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In dilute nitrobenzene solution, Fig. 6, the phenolic OH band appears at wave-lengths only slightly longer than it does in dilute benzene solution. In view of this fact one may predict that the hydrogen bridges between phenol and nitrobenzene, if indeed they form at all, are rather weak. Some may prefer to think of this, as well as the other cases of hydrogen bonding dis-

cussed here, not as the formation of definite complexes but merely as a special orientation of the molecules due to proton attraction.

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Potential Energy Curve of the Excited State of LiH

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A method developed by Klein has been applied to obtain the potential energy curve of the excited electronic state of LiH (state V). This curve crosses the Coulombic curve of Li^+H^- and indicates dissociation of excited LiH into $\text{Li}(^2P) + \text{H}$. The effect of this behavior on Mulliken's explanation of the unusual shape of the state V curve is discussed. The interaction of the Li^+H^- and $\text{Li}(^2P) \cdot \text{H}$ curves at moderately large interatomic distances is larger than Mulliken's estimate.

A PROCEDURE for obtaining the potential curve of a diatomic molecule to a sufficient degree of approximation and without the expenditure of an undue amount of time is highly desirable. The power series expansion in terms of the displacement of the atoms from their equilibrium position converges poorly for even moderately large displacements. While the Morse function is probably a fairly good approximation for most curves, for some abnormal ones, such as the curve considered here, it is useless and attempts to modify it can scarcely be expected to offer much improvement. Other types of potential functions have been suggested, but these frequently involve so many parameters that their applications are limited.

O. Klein¹ has given a semi-graphical method for obtaining the curve of a molecule directly from its observed energy levels. So far as the author is aware, this method has been applied only by Rydberg.² Since Rydberg has published no details of the application of the Klein method, it may be appropriate to discuss it somewhat fully.

¹ O. Klein, *Zeits. f. Physik* **76**, 226 (1932).

² R. Rydberg, *Zeits. f. Physik* **80**, 514 (1933).

Klein derives the following equation on the basis of classical mechanics:

$$S(U, \kappa) = \frac{1}{\pi(2\mu)^{1/2}} \int_0^{I'} (U - E(I, \kappa))^{1/2} dI,$$

in which U is a suitable value of the potential energy of the molecule, $E(I, \kappa)$ represents the energy of vibration and rotation as a function of the action variable I and the quantity κ (equal to $P^2/2\mu$), P is the angular momentum of the molecule, μ is its reduced mass, and I' is that value of I for which $U = E$. As Klein suggests, it is probably a good approximation to replace I and κ by their quantum-mechanical equivalents, $(v + \frac{1}{2})h$ and $(K(K+1)h^2)/(8\pi^2\mu)$. The maximum and minimum values of the interatomic distance for a molecule vibrating with the energy U are then given by

$$r_1, r_2(U) = (f/g + f)^{\pm 1/2},$$

in which $f = (\partial S / \partial U)$ and $g = -(\partial S / \partial \kappa)$. With r_1 and r_2 known for each of a series of U values, the curve for U as a function of r can be plotted. If the $U(r)$ curve for the rotationless state is wanted, the values $f = (\partial S / \partial U)_{\kappa=0}$ and $g = -(\partial S / \partial \kappa)_{\kappa=0}$ are to be used.

The quantity S for a given value of U and κ is obtained by plotting $(U-E)^{\frac{1}{2}}$ (computed from the set of observed energy levels) against I and then determining the value of the area under the curve by numerical integration. The values of S for a series of values of U with κ constant are plotted against U and the quantity f is found from the slope of this curve at any desired value of U . To get g , the values of S for a particular value of U are plotted against κ and the slope at the desired κ value is measured.

APPLICATION TO STATE V OF LiH

This method has been applied to the determination of a portion of the potential energy curve of the excited state (state V) of LiH. The excellent data of Crawford and Jorgenson³ were used. Unfortunately these data do not extend to energy levels high enough to permit the drawing of the curve near the dissociation energy. It was found that the curves of $(U-E)^{\frac{1}{2}}$ against I for $K=0$ and $K=2$ lie so close together even on a large scale plot that simple subtraction of one area from another was not precise enough. Accordingly the difference curve was plotted and integrated for each value of U which was used. The graph of S against κ was found to be a straight line for values of κ corresponding to small values of the rotational quantum number. Therefore $\Delta S/\Delta \kappa$ was substituted for $(\partial S/\partial \kappa)_{\kappa=0}$ in finding g . An error of 5 percent in g produces an error of only 1 percent in the value of r_{\max} and of less than 2 percent in r_{\min} . An error of 5 percent in f leads to one of 4 percent in r_{\max} and of 3 percent in r_{\min} . It is believed that the amplitudes of vibration here obtained are correct to within $\pm 0.03\text{\AA}$. For the two highest U values

TABLE I.

U (ev)	r_{\max} (\AA)	r_{\min} (\AA)
0.157	3.66	1.76
.189	3.76	1.74
.277	3.99	1.61
.410	4.25	1.51
.471	4.41	1.49
.519	4.47	1.45
.566	4.58	1.44
.614	4.75	1.45
.660	4.94	1.46

³ Crawford and Jorgenson, Phys. Rev. **47**, 932 (1935).

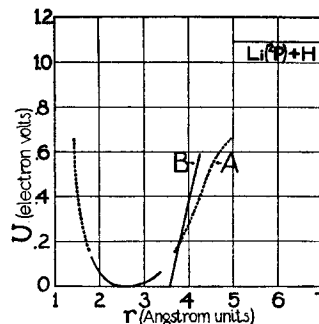


FIG. 1. Dotted part of curve A is portion obtained in present work; solid part is from series expansion of Crawford and Jorgenson (reference 4). Curve B is Coulombic curve of Li^+H^- (reference 5).

used in constructing the $U(r)$ curve, it appears likely that the r values are about 0.03\AA too large, since the computed r_{\min} values fall to the right of a reasonable extrapolation of the lower part of the left branch of the curve.

RESULTS AND DISCUSSION

The results of this application of the Klein method to state V of LiH are summarized in Table I and Fig. 1. The lower, solidly-drawn part of the curve was drawn by use of the series expansion given by Crawford and Jorgenson.⁴ The series expansion is most reliable in the region of small vibrational quantum numbers; it has been used here because the Klein method breaks down in just this region due to the small number of energy levels available. It will be observed that the upper and lower parts of the curve fit together excellently.

The chief point of interest about this curve is its unusual shape. It is an exceptionally flat curve which rises on both sides of the equilibrium interatomic distance faster than the osculating parabola. This behavior has been explained by Mulliken⁵ as the result of an interaction between two hypothetical unperturbed curves of which one is the Coulombic curve of Li^+H^- . This interaction was considered to be of such a nature that the resultant state V curve should not cross the Coulombic curve but should approach it asymptotically for moderately large values of r , as illustrated in Fig. 1 of reference 5. In this event the region in which the state V curve and

⁴ Crawford and Jorgenson, Phys. Rev. **49**, 745 (1936).

⁵ Mulliken, Phys. Rev. **50**, 1028 (1936).

the Li^+H^- curve reach the same slope should furnish the basis for an estimate of the dissociation energy of the normal state, since the energy difference between states V and N is known precisely from the spectroscopic data. From a rough estimate of the point at which the slope of the state V curve is closest to that of the Coulombic curve, the state N curve should be lifted with respect to its asymptote by about 0.2 ev above Mulliken's estimate of its position. This would make the dissociation energy of normal LiH about 2.3 ev.

According to the present computations, however, the state V curve is flatter at moderately large r values than Mulliken supposed, and must actually cross the Li^+H^- curve, apparently going to $\text{Li}(^2P)+\text{H}$. If Mulliken's value of 0.75 ev for the height of the state V curve above $\text{Li}(^2S)+\text{H}$ is accepted as a reasonable estimate, the crossing point is in the neighborhood of 3.8Å. This shows that the interaction of the Li^+H^- curve with the unperturbed $\text{Li}(^2P)\cdot\text{H}$ curve is much more intense near 5Å than is indicated by Fig. 2 of reference 5, so that state V dissociates quite definitely into $\text{Li}(^2P)+\text{H}$. Aside from this

quantitative change at large r values, the present results give no reason for altering Mulliken's interpretation of the nature of state V . The position of the Coulombic curve seems to make it unavoidable that state V be predominately of Li^+H^- character over a range of moderately large r values before it goes over into $\text{Li}(^2P)+\text{H}$.

These conclusions, unfortunately, do not help to fix a precise value of the dissociation energy of the normal state, a quantity which is particularly interesting because the values proposed for it are considerably below that required by Pauling's additivity rule.⁶ The value of 2.5 ev adopted by Mulliken is still a reasonable one and is compatible with the portion of the potential energy curve which has here been obtained. But the basis on which this value was reached has been made less certain. It may be said, however, that from the rate at which the state V curve beyond its inflection point is bending, a value less than 2.6 ev is more likely than a larger one.

I wish to record my thanks to Professor Mulliken for many valuable discussions.

⁶ Pauling, J. Am. Chem. Soc. **54**, 3570 (1932). This situation is discussed by Mulliken in reference 5.

The Low Temperature Heat Capacity of Gaseous Ethane

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The heat capacity of ethane has been determined at 163° and 143°K by the "hot wire" method and has been found not to level off as suggested earlier by Eucken and Weigert. This speaks against free interval rotation in ethane molecules.

SOME time ago Eucken and Weigert¹ employed the "hot wire" technique, devised by Schleiermacher² and since used repeatedly by others, to measure the heat capacity of ethane down to very low temperatures. The most significant result of this work was the observation that at the lowest temperature studied, *ca.* 140°K, the heat capacity curve of ethane gave indications of leveling off appreciably above the

classical value, $3R$, for the heat capacity due to rotation and translation. Quantum statistical calculations of Teller and Weigert³ showed that this behavior was to be expected if only a small hindrance to free internal rotation of the methyl groups in ethane was postulated. Eucken and Weigert concluded that a restraining potential of *ca.* 300 cal./mole fitted their observations best, meaning that at room temperature the methyl groups in an average ethane molecule are freely rotating.

¹ Eucken and Weigert, Zeits. f. physik. Chemie **B23**, 265 (1933).

² Schleiermacher, Wied. Ann. **26**, 287 (1886).

³ Teller and Weigert, Nachr. Götting. Ges. **218** (1933).