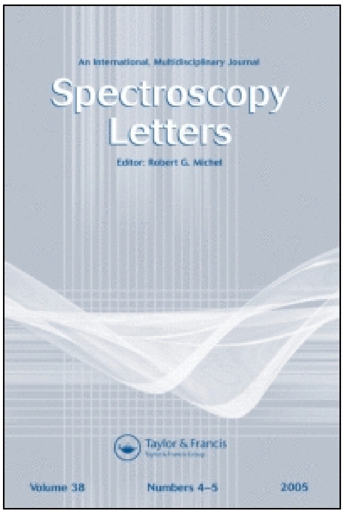

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An Infrared Spectroscopic Study of Rotational Diffusion and Intermolecular Interactions In Acetonitrile

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AN INFRARED SPECTROSCOPIC STUDY OF ROTATIONAL DIFFUSION AND INTERMOLECULAR INTERACTIONS IN ACETONITRILE

Key Words: infrared, rotational diffusion, intermolecular interactions, acetonitrile.

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INTRODUCTION

Several recent reviews[1-3] have emphasised the current interest in the study of infrared band shapes in condensed phases. Potentially such data can provide very valuable information[4-7] about the nature of the rotational and translational motions of individual molecules and about the intermolecular forces between them.[7] However, because of the possible ambiguities arising in the interpretation of such data, (for example, there may be several contributions to the overall band shape[7c,d]) it is clear that detailed studies on simple, symmetrical molecules are required before studies on more complex systems are attempted. This has been generally recognised and a number of simple (mostly linear and symmetric top) molecules have now been studied[4-10] in the compressed gas, liquid and solution phases. We have started a systematic study of simple nitriles and their weak molecular complexes. We report here some interesting data for the symmetric top molecule acetonitrile in the pure liquid and in solution in the "inert" solvent carbon tetrachloride. As far as we are aware the only previous work published on rotational diffusion in acetonitrile is the magnetic resonance work of Bopp.[11]

RESULTS

Acetonitrile belongs to the C_{3v} molecular point group[12] and its vibrations are divided into 4 a_1 modes and 4 e modes for which the transition moment is directed, respectively, along and perpendicular to the symmetry axis. It is found that the shapes of bands arising from a_1 and e modes have different overall shapes reflecting different rates of rotational diffusion about axes parallel and perpendicular to the symmetry axis. The a_1 modes give rise to bands which have a much smaller overall band width than those arising from e modes. We have been able to make detailed studies on the ν_4 (a_1) band near 920 cm^{-1} and on the $\nu_7(e)$ band near 1040 cm^{-1}. These bands, unlike the $\nu_1(a_1)$ band at 2258 cm^{-1}, are free from overlap with other bands and reasonably accurate transmission data (estimated accuracy ± 1%) have been obtained using a Grubb Parsons GS2A double beam spectrometer with digitised output facilities. The band envelopes have been Fourier inverted to yield the dipole autocorrelation function[1-3] ϕ as a function of time during the vibrational transition. Typical $\log\phi$-t plots are shown in Fig.1 while in Table 1 we have summarised the spectral parameters for the bands studied. The measurements were carried out at 25 ± 2°C. Our integrated intensity data for liquid acetonitrile are in good agreement with the data obtained using the dispersion technique.[13] The bands are relatively weak and no serious error is expected due to lack of a "dielectric field" correction.[5,6]

From Fig.1 it may be seen that the autocorrelation function can be divided into two parts showing short time and long time behaviour of the transition dipole as it rotates in the liquid. At short times, up to about 1 p sec, the decay of ϕ is essentially Gaussian and during the first ~ 1 p sec, therefore, essentially "free" rotation occurs. (There

TABLE 1

Spectral Data for Acetonitrile, Liquid and Carbontetrachloride Solution

	Liquid				Carbontetrachloride Soln.			
	Freq (cm^{-1})	$\Delta\nu_{\frac{1}{2}}{}^{a}$ cm^{-1}	B_i ^{c}	Previous B_i	Freq (cm^{-1})	$\Delta\nu_{\frac{1}{2}}{}^{a}$ cm^{-1}	B_i ^{c}	Previous B_i
$\nu_3(a_1)$	919	7 ± 1	180 ± 20	100	918	7 ± 1	155 ± 10	90
$\nu_7(e)$	1042	19 ± 1	710 ± 20	560	1039	20 ± 1	600 ± 30	250

c Intensity data in 1 $mole^{-1}$ cm^{-2} ("darks"), previous values from ref.13

is some evidence that this time may vary on going from liquid to solution). From then on intermolecular collisions occur leading to a randomisation of the molecular motion and exponential decay of ϕ is observed (the logϕ-t plot becomes linear). This linear part of the curve has a slope which gives the overall rotational damping constant γ. Following Favelukes et al[5] we have,

$$2.303 \log\phi(t) = -\gamma t = -(\beta_v + \beta_r)t \qquad (1)$$

where β_v and β_r are the damping constants for vibrational relaxation and rotational diffusion respectively. If we assume[5] that $\beta_v << \beta_r$ we may use the value of β_r to compute rotational diffusion coefficients along the principal axes of the molecule. Let the symmetry (C_3) axis be labelled x. The principal axes perpendicular to C_3 are then y and z. The diffusion coefficient D_y (or D_z) is obtained from the β_r value for the a_1 band since only "tumbling" rotation (simultaneously) about the y and z axes will lead to a rotation of the a_1 transition dipole.

So
$$D_y = D_z = \beta_r(a_1)/2 \qquad (2)$$

For the e mode the transition dipole is perpendicular to the symmetry axis and it shows the effect of rotation about the x, and either the y

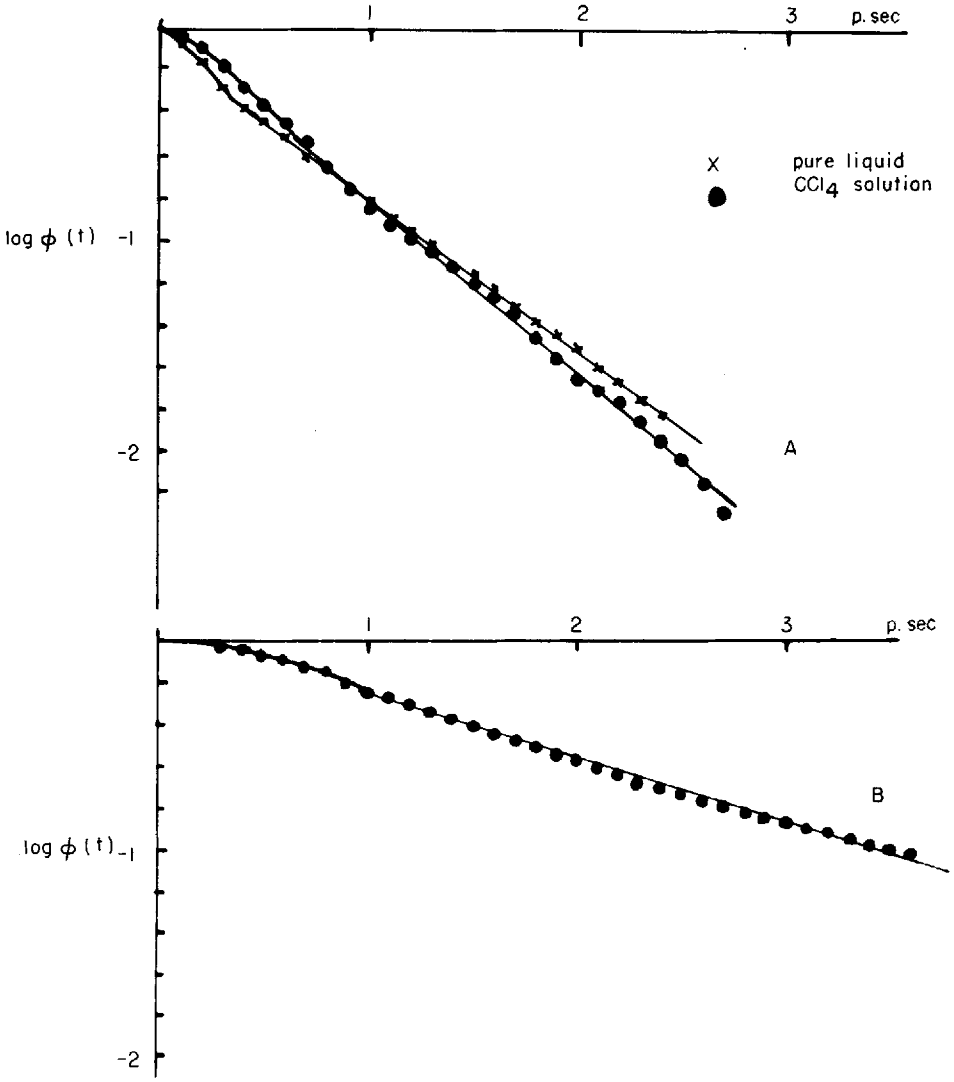

Fig. 1. Dipole autocorrelation functions for (A) ν_7 (e) band at 1042 cm^{-1} (B) ν_3 (a_1) band at 920 cm^{-1}. In case B the curves for pure liquid and carbontetrachloride solution could not be distinguished.

or z axes. The diffusion coefficient D_x is then

$$D_x = \beta_r(e) - \beta_r(a_1)/2 \qquad (3)$$

The results of these computations are shown in Table 2 along with the results obtained for other, similar molecules. The relevant moments of inertia are also included.

TABLE 2

Comparison of Rotational Diffusion Coefficients[a] for Acetonitrile and Methyl Iodide

	$\beta_r(a_1)$ (x 10^{-12} sec^{-1})	$\beta_r(e)$ (x 10^{-12} sec^{-1})	D_x (x 10^{-12} sec^{-1})	D_z (x 10^{-12} sec^{-1})	I_x amuÅ^2	I_z amuÅ^2	Ref
Acetonitrile (liq.)	0•73±0•04	1•66±0•10	1•29±0•10	0•37±0•02	3•2	55•0	-
Acetonitrile (CCl_4 soln)	0•71±0•04	1•96±0•10	1•61±0•10	0•34±0•02	3•2	55•0	-
Acetonitrile-d_3 (liq)			1•2[b]	0•14	6•4	64•3	11
Methyl Iodide (liq)	1•06	2•5	1•97	0•53	3•3	67•2	5

a. Our values obtained at ~ 25°C. b. values as low as 0•9 x 10^{12} sec^{-1} are possible. (see text).

DISCUSSION

It is very interesting to compare the results for acetonitrile with those obtained for acetonitrile-d_3[11] and methyl iodide.[5] Our results show that C_3 motion about the x axis is considerably easier than is "tumbling" motion about the y and z axes. This is what is expected for a molecule of this shape with moments of inertia shown in Table 2. Further, our results agree quite well with those obtained[11] for acetonitrile-d_3 using the magnetic resonance technique. (It should be noted that there is a large uncertainty involved in the determination of D_x by the NMR method because the necessary quadrupole coupling constants are "assumed"). However, the D values for acetonitrile are somewhat different from those for methyl iodide, even though the moments of inertia are very similar for the two molecules. The D values show that rotational diffusion is more rapid for methyl iodide although, from inertial effects alone, rotation would be expected to be somewhat more difficult. We are led to the conclusion that intermolecular forces in acetonitrile are considerably stronger than in methyl iodide. Such forces would cause a much slower decay of the autocorrelation function. This is, of course, to be expected since dipole-dipole interactions in acetonitrile will be of considerably greater strength than in methyl iodide (the liquid phase dipole moments[14] are 3•4D and 1•48D respectively). The relatively long period of "free" rotation in acetonitrile (1 p sec as compared with ~0•2 p sec in methyl iodide) supports the conclusions of Rothschild;[7d] that the formation of "clusters" in the liquid phase is unlikely to have a significant effect on the initial part of the autocorrelation curve. Thus, despite stronger intermolecular forces - which affect the function ϕ at long times - acetonitrile, with a smaller I_z value is able to rotate through a somewhat larger angle than is methyl iodide before collision induced diffusion begins to dominate. It is however, rather surprising to find so little difference between the D values for liquid acetonitrile and those for the carbontetrachloride solutions (between 2 and 5M). The implication is that the intermolecular forces are still very strong and we are now studying weaker solutions to test more fully these conclusions. We are also studying acetonitrile and related molecules in different solvents, with varying temperature, and in the presence of other interacting molecules and ions. Meanwhile this work emphasises the value of band shape studies in attempts to study molecule interactions in condensed phases.

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REFERENCES

1. B.L. Crawford, A.C. Gibby, A.A. Clifford and T. Fujiyama, Pure Appl. Chem., 18, 373 (1970).

2. R.P. Young and N. Jones, Chem. Review, 71, 219 (1971).

3. W.G. Rothschild and K.D. Möller, "Far Infrared Spectroscopy," Wiley-Interscience, 1971, Chapter 11.

4. T. Fujiyama and B.L. Crawford, J. Phys. Chem., 72, 2174 (1968).

5. C.E. Favelukes, A.A. Clifford and B.L. Crawford, J. Phys. Chem., 72, 962 (1968).

6. T. Fujiyama and B.L. Crawford, J. Phys. Chem., 73, 4040 (1969).

7. W.G. Rothschild, (a) Chem. Phys. Letters, 9, 149 (1971); (b) Macromolecules, 1, 43 (1968); (c) J. Chem. Physics, 55, 1402 (1971); (d) J. Chem. Physics, 53, 3265 (1970).

8. I. Rossi-Sonnichsen, J.P. Bauanich and N.V. Thank, Comptes Rendus, C273, 19 (1971).

9. J. Vincent-Geisse, J. Soussen-Jacob, N.T. Tai and D. Descout, Can. J. Chem., 48, 3918 (1970).

10. M. Chalaye, E. Dayan and G. Levi, Chem. Phys. Letters, 8, 337 (1971)

11. T.T. Bopp, J. Chem. Physics, 47, 3621 (1967).

12. J.C. Evans and H.J. Bernstein, Can. J. Chem., 33, 1746 (1955).

13. L. Nemes and W.J. Orville-Thomas, Trans. Faraday Soc., 61, 1839, 2612 (1965).

14. A.L. McOlellan, Tables of Experimental Dipole Moments, W.H. Freeman and Co., 1963.

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