

are not much more distant. An intricate network of hydrogen bonds connects the entire structure.

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Far-Infrared Studies of Intermolecular Forces. Dipole-Dipole Complexes

Sir:

Far-infrared spectra (between 150 and 50 cm^{-1}) of thirteen organic compounds have been obtained in this laboratory. A very broad absorption band in the range from 88 to less than 50 cm^{-1} has been observed in the spectra of those compounds which have a high dipole moment. These observations coupled with other evidence indicate that these broad, low frequency vibrations are vibrations involving the bond joining molecules together in dipole-dipole complexes. While considerable evidence has been reported previously¹⁻⁴ that highly polar organic molecules can undergo self-association or complexing, this evidence has usually been the result of classical, but indirect, studies of colligative properties or virial coefficients. The appearance of these low frequency bands gives a direct means of studying these complexing forces.

Observed frequencies for the compounds studied are listed in Table I along with the molecular weights and

TABLE I

VIBRATIONAL FREQUENCIES OF ORGANIC MOLECULES BETWEEN 50 AND 150 cm^{-1}

Compound	Molecular weight	Dipole moment, D. ⁵	Physical state	Frequencies, cm^{-1} ^a
Benzonitrile	103	3.9	Liquid	54 vbr
p-Chlorobenzonitrile	137	2.56	Liquid	113
Phthalonitrile	128	5.9 (calcd.)	Solid	72, 133
Terephthalonitrile	128	0	Solid	95, 154
Nitrobenzene	123	3.98	Liquid	<50 vbr
o-Dinitrobenzene	168	6.00	Solid	88, 113, 136
			Liquid	86 br
p-Dinitrobenzene	168	0	Solid	104, 125
Phenylacetylene	102	0.80	Liquid	
Acetonitrile	41	3.5	Liquid	87 vbr
			Vapor	65 vbr, w
Nitromethane	61	3.15	Liquid	60 vbr
Methyl thiocyanate	73	3.6	Liquid	68 vbr
Acetone	58	2.75	Liquid	<50 vbr
			Vapor	118
1-Bromobutane	136	1.97	Liquid	

^a v = very, br = broad, w = weak, italicized frequencies are those attributed to dipole-dipole interaction.

dipole moments⁵ of the compounds. These spectra were obtained with a Perkin-Elmer Model 301 double-beam spectrophotometer with a lower frequency limit of approximately 50 cm^{-1} . Since many of the observed bands have frequencies near 50 cm^{-1} and are extremely broad, it was difficult to observe the entire band and, therefore, to locate the center of the band accurately. For these bands, the frequency may be accurate only to $\pm 10 \text{ cm}^{-1}$.

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- (4) A. M. Saum, *J. Polymer Sci.*, **42**, 57 (1960).
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Low frequency absorptions such as those observed could also arise from internal molecular vibrations, lattice modes or other crystal effects, and/or torsional modes (e.g., methyl rotations). For the compounds listed in Table I, vibrational assignments have been made for benzonitrile,^{6,7} nitrobenzene,⁸ phenylacetylene,⁹ acetonitrile,¹⁰ acetone,¹¹ and nitromethane.¹² None of these assignments indicates an internal molecular vibration giving absorption below 130 cm^{-1} ; therefore, the observed bands below 88 cm^{-1} cannot be assigned to intramolecular vibrations.

Lattice modes can be eliminated in all the compounds examined as liquids, and the use of a polyethylene matrix to contain the sample¹³ minimizes possible crystallinity effects in the materials examined as solids.

Torsion modes can be eliminated from consideration in the cases of benzonitrile, where microwave studies¹⁴ have shown a linear CCN structure; nitrobenzene, where Raman data have been used to assign the nitro torsion at 130 cm^{-1} ; acetone, for which Fateley and Miller¹⁵ assign a weak band at 109 cm^{-1} to the methyl torsion; and methyl thiocyanate, for which Fateley and Miller¹⁶ assign a broad band at 131 cm^{-1} in both the liquid and solid to the methyl torsion. No methyl torsion would be expected in this region for acetonitrile due to the linear CCN structure.

The broad, low frequency band observed in liquid acetone is not seen in acetone vapor; instead we observe a much weaker, sharp band at 118 cm^{-1} (which is probably the very weak band reported Fateley and Miller¹⁵). This disappearance is consistent with dissociation of the dipole-dipole complexes, or clusters of complexes, in the vapor state. The broad band observed in liquid acetonitrile is still evident in the vapor spectrum, but is much less intense and apparently shifted somewhat to lower frequencies than in the liquid. This would be the expected behavior if the complex persisted in the vapor as has been postulated.^{1,2} Persistence of the complex in the vapor for acetonitrile, but not for acetone, is consistent with the relative magnitude of the dipole moments of these compounds.

We do not observe the broad absorption at 131 cm^{-1} reported by Fateley and Miller for liquid and solid methyl thiocyanate; instead our liquid spectrum shows a broad band centered near 68 cm^{-1} , while at 77°K. we find a band near 116 cm^{-1} . Such a frequency shift with decreasing temperature is consistent with the expected behavior of an intermolecular vibration, but is not consistent with a torsion mode. Coupling between the torsion and the dipole-dipole vibration may occur and would account, in part, for the extreme broadness of these bands.

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These arguments, though consistent and convincing, are completely overshadowed by the significant correspondence between these absorptions and the dipole moments of the compounds examined. The internal molecular vibrations of phenylacetylene⁹ are very close in frequency to those of benzonitrile^{6,7} (except for those involving the acetylenic proton). However, phenylacetylene has a dipole moment of 0.80 D. compared to 3.9 D. for benzonitrile. No absorption below 150 cm^{-1} is seen in phenylacetylene, while a broad band near 54 cm^{-1} is observed in benzonitrile. No bands below 95 cm^{-1} are evident in the spectra of *p*-dinitrobenzene and terephthalonitrile ($\mu \sim 0$). (Some absorptions above 95 cm^{-1} in these compounds could be ascribed in part to lattice modes, as these were examined as solid films rather than by the polyethylene matrix technique.) Both corresponding *ortho* isomers ($\mu \sim 6$) do show absorptions in the 70–88 cm^{-1} region. No low frequency absorption was observed in the spectrum of the slightly polar aliphatic compound, 1-bromobutane ($\lambda = 1.97$ D.). This compound, and others with intermediate dipole moments, may have such absorption bands at frequencies beyond the range of our instrumentation.

While it is impossible, at this time, to determine the exact mode of this vibration, the half-band widths (50–70 cm^{-1}) of these bands are similar to those seen in the O—H—O intermolecular hydrogen bond stretching vibration. This would support a dipole-dipole stretching vibration, similar to the hydrogen-bond stretching vibration. A motion corresponding to a coupled libration or to librations of a polymeric cluster of molecules could also be active in the infrared and give rise to the observed bands. Further work is needed to establish the exact nature of the vibrations.

This work points to a direct means of obtaining information about the nature of dipole-dipole complexes and indicates that the far-infrared spectral region may be extremely useful in studying intermolecular forces.

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Visible Absorption Spectra of Lithium, Sodium, and Potassium in Molten Lithium Chloride–Potassium Chloride

Sir:

In order to elucidate the nature of the species formed upon the addition of an alkali metal to an alkali halide melt, the absorption spectra obtained upon the addition of Li, Na, and K to molten LiCl–KCl were measured. The eutectic mixture of LiCl and KCl was used in order that the measurements be made at as low a temperature as possible. Although the attack of heated alkali metal vapors has restricted the use of silicate containers in such work, it was not found to be a primary problem. The absorption spectra obtained can all be characterized by a band with a peak maximum at 530 $\text{m}\mu$.

Quartz cuvettes, 1 cm. in diameter, were used as containers. Although heated alkali metal vapors react

with silicates, it was found that if the salts were anhydrous, the alkali metal would dissolve in the salt without discoloring that portion of the cell containing the melt. However, there were irreversible losses of alkali metal vapor for the following reasons: reaction of the metal with water on the container walls,¹ reaction of the metal with the glass cuvette itself, and distillation of the metal from the solvent to other parts of the evacuated container. The presence of adsorbed water on the glass container has been shown to be a source of decomposition in the preparation of alkali-metal-ammonia solutions.²

The cells were wrapped with Inconel heating strips and placed in an insulating container. The steady-state temperatures were controlled by means of a Variac to within $\pm 5^\circ$. The temperature of the system was measured by means of a platinum–rhodium (13%) thermocouple. All measurements were made at 400°.

The spectra were obtained by use of a Beckman DK, double-beam recording spectrophotometer. Each metal–salt mixture was compared to air in the reference compartment. The base line for the system was obtained by running the spectrum of the salt mixture alone when all the metal had left the system. In this way the problems in reproducing the exact temperature, concentration, and configuration of the sample cell were eliminated. The results obtained essentially enabled us to calculate a spectrum of the metal–salt system as compared with the identical salt system.

The standard preparation of molten salt halides was found to have inherent difficulties. In the salt melted *in vacuo*, washed with the appropriate halide gas, then with a dry inert gas, and filtered through Pyrex glass wool, it was found that not all hydrolysis products were removed and that often residual amounts of halogen gas reacted with the alkali metals added. In order to overcome the difficulties produced by heating the salt in the presence of water and by introducing halogen gases into the system, a new purification technique was used.³ It was found that anhydrous salts could be obtained by washing with liquid ammonia. This procedure eliminated the possibility of hydrolysis since the salt was not heated until all the water was removed. This procedure also eliminated the use of halide and halogen gases.

Preparation of Metal–Molten Salt Solutions.—Reagent grade LiCl and KCl were weighed out after vacuum drying to form the eutectic mixture (59 mole % LiCl). Removal of water from the salts was then done by washing with dry liquid ammonia. A system shown in Fig. 1 was used first to purify the salt mixture and then to prepare the metal–salt solution. After repeatedly washing the salt mixture in region B and pumping on the washed salt to remove residual ammonia, the potassium, and also the sodium, was distilled from region A into region C. The system was then sealed off at D while pumping. The salt mixture in region B was easily transferred into region C by tipping the ampoule and transferring the finely divided solid without heating. A heater was then placed about the

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