

simultaneously trapping small ions within it. We have taken both charge density and polymer radius as independent parameters and, as far as our calculations are concerned, we cannot predict a functional relationship between the two. Furthermore, we assumed the electrolyte solution to be so dilute that polymer-polymer interactions could be ignored. This may not be justifiable for what we call "dilute" polymer solutions in the laboratory. For example, consider a 0.01*N* solution of a polymer of degree of polymerization (D.P.) equal to 1000, where the concentration refers to the number of equivalents of monomer units per liter. If the total volume of solution is *V* cc, then the number of polymer

molecules, *N*, is:

$$N = \frac{(0.01)V(6 \times 10^{23})(10^{-3})}{(\text{D.P.})} = 6 \times 10^{15}V. \quad (30)$$

In the second calculation, a radius *R* was defined in terms of the average volume per polymer molecule:

$$(4/3)\pi R^3 = V/N = 1.7 \times 10^{-16} \text{ cm}^3. \quad (31)$$

This means that the radius *R* of the large sphere is of the order of 340 Å. However, the radius of the polyion itself would not be expected to be much smaller, so we can expect overlapping of molecules in solutions of moderate concentrations.

Raman Spectrum and Vibrational Assignments of Gaseous Dimethyl Ether

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The Raman spectrum of gaseous dimethyl ether has been obtained and that of the liquid reinvestigated. In the low-frequency region of the gas spectrum, two bands have been observed which are attributed to overtones of the torsional motions of the methyl groups. The assignment of vibrational frequencies is discussed on the basis of a C_{2v} symmetry in the molecule.

IN connection with a recent study of the HCl-dimethyl ether system, the Raman spectrum of gaseous dimethyl ether was obtained and that of the liquid reinvestigated. Since the Raman spectrum of this compound in the gas phase has not been previously reported and one or two new features of interest were found, it seems worth while to summarize the results briefly.

The spectrograph and light source used, and the details of handling the liquid have been described previously.¹ Dimethyl ether gas was examined at 5–6 atmos in a Raman cell 50 mm in diameter with an illuminated length of about 150 mm. Overlapping spectra were eliminated by filtering the exciting light with saturated sodium nitrite solution. A Rhodamine 5GDN extra dye solution was used in addition when the C–H stretching region was examined. With Eastman 103a-J plates, exposure times for the gas varied from 3 hr, which was adequate for the C–H stretching bands, to 48 hr for the weaker frequencies. Qualitative depolarization ratios for the liquid were obtained by the two exposure method and polaroid cylinders. The data shown in Table I represent the average of measurements made on several plates. Microphotometer tracings of the gas spectrum are shown in Fig. 1 in which the different portions of the figure were obtained at different expo-

surements and selected to show the best detail in each region.

The assumption of a C_{2v} symmetry for the dimethyl ether molecule results in the prediction of 21 fundamental modes of vibration distributed among four symmetry classes as follows: 7 A_1 , 4 A_2 , 6 B_1 and 4 B_2 . Frequencies belonging to all four classes are Raman active but the A_2 frequencies are forbidden in the infrared. A description of these modes together with a review of the experimental frequencies and their assignments appearing in the literature before about 1944 has been given by Herzberg² while normal coordinate treatments based on the same data have been made by Siebert³ and Ryskina.⁴ Identification of all frequencies and a complete assignment does not appear feasible without the help of isotopically substituted molecules and perhaps high resolution grating work because of the superposition of bands in several regions of the spectrum.

In the methyl group rocking region around 1000–1200 cm^{-1} , two new frequencies have been observed at 1053 and 1242 cm^{-1} . Both show a sharp *Q* branch in the gas spectrum which is usually characteristic of a totally symmetric vibration, and the second is also strongly polarized in the liquid. Siebert³ calculates a value of 1239 cm^{-1} for the A_1 rocking motion, ν_5 , (in Herzberg's

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¹ G. L. Vidale and R. C. Taylor, *J. Am. Chem. Soc.* **78**, 294 (1956).

² G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 353–354.

³ H. Siebert, *Z. anorg. Chem.* **271**, 65 (1952).

⁴ S. I. Ryskina, *J. Phys. Chem. (U.R.S.S.)* **22**, 21 (1948).

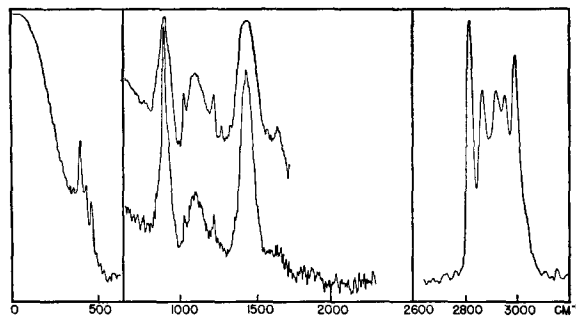


FIG. 1. Raman spectrum of gaseous dimethyl ether.

notation) which is close to the latter. However such an assignment would leave only the possibility of one of the A_1 methyl group deformation modes, ν_3 or ν_4 , for the 1053 cm^{-1} band. Since the likelihood of a deformation frequency being this low is not great, the assignment of 1053 cm^{-1} to the symmetric rock ν_5 , and 1242 cm^{-1} to the symmetric deformation, ν_4 , appears more satisfactory. There seems no reasonable possibility that these two bands are overtones or combinations. The B_1 skeletal motion ν_{17} also falls in this region and appears primarily responsible for the rather broad band with its maximum at 1122 cm^{-1} .

It seems pointless to attempt any detailed assignment of deformation frequencies in the region around 1450 cm^{-1} and likewise for the C—H stretching region despite the fact that five sharp and well resolved lines appear in the gas spectrum between 2800 and 3000 cm^{-1} . The difficulty in the latter case arises, at least in part, from the fact that the first overtones of several of the deformation frequencies fall right in the middle of the C—H region and give a complicated case of Fermi resonance with the two A_1 stretching fundamentals. One is tempted to assign the two most intense bands at 2821 and 2997 cm^{-1} to the two A_1 fundamentals ν_1 and ν_2 , respectively although the only basis for the assignment is their greater intensity. A band at 2889 cm^{-1} appeared in the liquid spectrum obtained with parallel polarized light in which the intensities of the principal bands were considerably reduced. It is therefore likely to be one of the antisymmetric stretching motions.

The two remaining modes of interest are ν_{11} and ν_{21} , respectively, the A_2 and B_2 torsional motions of the methyl groups. Herzberg² lists four Raman bands observed in the liquid at 160 , 300 , 583 , and 702 cm^{-1} as possibilities, and Pitzer⁵ has calculated that the first two are of the right order of magnitude to give agreement between thermodynamic and spectroscopic data. However, such motions are very difficult to observe

TABLE I. Observed Raman frequencies and assignments for liquid and gaseous dimethyl ether.

Gas frequency cm^{-1}	Liquid frequency cm^{-1}	Polarization (liquid)	Assignment	Species
413	420	pol.	ν_7	a_1
448	$2\nu_{11}$	A_1
478	$2\nu_{21}$	A_1
929	920	pol.	ν_6	a_1
1053	1046	...	ν_5	a_1
1122	1095	depol.	ν_{17}	b_1
1154	1147	depol.}	$\nu_{10}, \nu_{16}, \nu_{20}?$	
...	1167	...		
1242	1238	s. pol.		
1291	ν_4	a_1
1440	$\nu_{10}, \nu_{16}, \nu_{20}?$	
1456	1448	depol.}	ν_8, ν_9, ν_{14}	
1475	1479		ν_{15}, ν_{19}	
2821	2814	pol.	$\nu_2?$	a_1
2868	2865	pol.}	$2\nu_3, 2\nu_9, 2\nu_{14}$	A_1
2924	2921	pol.		
2959	2953	pol.}		
...	2889	depol.	$\nu_8, \nu_{12}, \nu_{13}, \nu_{18}?$	
2997	2991	pol.	$\nu_1?$	a_1

experimentally, particularly in the liquid state, and the polarization characteristics of the bands do not agree with those predicted so that a reasonable doubt of the correctness of the assignment exists. All the bands are listed by Herzberg as quite weak and were reported by one observer only. None were confirmed in this investigation either in the gas or liquid despite heavy exposures. A band at 270 cm^{-1} has been reported recently by Hadni⁶ in a grating infrared study which he assigns to ν_{21} , the B_2 motion.

In the gaseous spectra obtained in the present work, the region in the neighborhood of ν_7 , the skeletal A_1 bending mode, was observed to be considerably more complicated than anticipated. In particular, two relatively sharp satellites appeared on the high frequency side of the central Q branch. These satellites, which are shown clearly in Fig. 1, appeared in all exposures of the gas of sufficient length but were absent in the liquid spectra. This type of structure is not to be expected in the envelope of an A_1 band and the suggestion that they may be "hot" bands is likewise not reasonable. Their appearance is that of the Q branches of A_1 bands and consequently they are assigned as the first overtones of ν_{11} and ν_{21} which have borrowed intensity from the ν_7 fundamental by Fermi resonance. Their absence in the liquid spectrum is not unexpected since these motions would be easily perturbed and the resonance weakened. The values of the fundamentals so derived are in good agreement with estimates made from specific heat measurements and also are not too far from the value of 275 cm^{-1} accepted for the torsional frequency in ethane.

⁵ K. S. Pitzer, J. Chem. Phys. **10**, 605 (1942).

⁶ A. Hadni, Compt. rend. **239**, 349 (1954).