

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

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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  $1.08 \times 10^{-18}$  e.s.u. in the gas to about  $1.3 \times 10^{-18}$  in benzene, hexane and carbon tetrachloride, reported by F. Fairbrother<sup>3</sup> could be accounted for by the stretching of the molecule in solution.

Assuming the constancy of the expression  $\nu r^2$  where  $r$  is the internuclear distance, one finds that the greatest change in  $\nu$ , 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.

<sup>3</sup> 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*,<sup>1</sup> 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  $A = (1/2m_2)(\mu_1 \mu_2 \nu_1 \nu_2)^{\frac{1}{2}}$ ,  $\nu_1$  and  $\nu_2$  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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<sup>1</sup> N. Rosen, J. Chem. Phys. 1, 319 (1933).