

## The Nature of the Hydrogen Bond in KHF<sub>2</sub>

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and lithium in a sealed iron container. Only three of eighty cylinders tried withstood the temperature of a red heat. These conditions, inadequate to transform graphite to diamond, might conceivably have produced diamond directly by a process of polymerization.

Parsons,<sup>4</sup> in his Bakerian lecture to the Royal Society of London, states that he tried to repeat Hannay's work, but in the very long list of experiments described at the end of his paper he gives very few details about these particular experiments. With the improved facilities now available it would seem worth while to try to check and possibly to extend Hannay's work. In addition to the light paraffins previously used, other substances possessing more of the diamond structure such as derivatives of methane III,<sup>1-3</sup> cyclopropane,<sup>5</sup> and tricyclo (3.3.1.1).<sup>6</sup> decane (adamantane) might repay investigation along these lines.

<sup>1</sup> P. W. Bridgman, *J. Chem. Phys.* **15**, 92 (1947); P. L. Gunther, P. Geselle, and W. Reberich, *Zeits. f. anorg. allgem. Chem.* **250**, 357 (1943).

<sup>2</sup> J. B. Hannay, *Proc. Roy. Soc. (London)* **30**, 188 (1880).

<sup>3</sup> F. A. Bannister and K. Lonsdale, *Mineralog. Mag.* **26**, 309 (1943).

<sup>4</sup> C. A. Parsons, *Phil. Trans.* **A220**, 67 (1919).

<sup>5</sup> M. Beesley and J. Thorpe, *J. Chem. Soc.* **117**, 602 (1920); see also A. M. Patterson and L. Capell, *The Ring Index* (Reinhold Publishing Corporation, New York, 1940), p. 172, Compound 1191.

<sup>6</sup> W. Nowacki, *Helv. Chim. Acta* **28**, 1233 (1945); see also A. M. Patterson and L. Capell, *The Ring Index* (Reinhold Publishing Corporation, New York, 1940), p. 275, Compound 2034.

## The Nature of the Hydrogen Bond in $\text{KHF}_2$

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THE discovery of the residual entropy of ice at low temperatures, and its explanation in terms of a double minimum potential curve for the proton in the O—H—O hydrogen bond,<sup>1</sup> raised the question whether F—H—F system also had a double minimum potential curve. We had undertaken to answer this question by measuring the entropy of  $\text{KHF}_2$  by heat capacity measurements from low temperatures and from the reaction  $\text{KF}(s) + \text{HF}(g) = \text{KHF}_2(s)$ . This work was interrupted in 1943 and is only now being completed. However, the heat capacity curve for  $\text{KHF}_2$  was finished. In the interval the excellent measurements of Ketelaar<sup>2</sup> on the infra-red absorption and reflection spectra of  $\text{KHF}_2$  have become available to us. These more complete spectra make untenable the earlier postulate of Buswell, Maycock, and Rodebush,<sup>3</sup> which was followed by Glockler and Evans.<sup>4</sup> However, our heat capacities are not consistent with Ketelaar's explanation of his data. We wish to propose the following interpretation of all these data.

Solid  $\text{KHF}_2$  shows absorption and reflection peaks at 1450 and 1222  $\text{cm}^{-1}$  which are so much stronger than all others as to virtually assure the correctness of their assignment as fundamentals. The  $\text{HF}_2^-$  ion should have two infra-red active fundamentals,  $\nu_3$ , where the proton moves along the F—F line, and  $\nu_2$ , where the proton moves perpendicularly to the F—F line. The latter is degenerate. Also there is the inactive fundamental,  $\nu_1$ ,

which is a symmetrical F—F vibration. Ketelaar felt that the two observed peaks were too close together to be the two active fundamentals and that  $\nu_2$  would be "much lower than 600  $\text{cm}^{-1}$ ." Hence he assigned the 1450 and 1222  $\text{cm}^{-1}$  peaks to a doubling of  $\nu_3$  because of a double minimum potential curve. This is not possible because it would lead to a peak in the heat capacity curve near 20°K which is definitely not present<sup>5</sup> (see Fig. 1). Consequently,

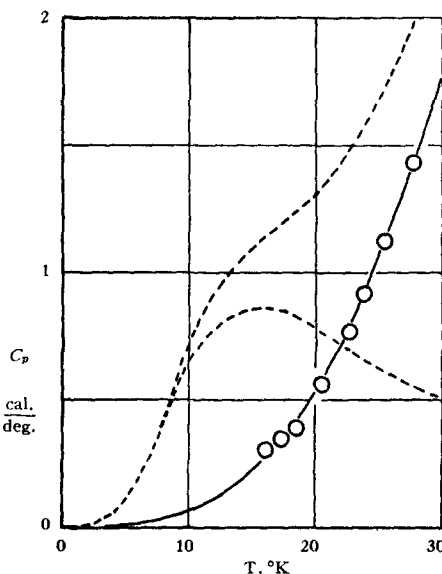


FIG. 1. The molal heat capacity of solid  $\text{KHF}_2$ : circles, experimental; solid line,  $T^3$  law for lattice vibrations; dotted curves, Ketelaar's model, lower the contribution from the  $\nu_3$  doublet above, upper the total including lattice vibrations.

we believe that 1450 and 1222  $\text{cm}^{-1}$  peaks represent, respectively, the  $\nu_3$  and  $\nu_2$  fundamentals. In our opinion the more surprising point is not that  $\nu_2$  is so high but that  $\nu_3$  is so low. However, this hydrogen bond is considerably shorter than those previously studied so that there is no evidence against the assignment.

The  $\text{HF}_2^-$  ion has a center of symmetry both internally and with respect to the crystal, hence  $2\nu_3$  is forbidden in the infra-red. The peak at 5099  $\text{cm}^{-1}$  seems most likely to be  $3\nu_3$ . If we assume the peak at 4232  $\text{cm}^{-1}$  to be  $2\nu_3 + \nu_2$ , then  $2\nu_3$  should be approximately 3010  $\text{cm}^{-1}$ . These levels show a large negative anharmonicity; indeed they approach somewhat the levels of an oscillator with a fourth power potential as calculated by Bell.<sup>6</sup> There is no indication of any double minimum character with the F—H—F potential. The possibility of a very small potential hill has not been eliminated; however it must not be much higher than the lowest energy level.

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<sup>1</sup> W. F. GIAUQUE and M. ASHLEY, *Phys. Rev.* **43**, 81 (1933); L. PAULING, *J. Am. Chem. Soc.* **57**, 2680 (1935); W. F. GIAUQUE and J. W. STOUT, *ibid.* **58**, 1144 (1936).

<sup>2</sup> J. A. A. KETELAAR, *Rec. Trav. Chim.* **60**, 523 (1941).

<sup>3</sup> A. M. BUSWELL, R. L. MAYCOCK, and W. H. RODEBUSH, *J. Chem. Phys.* **8**, 362 (1940).

<sup>4</sup> G. GLOCKLER and G. E. EVANS, *J. Chem. Phys.* **10**, 607 (1942).

<sup>5</sup> Other supporting arguments can be given for this conclusion, but they will be postponed until our full paper.

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