in the various solvents have been calculated, using the equations and methods presented there and elsewhere (36). Hard-sphere diameters used in the calculations were obtained from Weiderkehr and Drickamer (22). As before, a constant factor was utilized to obtain equality for $\tau_v^{\text{exp}}$ and $\tau_v^{\text{cal}}$ in the neat liquids. Shown also in the tables are values for $\tau_v^{\text{cal}}/\tau_v^{\text{exp}}$ for both bromomethanes studied here and for the analogous chloromethanes (7,34). To the extent that the simplified IBC model corrects for changes in $\tau_v$ due to nonspecific solute-solvent interactions, this ratio should be close to unity in non-associative solvents. A large increase in this quantity signifies a decrease in the relaxation time attributable to hydrogen bond formation.

Indeed, as seen from Tables XII and XIII, $\tau_v^{\text{cal}}/\tau_v^{\text{exp}}$ ranges from 0.7 to 1.6 in the non-interacting solvents (Nos. 1-5), but it increases to 3 or greater in the three basic solvents.

Based upon the above results, it can be concluded that, as in the earlier study of dichloromethane (7), a comparison between experimental and calculated relaxation times of the C-H band provides a far more reliable indication of hydrogen bond interactions of halomethanes than does measurement of the frequency displacements of this vibration.
Finally, it is of some interest to note that for a given solute, $\frac{\tau_{\text{cal}}}{\tau_{\text{exp}}}$ is greater in the stronger bases, pyridine and dimethylsulfoxide, than it is in acetone which, as noted earlier, generally forms weaker complexes. However, further study is necessary to determine whether relaxation times can provide a semiquantitative measure of hydrogen bond strengths in these systems.
CHAPTER NOTES


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