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The Raman Spectra of Some Simple Molecules in Solution*

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(Received October 12, 1936)

The Raman spectra of HCl, HBr, SO₂ and NH₃ in various nonionizing solvents indicate vibrational frequencies in the solute molecules of lower value than in the corresponding gaseous states, the relative diminution amounting, in the hydrogen halides dissolved in some solvents, to 3 percent of the gas frequencies. The frequency shift is smaller for the two polyatomic molecules. There seems to be a definite relation between the relative frequency displacement and the dielectric constant of the solvent for the dissolved molecules of HCl and HBr.

$\Delta\nu/\nu$ increases with solvent dielectric constant to a limiting value of 0.03. A similar trend is shown in SO₂ and for NH₃ it seems that other factors than the dielectric constant of the solvent are effective in determining the frequency displacement. Concentrated solutions of HCl and HBr in several ionizing solvents have no features in their Raman spectra which can be identified as vibrations in HCl or HBr molecules. The bearing of these results on the dissociation process of HCl in solvents is discussed.

THE great power of spectroscopic investigations in furthering the development of the theory of molecular structure in the gaseous state naturally suggests the utility of similar studies in the effort to gain an understanding of molecular properties in liquids and solutions. It is soon apparent, however, that in leaving the gaseous state for the condensed phase we nearly always lose one of the most important aids in the elucidation of molecular structure, the rotational structure associated with rotational-vibrational bands; for in all except molecules of very small moment of inertia, the frequency of rotation characteristic of the isolated molecule is less than the frequency of collision with other molecules in the liquid state and no well defined rotational frequencies are to be expected. But in spite of lack of unambiguous knowledge on such matters as internuclear distances and moments of inertia imposed by this handicap, it is still probable that since any changes in the energy states of molecules will be reflected in their spectra, valuable information may be obtained from spectral studies on the condition of molecules in liquids and on their interactions with their neighbors.

Our program included the investigation of the Raman spectra of the diatomic molecules HCl and HBr, and of the polyatomic molecules SO₂ and NH₃ in a number of nonionizing solvents and in a few ionizing solvents. At the same time it was realized that while the examination of the

Raman spectra might afford a quick and easy way of surveying the problem generally, the relatively small dispersion of the instruments available for this purpose kept precision low, and therefore, to confirm the Raman results with higher precision, as well as to observe any further phenomena which might exist, a detailed study has been made of the absorption spectra of HCl in a number of solvents in the near infrared by means of a grating spectrometer of high resolving power.

Woodward,¹ in the course of an investigation of the Raman spectra of solutions, had already examined the spectrum of HCl dissolved in carbon tetrachloride without observing any feature characteristic of HCl, a result he attributed to the low concentration of HCl in the solution he used. By using a temperature of -65°C we have prepared solutions of sufficient concentration to show the Raman line of the solute. Where the nature of the solvent permitted, the HCl concentration was determined by direct titration by means of standard alkali; in other cases solutions of given concentration were prepared with sufficient accuracy by measuring the volume of solvent and of solution in the calibrated Raman cell, assuming the volume of solution to be additive, and using the value of the density of liquid HCl at the temperature in question.²

HCl gas was prepared, with due precautions as to purity and dryness, (P₂O₅), by dropping concentrated sulphuric acid into concentrated hydrochloric acid. Hydrogen bromide was pre-

* A preliminary report of some of the experimental observations in this paper was made at the meeting of the American Chemical Society held in New York, April 1935.

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¹ L. A. Woodward, *Physik. Zeits.* **32**, 212 (1931).

² Landolt-Börnstein, *Tabellen*. II., p. 297.

pared by warming potassium bromide with phosphoric acid from which most of the water had been removed by boiling, freed from traces of bromine by means of moist red phosphorus, dried by P_2O_5 , condensed, fractionally distilled into a second receiver, from which it was distilled into the solvent. Special precautions were here necessary to avoid photo-oxidation during the exposure, as the resulting bromine absorbs the exciting and the scattered radiation. The air in the apparatus was displaced by oxygen-free nitrogen before the beginning of the generation. Sulphur dioxide and ammonia were obtained from commercial tanks.

The solutions were prepared by passing the gas into the solvent, contained in the Raman tube, 6" long, placed in a large Dewar containing dry ice; the temperature was kept at $-67^\circ \pm 3^\circ C$ by adjusting the supply of refrigerant. A 6" 220-volt mercury arc was focused on the cell, through a dilute iodine filter in CCl_4 to minimize the continuous radiation, and a potassium nitrite solution to absorb the ultraviolet. Two cameras were used in the spectrograph, one giving a dispersion of 270 cm^{-1} per mm, the other 90 cm^{-1} per mm at 4600A. Eastman Hyper Press Plates were used.

RESULTS

The results are summarized in Table I, in which D is the dielectric constant of the solvent,

ν is the Raman frequency, that is the wave number difference between the exciting and the incoherently scattered line, and $\Delta\nu/\nu$ the ratio of the difference in Raman frequencies of gas and solution to the Raman frequency of the gas. The Raman bands of HCl and HBr in solution are not sharp and in most solvents extend over some 30 cm^{-1} or more and some doubt exists as to which feature of the band should be measured. In HCl gas, for instance, the most intense feature of the Raman spectrum is the unresolved Q branch, the long wave limit of which represents the origin of the branch, but in liquids or solutions the nature of the spectrum is too little understood to justify our attaching a similar importance to the long wave limit. The Raman bands of HCl and HBr in solution are decidedly asymmetrical, with a maximum intensity nearer the long wave than the short wave edge and, somewhat arbitrarily, the measurements reported are for this maximum. Sulphur dioxide and ammonia have sharper and more symmetrical lines, and for these solutions the measurements refer to the centers of the lines.

In addition to the solutions listed in Table I, none of which conduct the electric current appreciably, certain electrically conducting solutions of HCl and HBr were examined. Along with all others who have reported the Raman spectrum of concentrated aqueous hydrochloric acid solutions we have found no feature in the spec-

TABLE I.

| SOLVENT | D | ν cm^{-1} | $\Delta\nu/\nu$ | SOLVENT | D | ν_1 | ν_2 | ν_3 | $\Delta\nu_2/\nu_2$ |
|----------------------------------|-------------|---------------------------|-----------------|------------------------------------------------|---------------------|--------------|-----------|--------------|-------------------------------|
| HCl SOLUTIONS | | | | NH ₃ SOLUTIONS ² | | | | | |
| HCl gas ¹ | | 2886 | | NH ₃ gas | | 3336 | | | |
| SiCl ₄ | 2.5 calc. | 2860 | -0.009 | Hexane | 1.8 | 3220 | 3315 | 3389 | -0.006 |
| PCl ₃ | 4.2 | 2828 | -0.020 | CHCl ₃ | 7.0 | 3211 | 3317 | 3382 | -0.006 |
| CHCl ₃ | 7.0 | 2826 | -0.021 | NH ₃ liquid ³ | 25.4 ₋₇₇ | 3210 | 3310 | 3380 | -0.008 |
| HCl liquid ¹ | 8.85(-90°C) | 2800 | -0.030 | CH ₃ OH(20°C) | 31 | 3207 | 3315 | 3389 | -0.006 |
| SO ₂ | 22.4 | 2798 | -0.031 | H ₂ O(20°C) | 80 | 3230 | 3311 | 3390 | -0.008 |
| C ₂ H ₅ Br | 14 | 2797 | -0.031 | | | ν_δ | ν_π | ν_σ | $\Delta\nu_\pi/\nu_\pi$ |
| CH ₃ CO.Cl | 20.3 | 2804 | -0.028 | | | | | | $\Delta\nu_\sigma/\nu_\sigma$ |
| HBr SOLUTIONS | | | | SO ₂ SOLUTIONS | | | | | |
| HBr gas ¹ | | 2559 | | SO ₂ gas ⁴ | | 525 | 1153 | 1361 | |
| CHCl ₃ | 7.0 | 2500 | -0.023 | C ₆ H ₅ .CH ₃ | 2.5 | | 1149 | 1342 | -0.003 |
| HBr liquid ¹ | 6.29(-80°C) | 2487 | -0.028 | CHCl ₃ | 7.0 | | 1153 | 1347 | -0.000 |
| C ₂ H ₅ Br | 14 | 2471 | -0.034 | HCl | 7.77 | | 1152 | 1345 | -0.000 |
| | | | | SO ₂ liquid | 22.4 | 522 | 1153 | 1346 | +0.001 |
| | | | | CH ₃ OH | 51.2 | 522 | 1147 | 1341 | -0.005 |
| | | | | H ₂ O(20°C) | 80(20°C) | | 1138 | 1342 | -0.013 |
| | | | | CH ₃ .COCl | 20.3 | | 1143 | 1329 | -0.009 |
| | | | | (CH ₃) ₂ CO | 28.9 | | 1138 | 1334 | -0.013 |

** See also W. West and P. Arthur, this journal 2, 215 (1924).

¹ E. O. Salant and A. Sandow, Phys. Rev. 37, 373 (1931).

² Cf. G. Jung and H. Gude, Zeits. f. physik. Chemie B18, 380 (1932).

³ P. Daure, Ann. d. Physik 12, 375 (1929).

⁴ C. R. Bailey, A. B. D. Cassie and W. R. Angus, Proc. Roy. Soc. A130, 133 (1930).

trum which can be identified with an HCl vibration, nor with an HBr vibration in hydrobromic acid solution. Long exposures on HCl in cold (-65°C) concentrated alcohol, and ether, and in acetic acid at room temperature were equally without result and it seems that even in concentrated solutions of HCl in these ionizing solvents not more than a small fraction of HCl can be left as diatomic molecules.

GENERAL RESULTS

All four of the solute molecules studied, when dissolved in nonionizing solvents, show Raman spectra of the same general type as the corresponding gases; that is they perform vibrations of about the same frequency as in the gaseous state. The vibrational frequency is diminished in solutions to a greater or less extent compared with that in the gas. In HCl and HBr solutions, there seems a definite connection between the frequency shift and the dielectric properties of the solvent; the relative shift, $\Delta\nu/\nu_{\text{gas}}$, increases with increasing dielectric constant of the solvent, reaching, however, a limiting value of about 0.03 in the hydrogen halides, at a solvent dielectric constant of about 14 beyond which increase in dielectric constant produces no further shift. The polyatomic molecules show several Raman frequencies which are differently affected by solutes.³ The shifts here are smaller than for the diatomic molecules; for SO_2 there is a trend toward greater shifts with increasing solvent dielectric constant, but with marked irregularities, particularly in the ionizing solvents methyl alcohol and water. In ammonia solutions, the relative shift in the vibration common to the gas and solution is small, nor do either our data on the Raman spectra nor the more complete data of Jung and Gude⁴ on the third, fourth and fifth overtones in absorption show any relation between the shift and the dielectric constant of the solvent.

It is of some interest to note how the different frequencies of SO_2 are affected by solvents. The three fundamental vibrations of this molecule are all active in the Raman spectrum, although the

slow "bending" frequency, ν_8 , in which the two oxygen atoms move symmetrically perpendicularly to the direction of the S—O bonds, is sometimes too feeble to measure. When observed, this frequency is very slightly altered by the solvent. ν_7 , the frequency of the symmetrical motion of the oxygen atoms along the bond direction while the sulphur moves symmetrically toward the oxygen, is less influenced by solvents than the corresponding antisymmetrical vibration ν_6 .

DISCUSSION

It will be observed that the change in frequency in passing from gas to solution is the same order of magnitude and may be numerically greater than the change in passing from a gas to the corresponding pure liquid. The solutions employed in the Raman investigation were relatively concentrated (mole fraction 0.2) and it is arguable that in the solvents of lower dielectric constant especially, the observed shift may largely have been attributable to the HCl itself. In fact, however, we shall show in the next paper that the shifts observed in the infrared absorption spectra of much more dilute solutions of HCl are within the limits of error the same as those observed in the Raman spectra whence we conclude that the shift, for the most part, is the result of solvent action on dissolved HCl molecules. It was very early noticed in Raman investigations that molecules possessing a permanent dipole undergo considerable diminution in vibrational frequency in changing from gas to liquid while those with no dipole moment are changed very little. For example, the vibrational frequencies of H_2 , O_2 , N_2 , CH_4 , CO_2 are almost the same in the gaseous and liquid states, while the liquefaction of HCl, HBr and HI is accompanied by a diminution of the vibrational frequency of about 3 percent of its value in the gas. It may be mentioned that we have found the frequencies of the nonpolar molecule CCl_4 to be unchanged on dissolving it in solvents of different dielectric constants. The diminution in frequency of polar molecules in solvents of high dielectric constant can probably therefore be correlated with the shift brought about by liquefaction, although in the latter case quantum-mechanical resonance effects may be superimposed on dielectric interaction. J. C.

³ Cf. A. F. Brodskii and A. M. Sack, this journal 3, 449 (1935).

⁴ G. Jung and H. Gude, Zeits. f. physik. Chemie B18, 380 (1932).

Kirkwood has given a theory capable of accounting for the essential observations in connection with frequency shifts in diatomic dipole molecules in solution, but as its discussion can be amplified from observations on the absorption spectra we shall postpone it to the next paper. Here we shall point out some qualitative conclusions of general interest which seem capable of being drawn from the observations.

In interpretation of the frequency shift it becomes important to settle the nature of the oscillator; i.e., whether it is an HCl molecule exposed to the fields of its neighbors or an oscillator in an associated $(\text{HCl})_n$ molecule or in a compound of HCl with solvent molecules. What physico-chemical data exist point to the existence of simple molecules in these solutions. Liquid hydrogen chloride itself seems largely to consist of simple molecules; its Trouton constant is nearly normal, although the Eötvös constant is lower than the normal value; and the equilibrium diagram for the $\text{HCl}-\text{SO}_2$ system shows no sign of a compound between these components. Although we have been unable to find complete equilibrium data for the other solvents, the low solubility, which does not differ greatly from the ideal, in these solvents is indicative of lack of compound formation.

If then we assume the reduced mass of the oscillator to be unaffected in solution, the diminution in vibrational frequency points to a diminution of force constant; the restoring force tending to prevent displacement of the H and Cl nuclei is diminished in solution by an amount, in the limiting case, of some 6 percent of its value in the gaseous state. It is also probable that this diminution of force constant is accompanied by an increase in the equilibrium internuclear distance; if the empirical rule of Morse, $\omega_0 r^3 = \text{constant}$, is applicable to HCl in the gaseous and dissolved states, the internuclear distance at equilibrium will increase from 1.279 Å in the gas to 1.292 Å in solution of high dielectric constant.

It may be noticed that there is a certain resemblance between the effects of dielectric interaction on simple polar molecules which we have deduced as existing from the observed action of

the solvent on the vibrational frequency, and the well-known effect of the dielectric constant of a solvent in diminishing the force of attraction between oppositely charged ions, postulated by J. J. Thomson and W. Nernst in explanation of the high ionizing power of solvents of high dielectric constant. But an essential result of the spectral observations is that the diminution in interatomic attraction caused by dielectric action on dissolved dipoles cannot exceed a value of, in the hydrogen halides, about 6 percent of the attractive force prevailing in the isolated molecule, however high the dielectric constant, i.e., no process of dissociation in these molecules can occur by purely electrostatic actions, and when electrolytic dissociation of HCl does actually occur, other actions must be in play. It is well known, of course, that HCl functions as a good electrolyte in ether ($D=4.3$ at 20°C) whereas in solvents of much higher dielectric constant, which contain no atom capable of combining with a proton, as nitromethane ($D=39.4$ at 20°) it is a nonelectrolyte.⁵ Although then our experiments throw no light on the mechanism of ionization of HCl in solution except insofar as they show what does not happen, our interpretation of the frequency shift in these solutions is in accord with those views of the electrolytic dissociation of HCl which see as the essential process the association of a hydrogen ion to some atom in the solvent molecule, usually the oxygen atom, by a definite homopolar chemical bond. Moreover, in the usual solvents in which HCl does act as an electrolyte, water, ether, alcohols, the absence of HCl Raman lines, and more conclusively, because of lower concentrations of HCl required for detection in absorption, the absence of infrared absorption bands of HCl, indicate that even in very concentrated solutions the electrolytic equilibrium is characterized by an almost complete absence of molecules of HCl.

⁵ We have observed a Raman line in nitromethane solutions of HCl, displaced as in other solutions of high dielectric constant. As however, slow precipitation of a crystalline compound takes place from this solution, we have not included the frequency in our discussion, though, in fact, it behaves quite normally.