

- ⁷ E. O. Wollan, W. L. Davidson, and C. G. Shull, *Phys. Rev.* **75**, 1348 (1949).
⁸ B. Kamb, *Acta Cryst.* **17**, 1437 (1964).
⁹ W. B. Kamb and S. K. Datta, *Nature* **187**, 39 (1960).
¹⁰ F. V. Shallcross and G. B. Carpenter, *J. Chem. Phys.* **26**, 782 (1957).
¹¹ J. E. Bertie, L. D. Calvert, and E. Whalley, *J. Chem. Phys.* **38**, 840 (1963).
¹² L. G. Dowell and A. P. Rinfret, *Nature* **188**, 1144 (1960).
¹³ H. König, *Z. Krist.* **105**, 279 (1944).
¹⁴ N. D. Lisgarten and M. Blackman, *Nature* **178**, 39 (1956).
¹⁵ B. Kamb, *Trans. Am. Cryst. Assoc.* **5**, 61 (1969).
¹⁶ G. Tammann, *Ann. Phys.* **2**, 1 (1900).
¹⁷ E. Whalley, J. B. R. Heath, and D. W. Davidson, *J. Chem. Phys.* **48**, 2362 (1968).
¹⁸ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **47**, 441 (1912).
¹⁹ P. W. Bridgman, *J. Chem. Phys.* **3**, 597 (1935).
²⁰ A. C. Larson, R. B. Roof, Jr., and D. T. Cromer, *LASL Report LA-3335* (1965).
²¹ Von R. Brill and A. Tippe, *Acta Cryst.* **23**, 343 (1967).
²² A. Kahane, J. Klinger, and M. Philippe, *Solid State Commun.* **7**, 1055 (1969).
²³ A. Yu. Namiot and E. G. Bukhgalter, *J. Struct. Chem. (USSR)* **6**, 873 (1965).
²⁴ L. Pauling, *The Nature of the Chemical Bond* (Cornell U. P., Ithaca, N.Y. 1960), 3rd ed., p. 514.

Anisotropic Intermolecular Force Effects in Spectra of H₂- and D₂-Rare-Gas Complexes*

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(Received 4 March 1971)

Spectra of H₂-Ar, H₂-Kr, and H₂-Xe Van der Waals complexes, accompanying the Q₁(0), S₁(0), Q₁(1), and S₁(1) transitions of the pressure-induced fundamental absorption band of hydrogen, have been studied in a path length of 165 m at temperatures in the range 85–158°K. At the low total gas densities used, 1–2 amagat, the lifetimes of the complexes were sufficiently long to show a great deal of new detail in the spectra. The R and P branches ($\Delta l = \pm 1$, where l is the angular momentum of the complex) accompanying the overlap-induced Q₁(0) transitions, could be analyzed on a nonrigid rotation model to give Lennard-Jones ϵ and σ parameters for the molecular pairs. The spectra accompanying the quadrupole-induced S₁(0), Q₁(1), and S₁(1) transitions show T and N ($\Delta l = \pm 3$) as well as P and R branches, and many of the lines are split by the anisotropy of the intermolecular forces. The splitting is qualitatively in agreement with a model with loose coupling between J, the angular momentum of the H₂ molecule, and I. Well-resolved spectra of D₂-Ar, D₂-Kr, and D₂-Xe complexes accompanying the S₁(0) transition of deuterium were also obtained; these show more bound states than the H₂-rare-gas spectra and anisotropic interaction effects are evident. The H₂-N₂ complex shows a spectrum with a diffuse structure not previously observed.

I. INTRODUCTION

The discovery of discrete spectral features corresponding to transitions between bound states of the Van der Waals complex (H₂)₂ by Watanabe and Welsh¹ revealed a promisingly direct new approach to the study of intermolecular forces of nonpolar molecules. Subsequently, the observation of such transitions in the H₂-Ar complex by Kudian *et al.*² led to the recent more extensive study of the spectra of the H₂-Ar, H₂-Kr, and H₂-Xe systems³; the latter paper will be referred to as I. The transitions in Van der Waals complexes are manifested as fine structure accompanying the various hydrogen transitions in the collision-induced fundamental absorption band of hydrogen and hydrogen-foreign-gas mixtures. The experiments are performed at low temperatures and densities; under these conditions a small fraction, i.e., a few percent, of the molecules in the gas are in the form of bound pairs at any instant. The usual broad collision-induced absorption lines which arise from short-lived binary collisions are then accompanied by relatively sharp features arising from transitions between bound states of the longer-lived complexes. In I, it was found that

the spectral width of these features, which is inversely proportional to the lifetime of the complex, decreased as the gas density was lowered over the density range investigated. The lifetime of the complex is thus collision limited, and appeared to have a mean value of the order of the collision time. The over-all structure of the spectra could be explained in terms of a nonrigid rotator model with an isotropic Lennard-Jones potential. However, deviations from the predictions of the model were clearly evident in the spectra and it was concluded that these must be due to effects of anisotropy of the intermolecular potential. Detailed calculations of the energy levels of dimers for a Lennard-Jones potential have been made for (H₂)₂ by Gordon and Cashion⁴ and for H₂-Ar and the general case by Cashion.^{5,6}

In the experiments reported here, we have examined the spectra of H₂-Ar, H₂-Kr, and H₂-Xe complexes at densities which are $\frac{1}{3}$ to $\frac{1}{5}$ of those used in I. Under these conditions, the resolution of the spectra is greatly improved and a wealth of new detail is observed. Included in this detail is a splitting of certain spectral lines which is a direct consequence of anisotropy in the H₂-rare-gas potential energy curve. A complete analysis