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The Double Minimum Problem Applied to Potassium Hydrogen Fluoride

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The doublet character of the infra-red absorption line at 2.67μ of solid potassium hydrogen fluoride is due to the "tunnel effect." The proton has two potential minima between the fluorine nuclei in the FHF^- ion. The distance of a minimum to the center of the ion is 0.26\AA . The height of the potential hill is $33,400$ calories.

THE infra-red absorption line of solid potassium hydrogen fluoride at 2.67μ has been found to have doublet character by Buswell, Maycock, and Rodebush.¹ The two lines are located at 2.649μ (3775.0 cm^{-1}) and 2.729μ (3664.4 cm^{-1}). Buswell *et al.* suggested that this doublet nature might be due to the "tunnel effect" on the supposition that the proton may oscillate between two potential minima located between the two fluorine nuclei and equidistant from a plane at right angles to the figure axis of the FHF^- ion at its midpoint.

A similar case in the ammonia molecule has been studied by several authors²⁻⁴ with a variety of potential energy expressions. The values of the total energy given by Wall and Glockler have been applied to the present case, after having solved them for all possible values of the parameter q . This quantity is given by

$$q^2 = (4\pi^2\mu\nu_0 l^2)/h, \quad (1)$$

where μ is $(1/38 + 1/1.008)$ or 0.982 , ν_0 is the average fundamental frequency (3719.7 cm^{-1}), l is the distance from the center of the ion to the

potential minimum, and h is Planck's constant. For the purpose of calculation the following abbreviations have been used:

$$A = 4q^2/(\pi)^{\frac{1}{2}} \int_0^{-q} \exp(-n^2) dn;$$

$$B = 4/(\pi)^{\frac{1}{2}} q \cdot \exp(-q^2);$$

$$C = \exp(-q^2);$$

$$D = (1 - 2q^2) \exp(-q^2).$$

$$W_{OS}/h\nu_0 = \frac{1}{2}[1 + (2q^2 - A - B)/(1 + C)]; \quad (2)$$

$$W_{OA}/h\nu_0 = \frac{1}{2}[1 + (2q^2 - A)/(1 - C)]; \quad (3)$$

$$W_{IS}/h\nu_0 = \frac{3}{2}[1 + (2q^2 - A - Bq^2)/(3 - 3D)]; \quad (4)$$

$$W_{IA}/h\nu_0 = \frac{3}{2}[1 + (2q^2 - A - 2B + Bq^2)/(3 + 3D)]. \quad (5)$$

The calculated values are shown in Fig. 1. The doublet separation is given by

$$\Delta h\nu_0 = W_{IA} - W_{IS} + W_{OA} - W_{OS} \quad (6)$$

and is plotted as a function of q in Fig. 2. From this graph a value of q can be found from the experimental doublet separation $\Delta h\nu_0/h\nu_0 = (3775.0 - 3664.4)/3719.7 = 0.03$. In the present case q is 2.7 . From Eq. (1), which can be written

$$l = 5.805q/(\mu\nu_0)^{\frac{1}{2}}, \quad (1a)$$

the distance (l) from the center to the potential minimum is found to be 0.26 angstrom .

¹ A. M. Buswell, R. L. Maycock, and W. H. Rodebush, *J. Phys. Chem.* **8**, 362 (1940).

² F. Hund, *Zeits. f. Physik* **43**, 805 (1927).

³ D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

⁴ See F. T. Wall and G. Glockler, *J. Chem. Phys.* **5**, 314 (1937) for further literature references.

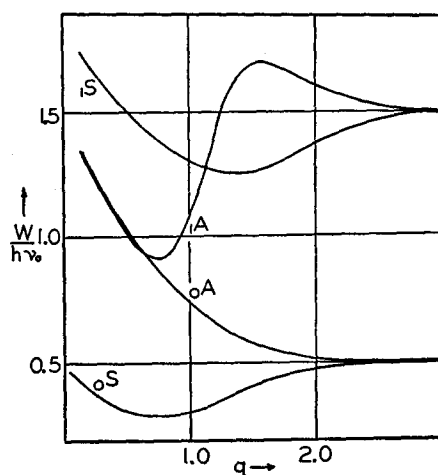


FIG. 1. Energy states (W) for double minimum problem. S =symmetric and A =antisymmetric levels; ν_0 =fundamental frequency; q =coordinate. (Applicable for values of the parameter q greater than about 2.)

In order for the whole consideration to be valid this distance must check reasonably well with the dimensions of the FHF^- ion as obtained from other sources. The following information has been found on the size of this ion. Bozorth⁵ studied the diffraction of x-rays from potassium hydrogen fluoride and found the $\text{F}-\text{F}$ distance to be 2.25 angstroms. He could not obtain the $\text{H}-\text{F}$ distance since protons usually do not scatter x-rays sufficiently to be observed. The distance from the center of the ion to a fluorine nucleus is then 1.13Å. Another value may be obtained from the application of the theory of small vibrations to the triatomic FHF^- ion. The line at 2.67μ is considered to be the asymmetric frequency:

$$\nu_3 = [(k \cdot p)/m]^{\frac{1}{2}} = 3719.7 \text{ cm}^{-1},$$

where k =force constant, m =mass of fluorine atom, M =mass of hydrogen, and $p = (2m + M)/m$. The simple valency force field has been used.⁶ The force constant calculated is 0.4 megadyne per cm. An application of Badger's rule⁷ to the hydrides of the first row of the periodic table shows that the rule holds very well and permits the calculation of the $\text{H}-\text{F}$ distance in FHF^- from the force constant. The value⁸ obtained is

⁵ R. M. Bozorth, J. Am. Chem. Soc. **45**, 2128 (1923).
⁶ K. W. F. Kohlrausch, *Der Smekal-Raman Effekt (Ergänzungsband)* (Julius Springer, Berlin, 1938), p. 64.
⁷ R. M. Badger, J. Chem. Phys. **2**, 128 (1934); **3**, 710 (1935).
⁸ Unpublished results.

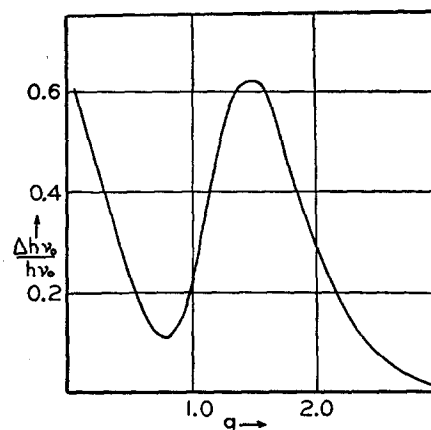


FIG. 2. Doublet separation in tunnel effect. ν_0 =fundamental frequency; q =coordinate. (Applicable for values of the parameter q greater than about 2.)

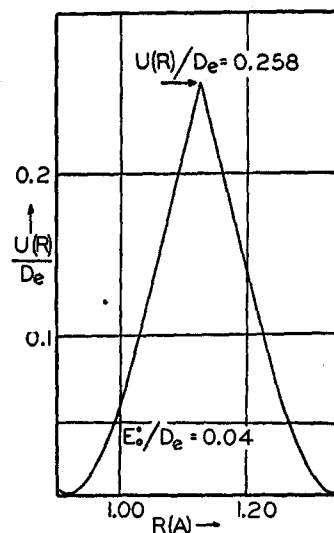


FIG. 3. Two Morse curves for HF. The F atom centers are 2.25Å apart as in FHF^- . $D_e = 6.4$ ev.

1.15Å which is, however, the distance from the center of the ion to a fluorine nucleus, because it is assumed in the application of the theory of small vibrations that the hydrogen atom resides midway between the fluorine nuclei and nothing in this calculation indicates two potential minima. Hence the half-distance between the fluorine atoms is 1.13Å from crystal structure study and 1.15Å from spectroscopy via the theory of small vibrations. The average of 1.14Å will be taken for the next consideration. Since the distance from the center of the ion to the potential minimum has been estimated to be 0.26Å, the $\text{H}-\text{F}$ distance is 0.88Å. This value does not seem unreasonable when compared with the $\text{H}-\text{F}$ distance in monomeric hydrogen

fluoride, 0.92A, obtained from its band spectroscopy.⁹ Another way of making the comparison is to say that the distance (l) from the ion center to the potential minimum would be 0.22A (1.14–0.92) if the proton remains at the same equilibrium distance from the fluorine nucleus in the FHF⁻ ion as in HF. These various possibilities are summarized in Table I. It appears that these values check sufficiently well to warrant the belief that the doublet under consideration is due to the "tunnel effect." It is to be expected in FHF⁻ and a further calculation of the potential hill also favors this view. The height of the potential barrier can be obtained from

$$V_{x=0} = \frac{1}{2}(h\nu_0 q^2) = 38,750 \text{ cal./mole,}$$

with $\nu_0 = 3719.7 \text{ cm}^{-1}$ and $q = 2.7$. The zero-point energy is one-half the fundamental frequency ν_3 multiplied by Planck's constant and amounts to 5316 calories. The barrier has a value of 33,400 calories. This quantity can be compared with the potential hill formed when two Morse curves for HF are approached in such a

⁹ G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 488.

TABLE I.

		Distance	Remarks
<i>a</i>	$\frac{1}{2}$ (F-F)	1.13A	Crystal structure of KHF ₂
<i>b</i>	H-F	1.15	$k = 0.4$ megadyne/cm from 3719.7 cm ⁻¹ and Badger's rule (Really $\frac{1}{2}$ (F-F) distance!)
<i>c</i>	$\frac{1}{2}$ (F-F)	1.14	Average: <i>a</i> and <i>b</i>
<i>d</i>	H-F	0.92	In HF monomer (band spectra)
<i>e</i>	l	0.22	<i>c</i> minus <i>d</i>
<i>f</i>	l	0.26	Tunnel effect
<i>g</i>	H-F	0.88	HF distance in FHF ⁻ ; <i>c</i> minus <i>f</i> .

way as to make the F-F distance 2.25A (see Fig. 3). The height calculated is 38,065 calories/mole. For the Morse curve¹⁰ the data on HF given by Herzberg⁹ were used. The heat of dissociation of HF is 6.4 ev and $\omega_e = 4141.305 \text{ cm}^{-1}$. The zero-point energy is calculated to be 5918 cal./mole. Hence the potential hill intervening is 32,150 calories/mole. This height is of the same order as the barrier in FHF⁻ as was to be expected. The problem of the FHF⁻ ion has been discussed by Pauling.¹¹

¹⁰ Reference 9, pp. 108–9.

¹¹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition, chapter 9.

The Elimination of Errors due to Electrode Polarization in Measurements of the Dielectric Constants of Electrolytes

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An investigation was made of the errors resulting from electrode polarization in measurements of the dielectric constants of solutions containing electrolytes. The applicability of two methods, one used by Fricke and Curtis and the other by Oncley, to eliminate these errors, was considered. There is introduced a modification of Oncley's method, which was found applicable at higher electrolyte concentrations than Oncley's method. The relative effectiveness of the modified method and that of Fricke and Curtis was tested by employing the two methods to correct experimental data obtained for aqueous solutions of glycine containing various amounts of electrolytes. The measurements were made at frequencies ranging from 10 to 5000 kc, and at conductivities ranging from 0.29×10^{-4} to $1.74 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$. The corrected values of the dielectric constant were compared with known values in the literature and found to be in good agreement. The limitations of the methods are considered and the usefulness of the methods in cases where the dielectric constant varies with frequency is discussed.

I. INTRODUCTION

THE polarization of dielectric constant cell electrodes is an important source of error in the determination of the dielectric properties

of dilute electrolyte solutions. This phenomenon becomes increasingly important as the frequency is lowered and as the conductivity of the solution is raised. Where precise dielectric constant