RAMAN AND NMR INVESTIGATION OF MOLECULAR REORIENTATION
AND INTERNAL ROTATION IN LIQUIDS

DISSEPTION

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

For the Degree of

DOCTOR OF PHILOSOPHY

By

Peng Yuan, B.S., M.S.
Denton, Texas
December, 1991
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Molecular rotational motions are known to influence both Raman scattering of light and nuclear spin relaxation. Therefore, the application of Raman bandshape analysis and NMR relaxation time measurements to probe molecular dynamics in liquids will provide us with a deeper understanding of the dynamical behavior and structure of molecules in the liquid phase.

Presented here are (i) studies of molecular reorientation of acetonitrile in the neat liquid phase and in solution by Raman bandshape analysis and NMR relaxation; (ii) studies of reorientational dynamics and internal rotation in transition metal clusters by NMR relaxation.

Based upon the results from both Raman and NMR experiments, the parallel diffusion coefficients of both \( \text{CH}_3\text{CN} \) and \( \text{CD}_3\text{CN} \) in the pure liquid can be well predicted by the Free Rotor model of reorientation, in both magnitude and dependence on temperature. In addition, the associative behavior of acetonitrile molecules is clearly manifested in the perpendicular diffusion coefficients of \( \text{CD}_3\text{CN} \) in solution.
In phenyl capped clusters, the slowed internal phenyl ring rotation can be used to probe intramolecular electronic and/or steric interactions by investigating the $^{13}$C NMR relaxation of the cluster. In $\text{Co}_3(\text{CO})_9(\mu_3\text{-CPh})$, the phenyl group rotates as rapidly as in benzene itself about its $C_2$ axis, which indicates there is no interaction between the phenyl group and the tricobalt skeleton. However, if a heterometal is introduced into the trinuclear skeleton, the splitting of the degenerate metal's orbitals will induce an electronic perturbation that leads to a small, but finite barrier to the internal rotation of phenyl group, which has first been demonstrated by the experimental results here in $\text{FeCo}_2(\text{CO})_9(\mu_3\text{-PPh})$ and $\text{Co}_2\text{NiCp}(\text{CO})_6(\mu_3\text{-CPh})$. Furthermore, a bridging carbonyl on the cluster's skeleton will interact with the phenyl group and create a barrier that stops the phenyl internal rotation, which were first proposed by Stone et al in $\text{CoFe}_2(\mu_2\text{-CO})(\text{CO})_8(\mu_3\text{-CC}_6\text{H}_4\text{Me}-4)$ and demonstrated here in $\text{Co}_3\text{Cp}_2(\mu_2\text{-CO})(\text{CO})_3(\mu_3\text{-CPh})$. 
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CHAPTER I

STUDIES OF MOLECULAR DYNAMICS IN LIQUIDS

A. Introduction

Since almost all chemical conversions proceed in solution, it is desirable to understand the structure, molecular dynamics, and other basic properties of liquids. The model obtained should provide one with a deeper understanding of the motional behavior of molecules and therefore of the course of chemical reactions in liquids. For many years, much effort has been devoted to approach this goal. At present, we still have only rather a crude understanding, largely based on simplified models. The difficulties arise from the fact that, in the liquid phase, the molecules are in motion, intermolecular separations are small, intermolecular interactions which are molecule specific come into play, and the macroscopic manifestation of the unique liquid phase characteristics is the bulk viscosity of the system. It is not like the molecule in the gas phase, where the rotational motion is essentially complete with the solution of Schrödinger equation for the free rotor, and the angular velocity is determined solely by the molecule's moment of inertia and the temperature. Nor is it like in the solid phase, for which experimental
observation based largely upon X-ray diffraction has provided us with a spongy spheres model for atoms and molecules, and bond lengths and bond angles can now be predicted with reasonable confidence. One aspect of the efforts toward understanding of the liquid state is the study of rotational reorientation of molecules in liquids, or molecular dynamics in liquids, and the basic model for description of this is rotational diffusion, which is constructed largely on the concepts of rotational Brownian motion.

There are many spectroscopic techniques which can be applied to the study of molecular reorientation in liquids.\textsuperscript{1} Raman and NMR spectroscopy are two of these spectroscopic methods. In Raman spectroscopy, the properties of concern are polarizability, the motions involved are molecular reorientations and vibrations, and in NMR spectroscopy, the properties of concern are nuclear magnetization, the motions involved are molecular reorientations and internal rotation in the liquid phase.

One major part in studies of liquid-phase molecular dynamics is to determine the dynamical parameters, using the concept of rotational diffusion, which characterizes the rotational motions (reorientation) experienced by molecules or moieties of molecules. The results can provide\textsuperscript{1,2} (i) an evaluation of the validity of current theoretical models
describing the rotational diffusion of molecules in condensed phases; (ii) the evidence of molecular interactions which interfere with the reorientations of molecules; (iii) information about the molecular structure, orientation, bonding, etc.\textsuperscript{3,4}.

In order to see how the rotational diffusion of $C_{3v}$ molecules will be influenced by temperature and solvents, we performed both Raman bandshape analysis and NMR relaxation time studies of molecular reorientation in acetonitrile\textsuperscript{5,6}. To determine how phenyl group will interact with metal and ligands, electronically or sterically, in phenyl group capped metal clusters, we investigated the reorientational dynamics of several metal clusters by utilizing NMR spin-lattice relaxation times\textsuperscript{3,4,7}. All of these studies will be discussed in detail in following chapters.

B. Reorientation of Molecules

1. Rotations and Symmetry of Molecules

Depending on the symmetry of the molecule in consideration, there are as many as three different rotations about the three orthogonal principal molecular axes. The simplest type of molecule is the spherical or spherical-top molecule in which all three rotations are identical. Therefore, the motion of the molecule is isotropic and can be characterized by only one dynamic
parameter. Molecules of tetrahedral or octahedral point groups are typical spherical molecules.

The other extreme is the asymmetric-top molecule. Rotations about the three axes are all different. A rank three tensor will be needed to fully describe the anisotropic rotations. Experimentally more effort is needed to solve the problem. Depending upon the shape of the molecule in consideration we will approximate it as a quasi-symmetric-top molecule. That simplifies the problem significantly, both experimentally and theoretically, in most cases.

A symmetric-top molecule is a molecule of axial symmetry which has at least a three-fold symmetry axis. For a symmetric-top molecule, two of the three rotations are identical and its anisotropic motion is classified into spinning (parallel) and tumbling (perpendicular) motions. The semi-axial lengths in a symmetric-top molecule are given by a, b, and c, where b and c are equal. The axial ratio, \( \rho = b/a \) or \( c/a \), plays a very important role in characterizing rotations of symmetric-top molecules. Most theories of molecular rotations treat prolate molecules \( (\rho < 1) \) and oblate molecules \( (\rho > 1) \) in different ways.

2. Reorientation of Molecules

The term reorientation is used to describe the orientational motion of a vector which lies along the chosen
axis (Z-axis for example). It is readily seen that rotation about the Z-axis itself will leave the vector invariant. Only rotations around the X- and Y-axes result in a change of the orientation of this vector. In other words, the reorientational motion describing the angle-change for a molecule-fixed axis arises from rotations of the molecule about the other two axes.

In the liquid phase, a molecule will be constantly acted upon by the neighbor molecules and its orientation will be changed from time to time in a randomized way. The motion of a vector embedded in the molecule can be represented as a random walk across the surface of a sphere drawn around the center of mass of the molecule. In this way reorientation results from a large number of very small angular jumps, and has been treated as rotational Brownian movement ever since Debye first proposed it.\(^9\)

Along with the molecular reorientational motion, the relative internal motion within the molecule will result from the relative rotation of two moieties in the molecule \(\sigma\) bonded to each other. This is a kind of motion for which we can investigate if there is any intramolecular interaction, electronically or sterically, present in the molecule. If there is no internal rotation or slowed internal rotation for a group \(\sigma\)-bonded relative to the rest of the molecule,
that will tell us definitely there is some kind of interaction existing.

In theoretical treatments of rotational relaxation in Raman spectroscopy, the relative transition moment (polarizability) is considered as a tensor positioned along a molecular-fixed axis. Since rotational relaxation is angle dependent, it is related to the angular fluctuations of the chosen axis of the tensor. For this reason, rotational relaxation is identified with molecular reorientational fluctuations. Therefore, reorientation is a type of rotational motion with emphasis on the change of angle (orientation) of chosen molecular axis (i.e., the vector in consideration) relative to external coordinate frame.

3. Diffusion Constants & Rotational Diffusion

As mentioned above, Debye\textsuperscript{9} seems to be the first person to consider the problem of rotational Brownian movement. In his first model of the phenomenon Debye considered an assembly of molecules, each carrying a permanent dipole moment, with each molecule compelled to rotate about an axis normal to itself. He further supposed that the electric interaction between each member of the assembly may be ignored so that on the average all molecules of the assembly behave in the same way. Thus it suffices to consider the behavior of one molecule only.
The diffusion equation is an appropriate description of molecular rotation in liquids. The rotational diffusion of a liquid molecule is viewed as reorientational motion of the molecule, which is hindered by a frictional viscous force operating at the molecular surface. The rotational diffusion constant is given by

\[ D_r = \frac{kT}{8\pi a^3\eta} \]  

In this expression, which is known as the Stokes-Einstein-Debye (SED) equation, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( a \) is the hydrodynamic radius of the molecule, and \( \eta \) is the shear viscosity of the medium.

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

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

\[ \langle \Delta \theta \rangle_{\text{rms}} = \langle \Delta \theta_i^2 \rangle^{1/2} = (2D_i \times \Delta t)^{1/2} \]

The value of \( \Delta t \) required for \( \langle \Delta \theta \rangle_{\text{rms}} \) to reach one radian is defined as \( \tau_\theta \). For spherical molecules, in which motion is isotropic, only a single diffusion constant is needed to describe the reorientational motion.

For totally asymmetric 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 reorientational motion ($D_1$ and $D_2$, which represent rotation parallel to the symmetry axis and the axis perpendicular to the top axis, respectively).

Molecular rotational motions are known to influence both Raman scattering of light and nuclear spin relaxation. In Raman scattering, the rotation and vibration of a molecule modulate its polarizability and, thus, the frequency distribution of the scattered light contains information about the rotational motion. In nuclear spin relaxation, molecular rotation is coupled to the nuclear spin by a number of mechanisms, and therefore by measuring the dynamical behavior of the spins, it is possible to draw conclusions about molecular rotations.

4. Factors which influence the molecular reorientation

Molecular reorientation in the liquid phase will depend on many factors, such as molecular size, symmetry and viscosity. If the molecule is small, it will rotate faster than a big molecule because of its moment of inertia ($I$); a symmetric molecule, which causes less disordering of the solvent as it rotates, will reorient more efficiently than an asymmetric one because of the steric hindrance. Viscosity is a measure of how difficult it is to displace the surrounding molecules when a molecule rotates, so it
will depend on both the solute and solvent. Temperature is a combined factor; when temperature is elevated, the molecule will rotate faster than at lower temperature due to the increase in kinetic energy and the lowered viscosity. If some kind of intermolecular interaction exists, molecular association, H-bonding, etc, slower molecular rotation will be expected.

C. Theoretical Models of Molecular Reorientation

In an attempt to describe liquid-phase molecular reorientation, several rotational diffusion models have been developed in past years, from which it is possible to obtain a priori estimates of the diffusion constants. A comparison with experimental values permits an evaluation of the validity of assumptions on which a model is based.

1. 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 in 1856. He showed that the friction constant is given by

$$\epsilon = \frac{\text{torque/angular momentum}}{8\pi a^3 \eta}$$

[3]

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

Debye extended its application. In the case of spherical molecules, the reorientational motion was treated
as rotational diffusion in a continuous viscous medium (the solvent) opposed by impulsive torques produced by the random interactions with neighboring molecules, similar to Einstein's picture of translational motion of Brownian particles. By comparing rotational Brownian motion with translational motion, he suggested\(^9\) that, for spherical molecules, the rotational diffusion constant \(D_r\) can be expressed, analogous to the Stokes-Einstein law\(^{12}\), as in equation \([1]\).

However, experimental evidence from many NMR relaxation studies reveal faster-than-predicted actual rates of rotations, 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.\(^{13}\)

2. The Perrin (Stick) Model

The earliest hydrodynamic theory of anisotropic reorientation was developed by Perrin\(^{14}\) who extended the SED model of a spherical molecule rotating in a viscous, continuous medium. This model assumes that the solvent molecules stick to the surface of the reorienting molecule, thus creating a viscous drag which retards its rotation. Perrin solved the Navier-Stokes equation\(^{11}\) to obtain diffusion constants, given by:
\[ D_i = (1/f_i)kT/(8\pi r^3\eta) \]  

In this equation, \( D_i = D_1 \) or \( D_1 \), \( f_i = f_1 \) or \( f_1 \), and \( r = \sigma/2 \), is the mean radius of the molecule, \( r = (a b^2)^{1/3} \). The remaining quantities have the same meaning as in the original SED expression (eq. [1]). The correction factors, \( f_i \) and \( f_1 \), 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 because of the overly strong viscosity dependence and it predicts rotational diffusion constants that are an order of magnitude smaller than the experimentally measured values.

3. The Microviscosity (MV) Model

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

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

where \( a_s/a \) is the ratio of solvent to solute radius; \( a_s \) is average radius of the solvent molecule and \( a \) is the longest semi-axis of the solute molecule.

One limiting case, \( a_s/a >> 1 \), corresponds to the "slip" boundary condition in which the rotating molecule slips through the solvent without retarding forces \((\epsilon = 0)\).
other limit, \( a_s/a \ll 1 \), corresponds to the "stick" boundary condition, in which the rotating molecule experiences a retarding force \( (\epsilon = 8\pi a^3 \eta) \). In pure liquids, \( a_s/a = 1 \), which corresponds to a microviscosity factor, \( f = 0.16 \), and represents a friction coefficient with 16% of the stick value. This model gives quite satisfying results for solutions in solvents of smaller molecular size; but for neat liquids the model is not as good because non-viscous intermolecular forces affecting the molecular reorientation are more likely to be present\(^{13}\).

4. 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 gas phase) at a rate controlled by its moment of inertia. The diffusion constant is given by\(^{13}\)

\[
(D)_{\text{FR}} = [6t_{\text{FR}}]^{-1}
\]

where

\[
t_{\text{FR}} = 2\pi(41/360)(I/kT)^{1/2}
\]

\( t_{\text{FR}} \) is the time for a "free rotor" to travel 41°, \( I \) is the molecular moment of inertia, \( k \) is Boltzmann's constant, and \( T \) is the temperature. The equation may be modified for symmetric-top molecule by replacing \( I \) with \( I_\perp \) and \( t_{\text{FR}} \) with
(τ_{FR})_1, one obtains D_⊥(FR) = 1/[6(τ_{FR})_1]. Similarly, D_\parallel = 1/[6(τ_{FR})_1] is obtained by replacing I with I_\parallel and τ_{FR} with (τ_{FR})_1.

This model gives quite satisfying results for D_\parallel when applied to C_3V molecules, like CH_3I, CD_3I, CH_3CN, CD_3CN and CCl_3CH_3^{5,19,20,21}, in pure systems. It is not, however, as good in solutions because of the interaction between the solvent and solute molecules.\textsuperscript{6}

5. The Hu-Zwanzig (Slip) Model

Hu and Zwanzig\textsuperscript{22} pointed out that the discrepancies between experimental diffusion constants and values predicted by the SED and Perrin models arise from application of the "stick" boundary condition in solving the Navier-Stokes equation to determine the friction coefficient. To overcome this deficiency, they introduced an alternative "slip" theory in which the sole resistance to reorientation is caused by displacement of solvent as the molecule rotates. They noted that the slip boundary condition with no tangential stress is probably more realistic for rotation on a molecular scale. Like the motion of a spherical molecule in the gas state, the spinning motion of a symmetric top molecule can be described by the "free rotor" treatment with vanishing friction. However, the tumbling motion is retarded since it requires displacement of solvent molecules. Using the slip boundary
condition, Hu and Zwanzig\textsuperscript{22} solved the equation numerically; the perpendicular diffusion constant given by

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

where \( a \) is the larger semi-axis length of the molecule, and \( f_{HZ} \) 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 coefficient, \( \epsilon^* \), in Table I of their paper.\textsuperscript{22}

Although one observes a marked improvement over the earlier stick model, diffusion constants calculated using the HZ theory are generally found to be significantly greater than experiment; i.e. the slip boundary condition underestimates the friction impeding molecular rotation.

6. The Hynes-Kapral-Weinberg (HKW) Model

More recently, Hynes, Kapral and Weinberg\textsuperscript{23,24} introduced a new formalism, intermediate between the "stick" and "slip" extremes, in which they incorporate a slip coefficient, \( \beta \), whose magnitude is dependent on the frictional torque exerted by the solvent. \( \beta = 0 \) 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\textsuperscript{24} to obtain an equation for the approximate calculation of \( \beta \).
Originally developed for spherical particles, Tanabe\textsuperscript{25,26} made an intuitive extension of the HKW theory in order to calculate the diffusion constants, $D_\perp$ and $D_\parallel$, of symmetric-top molecules. The modified HKW equations are expressed as

\[ D_\perp = \left(\frac{1}{f_\perp}\right) D_0 \left[1 + \frac{3\eta}{(\beta + \alpha_\perp\eta)}\right] \]  \tag{9} 

and

\[ D_\parallel = \left(\frac{1}{f_\parallel}\right) D_0 \left[1 + \frac{3\eta}{\beta}\right] \]  \tag{10} 

In these equations, $f_\perp$ and $f_\parallel$ are the Perrin coefficients\textsuperscript{14} and $D_0$ is the SED diffusion constant. The quantity $\alpha_\perp$ can be calculated via the relation

\[ \frac{\rho^2}{f_{HZ}} = \left(\frac{1}{f_\perp}\right)(1 + 3/\alpha_\perp) \]  \tag{11} 

The slip coefficient, $\alpha$, may be estimated from the Enskog theory as

\[ \alpha = \left[\frac{2\kappa}{\kappa + 1}\right] \left(2\mu_{12}kT/\pi\right)^{1/2} \rho_2 g_{12}(\sigma_{12}) \]  \tag{12} 

$\mu_{12}$ is the reduced mass of the solute-solvent pair; $\sigma_{12}$ is the mean diameter, $(\sigma_1 + \sigma_2)/2$, and $\rho_2$ is the solvent's number density. The radial distribution function, $g_{12}(\sigma_{12})$, may be calculated in the manner presented elsewhere\textsuperscript{2,9,25-31}. Finally, $\kappa = I_{\text{avg}}/m r^2$, where $I_{\text{avg}} = (2I_\perp + I_\parallel)/3$ and $m$ is the molecular mass.

The extended HKW model demonstrate considerable promise in narrowing the gap between calculated and experimental
rotational diffusion constants$^{17,32-35}$.

Summary

Numerous experiments have been performed to evaluate the validity of different models discussed above. For molecules that can be approximated by spheres, the Gierer-Wirtz model provides a good description of the motion for solutions in solvents of smaller molecular size. For molecules with cylindrical (spheroidal) symmetry, values for $D_\parallel$ calculated using the Hu-Zwanzig model are invariably more reliable than are calculated values of $D_\perp$. The Free Rotor model seems to be the best one in calculating the $D_\parallel$ for symmetric-top molecules. The HKW model could be the best of all in terms of the closeness of the calculated and experimental results. However, the essential molecular factors which govern solute rotation are not yet unambiguously identified.$^{13}$ Also it is ignored that there may be the interactions between molecules not reflected in the bulk viscosity but in some cases having a significant effect upon the rotation of molecules in consideration.


15. In a symmetric-top molecule, the semi-axis lengths of the volume ellipsoid are given by a, b, and c, where b = c.

CHAPTER II

RAMAN SPECTROSCOPY AND MOLECULAR DYNAMICS

A. Raman Spectroscopy

1. Theoretical Background

The Raman effect, named in honor of its discoverer C. V. Raman\textsuperscript{1,2}, is an inelastic light-scattering phenomenon in nature. In this process, the incident optical photon is absorbed by an atom of the molecule through dipole interaction with the electronic level; this is followed by a spontaneous photon emission as depicted in Figure 1.

When it experiences an electric field, the electron cloud in a molecule is periodically perturbed and redistributed relative to the nuclear framework. This distortion of the electron cloud results in an induced, alternating dipole moment. The polarization, \( P \), defined as the induced dipole moment per unit volume, is proportional to the incident electromagnetic field, \( E \), and can be expressed as

\[
P = \alpha E
\]  \hspace{1cm} [13]

where \( \alpha \) is the polarizability of the material. The electric field associated with the incident beam of frequency \( v_o \) can be written in its time-dependent form, according to
A. Raman Spectroscopy

1. Theoretical Background

The Raman effect, named in honor of its discoverer C. V. Raman, is an inelastic light-scattering phenomenon in nature. In this process, the incident optical photon is absorbed by an atom of the molecule through dipole interaction with the electronic level; this is followed by a spontaneous photon emission as depicted in Figure 1.

When it experiences an electric field, the electron cloud in a molecule is periodically perturbed and redistributed relative to the nuclear framework. This distortion of the electron cloud results in an induced, alternating dipole moment. The polarization, $P$, defined as the induced dipole moment per unit volume, is proportional to the incident electromagnetic field, $E$, and can be expressed as

$$ P = \alpha E $$

where $\alpha$ is the polarizability of the material. The electric field associated with the incident beam of frequency $v_0$ can be written in its time-dependent form, according to
Figure 1. Energy level diagram illustrating the fundamental processes of Raman scattering. The exciting line is of energy $h\nu_0$. Raman bands appear at $h(v_0 - v_1)$ and $h(v_0 + v_1)$. 
classical electromagnetic theory, as

$$E = E_0 \cos(2\pi v_0 t)$$  \[14\]

where $E_0$ is the amplitude of the external electromagnetic wave. In this case, the polarization will fluctuate as

$$P = \alpha E_0 \cos(2\pi v_0 t)$$  \[15\]

The Raman effect results from the variation of the polarizability, $\alpha$, at the frequency of the normal mode of the molecular vibration. The time dependency of $\alpha$ can be expressed as

$$\alpha = \alpha_0 + \sum_k \alpha_k \cos(2\pi v_k t)$$  \[16\]

The first term, $\alpha_0$, expresses the static polarizability for the molecule with a fixed nuclear position. The summation term expresses the polarizability changes which arise from the time-dependent normal modes of the molecule, and $v_k$ is the frequency of the $k^{th}$ vibration. Substituting the above expression for $\alpha$ into equation [15] gives

$$P = \alpha_0 E_0 \cos(2\pi v_0 t) +$$

$$\left(\frac{E_0}{2}\right) \sum_k \{ \cos[2\pi(v_0 + v_k)t] + \cos[2\pi(v_0 - v_k)t] \}$$  \[17\]

The first term gives rise to Rayleigh scattering describing a classical dipole radiating at frequency $v_0$ (see Figure 1). The second term contains two frequency-shifted radiations at frequencies $v_0 + v_k$ and $v_0 - v_k$ known as anti-Stokes and Stokes Raman scattering respectively.
process proceeds leads to a broadening or bandwidth increment, $\Delta \omega$, of the vibrational line as predicted by the energy-time uncertainty principle\textsuperscript{7}

$$\tau \Delta E = \hbar \text{ or } \tau \Delta \omega = 1$$  [18]

As a result, a frequency distribution around the unperturbed vibrational frequency is exhibited and this gives rise to a band profile. The extent to which a vibration band is broadened is governed by the relaxation process which in turn is dominated by the dynamic effects or the molecular motions. Consequently, the vibrational band profile serves as a probe of the molecular dynamics. Before 1964 useful quantitative theories were nonexistent. Only qualitative conclusions about molecular motion could be drawn from frequency and bandwidth data of some simple liquids because the spectra looked similar to those of the compressed gases.

The situation changed with the publication of R. G. Gordon's paper on the fundamental connection between spectral parameters of vibration bands in a liquid and rotational motion of its molecules\textsuperscript{8}. In his work the Raman linewidth was related quantitatively to molecular rotations \textit{via} the Heisenberg picture which leads to the definition of time correlation functions. Depending on various experimental techniques, the correlation functions for
different motions can be used to measure related molecular properties.

2. Bandshape Analysis, Line Broadening and Curve-fitting

Implied by equation [18] is an equivalent relationship between the bandwidth increment and relaxation time expressed as

\[ r = (\Delta \omega)^{-1} \]  \hspace{1cm} [19]

Qualitatively, a fast motion results in a fast relaxation (a short \( r \)) and, therefore, a larger bandwidth increment is exhibited in the spectral band profile. Quantitatively, if we could obtain the bandwidth we would be able to tell how fast the relaxation might be. The process of get the bandwidth is called bandshape analysis. Gordon's work,\(^8,9\) as mentioned earlier, was a milestone in the study of molecular dynamics. In recent years, analysis of Raman and/or IR bandshapes to determine dynamic properties of molecules has become a rapidly expanding field of study.

One major obstacle to bandshape analysis is the overlap of band contours of different vibrational modes due to a high extent of linebroadening. Fundamental vibrational bands might be overlapped, through Fermi resonance, with overtones or combinational bands arising from vibrational anharmonicity. This phenomenon gets worse as the size of the molecule gets bigger and its symmetry becomes lower. The band overlap due to line broadening also can result from
various factors including hot bands, isotope splitting, poor resolution, low intensity, etc.. All of these will add difficulties on the bandshape analysis and, in some cases, make it impossible. Another case is for doubly degenerate vibrational bands which contain two peaks at the same position but with different bandwidths and intensities.

Under the condition that there is no overlap other than the slitwidth broadening, we can get the bandwidth by hand measurement. However, in order to get a true bandwidth from the bandshape interfered with the factors mentioned above, these problems must be solved by a curve-fitting procedure with proper model based on theoretical and/or available experimental data to disentangle these band contours. The complete procedure includes baseline subtraction and bandwidth computation, along with slitwidth correction. We have been quite successful in solving the problems related with doubly degenerated peaks$^{10-13}$, isotope splitting$^{12,14}$ and hot bands$^{15,16}$.

(a) Baseline Subtraction

The baseline correction of the recorded spectrum was performed by 2-frequency baseline subtraction. Assuming a linear function of the frequency, i.e. $I_{BL}(\omega) = a + b\omega$, the baseline was calculated from two frequencies selected from each side of the peak contour. The coefficients, $a$ and $b$, were determined by least-square fit to seven points about
each selected frequency. The baseline subtracted spectrum, $I_{BS}(\omega)$, is obtained by

$$I_{BS}(\omega) = I_{exp}(\omega) - (a + b\omega)$$  \[20\]

(b) Slitwidth Correction

In general, the observed spectrum, $I_{exp}$, is a convolution of the true spectrum, $I_{true}(\omega)$, and the instrumental slit function, $S(\omega)$, given as

$$I_{exp}(\omega) = \int_{-\infty}^{\infty} I_{true}(\omega') S(\omega - \omega') d\omega'$$  \[21\]

where $\omega$ and $\omega'$ are the frequency displacements from the laser line. The convolution procedure is to find $I_{true}(\omega)$ after knowing $S(\omega)$ and $I_{exp}(\omega)$ by best fit to equation [21].

(c) Bandwidth Computation

The experimental intensities were fitted with theoretical Lorentzian lineshapes. The fitting was done computationally by using non-linear regression to minimize root-meant-square errors between experimental and computed data. Elimination of the effects of instrumental linebroadening was performed by convolution of the calculated spectra with a 19-point triangular slit function.

B. Correlation Function

The application of spectroscopic methods to studies of molecular motions is based on the Wiener-Khintchine theorem which states that, for any dynamic process, the power spectrum, $I(\omega)$, of this process and the corresponding
time correlation function, \( f(t) \), are mutual Fourier transforms.\(^{18}\) On one hand, these correlation functions can be obtained by numerical Fourier transform of experimental band contours; on the other hand, they can be predicted by theoretical modeling. Therefore, such correlation functions, which are rigorously defined in time-dependent statistical mechanics,\(^{19-23}\) provide an important link with theoretical studies of molecular dynamics in the condensed phase.

Although Raman and IR arise from different physical processes, the two kinds of spectra supply complementary vibrational information. Considering the similarity, we discuss their correlation functions together. Reorientational correlation functions of the polarizability and dipole moment derived from the small-step rotational diffusion theory\(^{24}\) are widely used to determine rotational diffusion constants from spectral bandwidths.

1. General Aspects

The fluctuation-dissipation theorem\(^{19,25}\) states that (ref 19, p. 85) the energy dissipated by a system when it exposed to an external field is related to a time-correlation function which describes the detailed way in which spontaneous fluctuations relax the system back to the equilibrium state, the correlation function is expressed in a one side average form\(^{26}\)
\[ f(t) = \langle m(0)m(t) \rangle \]  \[ \text{[22]} \]

where \( m(t) \) is the dynamical quantity of concern, which can be a unit vector along molecular transition dipole, or a tensor with trace components along the vibrational-rotational transition moment of the molecule.

In IR absorption, \( m(t) \) is identified with the first-rank dipole moment tensor (a vector), \( p^{(1)} \). The dipole moment correlation function, \( f_{p}(t) \), is

\[ f_{p}(t) = \langle p(0)p(t) \rangle \]  \[ \text{[23]} \]

Since \( p(t) \) is fixed in the molecular frame, variations resulting from molecular motions determine the time dependence of \( \langle p(0)p(t) \rangle \).

For Raman scattering, the polarizability tensor, \( \beta^{(2)} \), is involved and the polarizability correlation function is expressed in an analogous manner

\[ f_{\alpha}(t) = \langle \beta^{(2)}(0)\beta^{(2)}(t) \rangle \]  \[ \text{[24]} \]

Due to the second-rank nature, the polarizability tensor can be split into a product of two terms, an amplitude-dependent and an angle-dependent term.\(^{26,27}\) The amplitude-dependent part is related to vibrational relaxation, whereas the angle-dependent part is assigned to rotational relaxation.

2. Reorientational Correlation Functions

In the formalism of reorientational correlation functions, it is necessary to determine the ways in which
the dipole moment and polarizability change when the molecule rotates through an Eulerian angle. One general approach\textsuperscript{19,27-29} is to describe the reorientation of the tensor in question by the rotation of the molecular frame with respect to the laboratory reference coordinate system. This is done by expressing the Cartesian tensor elements in terms of Wigner rotation matrices.

The derived reorientational correlation functions for dipole moment and polarizability are given as\textsuperscript{18}

\begin{equation}
 f_p(t) = \sum_{m=-1}^{1} |p_m^{(1)}|^2 g_m^{(1)}(t) \tag{25}
\end{equation}

and

\begin{equation}
 f_\beta(t) = \sum_{m=-2}^{2} |\beta_m^{(2)}|^2 g_m^{(2)}(t) \tag{26}
\end{equation}

The coefficients in these two equations, $|p_m^{(1)}|$ and $|\beta_m^{(2)}|$, are spherical components of dipole moment and polarizability derivatives respectively. They are related to the Cartesian components in the molecular frame by\textsuperscript{19,28,30}

\begin{align*}
 p_0^{(1)} &= P_z \\
 p_{\pm}^{(1)} &= ±2^{-1/2}(p_x ± ip_y) \tag{27}
\end{align*}

and

\begin{align*}
 \beta_0^{(2)} &= (3/2)^{1/2}\beta_{zz} \\
 \beta_{\pm 1}^{(2)} &= \beta_{zx} ± i\beta_{yz} \\
 \beta_{\pm 2}^{(2)} &= -(1/2)(\beta_{xx} - \beta_{yy}) ± i\beta_{xy} \tag{28}
\end{align*}

Based on the small-step rotational diffusion theory\textsuperscript{24},
the reorientational correlation functions for IR absorption and Raman scattering, \( g_m^{(1)} \) and \( g_m^{(2)} \), are exponential functions specified by the correlation time, \( \tau_m^{(1)} \), and the following results are obtained:\( ^{18} \)

\[
f_p(t) = \sum_{m=-1}^{1} |P_m^{(1)}|^2 \exp(-t/\tau_m^{(1)}) \tag{29}
\]

and

\[
f_\beta(t) = \sum_{m=-2}^{2} |\beta_m^{(2)}|^2 \exp(-t/\tau_m^{(2)}) \tag{30}
\]

For symmetric-top molecules, the correlation time, \( \tau_m^{(1)} \), is related to rotational diffusion constants by\(^{18,31} \)

\[
1/\tau_m^{(1)} = 1(1 + 1)D_\perp + m^2(D_\parallel - D_\perp) \tag{31}
\]

3. Correlation Function with Inclusion of Vibrational Relaxation

After Gordon's introductory analysis of reorientational relaxation from molecular spectral bandshapes in 1964,\(^8 \) rotational relaxation times or diffusion constants for various molecules were first obtained on the assumption that the overall observed Raman band width can be attributed entirely to rotational relaxation.\(^9\) Bartoli and Litovitz\(^5 \) in 1971 showed that vibrational relaxation also plays an important role in the broadening of vibrational lines. The experimental bandwidth increment, \( \Delta_{\text{exp}} \), arises from the combination of vibrational relaxation, \( \Delta_{\text{vib}} \), and rotational relaxation, \( \Delta_{\text{rot}} \).
$$\Delta_{\text{exp}} = \Delta_{\text{vib}} + \Delta_{\text{rot}}$$  \[32\]

In order to calculate the diffusion constants from the bandwidth, it is necessary to obtain the vibrational bandwidth first, which can readily be done experimentally by utilizing isotropic Raman spectra$^{5,6,32}$ of totally symmetric vibrations. Theoretically, this feature comes from the tensor property of the polarizability, $\beta$. A Taylor series expansion of this second-rank tensor allows the vibrational-rotational correlation function to be written as the product of an amplitude-dependent and an angle-dependent factor.$^{18,26}$ The time dependent development of the amplitude-dependent factor is assigned to vibrational relaxation, whereas the angle-dependent factor is assigned to rotational relaxation. Assuming a statistically independent and exponentially decaying vibrational relaxation correlation function, $f_{\text{vib}}(t) = \exp(-t/\tau_{\text{vib}})$, the complete correlational function for Raman spectroscopy will be

$$F_{\text{Raman}}(t) = f_{\text{vib}}(t)f_{\text{rot}}(t) = \exp(-t/\tau_{\text{vib}})\left\{ \sum_{m=-2}^{2} |\beta_{m}^{(2)}|^{2}\exp(-t/\tau_{m}^{(2)}) \right\}$$ \[33\]

The complete correlation function for IR spectroscopy is obtained in a similar fashion.

4. Correlation Functions and Symmetry of Molecules

For molecules of $C_{3V}$ or higher symmetry, the following relationships between spherical components are valid$^{18}$
Thus eqs. [29] and [30] can be simplified to

\[ f_p^{(1)} = |p_0^{(1)}|^2 \exp(-t/\tau_0^{(1)}) \]
\[ + 2|p_1^{(1)}|^2 \exp(-t/\tau_1^{(1)}) \quad [36] \]

and

\[ f_\beta^{(2)} = |\beta_0^{(2)}|^2 \exp(-t/\tau_0^{(2)}) + 2|\beta_1^{(2)}|^2 \exp(-t/\tau_1^{(2)}) \]
\[ + 2|\beta_2^{(2)}|^2 \exp(-t/\tau_2^{(2)}) \quad [37] \]

Eqs. [36] and [37] show that a reorientational IR or Raman correlation function of a band contour is a linear combination of up to two or three independent time-dependent functions with coefficients being the squares of the spherical IR or Raman tensor components in the molecular coordinate system. In general one or more terms vanish due to symmetry properties. By reference to the character table, the number of nonvanishing \( m \)-mixed terms for a vibrational mode can be determined from the point group of the molecule in consideration via the transform properties of the spherical components shown in eqs. [27] and [28].

Take \( E^m \) vibrations in \( D_{3h} \) molecules as an example, for which

\[ \beta_0^{(2)} = (3/2)^{1/2} \beta_{zz} = 0 \quad [38] \]
\[ B_2^{(2)} = -(1/2)(B_{xx} - B_{yy}) + iB_{xy} = 0 \]  

[39]

Hence the total reorientational correlation function is a single exponential

\[ f_B^{E''}(t) = 2|B_1^{(2)}|^2 \exp(-t/\tau_1^{(2)}) \]  

[40]

and the complete correlational function will be

\[ F_{\text{Raman}}(t) = \exp(-t/\tau_{\text{vib}}) \{ 2|B_1^{(2)}|^2 \exp(-t/\tau_1^{(2)}) \} \]  

[41]

5. Bandwidth Increments and Correlation Times

The bandwidth, \( \Delta \), employed throughout this research is the full width at half maximum intensity (FWHM) in wavenumbers (cm\(^{-1}\)). Thus a conversion factor, \( \pi c \), is required to relate \( \Delta \) and the correlation time, \( \tau \), by

\[ \Delta = (\pi c \tau)^{-1} \]  

[42]

Thus, the bandwidth increment resulting from vibrational relaxation will be

\[ \Delta_{\text{vib}} = (\pi c \tau_{\text{vib}})^{-1} \]  

[43]

and the bandwidth increment resulting from rotational relaxation, \( \Delta_{\text{rot}} \), is related to rotational diffusion constants by combining eqs. [31] and [42]

\[ \Delta_{m}^{(1)}(\text{rot}) = (\pi c \tau_{m}^{(1)})^{-1} \]

\[ = (\pi c)^{-1}[1(1 + 1)D_\perp + m^2(D_\parallel - D_\perp)] \]  

[44]
6. Lorentzian Bandshapes

The small-step rotational diffusion theory\textsuperscript{24} proposed by Debye has been extensively applied to interpret reorientational spectra from IR and Raman studies of various condensed phase systems.\textsuperscript{19} The major conclusion from this theory is that both the vibrational and reorientational correlation function are exponential functions, $f_{\text{vib}}(t) = \exp(-t/\tau_{\text{vib}})$ and $f_{m}^{(1)}(t) = \exp(-t/\tau_{m}^{(1)})$, as stated earlier. The form of the correlation function is completely specified by the correlation times, $\tau_{\text{vib}}$ and $\tau_{m}^{(1)}$, which can be obtained simply as the inverse of the full width at half maximum intensity (HWHM), $\Delta$. An inverse Fourier transform of the exponential function gives a Lorentzian bandshape in the frequency domain, $I_{\text{Lor}}(\omega) = A/[1 + (\omega/\Delta)^2]$, as derived in the following calculations

\[
I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-t/\tau_{m}^{(1)}) \exp(-i \omega t) \, dt
\]

\[
= \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-\Delta |t|) \exp(-i \omega t) \, dt
\]

\[
= \frac{1}{2\pi} \left[ \int_{-\infty}^{0} \exp[t(\Delta-i\omega)] \, dt + \int_{0}^{\infty} \exp[t(-\Delta-i\omega)] \, dt \right]
\]

\[
= \frac{1}{2\pi} \left[ \frac{1}{\Delta-i\omega} + \frac{1}{\Delta+i\omega} \right] = \frac{(\Delta/2\pi)}{\Delta^2 + \omega^2}
\]

\[
= \frac{A}{1 + (\omega/\Delta)^2} \quad A = \frac{1}{2\pi\Delta}
\]
where $\Delta = 1/\tau$. Theoretically, it tells us that the contours of Raman spectra in the liquid phase will be the Lorentzian in nature.

The model we adopt in the curve-fitting procedure is that all the Raman spectra will be composed of one or sum of two or more Lorentzian-type peaks convoluted with slitwidth broadening.

C. Vibrational Bandshape Analysis in $C_{3v}$ Molecules

As we discussed earlier, the correlation function can be simplified according to the symmetry of the molecule under consideration. In $C_{3v}$ molecule, we will be interested in $A_1$ (symmetric) and $E$ (antisymmetric) vibrations (same motion preferred).

In $A_1$ modes, only $B_o^{(2)} = (3/2)^{1/2}B_{zz} \neq 0$. Therefore, we have only one term in the correlation function (eq. [33]), and after Fourier transformation we have ($l = 2, m = 0$)

$$\Delta_{\text{aniso}} = \Delta_{\text{vib}} + \Delta_{\text{rot}} = \Delta_{\text{vib}} + (\pi c)^{-1}(6D_1)$$  \[46\]

For $E$ vibration in $C_{3v}$ molecules, however, the only vanishing term is $B_o^{(2)} = (3/2)^{1/2}B_{zz} = 0$ and the total correlation function contains two exponential functions, which means that the Raman spectrum from the $E$ vibration will be sum of two Lorentzian peaks with the same peak frequency but different intensities and bandwidths.
1. **A₁ Modes**

**Determination of Δ_{rot}**

In Raman experiments, the isotropic spectrum ($I_{iso}$) is obtained from polarized and depolarized spectra ($I_{pol}$ and $I_{dep}$) by

\[ I_{iso} = I_{pol} - (4/3)I_{dep} \]  \[47\]

$I_{iso}$ is the angle-independent or orientation-independent component of the scattered light and results from vibrational relaxation only. Therefore, the isotropic bandwidth is equal to the bandwidth increment caused by vibrational relaxation, $Δ_{vib}$

\[ Δ_{iso} = Δ_{vib} \]  \[48\]

On the other hand, the depolarized or anisotropic spectrum arise from both vibrational and rotational effects. The bandwidth term can be expressed as

\[ Δ_{anis} = Δ_{dep} = Δ_{vib} + Δ_{rot} \]  \[49\]

From the above two equations, the bandwidth increment results from rotational relaxation, $Δ_{rot}$, can be obtained as

\[ Δ_{rot} = Δ_{anis} - Δ_{iso} \]  \[50\]

It is concluded that vibrational and rotational parts of the Raman scattering process can be separated both theoretically and experimentally. This is an overriding advantage to prefer Raman measurements over IR absorption experiments in bandwidth analysis.
Evaluation of the Tumbling Diffusion Constant

Analysis of isotropic and anisotropic linewidths of totally symmetric vibrations is a well established, reliable technique to determine the tumbling diffusion constants of symmetric-top molecules. For $A_1$ modes in $C_{3v}$ molecules, the anisotropic linewidth is expressed as

$$\Delta_{\text{anis}} = \Delta_{\text{vib}} + (\pi c)^{-1} D_1$$  \[46\]

Substituting equation [48] into equation [46] gives

$$D_1 = (\Delta_{\text{anis}} - \Delta_{\text{iso}}) \pi c / 6$$  \[51\]

This is a well established method to determine tumbling diffusion constants. Researchers have combined this Raman technique with NMR relaxation times or IR bandshapes to study a number of symmetric-top molecules.

2. E Modes

We already know that the reorientational correlation function for Raman vibrations of E symmetry in $C_{3v}$ molecules is the sum of two exponential terms. The total correlation function for Raman E vibrations in $C_{3v}$ molecules, $F_{\text{Raman}}^E(t)$, can be obtained from eq. [31]. It may be expressed as

$$F_{\text{Raman}}^E(t) = f_{\text{vib}}(t) f_{\text{rot}}^E(t)$$

$$= 2 |B_1(2)|^2 \exp(-t/\tau_{\text{vib}}) \exp[-t/\tau_1(2)]$$

$$+ 2 |B_2(2)|^2 \exp(-t/\tau_{\text{vib}}) \exp[-t/\tau_2(2)]$$  \[52\]
It is seen that $F^E_{\text{Raman}}(t)$ is a sum of two exponential terms with different coefficients.

Hence the Raman lineshape of the $E$ vibrations, derived from inverse Fourier transform of eq. [52], is a sum of two Lorentzian bands with the same peak center but different bandwidths, $\Delta_1^{(2)}$ and $\Delta_2^{(2)}$. Combining eqs. [42], [43] and [44], these bandwidths are related to rotational diffusion constants as

$$\Delta_1^{(2)} = \Delta_{\text{vib}} + \frac{(\pi c)^{-1}(5D_\perp + D_\parallel)}{2}$$  \hspace{1cm} [53]$$

and

$$\Delta_2^{(2)} = \Delta_{\text{vib}} + \frac{(\pi c)^{-1}(2D_\perp + 4D_\parallel)}{2}$$  \hspace{1cm} [54]$$

The relative intensities (areas) of the two Lorentzians is given by $|B_1^{(2)}|^2/|B_2^{(2)}|^2$.

In order to calculate the spinning diffusion constants, $\Delta_{\text{vib}}(A_1)$ obtained from the linewidth of the isotropic band profile must be used to estimate $\Delta_{\text{vib}}(E)$ since there is no isotropic scattering from $E$ vibrations. This is done by using the proportionality, $\Delta_{\text{vib}} \propto 1/\omega^2$, predicted by the Fischer-Laubereau IBC$^3$ model via the relationship

$$\Delta_{\text{vib}}(E) = \Delta_{\text{vib}}(A_1)[\omega(A_1)/\omega(E)]^2$$  \hspace{1cm} [55]$$

In this expression, $\Delta_{\text{vib}}(A_1)$ is the isotropic width of an $A_1$ mode involving the same motion as the $E$ vibration, and the second term on the right is the squared ratio of their frequencies.
In principle, various methods can be used to calculate $D_\|$ if both $\Delta_1^{(2)}$ and $\Delta_2^{(2)}$ can be obtained experimentally. Firstly, both eqs. [53] and [54] can be employed to evaluate $D_\|$ after $\Delta_{\text{vib}}$ and $D_\perp$ are obtained. Secondly, $D_\|$ (and possibly, $D_\perp$) can be determined by solving eqs. [53] and [54] simultaneously if $\Delta_{\text{vib}}$ is available. Alternatively, one can combine the IR bandwidth $\Delta_1^{(1)}$ with either eq. [53] or [54] to solve for $D_\|$ analogous to Kim and Lee's approach\cite{36} proposed for molecules of $D_{3h}$. However, all former research work\cite{5,28,39-41} failed for the $E$ vibrations in $C_{3v}$ molecules due to the difficulties in determination of $\Delta_2^{(2)}$.

Using the bandwidth of the narrower component, $\Delta_1^{(2)}$, to calculate $D_\|$ is applied in our approach. With $D_\perp$ obtained from Raman $A_1$ modes and $\Delta_\nu(E)$ from the corresponding $\Delta_\nu(A_1)$, $D_\|$ can be determined from eq. [53] in this manner

$$D_\| = (\Delta_1^{(2)} - \Delta_{\text{vib}}) \pi c - 5D_\perp \quad [56]$$

D. Vibrational Bandshape Analysis in Molecules of Other Symmetries

For all the molecules with a symmetry axis of 3-fold or higher, we can always use $A$-symmetry vibrational modes to get $D_\perp$, as discussed above. Other than the molecules with a symmetry of $C_3$, $C_{3v}$ and $D_{3d}$, the Raman lineshape of doubly degenerated $E$ vibration is only one Lorentzian band.
Therefore, if we can get linewidth of that vibration, which is a function of $D_\perp$ and $D_\parallel$, we can surely derive $D_\parallel$ from eq. [56]. For molecules with a 2-fold symmetry axis, the situation will be more complicated. Detailed discuss will not be provided here since that is not related with my research.

E. Advantage and Difficulties of the Raman Method in Studying of Molecular Recorientation Dynamics

As we already know, there are several spectroscopic techniques which can be applied to the study of molecular reorientation dynamics. Raman spectroscopy has its own advantages over other techniques. First of all, we can measure polarized and depolarized spectra for the A-symmetry vibrations, which allows us to separate the bandwidth due to purely vibration and rotation relaxations. This is a well-established technique to obtain $D_\perp$. The molecule being studied can be very symmetric and does not need to have a permanent electric dipole moment. Since the intensity distribution in a rotation-vibration Raman band is expressed as the Fourier transformation of a correlation function of the molecular rotational coordinates, an experimental Raman band contour can thus be Fourier analyzed to obtain the complete correlation function.

The interpretation of spectroscopic information is always based on the assignment of peaks in a spectrum to
transitions corresponding to different vibrational mode. Therefore, when we do not have a precise peaks assignment for a molecule, or it is difficult to get because there may be so many transitions or peaks may blend together to form a continuous band, to study the reorientation dynamics of that molecule will be impossible. As the molecule gets bigger and its symmetry becomes lower, the problems with overlap, line broadening and the difficulties with peak assignment will be detrimental to the Raman study of reorientational dynamics in liquid phase.
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CHAPTER III

NUCLEAR MAGNETIC RESONANCE RELAXATION AND MOLECULAR DYNAMICS

The concept of Nuclear Magnetic Resonance (NMR) was originally developed in the classic investigations of Purcell, Torrey, and Pound\textsuperscript{1} and Bloch, Hansen, and Packard,\textsuperscript{2} who independently observed the first NMR signals. Since then, the theory has been considerably modified and extended by a number of authors.\textsuperscript{3-7}

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. With the advent of modern pulsed Fourier transform NMR Spectrometers,\textsuperscript{5,8-11} the measurement of NMR spin-lattice relaxation times ($T_1$) has become routine\textsuperscript{12-16} and can furnish valuable information for the study of rotational diffusion constants. The nuclear relaxation process is subject to a variety of contributing relaxation mechanisms, which include dipole-dipole, spin-rotation, chemical shift anisotropy, quadrupolar relaxation, and scalar-coupling. Any combination of these mechanisms can operate in a given liquid.

A. Basic Theory

NMR spectroscopy is concerned with the atomic nuclei in
a molecule. When an atomic nucleus does not have an even atomic number and/or an even mass number (Protons and Neutrons both have a spin quantum number of 1/2), it will 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). The nuclear spin can have the values 0, 1/2, 1, -1, -1/2, ... etc (Depending upon how protons and neutrons pair up in the nucleus). Therefore, the nuclear magnetic momentum, $\mu$, is given by

$$\mu = \gamma I(I - 1)\hbar$$

where $\gamma$ is the magnetogyric ratio, which is a constant for a given nucleus, and $\hbar$ is Planck's constant divided by $2\pi$.

Consider the consequence of placing a nucleus in a magnetic field. A nucleus ($I \neq 0$) is a magnetic dipole ($\mu$), and when placed in a static field $H_0$ (traditionally assumed to be in the Z direction), there is an interaction between the nucleus and the field forcing the dipole to align parallel to the field, and consequently the nucleus will precess relative to the $H_0$ [known as Larmor Precession, see Figure 2(a)] and acquire energy from the field given by the following equation:

$$E = -\mu Z H_0$$

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 $M_I = -I$, ... $I$).
Figure 2. Precession of nuclei in a magnetic field.
(a) Precession of $\mu$ about $H_0$; (b) Precession of an ensemble of nuclei with $I = 1/2$. 
\(-I + 1, \ldots \) to \(+I\), which denotes the spin state of the nucleus. So the energy of each spin state of the nucleus in the magnetic field is

\[ E_m = -\gamma \hbar M_1 H_0 \]  

[59]

The energy difference of two adjacent spin states is

\[ \Delta E = \gamma \hbar H_0 \]  

[60]

Also, the transition between two adjacent states will be induced by a radiation with frequency satisfying \( \hbar v = \Delta E \), where \( v \) is so-called Larmor frequency with value

\[ v = (2\pi)^{-1} \gamma H_0 \quad \text{(in Hz)} \]  

[61]

or

\[ \omega = 2\pi v = \gamma H_0 \quad \text{(in rad.sec}^{-1}) \]  

[62]

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

\[ M_0 = N\theta^2 \hbar I(I+1) H_0/(3kT) \]  

[63]

where \( N \) is the density of nuclei. This magnetization is due to the preferential population of the lower energy level according to a Boltzmann distribution.

Suppose, now, that the magnetization is perturbed from its equilibrium position. The interaction between the magnetization, \( M \), and the magnetic field, \( H_0 \), will exert a torque on the nonequilibrium magnetization 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 $M$, the net result leads to a rotation of the direction of $M$ in a cone with its axis along $H_0$. Such movement is also called Larmor precession, shown in Figure 2(b), and described by\textsuperscript{17}

$$\frac{dM}{dt} = \gamma (M \times H_0)$$ [64]

under condition that there is no interaction between the spins or with their surroundings. The frequency with which the $M$ preceeds about $H_0$ is the Larmor frequency, $\omega_0 = 2\pi v_0 = \gamma H_0$. If we view this motion from a reference frame rotating at the Larmor frequency instead of the Lab frame, the magnetization appears to be a constant vector with components $M_z$ and $M_{x,y}$, which are parallel and perpendicular to the magnetic field, respectively ($M_{x,y} = M_x$ or $M_y$, in the equilibrium state, both are zero).

After the disturbance is removed, two kinds of relaxation processes will occur to bring the magnetization to its equilibrium state. $M_z$ will return to its original value $M_0$ by a process called spin-lattice relaxation

$$\frac{dM_z}{dt} = -(M_z - M_0)/T_1$$ [65]

Where $T_1$ is the time constant which tells how fast the energy is transferred from the nuclear spin system to its surroundings and rate of return of $M_z$ to equilibrium after a perturbation. Spin-lattice relaxation occurs via transition
which are stimulated by components of the local magnetic field, seen by a particular nucleus, which fluctuate at its Larmor frequency. Fluctuations in the local magnetic field are generated by variation in the orientation and relative distance of two interacting nuclei resulting from Brownian motion.\textsuperscript{18} The nonequilibrium component of magnetization, $M_{x,y}$, is also subject to relaxation and approaches zero at equilibrium. The relaxation is called spin-spin relaxation and can be expressed by

$$\frac{dT}{dt} = \frac{-M_{x,y}}{T_2}$$

Where $T_2$ represents the amount of time for $M_{x,y}$ to decay to $1/e$ of its original value. Spin-spin relaxation also occurs through local magnetic fields, but in a different way. If one nucleus undergoes a transition from one spin state to another then the local magnetic field changes at the same frequency to induce a transition in a second nucleus. If a second nucleus of the same type with opposite spin state is close by at this point in time, then the two nuclei will exchange energy. Such a process does not change the total system energy but affects the lifetime of the excited state. So the spin-spin relaxation is an entropy effect and spin-lattice relaxation is an energy effect.\textsuperscript{18}

$T_2$ is quite often shorter than $T_1$ and is never longer due to two effects. The first effect is due to static dipolar fields originating from other nuclei within the
sample, which only interact with $M_{x,y}$. In the case of liquids and gases such fields will be averaged out to zero because of the fast molecular motion; thus $T_1 = T_2$. In the solid state, where molecules are rigid, the first effect becomes very important, and $T_1 \gg T_2$. The second one arises from inhomogeneities in the basic magnetic field due to instrumental imperfection. That is not truly a $T_2$ process; however, it is very hard to distinguish such an effect from a genuine $T_2$ process. Since we are interested in molecular reorientation in the liquid phase, we will always have $T_1 = T_2$, and in the following discussion we will not mention $T_2$ unless it is necessary.

From the relaxation studies, the molecular reorientational correlation time $\tau_c$ is obtained. It is a useful property in describing random molecular motion, defined as the average time for a molecule to reorient itself by one radian. The rotational diffusion constants ($D_1$, $D_\parallel$, and $R$, internal rotation rate) of a molecule can be calculated from its rotational correlation time, as will be discussed later.

B. Relaxation Mechanisms

We already know that a perturbed nuclear spin system relaxes to its equilibrium state by first-order processes characterized by two relaxation times: $T_1$, the spin-lattice relaxation time; and $T_2$, the spin-spin relaxation time.
Relaxation occurs only if there is some specific interaction between the nucleus and its environment that can result in energy exchange. There are six types of interaction that have been identified so far:

1. Nuclear magnetic dipole-dipole interaction
2. Chemical shift anisotropy
3. Spin-rotation interaction
4. Nuclear electric quadrupole interaction
5. Scalar coupling effects
6. Effect of paramagnetic species

In fact, all the interactions may contribute to the overall relaxation process, and the experimental relaxation rate is usually considered as a summation of the specific rate of all the mechanisms involved. Fortunately, in many cases only one or two of the numerous possible mechanisms predominate and a quantitative interpretation can be carried out.

1. Dipole-Dipole (DD) Relaxation

The principal source of nuclear relaxation for spin 1/2 nuclei is via dipole-dipole interactions. Consider the relaxation of a nucleus I induced by another nucleus S. The local field generated at I by S is given by the classical equation

\[ H_{loc}^{DD} = \pm \frac{\mu_S (3 \cos^2 \theta - 1)}{r_{IS}^3} \]
in terms of $\mu_s$ (magnetic moment of S), the distance $r_{IS}$ between I and S, and the angle $\theta$ between the static field and the axis joining I and S. As the molecule tumbles in solution under the influence of Brownian motion, this field fluctuates in magnitude and direction.

Just as a precessing nuclear moment can interact with a coherently applied RF magnetic field, so it can interact with the component of a molecular magnetic field precessing at the Larmor frequency. Therefore, the relaxation arising from the fluctuating field will depend on the molecular motion, magnitudes of the nuclear moments and the distance between the interacting nuclei. A detailed treatment of the relaxation process shows that

$$\frac{1}{T_{1\text{RD}}} = \frac{\gamma_i^2 \gamma_j^2 h^2 S(S + 1)}{30 \pi^2 r_{ij}^6} \times$$

$$\left[ \frac{3\tau_c}{1 + \tau_c^2 \omega_I^2} + \frac{\tau_c}{1 + \tau_c^2 (\omega_I - \omega_S)^2} + \frac{6\tau_c}{1 + \tau_c^2 (\omega_I + \omega_S)^2} \right]$$

where $\gamma_i$ and $\gamma_j$ are the magnetogyric ratios for nuclei with nuclear spin I and S, respectively; $\tau_c$ is the reorientational correlation time; $\omega_I$ and $\omega_S$ are the Larmor frequencies for nuclear spins I and S.

When molecules are in rapid and random motion, which will lead to a very short $\tau_c$. The extreme narrowing condition, $\tau_c \ll 1/\omega_c$, is satisfied, and eq. [68] will be
simplified to give\textsuperscript{20}

\[
\frac{1}{T_{1DD}} = \frac{\gamma_i^2 \gamma_j^2 \hbar^2 S(S+1)}{3\pi^2 x_{ij}^6} \tau_c
\]  \hfill [69]

Eq. [69] tells us three things: Firstly, as the local
field depends on \(\mu_s\), the nucleus with the largest \(\gamma\) (such as \(^1\)H) must be the most powerful source of internuclear dipolar
relaxation. If present, an unpaired electron whose magnetic
moment is 860 times that of the proton is even more
efficient. Secondly, dipole-dipole relaxation is very much
a short range effect because of the inverse sixth power
dependence on the inter-dipole distance. Thirdly, dipole-
dipole relaxation is magnetic field independent and
temperature dependent. \(\tau_c\) remains invariant in different
magnetic fields but changes with temperature. At high
temperature, \(\tau_c\) is short, the efficiency of dipole-dipole
interaction is lowered. Thus, \(T_{1DD}\) is lengthened.

Nuclei \(i\) and \(j\) may be in the same molecule, in which
case it is molecular rotation that causes them to move
relative to each other and to the direction of \(H_0\). They may
be in different molecules and move when molecules undergo
translational motion. The results are analogous, however;
eqs. [68] and [69] are interpreted in terms of a rotational
correlation time in the first case and translational
correlation time in the second case.\textsuperscript{21}
2. Chemical Shift Anisotropy (CSA)

The magnetic field experienced by a nucleus is not the primary magnetic field but, instead, is modified by the molecule. This modification is expressed in terms of a shielding tensor $\sigma$; thus\(^\text{18}\)

$$H_{1oc} = H_0 \left[ 1 - (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3 \right] \quad [70]$$

The three components are not necessarily equal, therefore, the chemical shift is anisotropic. Since the molecule tumbles in solution, the average value of these three components is observed in the form of a chemical shift, the fluctuating magnetic field produced acts as a relaxation mechanism.

If $\sigma$ is axially symmetric, theory predicts that in the extremely narrowing limit

$$\frac{1}{T_{1CSA}} = \frac{2}{15} \gamma^2 H_0^2 (\sigma_\perp - \sigma_\parallel)^2 \tau_c \quad [71]$$

where $\sigma_\parallel = \sigma_{zz}$, $\sigma_\perp = \sigma_{xx} = \sigma_{yy}$. As we see from eq. [71], relaxation rate increases quadratically with increasing magnetic field. Therefore, the chemical shift anisotropy is not an efficient mechanism at low fields. For $^{13}$C, usually it is not dominant. However, in certain molecules relaxation occurs predominantly via the CSA process, as will be seen later.

3. Spin-Rotation (SR) Relaxation

The spin-rotation relaxation arises from magnetic
fields generated at a nucleus by the motion of a molecular magnetic moment, which is caused by the electron distribution in a 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 since it behaves like a circulating electric current. The field will be modulated by the change in direction and rotation due to molecular collisions and provide a relaxation process.

It can be shown that for molecules undergoing diffusional reorientation, the spin-rotation relaxation rate for a symmetric top molecule\textsuperscript{22} is given by

$$\frac{1}{T_{\text{ISR}}} = \frac{3kT}{3\pi^2h^2}[I_1 C_{11}^2(\tau_j)_1 + 2I_\perp C_{\perp\perp}^2(\tau_j)_\perp]$$ \[72\]

where $I_1$ and $I_\perp$ are components of the inertia tensor and $C_1$ and $C_\perp$ are components of the spin-rotation tensor with respect to the symmetry axis. The terms $(\tau_j)_1$ and $(\tau_j)_\perp$ are the angular momentum correlation times.

Since this effect is inversely proportional to the moment of inertia, in general we can anticipate that the smaller the molecule the more important will be the spin-rotation interaction. Furthermore, symmetric molecules with little or no intermolecular interaction will be affected because they will have rather greater angular velocities. For spherical molecules, $I_1 = I_\perp = I (\tau_j)_1 = (\tau_j)_\perp = \tau_j$, so
eq. [72] can be written as

\[ \frac{1}{T_{1\text{SR}}} = (2\pi I k T / \hbar^2) C_{\text{eff}}^2 \tau_J \]  

[73]

where \( C_{\text{eff}}^2 \) is the average component of the spin-rotation tensor and \( \tau_J \) is the angular momentum correlation time, which is a measure of the time a molecule spends in any given angular momentum state. \( \tau_J \) is related to the molecular reorientation correlation time \( \tau_c \) by the Hubbard relationship\(^{23}\)

\[ \tau_c * \tau_J = I / (6kT) \]  

[74]

As the sample temperature increases, \( \tau_c \) becomes shorter as discussed above, so \( \tau_J \) becomes longer. Therefore the best way to judge if the spin-rotation relaxation is dominant is to see if \( T_1 \) decreases as temperature increases.

Spin-rotation interaction is known to be the dominant relaxation mechanism for \(^{13}\)C in CS\(_2\) (except high \( H_0 \) and low \( T \)) and is important for \(^{13}\)C in methyl groups, which reorient rapidly by internal rotation, even in larger molecules. In general, spin-rotation interaction might be important with nuclei that have a large range of chemical shifts \( \text{e.g.,} \), \(^{19}\)F, \(^{13}\)C, \(^{15}\)N) because both the chemical shift and the spin-rotation of any given molecule depend on the electron distribution in a molecule. A distribution which results in large chemical shifts will also lead to large spin-rotation interactions.\(^{19}\)
4. Nuclear Electric Quadrupole Interaction

A spin 1/2 nucleus has a spherical charge distribution and no nuclei have electric dipole. But the electric charge distribution in nuclei with spin $I > 1$ is non-spherical, resulting in their having a quadrupole moment $Q$ ($Q > 0$, prolate charge distribution; $Q < 0$, oblate charge distribution). If such a nucleus was placed in an environment with asymmetric electronic charge distribution, relaxation will arise from the electric quadrupole interaction. This is because molecular tumbling causes fluctuating electric fields, which induce transitions among the nuclear quadrupole energy levels.

In the simplified case of rapid molecular tumbling and axial symmetry of the molecular electric field, the quadrupole relaxation rate is given by

$$\frac{1}{T_{1Q}} = \frac{3\pi}{10} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\xi^2}{3}\right) \left(\frac{e^2qQ}{\hbar}\right)^2 \tau_c$$

where $\xi$ is the quadrupole's asymmetry parameter and $q$ is the electric field gradient at the nucleus. The term $(e^2qQ/\hbar)$ is normally referred to as the quadrupole coupling constant. Since it depends on the electric field gradient present in the compound, its values can vary over a range even for a specific nucleus in different molecules. In the highly symmetric $^{14}\text{NH}_4^+$ ion, the QCC is zero for $^{14}\text{N}$, for asymmetric $^{14}\text{N}$ bond, QCC is generally a few MHz, leading
to $T_1$ in the range of a few msec. For Deuterium the range is typically 100-200 KHz$^{25,26}$.

In the liquid phase, quadrupole relaxation dominates except in highly symmetric environments. Since $T_{1Q}$ depends upon the rotational correlation time, it has the same relation as $T_{1DD}$ to temperature. If the quadrupole coupling constant is known (from nuclear quadrupole resonance in the solid or microwave spectroscopy in the gas phase), $T_{1Q}$ gives a simple measure of $\tau_c$. However, for the purpose of molecular reorientation study in liquid phase, the lack of direct determinations of nuclear quadrupole coupling constant or the uncertainties in applying known value from solid or gas phase measurements to the liquid phase frequently impose severe limitations on the interpretation of the data. Deuterium and nitrogen-14 are frequently used as probes in the study, uncertainties in QCC of these nuclei will keep the researchers from obtaining accurate result. Results from different nematic liquid phase also vary considerably. It is of interest to derive QCC directly from the liquid phase to compare with the value from the solid, gas, or nematic liquid phase. It has been shown that in liquid ClCN$^{34}$ the QCC of nitrogen-14 is in agreement with the solid instead of gas phase value, based on the fact the QCC of chlorine changes negligibly from gas to solid.
5. Scalar Relaxation

When a nucleus (I) is spin-spin coupled with another
nucleus (S) it is possible for S to provide a fluctuating
field. Thus, at nucleus I, relaxation will occur via scalar
interaction involving the bonding electrons. It is called
scalar relaxation because it relies on scalar spin coupling.
There are two sources causing the field fluctuation, first
one is from any time dependence of their spin coupling
constant resulting from chemical exchange; the second is
from the time dependence of the excited state of spin S. If
these fluctuation is rapid (in the order of Larmor
frequency), the relaxation will be efficient. The equations
for scalar relaxation are

\[ \frac{1}{T_{1\text{SC}}} = \frac{8\pi^2 J^2}{3} S(S + 1) \left[ \frac{T_1^S}{1 + (\omega_I - \omega_S)^2 (T_1^S)^2} \right] \]  \[ \text{[76]} \]

and

\[ \frac{1}{T_{2\text{SC}}} = \frac{4\pi^2 J^2}{3} S(S + 1) \left[ T_1^S + \frac{T_1^S}{1 + (\omega_I - \omega_S)^2 (T_1^S)^2} \right] \]  \[ \text{[77]} \]

Here S is the spin of nucleus S, \( \omega_I \) and \( \omega_S \) are the Larmor
frequencies of the two nuclei, and \( T_1^S \) is the longitudinal
relaxation time of S.

Eqs. [76] and [77] show that this mechanism can have
very different effects on \( T_1 \) and \( T_2 \) processes. In the
heteronuclear case, for example, in \( ^{13}\text{CH}_3\text{COOCD}_3 \) with \( T_1(H) \) = 12.5 sec and \( J_{\text{CH}} = 130 \text{ Hz}, T_1(^{13}\text{C}) = 19.2 \text{ sec, while} \)
\( T_2(^{13}\text{C}) = 6.1 \text{ sec.} \) \( T_1 \) and \( T_2 \) would have to be equal in the absence of the scalar coupling. In most cases, scalar relaxation does not contribute significantly to the overall \( T_1 \). The exceptions are when the Larmor frequencies of two nuclei are very close, e.g. \(^{13}\text{C}-^{81}\text{Br} \) in \( \text{CHBr}_3 \)\(^{30}\) and \(^{13}\text{C}-^{185,187}\text{Re} \) in \( \text{CpRe(CO)}_3 \).\(^{31}\)

6. Relaxation by paramagnetic species

Paramagnetic atoms or molecules are those with one or more unpaired electrons. An unpaired electron will generate a local magnetic field because it is a magnetic dipole. This local field will be randomly modulated by molecular motion and, consequently, it will provide a relaxation mechanism. The interaction is dipolar in nature and since the electron's magnetic moment is about \( 10^3 \) times larger than that of the proton, electron-nuclear dipolar relaxation could be \( 10^6 \) times more efficient than nuclear-nuclear dipolar relaxation. The most common paramagnetic relaxation agent is molecular oxygen which, when dissolved in a solution, can lead to line broadening. In proton spectra, line width below a few tenths of a Hertz normally can not be obtained without degassing the sample.\(^{32}\) In measuring \( T_1 \) relaxation time of \(^{13}\text{C} \), the error could be up to 100% without degassing oxygen. It is an unwanted effect for our purposes. However, it has important application in chemistry and biology.\(^{18}\)
C. Separation of Relaxation Mechanisms

The observed relaxation time is the sum of relaxation rates of all the various mechanisms discussed above. Each mechanism can offer different chemical information. Thus, in order to interpret the result from a study of relaxation data, the contribution of each mechanism must be resolved.

If a quadrupolar interaction is present, it will be predominant over other spin-lattice mechanisms in most cases. It could be four to five orders of magnitude more effective than any other mechanism in promoting relaxation. This is a most favored situation where we can easily pull out the information from $T_{1Q}$ and will not be bothered by other relaxation mechanisms.

1. Dipole-Dipole

The contribution from dipole-dipole relaxation to overall relaxation can be easily separated out by measuring nuclear Overhauser enhancement (NOE) effect.\(^\text{20}\)

The NOE is a property whose magnitude is directly proportional to the fraction of total relaxation that arises solely from the dipole-dipole mechanism. In general, it is field dependent.\(^\text{20}\) However, under the limiting condition $r_c \omega_c << 1$ and 100% dipole-dipole relaxation, the NOE effect reaches the maximum value: in the case of $^{13}$C-H,

$$\eta_{\text{max}} = \frac{\gamma_H}{(2\gamma_{C-13})} = 1.988,$$

which means the signal intensity of $^{13}$C can be enhanced by 3 fold when coupled to H.
It is important to point out that the enhancement factor depends on the sign of the magnetogyric ratio, e.g., it is negative for $^{29}\text{Si}$. Experimentally, we can obtain the NOE factor by observing the signal intensity with proton decoupling and without proton decoupling, named $I_E$ (enhanced) and $I_N$ (not enhanced), respectively, and it is expressed as

$$\eta_{\text{exp}} = \frac{I_E}{I_N} - 1 \quad [78]$$

The contribution of the dipole-dipole mechanism can be obtained by

$$T_{1DD} = T_1^{\text{all}} \ast (\eta_{\text{max}}/\eta_{\text{exp}}) \quad [79]$$

where $T_1^{\text{all}}$ is the measured spin-lattice relaxation time. For $^{13}\text{C-H}$, if $\eta_{\text{exp}}$ is less than 1.988, this is indicative that the relaxation of that particular carbon is not entirely dipolar. The relaxation due to other mechanisms can be obtained from

$$\frac{1}{T_1^{\text{other}}} = \frac{1}{T_1^{\text{all}}} - \frac{1}{T_1^{\text{DD}}} \quad [80]$$

Great care must be taken when apply homonuclear NOE technique. Paramagnetic species might be involved in the relaxation and it could override the NOE effect.

2. Chemical Shift Anisotropy

As we discussed earlier, CSA is a magnetic field dependent mechanism and only become prominent at high $H_0$ and without bonding to proton. It occurs quite frequently in
metal carbonyl complexes, as will be seen in later chapter. Experimentally we can measure the overall $T_1$ value at two different magnetic fields. According to eq. [71], we will have

$$1/T_1^\alpha = a + b(H_a)^2$$  \[81\]

and

$$1/T_1^\beta = a + b(H_B)^2$$  \[82\]

where $a = 1/T_1^{\text{other}}$, $b = (2/15)\gamma_c^2(\sigma_1 - \sigma_2)^2\tau_c$, and $H_a$ and $H_B$ represent two different magnetic fields. Mathematically we can solve the equations and obtain $T_1^{\text{CSA}}$, however, what we are really interested is the correlation time. In order to get $\tau_c$, we need to have the value of $(\sigma_1 - \sigma_2)$. In the liquid phase, the splitting due to CSA are averaged out by the fast molecular rotation, so we only see a single peak. One way to get $\Delta \sigma$ is to measure the NMR splitting in solid phase\textsuperscript{35} and in liquid crystal.\textsuperscript{36}

3. Scalar Coupling and Spin-Rotation

Scalar coupling is another magnetic field dependent mechanism. It is a rare phenomenon.\textsuperscript{30,31} However, when it is present in the overall relaxation, the difficulties in obtaining the correlation time will be increased significantly. We will need to have $T_1$ values from at least two different magnetic fields to separate scalar coupling from the overall relaxation process.
Spin-rotation is the only mechanism whose $T_1$ decreases monotonically with temperature. If a nucleus is relaxed partially by spin-rotation, it will show a non-Arrhenius behavior as a function of temperature. This enables spin-rotation to be detected in the presence of other relaxation mechanisms.

D. Relationship between $r_c$ and Diffusion Constants

In principle, magnetic relaxation measurement can provide a wealth of information about molecular motion on a microscopic scale. This is because molecular motion is coupled to the nuclear spins by a number of mechanisms. The correlation time, $r_c$, obtained from relaxation time measurement is a function of the rotational diffusion constants. The theory relating $r_c$ to the diffusion constants was developed in the 1960's by Shimizu\textsuperscript{37}, Woessner\textsuperscript{38} and Huntress\textsuperscript{39}.

For a symmetric-top molecule, we need two parameters, $D_\perp$ and $D_\parallel$, in general, to describe the molecular rotation. If the reorienting vector, which corresponds to the bond between two coupled nuclei, is along the unique axis ($Z$-axis), the correlation time is a function of $D_\perp$ only. $D_\parallel$ represents the rotation around the axis ($X$ or $Y$-axis) perpendicular to the unique axis.\textsuperscript{39}

$$r_c = 1/(6D_\perp) \quad [83]$$

If the reorienting vector is oriented at an angle $\theta$ relative
to the Z-axis, the correlation time will be the function of $D_1$ and $D_\parallel$, and it is given as

$$
\tau_c = \frac{A}{6D_1} + \frac{B}{5D_1 + D_\parallel} + \frac{C}{2D_1 + 4D_\parallel}
$$

[84]

$A = \frac{3\cos^2\theta - 1}{4}$, $B = 3\sin^2\theta \cos^2\theta$ and $C = 3\sin^4\theta / 4$, where $\theta$ is the angle between the symmetry axis of the molecule and the reorienting vector. If $\theta = 0$, that is the situation described by eq. [83].

If the molecule is a rigid body. By applying eqs. [83] and [84] we are able to get the rotational diffusion constants to fully describe the molecular reorientaion dynamics. If, additionally, the reorienting vector has an internal rotation relative to the molecule framework. The internal rotation will superpose on the motion of whole molecule and, denoted as $R$, can be incorporated into eq. [80] to give another relation.

$$
\tau_c = \frac{A}{6D_1} + \frac{B}{5D_1 + D_\parallel + R}
+ \frac{C}{2D_1 + 4D_\parallel + 4R}
$$

[85]

The $A$, $B$ and $C$ have the same meaning as in eq. [80]. In this case we need three $\tau_c$'s to calculate the $D_1$, $D_\parallel$ and $R$.

An even more general relationship was given by Woessner et al., in which the reorientation occurs about an arbitrary but fixed axis in the molecule, shown in Figure 3. The complete equation is very complex, a summation of 9 terms. However, it can be simplified in applications, for example, when the reorienting vector is perpendicular to the
Figure 3. The orientation of the relaxation vector $\mathbf{r}$ in the ellipsoid (unprimed coordinates). The vector rotates about the $z'$ axis with constant polar angle $\Delta$ and time-dependent azimuthal angle $\phi'(t)$. The $z'$ axis itself is fixed in the ellipsoid and has an angle $\alpha$ with the symmetry axis of the ellipsoid. $\theta(t)$ is the angle between $z$ axis and the vector.
axis about which it rotates. In this case, the equation will be reduced to six terms and given below

\[ \tau_c = \frac{C1}{6D_\perp} + \frac{C2}{6D_\perp + 4R} + \frac{C3}{5D_\perp + D_\parallel} + \frac{C4}{5D_\perp + D_\parallel + R} + \frac{C5}{2D_\perp + 4D_\parallel} + \frac{C6}{2D_\perp + 4D_\parallel + 4R} \]  

where \( C1 = (1 - 3\cos^2a)^2/16; \ C2 = 9\sin^4a/32; \ C3 = 3\sin^22a/16; \ C4 = 3(\sin^2a + 0.25\sin^22a)/8; \ C5 = 3\sin^4a/16; \) and \( C6 = 3[(1 + \cos^2a)^2 + 4\cos^2a]/32. \) \( a \) is the angle between unique axis and the axis about which the vector reorients (see Figure 3).

Experimentally we need \( \tau_c \) values from three geometrically nonequivalent nuclei to solve the rotational diffusion constants numerically.

For asymmetric molecules, we need three parameters to fully describe the molecular rotation, an extra one will be needed for internal rotation. It will be a nightmare to try to solve the problem because of the tremendous difficulties involved. However, often we can approximate an asymmetric molecule as a quasi-symmetric-top one. In doing so, the problem will be simplified significantly and we can apply all the relations above to obtain reasonable results.

E. Advantages and Difficulties of the NMR Method in Molecular Dynamics Studies

With the rapid development of Fourier Transform NMR spectrometers, it has been possible to easily measure
relaxation times of individual nuclei in complex molecules. The interpretation of these data has provided a great deal of new information on molecular structure and on molecular dynamics in the liquid phase. The advantage of applying NMR relaxation time in the studies of molecular dynamics in the liquid phase is that the molecule being studied can be big or small, and it can be symmetric or asymmetric in shape. As long as we can be able to measure the relaxation times of enough geometrically nonequivalent nuclei, we can obtain the dynamic parameters which fully describe the reorientational motion (isotropic or anisotropic) of the molecule.

The primary difficulty in extracting information about molecular motion from relaxation time is that the measured relaxation time is usually a composite of the relaxation times arising from several mechanisms of comparable efficiency. It is necessary to have a preliminary separation of the observed relaxation time into contributions from the different mechanisms. This separation can be difficult even in favorable cases. For spin 1/2 nuclei, three mechanisms -- DD, CSA, SR -- are important in general: small traces of paramagnetic impurities such as dissolved oxygen can make significant changes in the relaxation time; relative translational motion between molecules also contributes to the relaxation time. Additional effort is required to solve the problem.
For spin greater than 1/2 nuclei, the quadrupole interaction will be the predominant relaxation mechanism and all other mechanisms are negligible. The difficulties arise from the fact that we do not have the QCC value in the liquid phase, data from the measurements in nematic liquid crystals will vary in different liquid crystals. Uncertainty in calculation results from using the average of values from gas and solid phase measurements. Therefore, comparison of results from different techniques will be informative in clarifying conclusions about the reorientation dynamics of molecules in the liquid phase.
CHAPTER REFERENCES


21. Eqs. [68] and [69] apply strictly to two nuclei with different γ in the same molecule. Detailed expressions for other situations are give in ref. 3, chapter 8.


CHAPTER IV

RAMAN AND NMR STUDIES OF REORIENTATIONAL MOTION
IN ACETONITRILE

Introduction

As we already know, two dynamic parameters, $D_\perp$ and $D_\parallel$, are needed to characterize the reorientation of a symmetric-top molecule in the liquid phase. Analysis of the isotropic and anisotropic Raman linewidths of totally symmetric vibrations is a well established technique for the determination of $D_\perp$, the tumbling rotational diffusion coefficient, of symmetric-top molecules.\textsuperscript{1-3} More recently, the technique has been extended to the calculation of $D_\parallel$, the parallel rotational diffusion coefficient, from linewidths of doubly degenerate $E$ vibrations in molecules of $D_{3h}\textsuperscript{4-7}$ and $D_{6h}\textsuperscript{8,9}$ symmetry. In contrast, most attempts to extract $D_\parallel$ from the $E$ mode vibrational widths in $C_{3v}$ molecules have proved unsuccessful owing to the more complex dependence of the Raman bandshape upon $D_\perp$, $D_\parallel$ and $\Delta_{vib}$, the contribution of vibrational relaxation to the net linewidth.\textsuperscript{2,3,10}

Recently in our group, a new procedure involving curve-fitting has been introduced to study iodomethane\textsuperscript{11,12} and the results gave a physically realistic picture of the
spinning motion of this molecule in the liquid phase. Acetonitrile is another typical $C_{3v}$ molecule with large dipole moment. In order to test further the capability of the method to extract reliable diffusion coefficients in $C_{3v}$ symmetry molecules, we have analyzed the Raman spectra of CH$_3$CN and CD$_3$CN at various temperatures spanning the liquid range. The calculated diffusion coefficients for the deuterated molecule are compared with results obtained from Deuterium and Nitrogen-14 relaxation time measurements. Therefore, the reliability of the method can be evaluated by the information from different techniques.

In addition, it is well known that acetonitrile molecules will self-associate in the neat liquid phase$^{13,14}$ and they form donor-acceptor complexes in solution with chloroform, which has a weak hydrogen bond.$^{15-17}$ There have been a number of spectroscopic studies of molecular reorientation in the pure liquid$^{10,18-25}$ and in binary acetone/chloroform mixture.$^{26-28}$ There have, however, been relatively few comparative investigations of the motion of acetonitrile in both associative and 'inert' solvents.$^{28}$ We have measured the $^{14}N$ and $^2$H NMR relaxation times of acetonitrile-d$_3$ as a function of temperature in various solvents to determine the reorientational 'tumbling' and 'spinning' diffusion coefficients ($D_\perp$ and $D_\parallel$) to find out the effects of intermolecular association on both molecular motions.
Experimental

Acetonitrile was purchased from Aldrich Chemical Co. and purified by fractional distillation prior to use. Acetonitrile-d₃ was purchased from the same company and used as received.

A. Raman Experiment

The Raman spectra were acquired with a spectroscopic slitwidth of 5.1 cm⁻¹ and a frequency increment of 0.5 cm⁻¹ on a standard laser Raman spectrometer, Spex 14018 with argon-ion laser (4880 Å) as irradiation source, and interfaced with and controlled by an Apple-II+ computer. The sample was contained in a sealed melting point capillary tube which was inserted into a Harney-Miller cell. The temperature regulation was accomplished via liquid-nitrogen boil-off or heated air flow, and measured with an iron-constant thermocouple adjacent to the sample.²⁹,³⁰

Temperature-dependent polarized and depolarized (anisotropic) spectra of the v₁ symmetric stretching vibration of methyl group (at 2948 cm⁻¹ for CH₃ and 2120 cm⁻¹ for CD₃), and of the v₂ C≡N stretch (at 2257 cm⁻¹ for CH₃CN and 2266 cm⁻¹) for CD₃CN were acquired twice at each temperature. Polarized spectra of the doubly degenerate v₅ antisymmetric stretching vibration of methyl group (at 3008 cm⁻¹ for CH₃ and 2257 cm⁻¹ for CD₃) were also recorded twice at each temperature.
Following baseline subtraction, isotropic spectra of the $v_1$ and $v_2$ vibrations were calculated from eq. [45] on page 35. The isotropic and anisotropic linewidths, $\Delta_{iso}$ and $\Delta_{aniso}$, were determined from a fit of the experimental intensities by a model composed of a Lorentzian lineshape convoluted with a 19 point triangular slit function. The experimental intensities of the E-mode were fitted by a model which incorporated two Lorentzians, as discussed in Chapter II, with the same peak center and different widths, $\Delta_1^{(2)}$ and $\Delta_2^{(2)}$, convoluted with the slit function. As was observed in previous investigations,\textsuperscript{11,12} the broader width, $\Delta_2^{(2)}$, varied erratically and often diverged [$\Delta_2^{(2)} \rightarrow \infty$ and $I_2^{(2)} \rightarrow 0$]. In contrast, constant values were obtained for the narrower linewidth, $\Delta_1^{(2)}$, as indicated by the relatively small deviations between runs at each temperature. The resultant bandwidths as a function of temperature are present in table I; $\Delta_{aniso}$ of $v_1$ vibration is not shown since it was not used in the analysis.

B. NMR Experiments in Neat Liquid

Acetonitrile-d$_3$ was transferred to a 10 mm NMR sample tube, degassed by three freeze-pump-thaw cycles, and sealed under vacuum. Relaxation time measurements were performed on a JEOL FX90Q FT-NMR spectrometer operating at 13.8 MHz for $^2$D and at 6.5 MHz for $^{14}$N. The temperature was regulated by heated liquid nitrogen boil-off or heated air
Table I.
Temperature dependence of Raman linewidths and NMR relaxation times in acetonitrile

A. CH$_3$CN

<table>
<thead>
<tr>
<th>T/K</th>
<th>$\Delta_i(v_2)^b$</th>
<th>$\Delta_a(v_2)^b$</th>
<th>$\Delta_i(v_1)^b$</th>
<th>$\Delta_i^{(2)}(v_5)^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>233</td>
<td>2.43</td>
<td>6.43</td>
<td>4.33</td>
<td>24.5</td>
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<td></td>
<td>(0.07)</td>
<td>(0.29)</td>
<td>(0.05)</td>
<td>(0.5)</td>
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<tr>
<td>250</td>
<td>2.84</td>
<td>7.14</td>
<td>4.35</td>
<td>25.5</td>
</tr>
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<td>(0.03)</td>
<td>(0.10)</td>
<td>(0.06)</td>
<td>(0.7)</td>
</tr>
<tr>
<td>268</td>
<td>3.06</td>
<td>9.28</td>
<td>4.43</td>
<td>29.3</td>
</tr>
<tr>
<td></td>
<td>(0.01)</td>
<td>(0.02)</td>
<td>(0.01)</td>
<td>(0.1)</td>
</tr>
<tr>
<td>283</td>
<td>3.43</td>
<td>11.63</td>
<td>4.46</td>
<td>30.9</td>
</tr>
<tr>
<td></td>
<td>(0.05)</td>
<td>(0.18)</td>
<td>(0.02)</td>
<td>(0.1)</td>
</tr>
<tr>
<td>297</td>
<td>3.66</td>
<td>13.54</td>
<td>4.47</td>
<td>32.4</td>
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<td>(0.18)</td>
<td>(0.25)</td>
<td>(0.03)</td>
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<tr>
<td>312</td>
<td>3.91</td>
<td>15.55</td>
<td>4.76</td>
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<td>(0.03)</td>
<td>(0.13)</td>
<td>(0.01)</td>
<td>(1.7)</td>
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B. CD$_3$CN

<table>
<thead>
<tr>
<th>T/K</th>
<th>$\Delta_{i}(v_2)^{b}$</th>
<th>$\Delta_{a}(v_2)^{b}$</th>
<th>$\Delta_{i}(v_1)^{b}$</th>
<th>$\Delta_{i}^{(2)}(v_5)^{b}$</th>
<th>$T_{2}^{(14N)^{c}}$</th>
<th>$T_{1}^{(2D)^{d}}$</th>
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<tr>
<td>233</td>
<td>3.37</td>
<td>6.73</td>
<td>1.67</td>
<td>17.4</td>
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<td>(0.1)</td>
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<td>(0.20)</td>
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<td>250</td>
<td>3.47</td>
<td>8.72</td>
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<td>4.81</td>
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<td>(0.06)</td>
<td>(0.35)</td>
<td>(0.06)</td>
<td>(0.2)</td>
<td>(0.02)</td>
<td>(0.32)</td>
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<tr>
<td>268</td>
<td>3.82</td>
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<td>(0.02)</td>
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<td>(0.22)</td>
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<tr>
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<td>4.15</td>
<td>11.93</td>
<td>1.89</td>
<td>22.0</td>
<td>3.05</td>
<td>6.14</td>
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<td>(0.05)</td>
<td>(0.02)</td>
<td>(0.6)</td>
<td>(0.04)</td>
<td>(0.51)</td>
</tr>
<tr>
<td>297</td>
<td>4.53</td>
<td>13.94</td>
<td>2.12</td>
<td>25.7</td>
<td>3.68</td>
<td>6.74</td>
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<td>(0.14)</td>
<td>(0.01)</td>
<td>(0.5)</td>
<td>(0.05)</td>
<td>(0.08)</td>
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<td>4.90</td>
<td>15.82</td>
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<td>27.6</td>
<td>4.25</td>
<td>7.60</td>
</tr>
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<td>(0.10)</td>
<td>(0.95)</td>
<td>(0.03)</td>
<td>(1.9)</td>
<td>(0.07)</td>
<td>(0.29)</td>
</tr>
</tbody>
</table>

a) Quantities in parentheses represent the deviation between runs.

b) Linewidths (FWHM) in cm$^{-1}$.

c) $T_2$ in ms.

d) $T_1$ in s.
flow and measured with a thermometer inserted directly into another sample tube containing acetonitrile.

Nitrogen-14 spectra were acquired by accumulating 64 transients (with a $5T_1$ delay between $\pi/2$ pulses). The spin-spin relaxation time ($T_2$) was determined from $T_2 = (\pi\Delta v)^{-1}$, where $\Delta v$ is the measured linewidth (FWHM). Deuterium spin-lattice ($T_1$) rather than spin-spin ($T_2$) relaxation times were measured since the latter quantity is subject to possible errors arising from scalar coupling to $^{14}N$ and magnetic field inhomogeneities (due to the longer relaxation times and, hence, narrower linewidths of the deuterium nucleus). $T_1$ values were measured using the standard inversion recovery pulse sequence, $(\pi-\tau-\pi/2$-Acq.-D)$_n$, with a pulse delay, $D > 5T_1$, and $n = 8$ transients at each of 11 $\tau$ values plus $\tau \rightarrow \infty$, and determined by fitting the magnetization data, using a nonlinear least-square program, to the following three-parameter ($M_0$, $\cos \theta$ and $T_1$) equation:

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

Initial estimates for $T_1$ and $\cos \theta$ were obtained from the slope and intercept of a preliminary linear least-square fit. Three or four measurements of $T_1(^2D)$ and $T_2(^{14}N)$ were performed at each temperature. The average values for both nuclei, presented in the last two columns of Table IB, are in excellent agreement with recently published values.$^{26,27}$
Table II. Solvent and Temperature Dependence of Deuterium and Nitrogen-14 Relaxation Times in CD$_3$CN$^a,b$

A. $T_1(2^D)$

<table>
<thead>
<tr>
<th>T</th>
<th>CHCl$_3$</th>
<th>CCl$_4$</th>
<th>DMSO</th>
<th>Butanol</th>
<th>Propanediol</th>
</tr>
</thead>
<tbody>
<tr>
<td>312 K</td>
<td>5.4 s</td>
<td>7.0 s</td>
<td>2.74 s</td>
<td>3.4 s</td>
<td>1.83 s</td>
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<tr>
<td></td>
<td>(0.2)</td>
<td>(0.3)</td>
<td>(0.01)</td>
<td>(0.1)</td>
<td>(0.01)</td>
</tr>
<tr>
<td>297</td>
<td>5.20</td>
<td>5.89</td>
<td>2.57</td>
<td>2.50</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>(0.04)</td>
<td>(0.07)</td>
<td>(0.02)</td>
<td>(0.09)</td>
<td>(0.03)</td>
</tr>
<tr>
<td>283</td>
<td>4.55</td>
<td>4.97</td>
<td>2.26</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
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<td>(0.04)</td>
<td>(0.03)</td>
<td>(0.04)</td>
<td>(0.05)</td>
<td></td>
</tr>
<tr>
<td>268</td>
<td>3.88</td>
<td>3.8</td>
<td>1.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.02)</td>
<td>(0.1)</td>
<td>(0.04)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. $T_2(14N)$

<table>
<thead>
<tr>
<th>T</th>
<th>CHCl$_3$</th>
<th>CCl$_4$</th>
<th>DMSO</th>
<th>Butanol</th>
<th>Propanediol</th>
</tr>
</thead>
<tbody>
<tr>
<td>312 K</td>
<td>2.21 ms</td>
<td>2.77 ms</td>
<td>1.15 ms</td>
<td>1.06 ms</td>
<td>0.61 ms</td>
</tr>
<tr>
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<td>(0.08)</td>
<td>(0.05)</td>
<td>(0.02)</td>
<td>(0.03)</td>
<td>(0.01)</td>
</tr>
<tr>
<td>297</td>
<td>2.05</td>
<td>2.06</td>
<td>1.04</td>
<td>0.71</td>
<td>0.31</td>
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<td>(0.03)</td>
<td>(0.04)</td>
<td>(0.01)</td>
<td>(0.03)</td>
<td>(0.01)</td>
</tr>
<tr>
<td>283</td>
<td>1.57</td>
<td>1.66</td>
<td>0.84</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.04)</td>
<td>(0.05)</td>
<td>(0.01)</td>
<td>(0.01)</td>
<td></td>
</tr>
<tr>
<td>268</td>
<td>1.33</td>
<td>1.16</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.02)</td>
<td>(0.04)</td>
<td>(0.01)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Values represent the average of 2-3 measurements.
b) Quantities in parentheses are the mean deviation between runs.
C. NMR Experiments on CD$_3$CN in Solutions

The solvents, CHCl$_3$, CCl$_4$, dimethylsulfoxide (DMSO), n-propanol and 1,2-propanediol, were obtained commercially and used as received. Samples were prepared gravimetrically with an acetonitrile mole fraction, x=0.05 and transferred into 10 mm NMR tubes.$^{32}$ The samples were degassed by three freeze-pump-thaw cycles prior to sealing.

Deuterium and nitrogen-14 NMR spectra were acquired on a Varian VXR-300 FT-NMR spectrometer [$v_0$(2H) = 46.05 MHz and $v_0$(14N) = 21.67 MHz]. 14N spin-spin relaxation times [T$_2$(14N)] and 2H spin-lattice relaxation times [T$_1$(2H)] were measured using the same procedure as in neat liquid. Both T$_2$(14N) and T$_1$(2H) were determined 2-3 times in all solvents at each temperature. The results are listed in Table II.

Result and Discussion
A. Temperature Dependence of Reorientational Dynamics in Acetonitrile.

1. Perpendicular Diffusion Coefficients

The perpendicular diffusion coefficients in acetonitrile may be obtained directly from the isotropic and anisotropic bandwidths of any A$_1$ vibration from the simple expression:$^1$ $D_\perp = (\pi c/6)[A_a-A_i]$(eq. [49] on page 37. Shown in the second and third columns of Table III are values of D$_\perp$(Ram) for CH$_3$CN and CD$_3$CN at various temperatures as determined from the $v_2$ linewidths. The interpolated room
Table III. Rotational diffusion coefficients in acetonitrile$^{a,b}$

<table>
<thead>
<tr>
<th>T/K</th>
<th>$D_1$(Ram) (CH$_3$CN)</th>
<th>$D_1$(Ram) (CD$_3$CN)</th>
<th>$D_1$(NMR) (CD$_3$CN)</th>
<th>$D_1$(Ram) (CH$_3$CN)</th>
<th>$D_1$(Ram) (CD$_3$CN)</th>
<th>$D_1$(NMR) (CD$_3$CN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>233</td>
<td>6.3 (0.5)</td>
<td>5.3 (0.1)</td>
<td>5.2 (0.1)</td>
<td>161 (0.05)</td>
<td>123 (0.01)</td>
<td>112 (0.015)</td>
</tr>
<tr>
<td>250</td>
<td>6.8 (0.2)</td>
<td>8.2 (0.6)</td>
<td>7.2 (0.1)</td>
<td>168 (0.06)</td>
<td>140 (0.03)</td>
<td>126 (0.018)</td>
</tr>
<tr>
<td>268</td>
<td>9.8 (0.1)</td>
<td>10.6 (0.7)</td>
<td>8.9 (0.1)</td>
<td>188 (0.01)</td>
<td>123 (0.01)</td>
<td>118 (0.011)</td>
</tr>
<tr>
<td>283</td>
<td>12.9 (0.3)</td>
<td>12.2 (0.1)</td>
<td>10.6 (0.1)</td>
<td>186 (0.02)</td>
<td>130 (0.06)</td>
<td>125 (0.023)</td>
</tr>
<tr>
<td>297</td>
<td>15.5 (0.5)</td>
<td>14.8 (0.2)</td>
<td>12.7 (0.2)</td>
<td>188 (0.03)</td>
<td>150 (0.05)</td>
<td>127 (0.021)</td>
</tr>
<tr>
<td>312</td>
<td>18.3 (0.2)</td>
<td>17.1 (1.5)</td>
<td>14.8 (0.3)</td>
<td>192 (0.16)</td>
<td>155 (0.20)</td>
<td>137 (0.012)</td>
</tr>
</tbody>
</table>

$D(25°C)$ 15.3 (1.4) 15.0 (0.9) 12.7 (0.3) 190 (0.06) 144 (0.11) 130 (0.06)

$E_a^d$ 8.8 (0.8) 8.7 (0.5) 7.8 (0.2) 1.4 (0.3) 1.45 (0.7) 1.2 (0.4)

---

a) Diffusion coefficients are in units of $10^{10}$ s$^{-1}$. b) Quantities in parentheses represent one standard deviation. c) Values in square brackets were interpolated using Arrhenius equation. d) unit is kJ mol$^{-1}$
temperature coefficients, $D_x(25 \, ^\circ C)$, and activation energies determined from Arrhenius fits to the data are equal, to within experimental error, for the two molecules. This is not surprising since isotopic substitution has no effect on the molecular size and very little on the perpendicular moments of inertia.$^{21}$

The CH$_3$CN results are close to those of Griffiths,$^{22}$ who found $D_x(25 \, ^\circ C) = 16.1\times10^{10}$ s$^{-1}$ (interpolated from his data) and $E_a = 8.4$ kJ/mol from analysis of the $v_1$ mode at four temperatures. They agree also with the room temperature data of Tanabe and Hiraishi,$^{33}$ who report $D_x = 15.1\times10^{10}$ s$^{-1}$ as the average coefficient calculated from the four $A_1$ vibrations; $D_x = 12.2\times10^{10}$ s$^{-1}$ for CD$_3$CN$^{33}$ is somewhat lower than the value found here. Activation energies for the tumbling rotation determined from dielectric relaxation ($E_a = 8.3$ kJ/mol)$^{34}$ and from Rayleigh scattering ($E_a = 8.8$ kJ/mol)$^{22b}$ agree well with the current results, as does the value predicted from hydrodynamic theories of reorientation; $E_a(\eta/T) = 8.7$ kJ/mol.$^{19}$

NMR Quadrupolar relaxation times have been widely used to investigate rotational diffusion in liquids.$^{35,36}$ For a spin $I=1$ nucleus such as $^{14}$N or $^2$D, the relaxation time ($T_1$ or $T_2$) is related to the reorientational correlation time, $\tau_c$, of the vector containing the bond (C-D or C=N) by:$^{37}$
\[
\frac{1}{T_1} = \frac{1}{T_2} = \frac{3 \pi^2}{10} \frac{2I+3}{I^2(2I-1)} \left( 1 + \frac{\xi^2}{3} \right) \chi^2 \tau_c(\theta)
\]

[88]

\[
\frac{3 \pi^2}{2} \chi^2 \tau_c(\theta)
\]

In this equation, \( \xi \) is the electric field gradient (efg) asymmetry (we have assumed \( \xi \approx 0 \), which is rigorous for the \(^{14}\text{N} \) nuclei in \( \text{CD}_3\text{CN} \) and reasonable for the \(^2\text{H} \) nuclei), and \( \chi \) is the Quadrupole Coupling Constant (in Hz). \( \tau_c(\theta) \) is the reorientational correlation time for the principal axis of the efg vector (approximately parallel to the bond containing the quadrupolar nucleus). This quantity is dependent upon the angle, \( \theta \), between the vector and the symmetry axis, and on the reorientational diffusion coefficients, \( D_\perp \) and \( D_\parallel \); the relationship was given on page 67 as eq. [84] and shown again below:

\[
\tau_c(\theta) = \frac{(1/4)(3\cos^2\theta-1)^2}{6D_\perp} + \frac{3\sin^2\theta\cos^2\theta}{5D_\perp + D_\parallel}
\]

[84]

\[
+ \frac{(3/4)\sin^4\theta}{2D_\perp + 4D_\parallel}
\]

Since the C=N bond in \( \text{CD}_3\text{CN} \) lies parallel to the symmetry axis, \( \theta = 0^\circ \), and, hence, the correlation time from \( T_2(^{14}\text{N}) \) (determined from Eq. [88]) is related directly to the perpendicular ('tumbling') diffusion constant by: \( \tau_c(0^\circ) = \left[ 5D_\perp \right]^{-1} \) (eq. [83] page 66).

The application of these equations requires an estimate for \( \chi \). For acetonitrile, two values, \( \chi(^{14}\text{N}) = 4.22 \text{ MHz} \)
(gas)\textsuperscript{39a} and $\chi(^{14}\text{N})=3.74$ MHz (solid),\textsuperscript{39b} have been reported; in the absence of any determinations in liquid crystalline solvents, it is generally assumed that for $^{14}\text{N}$ the liquid phase QCC lies closer to solid state result.\textsuperscript{40} Using the latter value, together with the nitrogen-14 relaxation times yields the perpendicular diffusion constants, $D_{\perp}(\text{NMR})$, shown in the fourth column of Table III. The results are found to agree acceptably with $D_{\perp}(\text{Ram})$ for CD$_3$CN, lying an average of 15\% below the latter quantities. We would note that raising the assumed QCC to $\chi(^{14}\text{N})=4.0$ MHz (approximately midway between the two reported values) would yield virtually perfect agreement between the two experiments. One observes, too, that the two activation energies are within 10\% of each other. Hence, it may be concluded that perpendicular diffusion coefficients in CD$_3$CN determined from Raman bandwidths and NMR relaxation times are approximately equal to within the experimental error resulting from uncertainties in the liquid phase $^{14}\text{N}$ Quadrupole Coupling Constant.

2. Parallel Diffusion Coefficients

Assuming rotational diffusion, the Raman bandshape of degenerate vibrations in C$_{3v}$ symmetric tops consists of two Lorentzians with the same peak center and relative widths, $\Delta_{2}^{(2)} < \Delta_{1}^{(2)}$ (if $D_{\|} > D_{\perp}$). As found in iodomethane,\textsuperscript{11,12} and other systems,\textsuperscript{10} the latter component is often found to be
broader than may be explained solely on the basis of molecular reorientation and vibrational relaxation; it has been suggested that the additional width may result from collision induced scattering in the wings of the spectrum.\textsuperscript{10,41} The width of $\Delta_1^{(2)}$ is related with diffusion coefficients by eq. [51] on page 38 and again given here:\textsuperscript{2}

$$\Delta_1^{(2)} = \Delta_v + (\pi c)^{-1}[5D_v + D_1]$$ [51]

Application of this equation to calculate $D_1$ requires knowledge of $\Delta_v$, the contribution of vibrational relaxation to the linewidth. This quantity cannot be measured directly since non-symmetric vibrations do not scatter isotropically. However, $\Delta_v$ for $v_5$ may be estimated from the isotropic width of the similar $v_1$ mode by using the relation (from the IBC model of vibrational dephasing)\textsuperscript{8,9,42}, $\Delta_v \propto 1/\omega^2$, where $\omega$ is the vibration's peak frequency. Therefore, one may write $\Delta_v = \Delta_1(v_1) \times (\omega_1/\omega_5)^2$.

Eq. [51] has been used with the experimental linewidths, $\Delta_1^{(2)}$, and perpendicular diffusion constants to calculate $D_1$(Ram) for CH$_3$CN and CD$_3$CN as a function of temperature. One observes (Table III and Figure 4) that, in contrast to $D_1$, the parallel diffusion coefficients are substantially lower in the deuterated molecule, although the activation energies are equal. Significantly, as found earlier in iodomethane,\textsuperscript{11,12} the experimental diffusion constants in both species are in almost quantitative
Figure 4. Parallel diffusion coefficients in Acetonitrile;
(a) $D_{1(\text{FR})}$ in CH$_3$CN(-), (b) $D_{1(\text{Raman})}$ in CH$_3$CN(■),
(c) $D_{1(\text{FR})}$ in CD$_3$CN(-), (d) $D_{1(\text{Raman})}$ in CD$_3$CN(●)
(e) $D_{1(\text{NMR})}$ in CD$_3$CN(▲).
agreement with values predicted by the Free Rotor model of reorientation (see eq. [6] in Chapter I). In addition, the activation energy for $D_1$ calculated assuming freely spinning molecules, $E_a(\text{FR})=1.1 \text{ kJ/mol}$, lies within a standard deviation of the experimental results for both molecules. Thus, the parallel rotation rates in CH$_3$CN and CD$_3$CN are determined solely by their relative moments of inertia ($I_1$) rather than by interactions in the liquid phase, as we have discussed in Chapter I.

Tanabe and Hiraishi$^{33}$ studied the room temperature IR linewidths of various $E$ vibrations in acetonitrile. Their derived values of $D_1(\text{IR})$ ranged from $140 \times 10^{10}$ s$^{-1}$ to $161 \times 10^{10}$ s$^{-1}$ in CH$_3$CN and from $116 \times 10^{10}$ s$^{-1}$ to $150 \times 10^{10}$ s$^{-1}$ in CD$_3$CN, which display the same relative trend but lie somewhat below the values observed here. The differences may result from a different method for accounting for vibrational relaxation in the two investigations or the fact that some of the degenerate IR bands in acetonitrile are superposed upon a broad background absorption, complicating the analysis.

It is possible to use deuterium relaxation times in CD$_3$CN to obtain independent estimates of $D_1$ if one has a suitable estimate for $\chi^{(2)}(\text{D})$ in the liquid phase. There are four determinations of the deuterium QCC in liquid crystalline solvents; 152.5 kHz$^{43a}$, 156.9 kHz$^{43a}$, 165 kHz$^{43b}$ and 172.5 kHz.$^{43c}$ The variation results from the fact that
the measured value is dependent both upon the particular solvent and the method of analysis.\(^4\) We have assumed that \(\chi(2D)=162\ kHz\), the average of the above measurements; we have also used \(\theta=109.5^\circ\).\(^{21a}\)

Unlike the Raman bandwidth, which is a linear function of the two diffusion coefficients (eq. [51]), the non-linear dependence of \(T_1(2D)\) on \(D_\perp\) and \(D_\parallel\) (eqs. [83] and [84]) causes calculated values of the latter quantity to be sensitively dependent upon the value of \(D_\perp\) used in eq. [80]. Therefore, in order to reduce scatter in \(D_\parallel\text{(NMR)}\), we have used interpolated perpendicular diffusion constants (in square brackets in Table III).

Parallel diffusion coefficients in CD\(_3\)CN calculated from \(^2D\) relaxation times are displayed in the last column of Table III and in Figure 4. Considering uncertainties in the deuterium QCC, values for \(D_\parallel\text{(NMR)}\) are in satisfyingly close agreement to those determined from the Raman linewidth; the measured activation energies for \(D_\parallel\) from the two experiments also agree to within well under one standard deviation.

**B. Solvents Dependence of Reorientational Dynamics in CD\(_3\)CN**

The observed \(^2H\) and \(^{14}N\) relaxation times of CD\(_3\)CN in different solvents are displayed in Table 2. Values in the table represent the average of the measurements and the quantities in parentheses are the mean deviation between runs. Due to very high sample viscosity, \(^{14}N\) linewidths
Table IV. Solvent and Temperature Dependence of Reorientational Diffusion Coefficients in CD$_3$CN$^a$.

A. $D_\perp/10^{10}$ s$^{-1}$

<table>
<thead>
<tr>
<th>T</th>
<th>Neat</th>
<th>CHCl$_3$</th>
<th>CCl$_4$</th>
<th>DMSO</th>
<th>Butanol</th>
<th>Propanediol</th>
</tr>
</thead>
<tbody>
<tr>
<td>312 K</td>
<td>14.8</td>
<td>7.6</td>
<td>9.6</td>
<td>3.95</td>
<td>3.7</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>(0.5)</td>
<td>(0.1)</td>
<td>(0.06)</td>
<td>(0.1)</td>
<td>(0.03)</td>
<td></td>
</tr>
<tr>
<td>297</td>
<td>12.7</td>
<td>7.09</td>
<td>7.1</td>
<td>3.59</td>
<td>2.4</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>(0.09)</td>
<td>(0.1)</td>
<td>(0.03)</td>
<td>(0.1)</td>
<td>(0.02)</td>
<td></td>
</tr>
<tr>
<td>283</td>
<td>10.6</td>
<td>5.4</td>
<td>5.7</td>
<td>2.90</td>
<td>1.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.2)</td>
<td>(0.2)</td>
<td>(0.04)</td>
<td>(0.05)</td>
<td>(0.05)</td>
<td></td>
</tr>
<tr>
<td>268</td>
<td>8.9</td>
<td>4.58</td>
<td>4.0</td>
<td>2.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.06)</td>
<td>(0.1)</td>
<td>(0.02)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_\perp(25^\circ\text{C})$</td>
<td>12.8</td>
<td>6.7</td>
<td>7.5</td>
<td>3.5</td>
<td>2.6</td>
<td>1.1</td>
</tr>
<tr>
<td>$\eta(25^\circ\text{C})$</td>
<td>0.34 CP 0.54 CP 0.90 CP 2.00 CP 2.63 CP 44.3 CP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. $D_\parallel/10^{10}$ s$^{-1}$

<table>
<thead>
<tr>
<th>T</th>
<th>Neat</th>
<th>CHCl$_3$</th>
<th>CCl$_4$</th>
<th>DMSO</th>
<th>Butanol</th>
<th>Propanediol</th>
</tr>
</thead>
<tbody>
<tr>
<td>312 K</td>
<td>137</td>
<td>154</td>
<td>205</td>
<td>76</td>
<td>154</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>(02)</td>
<td>(28)</td>
<td>(02)</td>
<td>(08)</td>
<td>(02)</td>
<td></td>
</tr>
<tr>
<td>297</td>
<td>127</td>
<td>156</td>
<td>211</td>
<td>73</td>
<td>138</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>(04)</td>
<td>(08)</td>
<td>(03)</td>
<td>(22)</td>
<td>(05)</td>
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</tr>
<tr>
<td>283</td>
<td>125</td>
<td>153</td>
<td>193</td>
<td>73</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(23)</td>
<td>(10)</td>
<td>(03)</td>
<td>(12)</td>
<td>(12)</td>
<td></td>
</tr>
<tr>
<td>268</td>
<td>118</td>
<td>145</td>
<td>174</td>
<td>69</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(06)</td>
<td>(19)</td>
<td>(04)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_\parallel(25^\circ\text{C})$</td>
<td>130</td>
<td>154</td>
<td>202</td>
<td>74</td>
<td>130</td>
<td>54</td>
</tr>
<tr>
<td>$\eta \cdot D_\parallel(25^\circ\text{C})$</td>
<td>44</td>
<td>83</td>
<td>182</td>
<td>148</td>
<td>342</td>
<td>2400</td>
</tr>
</tbody>
</table>

a) Values represent the average of 2-3 measurements.
b) Quantities in parentheses are the mean deviation between runs.
were too broad to be measured accurately for solutions in n-butanol at 268 K and in 1,2-propanediol at either of the two lower temperatures. There was no reason, therefore, to determine \( T_1(\textsuperscript{2}H) \) at these temperatures.

Both deuterium and nitrogen-14 are spin I=1 nuclei. Therefore, their relaxation is purely by quadrupolar interactions and given by eq. [88]. By using the same procedure as in neat liquid, the calculated tumbling diffusion coefficients of acetonitrile as a function of temperature in the various solvents are displayed in Table IVA; for comparison, we include \( D_\perp \) in neat acetonitrile, from our earlier investigation.\(^{25}\) Also included are the interpolated (from an Arrhenius plot) values at 25 °C, as well as the room temperature viscosities, \( \eta \), of each of the solvents.

One observes from the data in Table IV that \( D_\perp \) in the neat liquid is greater than in any of the solutions, and that the tumbling of CD\(_3\)CN in chloroform is more rapid than in all but one of the other solvents. This would, at first appearance, seem to be inconsistent with intermolecular association in these two systems. However, simple inspection of the relative diffusion constants does not take into account the expected dependence of \( D_\perp \) upon solution viscosity.

In order to separate the effects of viscous drag and associative interactions on the molecular tumbling rate, we
have used the classic Gierer-Wirtz (GW) Microviscosity model of rotational diffusion to predict the dependence of the diffusion constant on viscosity. They have shown that, for spherical molecules, the rotational diffusion constant for a solute of radius \( a \) rotating in a medium containing solvent molecules of radius \( b \) may be obtained from the expression:

\[
D_\perp(GW) = \frac{1}{f_{GW}} \frac{kT}{8\pi a^3\eta}
\]

where, \( f_{GW} \), is the microviscosity factor, given by

\[
f_{GW} = [6(b/a) + (1 + b/a)^{-3}]^{-1}
\]

Although, as noted, this expression is strictly valid only for spherical tops, it has been demonstrated that the microviscosity model accurately predicts the perpendicular (but not parallel) diffusion constants in symmetric top molecules if one replaces the molecular radius by the semi-axis length of the symmetry axis, which for acetonitrile is \( a = 5.92 \) Å.

We have used the Microviscosity model to calculate \( D_\perp \) as a function of temperature in the various solvents. The calculated values are in semi-quantitative agreement with experiment in the non-associative solvents. However, to correct for errors resulting from the sensitivity of \( D_\perp(GW) \) to the choice for \( a \), and for simplifications in the model, we further introduced a correction factor,

\[
D_\perp(cal) = \alpha D_\perp(GW)
\]

The value of \( \alpha \) (the same for all solutions) was chosen to give the closest quantitative
agreement between $D_\perp$(cal) and $D_\perp$(exp) for rotation of CD$_3$CN in CC$_4$ (an 'inert' solvent) at the four measured temperature; it was determined that $\alpha = 1.82$.

We have plotted $D_\perp$(cal) versus $D_\perp$(exp) for acetonitrile in solutions and in the neat liquid in Figure 5. One sees that, in addition to CC$_4$ solution (filled squares), the calculated and experimental values are in good to excellent agreement in the solvents DMSO (open squares) and n-butanol (filled triangles). In contrast, calculated diffusion coefficients are substantially greater than experiment both in the pure liquid$^{25}$ (open circles) and in solution in chloroform (closed circles). Thus, the well-known associative interactions present in these systems$^{13-17}$ are manifested quite clearly in the perpendicular diffusion coefficients, when the experimental values are compared to those computed with a viscosity based theory of molecular reorientation.

One observes also from Figure 5, the opposite trend for acetonitrile in 1,2-propanediol; e.g. at 297 K, $D_\perp$(exp) = 1.1x$10^{10}$ s$^{-1}$, which is almost an order of magnitude greater than $D_\perp$(cal) = 0.14x$10^{10}$ s$^{-1}$. The far more facile rotation than predicted by theory is an example of the well-known 'saturation' effect, in which microscopic boundary layer effects diminish the efficiency of angular momentum transfer between solvent and solute in highly viscous media.$^{28}$
Figure 5. Calculated versus experimental perpendicular diffusion coefficients of CD$_3$CN in solutions: Pure CD$_3$CN - Open circles; CHCl$_3$ - Filled circles; CCl$_4$ - Filled squares; DMSO - Open squares; n-Butanol - Filled triangles; 1,2-Propanediol - Open triangles.
The vector governing quadrupolar relaxation of the deuterium nuclei in CD$_3$CN (along the C-D bond) lies at an angle of 109.5° relative to the symmetry axis. Thus, from eq. [84], the correlation time determined from $^2$H relaxation is dependent upon both $D_\perp$ and $D_\parallel$ (the parallel diffusion coefficient, which characterizes 'spinning' of the molecule about its symmetry axis). Assuming $\chi(^2\text{H}) = 160$ kHz, we have used $T_1(^2\text{H})$ to determine $\tau_c(109.5^\circ)$ (eq. [88]) which, together with the experimental values of $D_\perp$, have been fit to eq. [84] to determine $D_\parallel(\text{exp})$ as a function of temperature in the various solvents; the results are contained in Table IVB.

One observes that, as expected for methyl rotors the parallel diffusion constant is at least one order of magnitude greater than $D_\perp$, indicating that the spinning rotation is closer to that of an isolated inertially controlled Free Rotor. However, it is clear also that $D_\parallel$ is sensitive to medium effects since its magnitude varies by as much as a factor of four between solvents.

As discussed above for $D_\perp$, both solution viscosity and molecular association can potentially influence $D_\parallel$. One cannot utilize Microviscosity to isolate the latter factor, though, since this model has been shown to be inadequate to characterize the spinning of symmetric tops. One can, however, roughly account for viscous effects by
noting that all hydrodynamic theories predict that $D \propto 1/\eta$. Therefore, one expects that the product $D_1 \cdot \eta$ should be constant at a given temperature. We have tabulated this quantity at 25°C (last row in Table IVB). One observes that, indeed, $\eta \cdot D_1$ is substantially lower in neat CD$_3$CN and in CHCl$_3$ solution than in either CCl$_4$ or DMSO, most likely as a result of intermolecular association in the two former systems. One finds that the product is far higher in 1,2-propanediol, indicating that $D_1$ is significantly greater than expected on the basis of viscosity, which probably is, again, a manifestation of the saturation effect in viscous media. However, $D_1$ in n-butanol, too, is higher than one would expect on the basis of viscous forces, in contrast to the tumbling diffusion constant; as discussed above, there is close agreement between $D_1$(exp) and $D_1$(cal) in this solvent (Figure 5).

On the basis of these results, it appears that the spinning rotational diffusion coefficient may be dependent upon molecular association. However, interpretation of the data is less unambiguous than found above for the tumbling diffusion constant, indicating that the latter quantity is better used to monitor intermolecular interactions.

Conclusion

In conclusion, we have observed that the parallel diffusion coefficients in acetonitrile and acetonitrile-d$_3$
calculated from analysis of the Raman bandshape of the antisymmetric CH\textsubscript{3} (CD\textsubscript{3}) stretching vibrations are both physically realistic and lend further support to the conclusion that the spinning of this molecule about its symmetry axis is unhindered by intermolecular interactions in the liquid phase. Diffusion constants calculated from NMR relaxation times agree well with those from the Raman lineshapes, providing additional evidence for the accuracy of parallel diffusion constants calculated from the degenerate vibrational modes of molecules of C\textsubscript{3v} symmetry.

Molecular dynamics study of acetonitrile in different solvents shows that the acetonitrile molecules will associate with the molecules of associative solvents, which is clearly manifested in the tumbling diffusion constants. The saturation effect, in which microscopic boundary layer effects diminish the efficiency of angular momentum transfer between solvent and solute in highly viscous solvent, proposed by Nishida et al\textsuperscript{28} is again observed by faster than predicted rotation of acetonitrile molecules in 1,2-propanediol.


(b) Bull, T. E., ibid. 1975, 62, 222.
(b) Patterson, G. D.; Griffiths, J. E. ibid, 1975, 63, 2406.
32. Acetonitrile in 1,2-propanediol was prepared at a higher mole fraction, $x^* = 0.10$, due to the broader linewidths and, hence, lower sensitivity in this solvent.


47. This value for $a$ was obtained from the molecular volume ($V_{\text{mol}} = 47.1 \, \text{Å}^3$) and axial ratio ($\rho = 0.66 - \text{prolate}$) given in ref. 36.

CHAPTER V

NMR STUDY OF REORIENTATIONAL DYNAMICS AND INTERNAL ROTATION IN TRANSITION METAL CLUSTERS

Introduction

The growth of organometallic chemistry since the discovery of the cyclopentadienyl metal compounds has been one of the dominant forces in the development of our science. Many polynuclear complexes have been prepared in which transition metal atoms are bonded to each other. Halpern\(^1\) seemed to be the first one to appreciate that certain inorganic and organic groups are electronically equivalent. He drew attention to similarity in the reactivity patterns of alkyl radicals and the pentacordinate Cobalt(II) species \(\text{Co(CN)}_5^{3-}\), and similarity between carbenes and tetracoordinated \(d^8\)-metal complexes. Through structure studies of \([\text{AsCo(CO)}_3]\) and \([\text{As}_2\text{Co}_2\text{(CO)}_6]\), Dahl\(^2\) pointed out the similarity in bonding mode of arsenic atoms and \(\text{Co(CO)}_3\) groups in tetrahedral clusters. Wade\(^3\) and Mingos\(^4\), recognizing a similarity in the bonding properties of \(\text{Ru(CO)}_3\) and \(\text{BH}\) groups, developed a skeletal electron-pair theory which related the structure of certain polynuclear carbonyl metal species with those of polyhedral borane. In 1979, F. Gordon A. Stone's group\(^5\) noticed the ability of
Pt(PMe$_3$)$_2$ groups to bond to Chromium and Tungsten compounds containing metal-carbon double- or triple-bonds in a manner long known for alkenes and alkynes. R. Hoffmann$^6$ introduced the isolobal model which is very useful in relating the structures of metal complexes with those of simple organic molecules. Nowadays it is widely used as a predictive tool for the synthesis of transition metal complexes.

The interest in transition metal clusters arises from both theoretical consideration and practical applications. The long-range goal is to combine the reactivity of metal surfaces with the control achievable in homogeneous systems. In particular, heterometallic clusters have been prepared in the hope that chiral clusters may find a use in asymmetric synthesis. A new interest stems from the potential of polynuclear clusters to function as building blocks in the development of unusual electronic, magnetic, and optical materials. Much effort has been devoted to improving our understanding of organo transition metal clusters.

In the study of transition metal clusters, one problem commonly encountered is cluster fragmentation to mononuclear species which are also responsible for the observed reactivity in the catalytical processes. Fragmentation reactions can, in principle, be retarded through the use of nonfluxional capping ligands.$^7,^8$ The capping group, in addition to maintaining the cluster's integrity during
catalytic reactions\textsuperscript{7,8} and multielectron redox processes,\textsuperscript{9} can interact electronically with metal and ligand orbital electrons,\textsuperscript{10} thereby affecting bonding properties of these complexes.

In phenyl group capped (e.g. Phosphinidene, benzyldyne) clusters, one expects electronic (or steric) interactions to slow the rate of internal ring rotation. Qualitative information about molecular rotation could be derived simply from \textsuperscript{13}C NMR spectra by observing the occurrence of chemical shift splitting of meta- and/or ortho-carbons in the phenyl ring, which usually are averaged by fast molecular rotation. In the past several years, there have been conflicting data on whether a bridging carbonyl on the cluster's skeleton can interact electronically with the capping phenyl group, to slow its rotation. Stone et al,\textsuperscript{11} observed splitting of the ortho and meta resonance in the \textsuperscript{13}C NMR spectra of phenyl ring in CoFe\textsubscript{2}(\mu\textsubscript{2}-CO)(CO)\textsubscript{8}(\mu\textsubscript{3}-C\textsubscript{6}H\textsubscript{4}Me-4) when cooled to -80°C in CD\textsubscript{2}Cl\textsubscript{2}. They attributed this result to interaction of the \(\mu\textsubscript{2}\)-CO's \(\pi^*\) orbital with the phenyl \(\pi\) system through the metal 2e and carbonyl 2p orbitals, which leads to the immobility of phenyl ring in the cluster. However, it has been suggested that the observed \textsuperscript{13}C NMR behavior in the Stone cluster derives from the presence of a second isomer as a result of slowed carbonyl exchange.\textsuperscript{12} In contrast,
McGlinchey and co-workers\textsuperscript{12} found no splitting in the low temperature NMR spectra of a series of clusters with bridging carbonyls, \( \text{Cp}_2\text{Co}_3(\mu_2-\text{CO})(\text{CO})_3(\mu_3-\text{Car}) \), where \( \text{Cp} = \) cyclopentadienyl and \( \text{Ar} = \text{Ph}, \text{Tol}, \text{Xyl} \). Therefore they were able to conclude that there is no hindrance to the ring rotation on the NMR chemical shift time scale. According to Schilling and Hoffmann\textsuperscript{10}, the barrier to internal rotation of the capping group should be small to nonexistent in trimetallic clusters of the type \([\text{Co}_3(\text{CO})_9(\mu_3-\text{CCR}_2)^+]\) (where \( \text{R} = \text{H, alkyl} \)), which contain only terminal carbonyls.

NMR spin-lattice relaxation times,\textsuperscript{13} which are sensitive to molecular motions on a sub-nanosecond time scale, offer a simplifying alternative to the dynamic NMR technique when rotation barriers are too low to be conveniently obtained, and the information obtained can be quantitative, which allows us to investigate reorientation and bonding in these cluster systems.

Recent NMR relaxation investigations\textsuperscript{14,15} in our group have demonstrated that internal phenyl group rotational rates span a broad range, varying from total immobility \([\text{in Co}_4(\text{CO})_{10}(\mu_4-\text{PPh})_2]\)\textsuperscript{14} to completely free rotation, as rapid as in benzene itself \([\text{in Co}_3(\text{CO})_9(\mu_3-\text{CPh})]\)\textsuperscript{15}.

In an effort to establish, on a much shorter time scale, whether there exists an electronic or steric interaction with a phenyl group sufficiently strong to slow
Figure 6. Structures of the trinuclear clusters, Co₃CP₂(μ₂-CO)(CO)₃(μ₃-CPh) [I], FeCo₂(CO)₉(μ₃-PPh) [II] and Co₂NiCP(CO)₆(μ₃-CPh) [III].
the rate of internal ring rotation, we have undertaken an investigation of $^{13}$C NMR relaxation times of the clusters \( \text{Cp}_2\text{Co}_3(\mu_2-\text{CO})(\text{CO})_3(\mu_3-\text{CPh})^{38a} \) [I], \( \text{FeCo}_2(\text{CO})_9(\mu_3-\text{PPh})^{38b} \) [II] and \( \text{CpNiCo}_2(\text{CO})_6(\mu_3-\text{CPh})^{38c} \) [III]. The structures of these compounds are shown in Figure 6.

Experimental

A. Synthesis

All the clusters are synthesized in Professor Michael G. Richmond's laboratory.

The tricobalt cluster \( \text{Cp}_2\text{Co}_3(\mu_2-\text{CO})(\text{CO})_3(\mu_3-\text{CPh}) \) [I] was prepared according to the procedure of Robinson et al.\textsuperscript{16} by using \( \text{Co}_3(\text{CO})_9(\mu_3-\text{CPh}) \).\textsuperscript{17}

\( \text{FeCo}_2(\text{CO})_9(\mu_3-\text{PPh})^{19} \) [II] was synthesized according to the procedure of Müller and Vahrenkamp. Phenylphosphine\textsuperscript{18}, used in the reaction, was prepared from dichlorophosphine (Aldrich Chemical).

\( \text{Co}_2\text{NiCp}(\text{CO})_6(\mu_3-\text{CPh}) \) [III] was prepared according to the procedure of Vahrenkamp\textsuperscript{20} using \( \text{Co}_3(\text{CO})_9(\mu_3-\text{CPh}) \).\textsuperscript{17} Dicobalt octacarbonyl and \( \text{(CpNi(\text{CO})}_2 \), used in the reaction, were purchased from the Pressure Chemical and used as received.

B. NMR Samples

All the NMR samples were prepared in 5 mm NMR tubes except \( \text{FeCo}_2(\text{CO})_9(\mu_3-\text{PPh}) \), which was prepared in a 10 mm NMR tube. \( \text{CDCl}_3 \), used as solvent, was distilled from \( \text{P}_2\text{O}_5 \) and stored under argon using Schlenk techniques.\textsuperscript{21} The
concentrations of the samples were 0.2 M for both 
$\text{Cp}_2\text{Co}_3(\mu_2-\text{CO})(\text{CO})_3(\mu_3-\text{CPh})$ and $\text{Co}_2\text{NiCp}(\text{CO})_6(\mu_3-\text{CPh})$ and 
0.24 M for $\text{FeCo}_2(\text{CO})_9(\mu_3-\text{PPh})$, and the tubes were freeze-
pump-thaw degassed three times prior to flame sealing.

C. NMR Experiments

The NMR samples were observed to be stable in CDCl$_3$ for 
the duration of NMR study, as judged by reproducible $T_1$'s 
and the line widths associated with the clusters' and 
solvent's $^{13}\text{C}$ resonances. Thus, we conclude that the 
cluster fragmentation is negligible. $^{13}\text{C}$ spin-lattice 
relaxation times were measured (at natural abundance) by 
using the standard IRFT pulse sequence, and $T_1$'s were 
calculated via nonlinear regression using a three parameter 
magnetization equation (eq. [87] on page 81). All 
measurements were repeated at least twice at each 
temperature. The probe temperature was regulated by cooled 
Nitrogen or heated air flow and measured with a thermocouple 
that was calibrated by using NMR thermometer.

1. $\text{Cp}_2\text{Co}_3(\mu_2-\text{CO})(\text{CO})_3(\mu_3-\text{CPh})$

The $^{13}\text{C}$ NMR spectra were acquired at $B_o = 7.05$ T ($v_o = 
75.44$ MHz) on a Varian VXR-300 NMR spectrometer.
Measurements on the terminal carbonyl ligands were also 
performed at $B_o = 4.70$ T ($v_o = 50.29$ MHz) on a Varian 
Gemini-200 spectrometer. Chemical shifts were measured 
relative to CDCl$_3$ ($\delta = 77.0$ ppm) and reported in ppm
Table V. $^{13}$C NMR Relaxation Times in 
$\text{Cp}_2\text{Co}_3(\text{CO})_4(\mu_3\text{-CPh})^{a,b,c}$

<table>
<thead>
<tr>
<th>T/K</th>
<th>$T_{1\text{O}}$(Ph)</th>
<th>$T_{1\text{H}}$(Ph)</th>
<th>$T_{1\text{P}}$(Ph)</th>
<th>$T_{1\text{P}}$(Cp)</th>
<th>$T_{1\text{P}}^A$(CO)$^d$</th>
<th>$T_{1\text{P}}^B$(CO)$^e$</th>
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<td>0.22 s (0.01)</td>
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<td>[0.83]</td>
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<td>0.23 (0.02)</td>
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<td>0.70 (0.05)</td>
<td>3.06 (0.14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>[2.79]</td>
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</tr>
<tr>
<td>298</td>
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<td>1.51 (0.02)</td>
<td>1.20 (0.09)</td>
<td>4.07 (0.06)</td>
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<td>[1.12]</td>
<td>[3.94]</td>
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<td>[2.05]</td>
<td>[1.55]</td>
<td>[5.28]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) All relaxation times represent the average of two measurements.

b) Quantities in parentheses represent the mean deviation of the two runs from the average.

c) Quantities in square brackets were obtained from least squares fit of the relaxation times by the Arrhenius equation. These values were used in all further calculations.

d) Measured at $B_0^A = 7.05$ T ($v_0 = 75.44$ MHz).

e) Measured at $B_0^B = 4.70$ T ($v_0 = 50.29$ MHz).
downfield from TMS. The phenyl region resonances were observed at $\delta = 128.4$, 127.7, and 127.0 ppm, for the ortho, meta and para carbons, respectively. The cyclopentadienyl and carbonyl peaks are located at $\delta(Cp) = 88.0$ ppm and $\delta(CO) = 199.2$ ppm.

Nuclear Overhauser enhancements were determined for the phenyl and cyclopentadienyl carbons, using standard procedures.$^{22}$ The enhancements were found to be complete, $\eta = \eta_{\text{max}} = 2.0$, to within experimental error, indicating that these carbons are relaxed exclusively via dipolar coupling to the attached protons.$^{23}$

Carbonyl relaxation times were measured only at the lowest temperatures. Measurements at higher temperature were prohibited due to broadening of the resonances by $^{13}$C-$^{59}$Co scalar coupling (very short $T_2$).$^{24,25}$ In addition, the three terminal carbonyls are exchanging rapidly as evidenced by the appearance of a single peak in this region of the spectrum.$^{26,27}$ Because of the CO exchange, one obtains an average for the relaxation rate, $T_1^{-1}$. There is no exchange with the bridging CO at low temperature, since one observes a separate resonance for this carbonyl. All the experimental data were listed in Table V.

2. FeCo$_2$(CO)$_9$(μ$_3$-PPh)

$^{13}$C NMR relaxation time and nuclear Overhauser enhancement measurements of phenyl ring carbons were
<table>
<thead>
<tr>
<th>T [K]</th>
<th>$T_{10}^{a,b}$ [s]</th>
<th>$T_{1H}^{a,b}$ [s]</th>
<th>$T_{1P}^{a,b}$ [s]</th>
</tr>
</thead>
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<tr>
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<td>1.93 (0.15)</td>
<td>1.76 (0.11)</td>
<td>0.56 (0.06)</td>
</tr>
<tr>
<td>263</td>
<td>2.71 (0.04)</td>
<td>2.39 (0.22)</td>
<td>0.74 (0.01)</td>
</tr>
<tr>
<td>283</td>
<td>3.79 (0.19)</td>
<td>3.64 (0.26)</td>
<td>1.06 (0.09)</td>
</tr>
<tr>
<td>298</td>
<td>4.23 (0.02)</td>
<td>4.30 (0.05)</td>
<td>1.30 (0.13)</td>
</tr>
<tr>
<td>323</td>
<td>5.43 (0.12)</td>
<td>5.70 (0.19)</td>
<td>1.54 (0.04)</td>
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</tbody>
</table>

a) Reported relaxation times are the average of two measurements at each temperature.

b) Quantities in parentheses represent the mean deviations between runs.
performed at $v_0^{(13C)} = 75.44$ MHz on the Varian VXRX-300 NMR spectrometer over the temperature range from 247 K to 323 K using the same procedure as above. The $T_1$'s are presented in Table VI. The Overhauser enhancements were found to be complete ($\eta = \eta_{\text{max}} = 2.00$), indicating that dipolar interaction with the attached protons is the sole mechanism of $^{13}$C relaxation.\(^3\)

3. CpNiCo$_2$(CO)$_6$(μ$_3$-CPh)

The ortho, meta and para phenyl (at $\delta = 128.6$, 127.9 and 127.2 ppm downfield from TMS) and cyclopentadienyl (at $\delta = 91.0$ ppm) carbon-13 relaxation times and nuclear Overhauser enhancements (NOE's) were measured at various temperatures between 215 K and 303 K on the Varian VXRX-300 FT-NMR spectrometer. In addition, the carbonyl (at $\delta = 199.0$ ppm) $^{13}$C $T_1$'s were determined at the three lowest temperatures at $B_0 = 7.05$ T and $B_0 = 4.70$ T (on a Varian Gemini-200 spectrometer); the latter measurements were prohibited at high temperature due to spectral broadening resulting from $^{59}$Co-$^{13}$C scalar coupling. All the experiment data are present in Table VII.

NOE's of both phenyl and Cp carbons were found to be complete ($\eta = \eta_{\text{max}} = 2.0$) at all temperatures, indicating that dipole-dipole relaxation by the attached protons is the sole operative mechanism.\(^3\) The increase in $T_1$ of carbonyl with diminishing field strength reveals that, as expected,
Table VII. $^{13}$C NMR Relaxation Times in 
CpNiCo$_2$(CO)$_6$(µ$_3$-CPh)$^{a,b,c}$

<table>
<thead>
<tr>
<th>T/K</th>
<th>$T_{1M}$(Ph)</th>
<th>$T_{1O}$(Ph)</th>
<th>$T_{1P}$(Ph)</th>
<th>$T_{1}$(Cp)</th>
<th>$T_{1}^{A}$(CO)$^{d}$</th>
<th>$T_{1}^{B}$(CO)$^{e}$</th>
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<td>1.3 s</td>
<td>1.20 s</td>
<td>1.97 s</td>
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<td>(0.03)</td>
<td>(0.04)</td>
<td>(0.04)</td>
<td>(0.1)</td>
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<td>(0.02)</td>
</tr>
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<td>[0.79]</td>
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<td>[1.37]</td>
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<td>0.39</td>
<td>1.8</td>
<td>1.46</td>
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</tr>
<tr>
<td></td>
<td>(0.04)</td>
<td>(0.03)</td>
<td>(0.03)</td>
<td>(0.1)</td>
<td>(0.03)</td>
<td>(0.2)</td>
</tr>
<tr>
<td></td>
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<td>[0.35]</td>
<td>[1.64]</td>
<td></td>
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<td></td>
</tr>
<tr>
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<td></td>
<td>(0.09)</td>
<td>(0.04)</td>
<td>(0.01)</td>
<td>(0.1)</td>
<td>(0.08)</td>
<td>(0.01)</td>
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<td>2.23</td>
<td>0.70</td>
<td>3.1</td>
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<tr>
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<td>(0.3)</td>
<td>(0.07)</td>
<td>(0.05)</td>
<td>(0.1)</td>
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</tr>
<tr>
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<td>[2.17]</td>
<td>[0.76]</td>
<td>[3.17]</td>
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<td>3.00</td>
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<td>(0.0)</td>
<td>(0.03)</td>
<td>(0.2)</td>
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<td>3.3</td>
<td>3.30</td>
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<td>2.8</td>
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<tr>
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<td>(0.2)</td>
<td>(0.07)</td>
<td>(0.03)</td>
<td>(0.2)</td>
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<tr>
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<td>[3.63]</td>
<td>[3.63]</td>
<td>[1.27]</td>
<td>[5.08]</td>
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<tr>
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<td>4.60</td>
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<td>6.50</td>
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<td></td>
<td>(0.2)</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>(0.02)</td>
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<tr>
<td></td>
<td>[4.47]</td>
<td>[4.47]</td>
<td>[1.56]</td>
<td>[6.18]</td>
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<td></td>
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</table>

a) All relaxation times represent the average of two measurements.

b) Quantities in parentheses represent the mean deviation of the two runs from the average.

c) Quantities in square brackets were obtained from least squares fit of the relaxation times by the Arrhenius equation. These values were used in all further calculations.

d) Measured at $B^A_0 = 7.05$ T ($\nu_o = 75.44$ MHz).

e) Measured at $B^B_0 = 4.70$ T ($\nu_o = 50.29$ MHz).
Chemical Shift Anisotropy (CSA) is the predominant relaxation mechanism for this kind of carbon.\textsuperscript{23a}

Calculations

The phenyl group in phenyl capped clusters constitutes a particular useful probe for the study of motional anisotropy and internal rotation.\textsuperscript{28} The $T_1$ of the para-carbon, uninfluenced by internal rotation of the group about its $C_2$ axis (if there is any), reflects the rate of the overall molecular tumbling rotation, whereas the $T_1$'s of ortho- and meta-carbon are influenced by such motion. Separation of these relaxation contributions could provide us the possibility of calculating potential barriers to phenyl rotation, and of gaining an insight into the electronic and/or steric interactions present in molecules containing phenyl rotors. The separation can be achieved by using eqs. [83] and [85] (pages 66 & 67).

\[
T_{1P}^{-1} = \frac{\gamma_C^2 \gamma_H^2 h^2}{4\pi^2 r_{CH}^6} \left( \frac{1}{6D_\perp}\right) = \frac{3.781 \times 10^9}{D_\perp} \quad [88]
\]

and

\[
\chi = \frac{64}{1 + \frac{216}{5 + \sigma} + \frac{162}{2 + 4\sigma}} \quad [89]
\]

Where $\chi = (T_{1M}/T_{1P}) = (T_{10}/T_{1P})$ and $\sigma = D_\parallel/D_\perp$ ($D_\parallel = R + D_1$), where $R$ is the internal rotation rate of phenyl. $D_\parallel$ is the total spinning rate of the phenyl group about its $C_2$ axis).

It is straightforward to determine $\sigma$ from the experimental
value of $\chi$ using a simple iterative algorithm. Then, with $D_\perp$ calculated from eq. [88], we may obtain $D_\parallel$ from $\sigma$.\textsuperscript{14,15}

The parallel diffusion coefficient for overall spinning of the cluster may be determined if one can measure the rotational correlation time, $\tau_c$, for a vector attached rigidly to the molecular skeleton. In this case, $\tau_c$ is a function of $\theta$, its angle from the top axis, and of the diffusion coefficients, $D_\perp$ and $D_\parallel$:\textsuperscript{34}

$$\tau_c(\theta) = \frac{A(\theta)}{6D_\perp} + \frac{B(\theta)}{5D_\perp + D_\parallel} + \frac{C(\theta)}{2D_\perp + 4D_\parallel}$$  \[84\]

The coefficients are given by: $A = (1/4)(3\cos^2\theta - 1)^2$, $B = 3\sin^2\theta\cos^2\theta$, $C = (3/4)\sin^4\theta$. With $\tau_c(\theta)$ and $D_\perp$, we are able to solve for $D_\parallel$ using an iterative program,\textsuperscript{35} and consequently obtain the internal rotation rate; $R = D_\parallel - D_\perp$.

1. \textit{Cp\textsubscript{2}Co\textsubscript{3}(\mu\textsubscript{2}-CO)(CO)\textsubscript{3}(\mu\textsubscript{3}-CPh)}

\textit{Cp\textsubscript{2}Co\textsubscript{3}(CO)\textsubscript{4}(CPh)} is an asymmetric top molecule and, thus, in principle requires three independent diffusion coefficients to characterize its overall rotational motion. However, from its structure,\textsuperscript{12} one finds that the two semi-axis lengths in the Co\textsubscript{3} plane are close to equal and somewhat shorter than the vertical axis length. Therefore, in order to make the calculations tractable, it is assumed that this molecule approximates a prolate pseudo-symmetric top, with the unique axis perpendicular to the Co\textsubscript{3} plane and
containing the $C_1$ and $C_4$ phenyl carbons. Its overall skeletal rotation is then specified by the 'tumbling' and 'spinning' diffusion coefficients, $D_\perp$ and $D_\parallel$, corresponding to rotation perpendicular and parallel to the unique axis. To completely characterize its reorientational dynamics, one must introduce the additional coefficients, $R(\text{Ph})$ and $R(\text{Cp})$, which measure the internal rotation rates of the phenyl and cyclopentadienyl rings, respectively (see Figure 7).

The coefficients $D_\perp$, $R(\text{Ph})$ and $R(\text{Cp})$, exhibit a very non-linear dependence upon the experimental relaxation times, as shown in eqs. [84], [85] and [86] (page 67 & 69). This tends to exaggerate variations in the experimental

![Figure 7. The reorientational motions of Co$_3$Cp$_2$(μ$_2$-CO)(CO)$_3$(μ$_3$-CPh)]
data, yielding relatively large fluctuations in the coefficients, which tend to mask trends in their dependence upon temperature. To minimize scatter in the derived coefficients, we have fit the experimental phenyl and cyclopentadienyl $T_1$'s to the Arrhenius equation and have used the least-squares best fit values (in square brackets in Table V) in the calculations.

**Determination of $D_\perp$ and $D_s(Ph)$**

The dipolar relaxation of the para carbon [$T_{1P}$] is a function solely of the tumbling diffusion constant, $D_\perp$, whereas relaxation of the ortho and meta carbons [$T_{1O}$ and $T_{1M}$] depend, in an equivalent fashion, upon both $D_\perp$ and the sum of the parallel and internal rotation coefficients, $D_s(Ph) = D_\perp + R(Ph)$.

The straightforward calculation of $D_\perp$ and $D_s(Ph)$ from $T_{1P}$ and the ratio, $\chi = T_{1O}/T_{1P} (= T_{1M}/T_{1P})$ can be achieved by using the procedure discussed above (eqs. [88] and [89]).

It must be noted that, from Table V, $T_{1O} \approx T_{1M}$ at all but the two highest temperatures, where it is seen that $T_{1O} > T_{1M}$. This indicates a possible breakdown in the assumption that the skeletal rotation is that of a symmetric top, in which case the ortho and meta C-H vectors are no longer equivalent. However, there is insufficient data to analyze the system on the basis of completely anisotropic reorientation (requiring three diffusion coefficients) with superposed internal rotation of the phenyl group.
Calculation of $D_1$

This calculation can be performed via $T_1(^{13}\text{C})$ measurements on the three carbonyls attached to the Co not containing the Cp groups. From the crystal structure, the relevant CO bond vectors lie at angles of $69.6^\circ$, $77.5^\circ$ and $162.7^\circ$ from the unique axis.

These carbons are relaxed predominantly by Chemical Shift Anisotropy (CSA), which is magnetic field dependent, with a second contribution from Spin Rotation, which is independent of $B_0$. The net relaxation rate, therefore, is given by:

$$T_1^{-1} = T_{1CSA}^{-1} + T_{1SR}^{-1} = (2/15) \gamma^2 (\Delta \sigma)^2 \tau_c B_0^2 + T_{1SR}^{-1} \quad [90]$$

Thus, measurement of $T_1$ at two values of $B_0$ permits one to obtain the quantity, $(2/15) \gamma^2 (\Delta \sigma)^2 \tau_c$. Calculation of the correlation time, $\tau_c$, then requires that one have a value for the chemical shift anisotropy, $\Delta \sigma = \sigma_1 - \sigma_4$, of the carbonyl carbon. $\Delta \sigma$ has not been measured for this system, but may be estimated from the carbonyl's chemical shift relative to free carbon monoxide, and the near cylindrical symmetry of terminal CO ligands in metal carbonyls, which implies that the paramagnetic contribution to $\sigma_1$ is approximately zero. This procedure, which has been outlined elsewhere, yields $\Delta \sigma = 416$ ppm for the terminal carbonyls in $\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})$. 
A slight complicating feature is that the three carbonyls are exchanging between sites at different angles, $\theta_i$, relative to the axis. The exchange is rapid relative to $T_1$, but much slower than molecular reorientational times. Therefore, one obtains the average relaxation rate, and, hence, average correlation time, $\tau_c(\text{avg})$. This quantity is related to the individual correlations times for the three vectors by:

$$\tau_c(\text{avg}) = \left(\frac{1}{3}\right) \left[ \tau_c(\theta_1) + \tau_c(\theta_2) + \tau_c(\theta_3) \right]$$  \hspace{1cm} [91]

where the $\tau_c(\theta_i)$ are given by eq. [84].

The procedure for the calculation of $D_1$, then, is to measure $T_1^A$ and $T_1^B$ at two field strengths, $B_0^A$ and $B_0^B$, from which one obtains $\tau_c(\text{avg})$ from eq [90] and $\Delta\sigma$. With $D_1$ from phenyl group relaxation times, one then fits eqs [84] and [91] to find the value for the parallel diffusion coefficient, $D_1$, which minimizes the deviation between the experimental and calculated correlation time.$^{35}$

**Calculation of $R(Cp)$**

Like the phenyl group, the cyclopentadienyl rings can undergo internal rotation (about their $C_5$ axes). However, since the internal rotation axis is not coincident with the unique axis, the analysis is somewhat more complicated.

The correlation time for rotation of the Cp's C-H vectors may be obtained from their relaxation times by:
\[ T_1^{-1} = \frac{\gamma_C^2 \gamma_H^2 h^2}{4\pi^2 r_{CH}^6} \tau_c = 2.269 \times 10^{10} \tau_c \]  

[92]

where the numerical coefficient was calculated using standard values for Planck's constant (h), the magnetogyric ratios, \( \gamma_C \) and \( \gamma_H \), and \( r_{CH} = 1.08 \text{ Å} \).\(^{36}\)

Woessner et al.\(^{37}\) have developed a general expression for the correlation time undergoing internal rotation in a symmetric top molecule as a function of the overall and internal diffusion coefficients, \( D_\perp \), \( D_\parallel \) and \( R \), and \( \alpha \) and \( \Delta \), which signify the angle between the symmetry and internal rotation axis and the angle between the latter axis and the rotating vector, respectively. For the CH vector in the cyclopentadienyl ring, \( \Delta = 90^\circ \); the Woessner equation\(^{37}\) (see pages 68 and 69) then reduces to:

\[
\tau_c = \frac{C_1}{6D_\perp} + \frac{C_2}{6D_\perp + 4R} + \frac{C_3}{5D_\perp + D_\parallel} + \frac{C_4}{5D_\perp + D_\parallel + 4R} \\
+ \frac{C_5}{2D_\perp + 4R} + \frac{C_6}{2D_\perp + 4D_\parallel + 4R} \tag{86}
\]

Where

\( C_1 = (1 - 3\cos^2\alpha)^2/16; \ C_2 = 9\sin^4\alpha/32; \ C_3 = 3\sin^22\alpha/16; \ C_4 = 3(\sin^2\alpha + 0.25\sin^22\alpha)/8; \ C_5 = 3\sin^4\alpha/16; \) and

\( C_6 = 3[(1 + \cos^2\alpha)^2 + 4\cos^2\alpha]/32. \)

With \( \alpha = 85^\circ \) (calculated from the crystal structure\(^{12}\)) and the diffusion constants, \( D_\perp \) and \( D_\parallel \), from earlier calculations, it is straightforward to determine the value
Table VIII. Diffusion Coefficients in \( \text{Cp}_2 \text{Co}_3(\text{CO})_4(\mu_3-\text{CPh})^a \)

<table>
<thead>
<tr>
<th>T</th>
<th>( D_\perp )</th>
<th>( D_{\text{S(Ph)}} )</th>
<th>( D_{\text{S(Bz)}} )</th>
<th>( D_1^b )</th>
<th>( R(\text{Ph}) )</th>
<th>( R(\text{Cp}) )</th>
</tr>
</thead>
<tbody>
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<td>1.5 ns(^{-1})</td>
<td>15 ns(^{-1})</td>
<td>1.6 ns(^{-1})</td>
<td>( \approx 0 ) ns(^{-1})</td>
<td>11 ns(^{-1})</td>
</tr>
<tr>
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<td>1.9</td>
<td>18</td>
<td>1.9</td>
<td>( \approx 0 )</td>
<td>12</td>
</tr>
<tr>
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<td>3.8</td>
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<td>3.9</td>
<td>( \approx 0 )</td>
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<td>323</td>
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<td>97</td>
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<td>( \approx 3)^c</td>
<td>41</td>
</tr>
</tbody>
</table>

a) Values in the table are presented to two significant digits. However all calculations were performed prior to roundoff.

b) \( D_1 = 2.2D_\perp \). See text on page 130.

c) See explanation on pages 119 and 130.
of R in eq [86] which minimizes the deviation between the calculated and experimental correlation times.\textsuperscript{35} We term this quantity \( R(Cp) \) to distinguish it from the phenyl ring internal rotation coefficient.

Listed in Table VIII are the calculated values of \( D_\perp \), \( D_\parallel \), \( R(\text{Ph}) \) and \( R(Cp) \).

2. \textit{FeCo}_2(\textit{CO})_9(\mu_3-\text{PPh})

By using the same procedure (eq. [88]) in our earlier calculations, the dipolar relaxation time of the para phenyl carbon was used to calculate the overall tumbling coefficients, \( D_\perp \), of the complex. This value, together with the ratio, \( T_{10}/T_{1P} \) (or \( T_{1M}/T_{1P} \)), permits determination of the total 'spinning' rate, \( D_s \), of the aryl ring. As discussed above, this latter value is composed of contributions from overall parallel reorientation of the cluster's framework, \( D_\parallel \), and internal rotation, \( R \), of the phenyl group relative to the skeleton; \( D_s = D_\parallel + R \). We note that implicit in the decomposition of the rotational dynamics into parallel and perpendicular diffusion components is the presumption that the molecule's reorientation approximates that of a symmetric top.\textsuperscript{13} The structure of the complex and the fact that one observes no systematic deviations between \( T_{10} \) and \( T_{1M} \) (Table VI) provide evidence that this approximation, required for analysis of the results, is reasonable.\textsuperscript{13}

The tumbling and spinning diffusion coefficients of \( \text{FeCo}_2(\text{CO})_9(\mu_3-\text{PPh}) \) as a function of temperature in
Table IX. Rotational Diffusion Coefficients in FeCo$_2$(CO)$_9$(μ$_3$-PPh) and related systems.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>$D_\perp^a$ [ns$^{-1}$]</th>
<th>$D_S$(FeCo$_2$)$_a$ [ns$^{-1}$]</th>
<th>$D_S$(Co$_3$)$_b$ [ns$^{-1}$]</th>
<th>$D_S$(Bz)$_c$ [ns$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>247</td>
<td>2.1</td>
<td>21</td>
<td>4</td>
<td>33</td>
</tr>
<tr>
<td>263</td>
<td>2.8</td>
<td>29</td>
<td>5</td>
<td>43</td>
</tr>
<tr>
<td>283</td>
<td>4.0</td>
<td>39</td>
<td>8</td>
<td>59</td>
</tr>
<tr>
<td>298</td>
<td>4.9</td>
<td>48</td>
<td>10</td>
<td>72</td>
</tr>
<tr>
<td>323</td>
<td>5.8</td>
<td>60</td>
<td>14</td>
<td>97</td>
</tr>
</tbody>
</table>

a) Diffusion coefficient of FeCo$_2$(CO)$_9$(PPh) in chloroform.
b) Diffusion coefficient of Cp$_2$Co$_3$(CO)$_4$(CPh) in chloroform (interpolated by least squares fit of the data by Arrhenius equation).
c) Diffusion coefficient of benzene in chloroform (ref 43).

chloroform are presented in the second ($D_\perp$) and third ($D_S$) columns of Table IX. For comparison (vide infra), values of $D_S$ for Cp$_2$Co$_3$(CO)$_4$(CPh) and benzene are also shown in the table.
3. \( \text{CpNiCo}_2(\text{CO})_6(\mu_3-\text{CPh}) \)

The various relaxation times as a function of temperature are displayed in Table VII. The numbers in square brackets are the relaxation times calculated by a semi-logarithmic Arrhenius fit of the data. These values, which, generally, are close to the individual experimental results, were used in all further calculations in order to minimize the propagation of error from scatter in the measurements.

\( \text{CpNiCo}_2(\text{CO})_6(\mu_3-\text{CPh}) \) is also an asymmetric top molecule. However, from its structure,\(^{39}\) the two semi-axis lengths of its volume ellipsoid in the NiCo\(_2\) plane are

\[\text{Figure 8. The reorientational motions of Co}_2\text{NiCp(CO)}_6(\mu_3-\text{CPh}).\]
almost identical \((b = 5.52 \, \text{Å} \text{ and } c = 5.54 \, \text{Å})\), and slightly longer than the unique axis, perpendicular to the plane \((a = 5.26 \, \text{Å})\). Thus, the molecule may be treated as a pseudo-symmetric top, requiring only two diffusion coefficients, \(D_x\) and \(D_y\), to characterize the tumbling and spinning motions of the molecule in solution. To completely specify its rotational dynamics, one must introduce, in addition, two internal rotational diffusion coefficients. \(R(\text{Ph})\) represents the rate of rotation of the phenyl group about its \(C_2\) axis and \(R(Cp)\) is the rate of spinning of the cyclopentadienyl group about its \(C_5\) axis.

Figure 8 illustrates the various rotations in the cluster.

**Molecular Reorientation**

The C-H vector of the phenyl ring's para carbon lies along the principal molecular axis \((a)\). Therefore, the correlation time, \(\tau_c\), determined from \(^{13}\text{C}-\text{H} \) dipolar relaxation depends solely upon \(D_x\), the tumbling diffusion coefficient.\(^{28}\) We have used the measured values of \(T_{1p}(\text{Ph})\) to calculate \(D_x\) as a function of temperature. The results are displayed in Table X.

Calculation of the parallel diffusion coefficient, \(D_y\), requires determination of the rotational correlation time of a second vector, anchored on the molecular skeleton, at a finite angle relative to the unique axis.\(^{14,34}\) The
contribution to relaxation of the carbonyl carbons by chemical shift anisotropy is governed by rotation of the vector along the MCO bond; the angle of this vector differs for the three non-equivalent CO's. However, due to their rapid exchange, which results in a single carbonyl resonance, the mean relaxation rate which, in turn, depends upon the average correlation time were obtained. Using methods described on pages 120 and 121, we have used \( T^A(CO) \) and \( T^B(CO) \) [Table VII] to calculate \( \tau_c(\text{avg}) \) and, thence, \( D_\parallel \) at the three lowest temperatures. As noted above, measurement at higher temperature was not possible due to extensive \(^{59}\text{Co}-^{13}\text{C} \) scalar coupling. It was found that the average ratio of the parallel to perpendicular diffusion coefficients is \( D_\parallel /D_\perp = 2.85 \pm 0.14 \). We have used this ratio to estimate the parallel diffusion constant at the various temperatures; the results are given in Table X.

**Internal Rotation**

The C-H vectors of the ortho and meta phenyl carbons lie at (equivalent) angles of 120° and 60° relative to the principal axis. It has been shown that the ratio \( \lambda = T_{1O}/T_{1P} = T_{1M}/T_{1P} \), is a function of \( \theta \) (the angle between the vector and the axis), \( D_\perp \), and \( D_S \); \( D_S = D_\parallel + R(\text{Ph}) \) is the coefficient representing the net spinning rate of the phenyl ring. We have used these ratios to determine \( D_S \) and \( R(\text{Ph}) \) as a function of temperature; the results are shown in Table X.
Table X. Diffusion Coefficients in CpNiCo₂(CO)₆(μ₃-CPh)\textsuperscript{a}

<table>
<thead>
<tr>
<th>T/K</th>
<th>D\textsubscript{1}</th>
<th>D\textsubscript{1}\textsuperscript{b}</th>
<th>D\textsubscript{R}</th>
<th>R(Ph)</th>
<th>R(Cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>215</td>
<td>1.1 ns\textsuperscript{-1}</td>
<td>3.0 ns\textsuperscript{-1}</td>
<td>8.4 ns\textsuperscript{-1}</td>
<td>5.4 ns\textsuperscript{-1}</td>
<td>19 ns\textsuperscript{-1}</td>
</tr>
<tr>
<td>220</td>
<td>1.3</td>
<td>3.8</td>
<td>11</td>
<td>7.2</td>
<td>20</td>
</tr>
<tr>
<td>228</td>
<td>1.8</td>
<td>5.0</td>
<td>14</td>
<td>9.1</td>
<td>22</td>
</tr>
<tr>
<td>248</td>
<td>2.9</td>
<td>8.2</td>
<td>23</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>268</td>
<td>4.0</td>
<td>11</td>
<td>32</td>
<td>21</td>
<td>38</td>
</tr>
<tr>
<td>283</td>
<td>4.8</td>
<td>14</td>
<td>38</td>
<td>24</td>
<td>44</td>
</tr>
<tr>
<td>303</td>
<td>5.9</td>
<td>17</td>
<td>48</td>
<td>31</td>
<td>52</td>
</tr>
</tbody>
</table>

E\textsubscript{a} (kcal/mol) 2.5\textsuperscript{(0.3)} \textsuperscript{c} 2.5\textsuperscript{(0.3)} \textsuperscript{c} 2.5\textsuperscript{(0.3)} \textsuperscript{c} 2.5\textsuperscript{(0.3)} \textsuperscript{c} 1.5\textsuperscript{(0.1)} \textsuperscript{c}

\textsuperscript{a) Values in the table are presented to two significant digits. However all calculations were performed prior to roundoff.  
\textsuperscript{b) D\textsubscript{1} = 2.85D\textsubscript{1}. See text.  
\textsuperscript{c) Quantities in parentheses are 95% confidence limits.}
Unlike the phenyl ring, the internal rotation axis of the cyclopentadienyl group is not coincident with the principal axis of the molecular framework. Therefore, the correlation time governing rotation of the Cp's C-H vectors is a somewhat more complex function of $\alpha$, $D_\perp$, $D_\parallel$ and $R(Cp)$; $\tau_c = f[\alpha, D_\perp, D_\parallel, R(Cp)]$ (eq. [86]). However, with values of $\tau_c$ [from $T_1(Cp)$], $R(Cp)$ can be determined by solving eq. [86]. The results are given in the final column of Table X.

Results and Discussion

1. $\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})\ [I]$

   The $D_\perp$ and $D_\parallel(\text{Ph})$ of the phenyl group in [I] are shown in the second and third columns of Table VIII and in the Figure 9 (lines A and B). One finds that their ratio remains approximately constant at $D_\parallel(\text{Ph})/D_\perp \approx 2.1$-2.2 at all but the highest temperature, where it rises to 2.7. We believe that the inconsistency of this point with the other data may arise from the possible breakdown of the assumption of symmetric top behavior at higher temperature (vide supra).

   It is most informative to compare the spinning rate of the phenyl group with the rate of the equivalent rotation of benzene itself (about its $C_2$ axis) in the same solvent. The latter quantity is displayed as $D_\parallel(\text{Bz})$ in Table VIII and in Figure 9 (line D). One sees clearly that the rotation of
Figure 9. Temperature dependence of rotational diffusion coefficients in $\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})$ and related systems:
(A) $D_1$ (solid line and filled squares);
(B) $D_8(\text{Ph})$ (dashed line and filled circles);
(C) $D_1$ (solid line and open circles);
(D) $D_8(\text{Bz})$ (solid line);
(E) $D_8(\text{Ph})$ in $\text{Co}_3(\text{CO})_9(\text{CPh})$ (filled triangles). (ref.14)
the phenyl group about its $C_2$ axis in this cluster is markedly below the rate observed for free benzene in chloroform, by approximately one order of magnitude. Shown also in Figure 9 (points E) is the phenyl rotation rate which was reported recently for $\text{Co}_3(\text{CO})_9(\mu_3\text{-CPh})$ in CDCl$_3$.$^{14}$ This latter cluster contains no bridging carbonyls, and Schilling and Hoffmann$^{10}$ have predicted, on the basis of symmetry and EHMO calculations, that the capping group has no preferred orientation in complexes of this type. This is verified experimentally since, from the figure, one sees that $D_s(\text{Ph}) \approx D_s(\text{Bz})$ at all temperatures.

From the above comparison, it is quite clear that the rate of phenyl group spinning in [I] is substantially slowed compared to systems in which there are no electronic or steric barriers to internal ring rotation. As discussed in the introduction, McGlinchey et al.$^{12}$ found in this and related clusters that the aryl group is completely mobile on the NMR chemical shift time scale. We see, therefore, that on the much shorter time scale spin-lattice relaxation times offers a far more sensitive probe of internal rotational rates in capped transition metal clusters.

The Barrier to Internal Phenyl Group Rotation

As is discussed, phenyl carbon relaxation times yield only the sum of the parallel and internal rotation diffusion coefficients, $D_s(\text{Ph}) = D_f + R(\text{Ph})$. Therefore, the actual
rate of internal rotation, $R(\text{Ph})$, depends upon the magnitude of $D_\perp$. For example, if $D_\parallel \approx D_\perp$, then $R(\text{Ph})$ is finite on the nanosecond time scale; e.g. at 298 K, $R(\text{Ph}) \approx 5 \text{ ns}^{-1}$ (Table VIII). Alternatively, if $D_\parallel \approx D_\set{S}(\text{Ph})$, then $R(\text{Ph}) \approx 0$ (i.e. less than approximately 1 ns$^{-1}$). We have obtained the following results: At 211 K, $D_\parallel = 1.7 \text{ ns}^{-1}$, and $D_\parallel/D_\perp = 2.4$; at 218 K, $D_\parallel = 1.8 \text{ ns}^{-1}$, and $D_\parallel/D_\perp = 2.0$. As discussed, $^{13}\text{C}-^{59}\text{Co}$ scalar coupling prohibits carbonyl relaxation time measurements at higher temperatures. Therefore, we have estimated $D_\parallel$ as a function of temperature by assuming the average ratio, $D_\parallel/D_\perp = 2.2$. The results are shown in the fifth column of Table VIII and in Figure 9 (line C).

At all but the highest temperature, where we suspect the results are not accurate (vide supra), one finds that $D_\parallel \approx D_\set{S}(\text{Ph})$ to within 0.1 ns$^{-1}$. Therefore, the internal rotation rate, $R(\text{Ph}) \approx 0$ on a nanosecond time scale. We must note, however, that this conclusion must be viewed with a degree of caution since the calculation of $D_\parallel$ is very sensitive to the value of $D_\perp$, due to the non-linear relationship between the two diffusion coefficients (eq. [84]). For example, if $D_\perp$ at 211 K is increased or decreased by 5%, the ratio, $D_\parallel/D_\perp$, will decrease or increase by approximately 15%. The ratio is also sensitive to the value of the correlation time, $\tau_c$, which itself depends upon the estimated value of $\Delta \sigma$. 
It is possible to use the results of this investigation to obtain an estimated range for the barrier to internal rotation, $V_0$, through application of the equation:

$$ R = R_0 e^{-V_0/R_0 T} \quad [93] $$

$R_G$ is the gas constant. $R_0$ is the diffusion coefficient of a benzene molecule rotating freely about its $C_2$ axis. Its value may be obtained from $R_0 = (5/3)(k_B T/I)^{1/2}$; $k_B$ is Boltzmann's constant and $I$ is the moment of inertia, $I = 1.48 \times 10^{-38}$ g-cm$^2$. For example, at $T = 298$ K,

$$ R_0 = 2.78 \times 10^{12} \text{ s}^{-1}. $$

An estimate for the minimum barrier height may be calculated directly from eq [93] by assuming that $R < 1 \text{ ns}^{-1}$ at 298 K, which leads to $V_0(\text{min}) > 4.7$ kcal/mol. One may also obtain a maximum for $V_0$ from the fact that one does not observe any splitting in the ortho or meta NMR resonances at the lowest temperature studied (211 K). This indicates that, at this temperature, $R$ is greater than the rate required to induce coalescence. This rate may be obtained from the standard relation, $R = 2\pi \delta \nu / \sqrt{\delta}$, where $\delta \nu$ is the static frequency difference between the two peaks (in s$^{-1}$). Assuming a static splitting of approximately 2 ppm$^{11}$ corresponds to $\delta \nu = 150$ s$^{-1}$ [for $\nu_{(13C)} = 75$ MHz] and $R > 670$ s$^{-1}$. Use of eq. [93] then gives

$$ V_0(\text{max}) < 9.2 \text{ kcal/mol}. $$

As noted in the introduction, the ortho and meta aryl resonances in the carbonyl bridged cluster,
CoFe₂(μ₂-CO)(CO)_8(μ₃-CC₆H₄Me-4),¹¹ were split at -80 °C, but not split in the room temperature spectrum. Therefore, approximate barrier limits in this cluster are:

9 kcal/mol < \( V_\circ \) < 13 kcal/mol.⁴⁷ It is interesting to note that this range lies reasonably close to the barrier height, \( V_\circ = 14 \) kcal/mol, which they predicted by simple Extended Hückel MO calculations.¹¹ The range in [I], 5 kcal/mol < \( V_\circ \) < 9 kcal/mol, is somewhat lower. However, the barriers may be of similar magnitude if \( V_\circ \) in the latter complex is nearer the upper limit.

The Nature of the Barrier

The frozen aryl group rotation in CoFe₂(μ₂-CO)(CO)_8(μ₃-CC₆H₄Me-4) at low temperature was explained in terms of an electronic interaction of the \( \mu_2 \)-CO's π* orbital with the 2e metal orbitals, which splits their degeneracy, leading to an asymmetric interaction with the carbyne's 2p orbital and, thence, to preferred orientation of the ring parallel to the bridging carbonyl.¹¹ It is tempting to invoke a similar electronic interaction between the bridging carbonyl and the phenyl ring, through the metal 2e and carbyne 2p orbitals, to explain the large barrier to phenyl rotation in [I]. However, McGlinchey and coworkers,¹² from the crystal structure of this complex, pointed out that, although they expected no significant steric interaction between the phenyl and cyclopentadienyl
groups, the ortho protons of the two rings can approach to within 1.3 Å of one another for the appropriate orientation of the two groups. Since this is well below the sum of their van der Waal's radii \(2r_H \approx 2.8\,\text{Å}\), one cannot exclude a mutual steric obstruction of the phenyl and cyclopentadienyl rings' rotation via a 'gear' type mechanism, similar to that found by Mislow and Norton.

If the two rings do interfere sterically with one another's internal rotation, then one should observe slowed rotation of the cyclopentadienyl group about its \(C_5\) axis. To test this possibility, we have measured the relaxation times of the Cp carbons as a function of temperature. As outlined earlier, this data, together with the overall diffusion coefficients, \(D_\perp\) and \(D_\|\), were used to calculate the internal rotation rates of the cyclopentadienyl ring, \(R(\text{Cp})\). The results are shown in the last column of Table VIII.

One sees from the Table that \(R(\text{Cp}) \gg R(\text{Ph})\) at all temperatures, supporting the independent rotation of the cyclopentadienyl rings relative to the phenyl ring. One would expect any steric interaction between the two rings to be reflected by an equivalent reduction in \(R(\text{Cp})\). From this result, we believe that one may reasonably eliminate steric hindrance as the basis of the observed phenyl rotation barrier in \([I]\), which may, therefore, be attributed
primarily to electronic orbital interactions between the bridging CO and capping phenyl group.\textsuperscript{11,12,15}

2. \textit{FeCo}_{2}(CO)_{9}(\mu_{3}-PPh)\textsubscript{2}[II]

It is informative to compare the results for this complex with those obtained above for cluster [I]. The tumbling rate of the heterometallic cluster [II] is quite close to that of the tricobalt complex [I]; e.g. at 298 K, $D_{f}[II] = 4.9$ ns$^{-1}$ versus $D_{f}[I] = 4.2$ ns$^{-1}$.\textsuperscript{4} This result is expected, considering the similar dimensions of the two species. In contrast, as shown in Table IX and Figure 9 (lines A and B), the rate of phenyl group spinning in [II] is from four to six times more rapid than in [I]. This shows clearly that there is a substantially lower barrier to internal rotation in the former complex.

To determine whether there is any measurable hindrance to rotation of the phenyl ring, one may compare $D_{S}[II]$ to the rate of the equivalent rotation of free benzene (about its C$_2$ axis) in chloroform,\textsuperscript{43} which we denote as $D_{S}(Bz)$. As seen in Table IX and Figure 10 (lines B and C), the phenyl spinning rate in [II] is somewhat lower, by about 35%, than the rate of rotation of benzene in the same solvent. $D_{S}[II]$ is also below the rotational rate found in an earlier study\textsuperscript{14} of the complex, Co$_3$(CO)$_9$(\mu$_3$-CPh) (points D in Fig. 10), where, as noted above, it was found that $D_{S}$ of the phenyl group is equal to that of benzene, to within
Figure 10. Temperature dependence of the "spinning" diffusion coefficients, $D_s$:

(A) $\text{Cp}_2\text{Co}_3(\mu_2-\text{CO})(\text{CO})_4(\text{CPh})(\bullet)$;
(B) $\text{FeCo}_2(\text{CO})_9(\text{PPh})(\ast)$;
(C) benzene(-);
(D) $\text{Co}_3(\text{CO})_9(\text{CPh})(\triangle)$. 
experimental error, in agreement with the theoretical calculations of Schilling and Hoffmann.\textsuperscript{10}

Based upon the above comparisons, it appears that the replacement of a Co(CO)\(_3\) and \(\mu_3\)-CPh fragment with an Fe(CO)\(_3\) and a \(\mu_3\)-PPh fragment, respectively, does induce an electronic perturbation in the metal's orbitals which leads to a small, but finite barrier to internal rotation of the capping phenyl group. However, it is clear, too, that this barrier is much smaller than that found in earlier investigations of carbonyl bridged clusters.\textsuperscript{11,38a} In addition, we must add the caveat that it is possible, but not likely, that the relatively small hindrance to ring rotation might be attributable, instead, to another effect such as preferential solvation of the phenyl group in [II], although this was not seen in the previous investigation of Co\(_3\)(CO)\(_9\)(\(\mu_3\)-CPh).

3. CpNiCo\(_2\)(CO)\(_6\)(\(\mu_3\)-CPh)·[III]

The perpendicular diffusion constants in this complex are somewhat greater than found in the earlier investigation of the tricobalt cluster [I]. For example, the results at 25 °C are \(D_\perp[III] = 6.1\) ns\(^{-1}\) (interpolated) and \(D_\perp[I] = 4.2\) ns\(^{-1}\), respectively. This difference may be understood by the fact that the unique semi-axis length (a), is longer (6.14 Å[I] vs. 5.26 Å[III]) and, hence, the rotation slower in the latter complex. Indeed, the classic
Gierer-Wirtz (GW) Microviscosity model\textsuperscript{50} of molecular reorientation yields calculated diffusion constants that are in near quantitative agreement with experiment; e.g. at 25 °C, one finds that $D_{\perp}(GW)=6.2$ ns\textsuperscript{-1} in [III] and $D_{\perp}(GW)=3.5$ ns\textsuperscript{-1} in [I].

The dependence of $D_{\perp}$ on temperature is the same in [III] and [I]; $E_a(D_{\perp}) = 2.5$ kcal/mol in both clusters. This activation energy is also within experimental error (±0.3 kcal/mol) of the value predicted by the Gierer-Wirtz model (and other hydrodynamic theories);\textsuperscript{13b,51} $E_a(GW) = 2.3$ kcal/mol.\textsuperscript{14}

On the basis of its overall dimensions, one would expect the molecular reorientation to be close to isotropic [$D_{||} \approx D_{\perp}$], since $a \approx b = c$. However, $D_{||}/D_{\perp} = 2.85$ (see page 128) has been obtained. Similar motional anisotropy, ($D_{||}/D_{\perp} = 2.2$) has been observed in the tricobalt complex [I],\textsuperscript{38b} which is also close to spherical in shape. The comparatively rapid parallel rotation in these two clusters probably reflects the fact that spinning of these molecules about their principal axes, unlike their tumbling, requires little or no displacement of solvent. Indeed, in the 'slip' limit of rotation,\textsuperscript{52} it is this factor alone which determines the magnitude of the frictional forces impeding molecular reorientation.

Shown in Figure 11 are the spinning diffusion constants, $D_s$, for a number of trinuclear metal carbonyl
Figure 11. Temperature dependence of the phenyl spinning diffusion coefficients in metal clusters:

(A) Co$_3$Cp$_2$(CO)$_4$(CPh) [open circles and solid line];

(B) Co$_2$NiCp(CO)$_6$(CPh) [filled circles and solid line];

(C) FeCo$_2$(CO)$_9$(PPh) [open squares and dashed line];

(D) Co$_3$(CO)$_9$(CPh) [filled squares and dashed line];

(E) Benzene [solid line].
clusters that have been investigated in our group,\textsuperscript{14,38} and
the rate of the equivalent rotation of benzene in chloroform
[\textsuperscript{line E}].\textsuperscript{43} One observes immediately that the rate of
spinning of the aryl ring in [\textsuperscript{III}][\textsuperscript{line B}] is much greater
than in [\textsuperscript{I}][\textsuperscript{line A}]; e.g. at 298 K,
\[ D_s[\text{III}] = 49 \text{ ns}^{-1} \gg D_s[\text{I}] = 9 \text{ ns}^{-1}.\textsuperscript{4} \] This provides further
substantive evidence that the slowed internal rotation in
[\textsuperscript{I}] results from electronic orbital interactions between the
phenyl group and the bridging carbonyl in the complex.

\[ D_s \] in [\textsuperscript{I}] is not as large, however, as observed in an
earlier investigation of the analogous homonuclear
benzylidyne capped cluster, \( \text{Co}_3(\text{CO})_9(\mu_3\text{-CPh}) \)[\textsuperscript{line D}],\textsuperscript{14} in
which it was found that the phenyl ring rotation is as rapid
as that of free benzene in the same solvent.\textsuperscript{28} Rather, the
spinning rates found here are virtually identical at all
temperatures as those in [\textsuperscript{II}][\textsuperscript{line D}]. In the latter
system, the slowed internal rotation was attributed to a
barrier created by the heteroatom, which splits the
degeneracy of the metals' 2e orbitals, inducing an angle
dependent electronic interaction between the ring and metal
framework. From the results found in this investigation,
one concludes that an equivalent internal rotation barrier
exists in [\textsuperscript{III}].

The rotation of the Cp group about its \( C_5 \) axis is quite
facile, with values of \( R(\text{Cp}) \) somewhat greater than found in
the earlier investigation of[\textsuperscript{I}]; e.g. at 298 K,
R[III] = 50 ns\(^{-1}\) (interpolated) and R[I] = 33 ns\(^{-1}\).\(^{38a}\) The rapid internal rotation of the Cp ring provides evidence that there is little or no phenyl/cyclopentadienyl inter-ring interaction. This is not surprising, since the distance of closest approach of protons on the two groups is \(~2.3\ \text{Å}\), which is approximately equal to the sum of the van der Waal's radii (\(2R_H=2.4\ \text{Å}\)).\(^{48}\)

Finally, we note that the activation energy determined for \(R(\text{Cp})\), \(E_a=1.5\ \text{kcal/mol}\), is quite similar to that found in [I] (1.6 kcal/mol), and substantially less than the activation energy for \(R(\text{Ph})\). This probably results from the fact that, unlike the phenyl ring rotation about its \(C_2\) axis, spinning of the Cp group about its \(C_5\) axis does not require displacement of solvent. Thus, there is less of an intermolecular barrier retarding rotation of the latter ring.

Summary

We have utilized \(^{13}\text{C}\) NMR spin-lattice relaxation times to investigate the overall and internal rotation dynamics in \(\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})\),\(^{38a}\) \(\text{FeCo}_2(\text{CO})_9(\mu_3-\text{PPh})\)\(^{38b}\) and \(\text{CpNiCo}_2(\text{CO})_6(\mu_3-\text{CPh})\)\(^{38c}\) as a function of temperature in the solvent chloroform.

In \(\text{Cp}_2\text{Co}_3(\text{CO})_4(\text{CPh})\),\(^{38a}\) the molecular tumbling diffusion coefficient, \(D_1\), and the total phenyl ring spinning rate, \(D_\text{s}(\text{Ph}) = D_1 + R(\text{Ph})\), were obtained from phenyl carbon \(T_1\)'s.
$D_s(\text{Ph})$ in the complex was found to be an order of magnitude lower than both (a) the equivalent rotational rate of free benzene in chloroform,$^{43}$ and (b) the measured values of $D_s(\text{Ph})$ in $\text{Co}_3(\text{CO})_9(\mu_3-\text{CPh}),^{14}$ a cluster with neither electronic or steric interactions between the ring and molecular skeleton.

The parallel diffusion constant, $D_||$, of the cluster's framework was obtained by using $^{13}\text{C}$ relaxation times of the terminal carbonyl ligands, measured at two magnetic field strengths. It was observed that, to within experimental error, $D_|| = D_s(\text{Ph})$, from which it was concluded that the internal phenyl rotational rate, $R(\text{Ph}) \approx 0$ on a nanosecond time scale. This result permitted the determination of an estimated range for the barrier, $V_0$, to phenyl internal rotation: $5 \text{ kcal/mol} < V_0 < 9 \text{ kcal/mol}$.

To determine whether the hindrance to internal rotation of the phenyl group in the cluster might be due to a gear type mutual interaction of the phenyl and cyclopentadienyl rings, $^{13}\text{C}$ $T_1$'s of the Cp carbons were used to calculate the internal rotation rate of this ring about its $C_5$ axis. It was found that $R(\text{Cp}) \gg R(\text{Ph})$ at all temperatures, from which one may reasonably conclude that the barrier is not due to inter-ring steric effects. Rather, the rotational barrier can be attributed to electronic interaction of the bridging CO's $\pi^*$ orbital with the aryl $\pi$ system through the
metal 2e orbitals, as proposed recently by Stone et al.\textsuperscript{11} to explain the slowed ring rotation in 
\[ \text{CoFe}_2(\mu_2-\text{CO})(\text{CO})_8(\mu_3-\text{CC}_6\text{H}_4\text{Me}-4). \]

To our knowledge, this is only the second metal carbonyl cluster in which an orbital interaction between a bridging CO and capping ligand has been observed experimentally and the first for which the barrier range to internal rotation has been determined.

In FeCo\textsubscript{2}(CO\textsubscript{9}(\mu_3-\text{PPh}), derived values of the 'spinning' diffusion coefficient, \(D_s\), were approximately 30% lower than those found earlier in the structurally similar tricobalt cluster, Co\textsubscript{3}(CO\textsubscript{9}(\mu_3-\text{CPh}),\textsuperscript{14} and for free benzene in the same solvent.\textsuperscript{43} Thus, introduction of a Fe(CO\textsubscript{3} unit into the cluster polyhedron induces an electronic perturbation which creates a finite barrier to aryl ring internal rotation. The barrier most likely arises from the loss of degeneracy of the metal 2e molecular orbitals, resulting in a preferred orientation of the phosphinidene aryl group. This study represents the first investigation of the barrier to internal rotation in a heterometallic tetrahedrane cluster.

In CpNiCo\textsubscript{2}(CO\textsubscript{6}(\mu_3-\text{CPh}), the net phenyl spinning rates, \(D_s = D_I + R(\text{Ph})\), were found to be significantly below values observed earlier in the isolobal cluster, Co\textsubscript{3}(CO\textsubscript{9}(\mu_3-\text{CPh}).\textsuperscript{14} The slowed internal rotation has been attributed to
a barrier created by the Ni heteroatom, which splits the
degeneracy of the metals' 2e orbitals, inducing an
asymmetric electronic interaction between the ring and the
metal framework. In contrast, the spinning rate of the Cp
group is quite facile, indicating that there is no
appreciable barrier to internal rotation of this ring.

The results of this investigation illustrate the
powerful utility of the NMR relaxation time technique to
probe reorientational and internal rotation dynamics on a
nanosecond time scale. These measurements permit the
observation and estimation of barriers to phenyl internal
rotation which can not be detected using conventional
temperature dependent $^{13}$C NMR spectroscopy.
CHAPTER REFERENCES


30. Reference 23a, Chapter 8.


35. The calculation of Dij (from eqs. [80] and [86]) and R(Cp) (from eq. [82]) were performed by using iterative programs written for an IBM compatible PC in Turbo Basic.

36. rCH for Cp is often quoted as 0.95 Å. However, Churchill (Churchill, M. R. Inorg. Chem., 1973, 12, 1213) has noted that this value, determined from X-ray diffraction, corresponds to the distance between maxima in the electron density. He points out that for applications requiring the internuclear distance, one should use the spectroscopically determined value, 1.08 Å.

(c) Yuan, P.; Don, M. J.; Richmond, M. G.; Schwartz, M. *Inorg. Chem.*, (submitted).

39. (a) The structure of $\text{Co}_2\text{NiCp(CO)}_6(\mu_3\text{-CPh})$ has not yet been reported. Dimensions were calculated from the crystal structure of the similar complex, $\text{Co}_2\text{NiCp(CO)}_6(\mu_3\text{-CCO}_2\text{Me})$, together with standard CPh bond lengths and angles.

40. From the structure (ref. 39), we find that $\theta_1 = 71.4^\circ$, $\theta_2 = 82.4^\circ$, and $\theta_3 = 169.3^\circ$.

41. The chemical shift anisotropy ($\Delta \sigma$), required to determine $r_0(\text{avg})$ was calculated to be $\Delta \sigma = 415.8$ ppm, using the approximation method outlined in ref. 33.

42. From the structure (ref. 39), the angle between the Cp axis and the principal axis is $\alpha = 99.2^\circ$.

(b) Tanabe, K. *ibid.* 1979, 38, 125. These references report a room temperature diffusion coefficient of 72 ns$^{-1}$. The temperature dependence of $D_g(Bz)$ was calculated by assuming an activation energy, $E_g(\eta/T) = 2.27$ kcal/mol, where $\eta$ is the viscosity of the solvent chloroform.

(b) Lyerla, J. R. Jr; Grant, D. M. J. *Phys. Chem.*, 1972, 76, 3213.


47. In calculating $V_0(\text{min})$, we have assumed that $R < 100$ s$^{-1}$ at $-80^\circ$C, since one can observe 2 ppm splittings in the phenyl resonances. We have assumed further that the experiment were performed at $v_0(^{13}\text{C}) = 75$ MHz, since the spectrometer frequency was not given in ref. 11; these assumptions have only a small effect on the estimated barrier limits.


   (b) The GW microviscosity model was originally derived to describe the reorientation of spherical molecules. It has been shown that its application to determine $D_x$ in symmetric top molecules yields the most accurate results if one uses half the length of the principal axis rather that the mean radius. See, for example, Gillen, K. T.; Griffiths, J. E. Chem. Phys. Lett., 1972, 17, 359.


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