142. Concerning the 'Non-Specific' Far Infrared Absorption of Polar Liquids

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Summary. The far infrared spectra of dimethyl sulfoxide and several aliphatic nitriles have been studied with a view towards elucidating the mechanism responsible for the intense absorption bands which have been observed in this region. Spectra of pure liquids, solid DMSO, DMSO-d_6, CD_3CN, and dilute solutions in non-polar solvents are presented. The results are discussed in terms of the possible mechanisms proposed for these absorptions.

Introduction. – Several recent reports have shown conclusively that far infrared spectra ($\tilde{\nu} < 100$ cm^{-1}) of many organic liquids show considerable absorption which cannot be explained in terms of pure rotations or intramolecular vibrations [1–6]. The explanations which have been suggested may be summarized as follows: 1 - The observed bands are due to the high frequency end of the DEBYE absorption, well known from microwave dielectric measurements on liquids [1] [7] [8]; 2 - the bands are due to a vibration of a liquid lattice [4] [9]; 3 - the absorption arises from a hindered rotation of the molecule in the cage of its neighbors [6] [10] (this explanation is very similar to that of number two); 4 - the bands arise from a vibration involving dipole-dipole complexes [3].

That the first proposal is not the whole answer, even in the case of highly polar liquids, has now been established by the further work of LEROY & CONSTANT [11] as well as by GEBBIE's measurement [4] for monohalogenated benzenes. These show that the absorption in the far infrared is considerably greater than the plateau value expected from the DEBYE relaxation process.

It is possible that a sort of short lived lattice does exist in polar liquids, and that the large half-band widths of the bands in the far infrared (ca. 60 cm^{-1}) result from the short lifetime of the lattice. GEBBIE has further shown that in the case of chlorobenzene the lattice vibration frequencies of the solid fall in the same region of the spectrum as the broad absorption band. More conclusive proof has, however, not yet been presented.

In distinguishing the idea of a short lived lattice from a dipole-dipole complex, one must realize that an important influence on the lattice vibrations of a polar solid such as dimethyl sulfoxide will be the strong interactions between neighbouring dipoles in the unit cell. The crystal structure of dimethyl sulfoxide (DMSO) [11], which reveals

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corrugated layers of antiparallel dipoles with short intermolecular distances, reflects this strong interaction. Nonetheless, it is shown in the following work that one can make a distinction between an absorption arising from such an array of antiparallel dipoles in a *lattice*, and an absorption originating in a tightly bound *dimeric* species in solution.

In this work evidence is given for the view first presented by JAKOBSEN & BRASCH [3], that these absorption bands arise from dipole-dipole complexes, and not from a liquid lattice or any other formulation requiring long range order in polar liquids.

Of many available polar liquids, this paper treats dimethyl sulfoxide and several aliphatic nitriles. DMSO was selected for observation because its crystal structure is known, its vibrational spectrum and assignment have been rather well established [13], and there are no low-lying vibrational frequencies which can complicate the spectrum in the region of interest. The nitriles are well known as a case where dipole-dipole complexes have long been thought to exist on the basis of viscosities and other data (see, for example, [14]).

Results and Discussion. – When a 25 micron thick film of DMSO is examined in the far infrared region, a band is observed which is centered at 83 ± 3 cm^{-1}, with a half-band width of ca. 60 cm^{-1}. There appears to be a weak shoulder on the low frequency side of the band, however the breadth of the band makes it difficult to determine both the exact position of the broad maximum and the nature of weak features. It should be emphasized that all the spectra discussed here are double beam spectra (see Experimental section for details of how these were obtained), and represent the manually computed average of several runs.

The DMSO absorption band is very intense in comparison with organic liquids (1000 × as intense as CCl_4, for example) which have been reported previously [1–6]; indeed, a 50 micron film transmits less than 1% of the energy at the band center. In the hexadeuterated DMSO-d_6 there is an isotope shift of about 10% of the original frequency. The overall intensity and breadth of the band remain essentially unchanged, however.

The lattice vibrational spectrum of crystalline DMSO was examined at 100 K. Bands were found which had the following frequencies and relative intensities: 142 (*s*), 128 (*m*, shoulder), 95 (*m*), 74 (*m* - strongly overlapped by polyethylene band), and 48 (*w*) cm^{-1}. Exact determination of the relative intensities was complicated by a rapidly sloping background due to scattering from the polycrystalline sample. These results agree with those of GEBBIE in that the lattice vibration frequencies fall in the same spectral region as the broad liquid absorption band. It might be noted, however, that the most intense band in the lattice spectrum falls at considerably higher frequency than does the absorption maximum in the liquid.

To further test the liquid lattice hypothesis, the spectrum of dilute solutions of DMSO in such non-polar solvents as CCl_4, benzene, and cyclohexane were examined. Concentrations were such that the product of (concentration) · (pathlength) was kept constant. Even in dilutions as great as 0.25% DMSO in CCl_4 or cyclohexane (10 mm path) it was not possible to measure a decrease in the intensity of the absorption band. Not only was this result independent of solvent and cell window material, but it was also found for DMSO-d_6 and acetonitrile. In the acetonitrile case the band even appears to become more intense in solution, but this may be due to a slight decrease in half-band width[3]).

This persistence of the strong absorption band in dilute solutions in non-polar solvents is inconsistent with the concept of a lattice of any sort. Therefore we are forced to turn to other models for possible explanation.

Consideration of a simple monomer-dimer equilibrium reveals that if one has an association constant of ca. 10^3, the pure liquids are almost completely associated and there will be a decrease in dimer concentration of only about 5% upon 500 fold dilution. However, when a system which is only partially associated is examined, dilution will effect complete dissociation into monomers.

To test the hypothesis that the observed bands are due to a vibration originating from an associated complex, the spectra of five aliphatic nitriles were examined. Figures 1 and 2a–d show these spectra, as well as the slight isotope shift between CH_3CN and CD_3CN. One can see that acetonitrile, propionitrile, and capronitrile all show broad, reasonably symmetrical absorption bands, with center between 85 and 90 cm^{-1}. The butyronitrile spectrum is clearly complicated by an overlapping band, which is probably a fundamental mode of the isolated molecule. The same may be true of the valeronitrile band, which is clearly asymmetrical to the low frequency side.

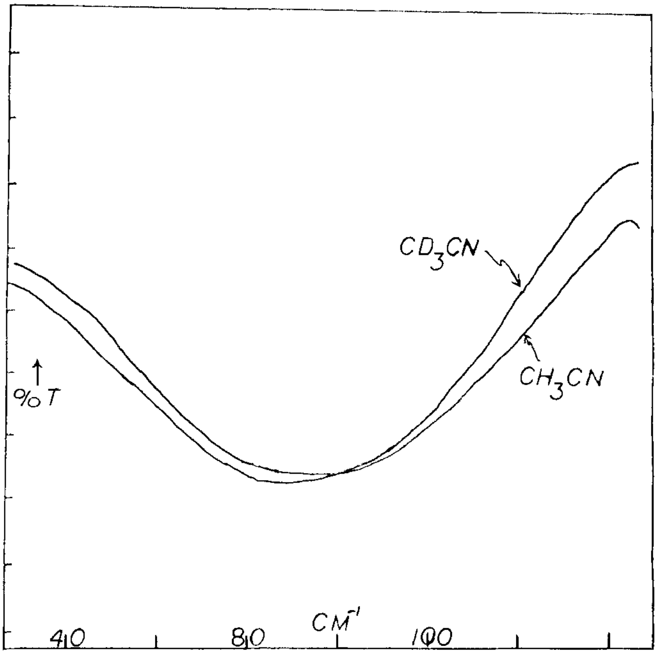

Figure 1. *Far infrared spectra of 25 μ thick films of acetonitrile and acetonitrile-d_3*

To measure the dependence of absorbance on chain length, a baseline technique [15] was used. Because the butyronitrile spectrum could not be treated directly due to

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[3]) We did not observe the shift to lower frequency in solutions of acetonitrile found by KROON & VAN DER ELSKEN (see [7]).

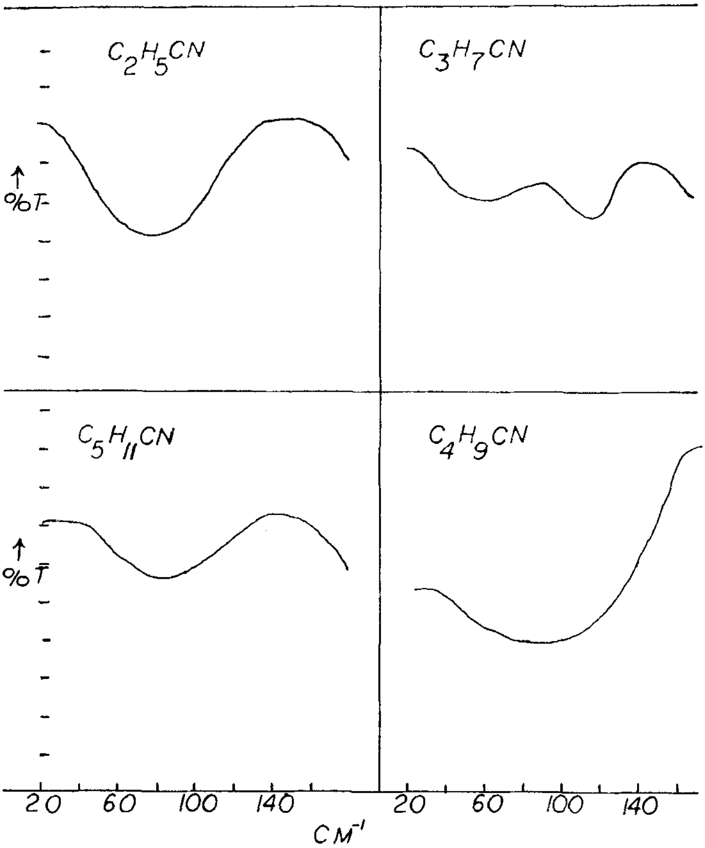

Figure 2. *Far infrared spectra of aliphatic nitriles*
All are 25 micron thick films except for C_4H_9CN, which is 50 microns thick

the overlapping band, a different approach was sought. If, as proposed by SAUM [14], this represents a case of only 76% association, then a sufficiently dilute solution can be prepared which should cause the dimer band to disappear. Such is indeed the case. Figure 3 shows the bands of pure butyronitrile, a 0.25% solution of butyronitrile in cyclohexane, and a difference curve obtained from a point by point subtraction of the two spectra. *This difference curve is clearly a band similar in shape and frequency maximum to the bands of the other nitriles.* It is the absorbance of this newly computed band which is used to compare to the fraction of dimer in butyronitrile. The value thus computed is a very reasonable one, and the $A_2 \rightarrow 2\,A$ behavior of the band upon dilution, coupled with the previously discussed dilution properties of the acetonitrile and DMSO spectra, offers rather conclusive evidence for the association formulation of the absorption band.

Figure 4 summarizes the results of this series of experiments. When the absorbance is corrected in each case for differing density and molecular weight, a regular decrease in the absorbance with chain length is observed. From the observed noise levels and subsequent arithmetic calculations, we estimate an uncertainty of ± .01 in the values

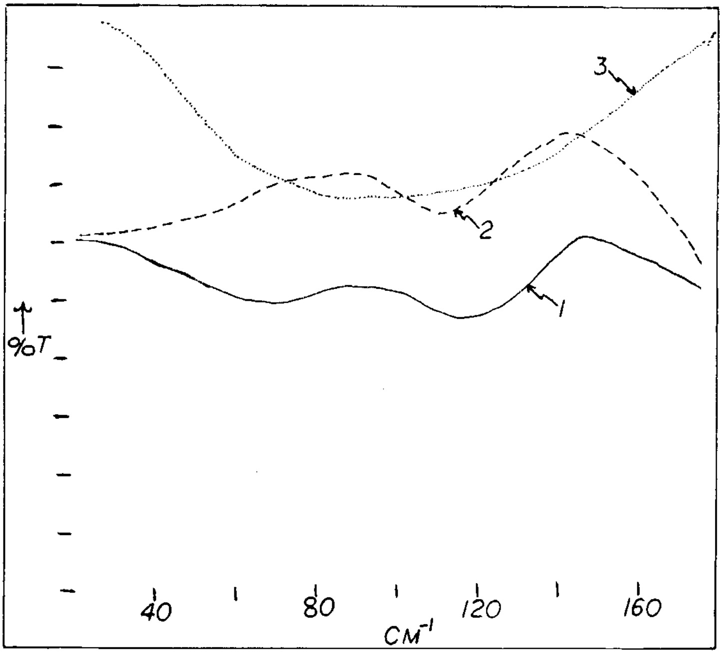

Figure 3. *Effect of dilution upon the far infrared spectrum of butyronitrile* C_3H_7CN
1. (———): 25 micron thick film of pure butyronitrile; 2. (- - - - -): 25% solution of butyronitrile in cyclohexane; 3. (......): difference spectrum obtained from subtraction of curve 2 from curve 1. The intermolecular vibration band disappears on dilution, but the intramolecular vibration band remains.

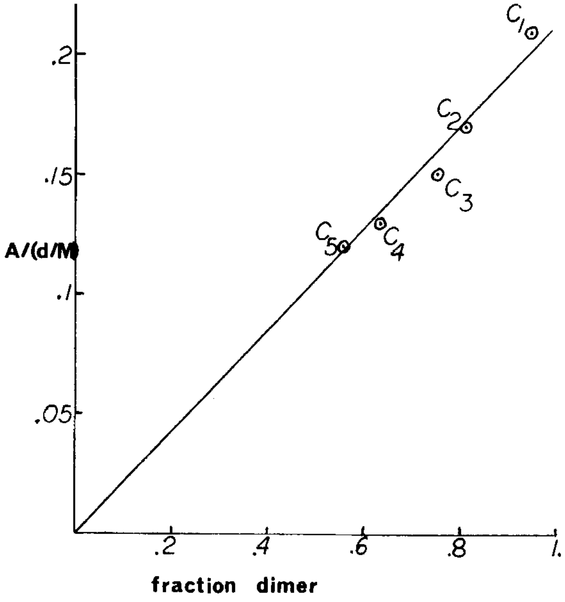

Figure 4. *Absorbances of aliphatic nitriles* (corrected for differing density, pathlength, and molecular weight) vs. *the fraction of dimer*[3])
The experimental points are identified by the length of the alkyl chain

of A(d/M) shown in Figure 4, except in the butyronitrile case where the additional subtraction step greatly increases the uncertainty. These results are thus not intended to be a quantitative determination of dipole-dipole complex concentration at this time. This must await the result of additional computer averaged and integrated spectra. This regular decrease in absorbance is, nonetheless, evidence for the presence of strong dipole-dipole complexes in polar liquids. The fact that the absorbance in butyronitrile disappears in dilute solution is further good evidence for an association complex as the origin of these absorption bands.

At present not enough is known about these dimers to set up a force field model which will reproduce the small isotope shifts observed. Further work in this direction, as well as spectral measurements on these and other systems, is in progress.

The interest and hospitality of Prof. Dr. Hs. H. GÜNTHARD of the ETH, Zürich, are gratefully acknowledged. Mr. P. BACHMANN and Mr. J.-P. PORCHET are thanked for assistance with aspects of the experimental work. The author thanks the NATIONAL SCIENCE FOUNDATION for a Postdoctoral Fellowship to support this study.

Experimental. – *Liquids:* All liquids were of the highest purity available from FLUKA A.G. These were stored for at least one week on LINDE 4 A Molecular Sieves, distilled *in vacuo* on to freshly regenerated sieves, and finally distilled directly into the liquid cell described below. Because of their low volatility, DMSO and DMSO-d_6 could not be distilled and were examined in fixed thickness liquid cells filled under nitrogen. Extreme precautions were taken to assure the dryness of the samples, and no water was detectable using the 1.9 micron band of water in the near infrared. CCl_4, benzene, and cyclohexane were stored for at least one week on molecular sieves and distilled *in vacuo* immediately prior to use.

Instrumentation: Spectra were obtained on a PERKIN-ELMER Model 301 far infrared grating spectrometer. The instrument was purged thoroughly with dry nitrogen, and was operated at a spectral slit width of 1–3 cm^{-1}. For spectra of pure liquids, no reference beam compensation was used, and the spectrum of the empty cell, without spacer, served as the background (I_0). For dilute solutions, the sample was run *vs.* a reference of pure solvent in the same thickness, and then the pure solvent was run in both beams for the I_0 spectrum. Spectra were run several times and the results averaged to reduce uncertainty. This was still fairly large however, as discussed above.

Cells: Pure liquids were run in a variable temperature cell similar in design to that described by BÜRER & GÜNTHARD [16]. Crystal quartz windows, cut parallel to the optic axis and wedged (1.0 to 1.7 mm, 40 mm diameter) to eliminate interference fringes, were used with a spacer made from spots of lead foil. The liquid cell cavity itself was evacuated to less than 10^{-3} Torr, then cooled to 0° C. The thoroughly deaerated liquid readily distilled to fill the space between the windows.

Spectra of dilute solutions were obtained in cells of 1, 3, 5, and 10 mm thickness, using teflon spacers and either crystal quartz or Rigidex polyethylene windows. The cells were filled under nitrogen or dry air.

Preparation of Dilute Solutions: Solutions of 0.25% DMSO or nitrile, by volume, were prepared using a HAMILTON 100 microliter syringe to measure the small volume of solute required. In a typical experiment, 25 μl of acetonitrile was mixed with 10 ml of cyclohexane, and a spectrum taken in a 10 mm cell.

Spectrum of Solid DMSO: A cell similar to that described by WERDER, FREY & GÜNTHARD [17] was operated at 100 K, using liquid nitrogen as a coolant. Pure liquid DMSO was sealed in a 0.1 mm polyethylene cell manufactured by BARNES ENGINEERING. A small copper-constantan thermocouple was sealed directly into the liquid cell to measure the temperature of the DMSO directly. The cells were sealed either with heat, or (preferably) by use of EPIBOND 128, hardener 9822[4]). These cells were vacuum tight and could be cooled several times without any observable change in the sample. Thus measurements could be made on the same sample as liquid and solid.

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[4]) A sample of this material, manufactured by FURANE PLASTICS, was kindly supplied by Mr. V. THORNTON of PHILLIPS PETROLEUM.

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143. Kernresonanzspektren des Cyclohexa-2,5-dien-1-on-Systems (para-Dienone)

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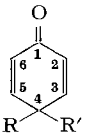
Summary. Proton and fluorine NMR. spectra of several *para*-dienones (4-allyl-4-methylcyclohexa-2,5-diene-1-one and its 2- and 3-fluoro derivatives, a spirocyclic bis-dienone and two dienone alkaloids) have been analysed using multiple resonance, solvent effects, and computer techniques. The relative signs of all the H,H- and H,F-coupling constants of the *para*-dienone system have been determined. The nature and significance of long range coupling in cyclic and openchain cross-conjugated dienones is discussed in comparison with related systems of aromatic character.

Das Cyclohexa-2,5-dien-1-on-System **1** (*para*-Dienone) ist in den letzten Jahren in verschiedenartigen chemischen Arbeiten vermehrt in Erscheinung getreten. Erwähnt sei hier das Vorkommen dieses Chromophors in Naturstoffen (Terpene, Steroide, Proaporphin-Alkaloide [1]), seine Bildung durch Desaromatisierungsreaktionen, die Dienon-Phenol-Umlagerung und die Synthese des neuartigen spiro-bis-Dienons **4** [2]. Eine Zusammenfassung der Fortschritte auf dem Gebiet der Chemie der Cyclohexadienone ist von WARING gegeben worden [3]. Die Bedeutung der Kernresonanzspektroskopie zur Charakterisierung von *para*-Dienonen wurde bereits frühzeitig er-



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