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LETTERS TO THE EDITOR

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Raman Spectra of HCl in Non-Ionizing Solvents

In the course of study of the nature of dissolved molecules we have investigated the Raman effect of HCl dissolved in various solvents. The results here communicated are for the vibration frequency of HCl in some non-ionizing solvents. Woodward¹ has reported his inability to observe the Raman spectrum of HCl dissolved in carbon tetrachloride, benzene and xylene, pointing out, however, that the negative result was probably to be ascribed to the low solubility of HCl in these solvents. This difficulty we have circumvented by the obvious device of examining the scattered spectra at a temperature at which the solubility of HCl in the various solvents was adequate, the mol. fraction of HCl in the solutions being about 0.2 and the temperature -65°C . By ν in Table I is indicated the frequency difference between the exciting line (Hg 4047) and the long wave side of the HCl band, which, if the latter is an unresolved Q branch with the same relation of rotational lines as in the gas, corresponds approximately to the vibrational frequency of the molecule in the lowest state. $\Delta\nu$ describes the difference between ν in solution and ν observed by Wood and Dieke and by Salant and Sandow for the gas (2886).

TABLE I.

Solvent	Electric moment $\times 10^{18}$	Diel. Const. at -65°	ν cm^{-1}	$\Delta\nu$
Silicon tetrachloride	0		2860	26
Phosphorus trichloride	0.90	10.3	2824	62
Chloroform	1.03	7	2826	60
HCl liquid (Salant and Sandow) ²	1.08	8.8(-90°C)	2800	86
Sulphur dioxide	1.63	25	2798	88
Ethyl bromide	1.83	14	2797	89
Acetyl chloride	2.7	20.5	2804	82

The electric moments listed are for the solvents in the gaseous state or in dilute solution in nonpolar solvents. When ν is plotted against the electric moment of the solvents, a straight line is obtained, within the accuracy of the measurement of ν , $\pm 5 \text{ cm}^{-1}$, up to the value of μ for

ethyl bromide. It is not at all surprising that the shift in frequency should cease to be proportional to the electric moment of solvent molecules of high electric moment as measured in the attenuated state, for it is well known that the polarization of complicated molecules of large electric moment may diminish very markedly with concentration. The approximate proportionality of the frequency shift with the electric moment of the molecules of the solvent would seem to indicate that a large part of the shift is due to dipole interactions between solvent and solute molecules, and as the frequency of liquid HCl is of the same order as in solvents of the same electric moment as HCl, the shift between gas and liquid in this case can also be largely attributed to dipole action, as indeed is suggested by the fact that the frequency difference between gas and liquids for the nonpolar mols H_2 , O_2 , N_2 , CH_4 is much smaller than for polar molecules.

The results have some bearing on the nature of the ionization process in HCl molecules. The diminution in vibration frequency with increasing dipole moment of the solvent indicates a diminution of the force constant for the vibration, i.e., a diminution of the strength of binding between the hydrogen and chlorine nuclei. The HCl molecule in a polar environment may be regarded in a state of incipient dissociation, and the diminution of binding strength is in a sense the effect recognized by Nernst and J. J. Thomson in their correlation between ionizing power and the dielectric constant of solvents; but it is also very obvious from our results that electrolytic dissociation by pure dipole interaction would require a solvent of enormously greater electric moment than any yet found. Where electrolytic dissociation of HCl actually occurs in the solvents in what it has been observed, many of which, like water, alcohol, ether, have electric moments lower than some of these investigated by us, the essential process is probably, as has often been stated, the attach-

¹ Woodward, Phys. Zeits. **32**, 777 (1931).

² R. W. Wood and G. H. Dieke, Phys. Rev. **35**, 1355 (1930); E. O. Salant and A. Sandow, Phys. Rev. **37**, 373 (1931).

ment of a H^+ by valence forces to the oxygen atom of the solvent molecules.

It is also of some interest to inquire if the increase of the electric moment of HCl from a value of 1.08×10^{-18} e.s.u. in the gas to about 1.3×10^{-18} in benzene, hexane and carbon tetrachloride, reported by F. Fairbrother³ could be accounted for by the stretching of the molecule in solution.

Assuming the constancy of the expression νr^2 where r is the internuclear distance, one finds that the greatest change in ν , in highly polar solvents, corresponds to an increase in r of some 3 percent and in nonpolar solvents it would be much less. An increase of 20 percent, to 30

percent in the electric moment of HCl dissolved in non-polar solvents cannot be attributed to the elongation of the molecule which takes place on solution.

The investigation is being extended to the other hydrogen halides both by the study of Raman and infrared spectra.

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February 20, 1934.

³ F. Fairbrother, J. Chem. Soc., p. 43 (1932).

On the Calculation of the Probability of the Spontaneous Decomposition of Linear Triatomic Molecules

In his paper *Lifetimes of Unstable Molecules*,¹ N. Rosen has calculated the probability of spontaneous decomposition of the "quasi-molecule" HO_2 into the molecule O_2 and atom H.

His method of calculation is as follows: When we treat the molecule HO_2 as linear, the wave equation of the system may be represented in the following form:

$$\left\{ -\frac{\hbar^2}{8\pi^2} \left[\frac{1}{\mu_1} \frac{\partial^2}{\partial r_1^2} + \frac{1}{\mu_2} \frac{\partial^2}{\partial r_2^2} - \frac{2}{m_2} \frac{\partial^2}{\partial r_1 \partial r_2} \right] + V_1(r_1) + V_2(r_2) \right\} \times \psi(r_1, r_2) = E\psi(r_1, r_2), \quad (1)$$

where $r_1 = x_2 - x_1$, $r_2 = x_3 - x_2$ (x_1 , x_2 and x_3 are the distances of atoms m_1 , m_2 and m_3 from a certain fixed point), $\mu_1 = m_1 m_2 / (m_1 + m_2)$, $\mu_2 = m_2 m_3 / (m_2 + m_3)$ and $V_1(r_1)$, $V_2(r_2)$ are the potential energies of the two end-atoms with the middle one (the interaction between the end-atoms is neglected).

The term,

$$T = (\hbar^2 / 4\pi^2 m_2) (\partial^2 / \partial r_1 \partial r_2) = (1/m_2) p_1 p_2 \quad (2)$$

is considered by Rosen as the perturbation energy; in this case the variables in the Eq. (1) can be separated and the probability of spontaneous decomposition of the molecule is defined in the usual way through the matrix elements of (2).

The perturbation method can be applied, however, only in that case, when the matrix elements of the perturbation energy are sufficiently small compared with the energy differences of the states under consideration, i.e., when:

$$|T_{n, n^1}| \ll |W_n - W_{n^1}|. \quad (3)$$

For the sake of simplicity we approximate the wave functions of the unperturbed problem referring to the discrete states by the wave functions of two harmonic oscillators (which is certainly valid for not too large values of the quantum numbers, n_1 and n_2). The nonvanishing

matrix elements of the perturbation energy are in this case those corresponding to transitions $n_1 \rightarrow n_1 \pm 1$, $n_2 \rightarrow n_2 \pm 1$. We shall restrict ourselves to the case of two opposite jumps corresponding to the smallest values of the difference $W_n - W_{n^1}$. We get in this case:

$$\begin{aligned} T_{n_1 n_1^1; n_2, n_2^1} &= (1/m_2) p_{n_1, n_1^1; n_2, n_2^1} \\ &= \hbar A [n_1(n_2+1)]^{\frac{1}{2}}, \text{ if } n_1^1 = n_1 - 1, n_2^1 = n_2 + 1 \\ &= \hbar A [n_2(n_1+1)]^{\frac{1}{2}}, \text{ if } n_1^1 = n_1 + 1, n_2^1 = n_2 - 1, \end{aligned}$$

where $A = (1/2m_2)(\mu_1 \mu_2 \nu_1 \nu_2)^{\frac{1}{2}}$, ν_1 and ν_2 being the frequencies of the respective bonds. The condition (3) assumes the following form:

$$\left. \begin{aligned} A[n_1(n_2+1)]^{\frac{1}{2}} &\ll |\nu_1 - \nu_2| \\ A[(n_1+1)n_2]^{\frac{1}{2}} &\ll |\nu_1 - \nu_2| \end{aligned} \right\} \quad (3')$$

Now it can easily be seen that this condition is *not* fulfilled either for the "quasi-molecule" HO_2 or for linear triatomic molecules known.

For the "quasi-molecule" HO_2 we have $A = 0.6 \times 10^{13}$, $|\nu_1 - \nu_2| = 6 \times 10^{13}$ for the values of n ($n_1 = 4, 3, 2, 1$; $n_2 = 16, 17, 19, 21$) used by Rosen both sides of the inequality (3') are of the same order of magnitude. For the molecule N_2O , we have: $A > |\nu_1 - \nu_2|$, ($A = 1.63$; $|\nu_1 - \nu_2| = 1.36$). For the symmetrical molecules CO_2 and CS_2 $|\nu_1 - \nu_2| = 0$, the term $A[n(n+1)]^{\frac{1}{2}}$ is, however, > 0 .

It follows that by dropping in Eq. (1) the "perturbation energy" (2) we do not obtain any approximations to the actual stationary states of the molecules, so that Rosen's perturbation method cannot be applied.

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February 8, 1934.

¹ N. Rosen, J. Chem. Phys. 1, 319 (1933).