



FIG. 1. The ground state energy (K) of solid H₂ vs. molar volume (cm³).

Using the anisotropic interaction of equations (2) and (3) we find curve C of Fig. 1; A is experimental⁷ and B is from reference 4, corresponding to $V_{\text{ani}} \equiv 0$. The dashed curve is the calculation of Krumhansl and Wu³ also employing the *E*-6 potential. From the plot we see that the introduction of V_{ani} improves the agreement of theory and experiment but that there is still a significant discrepancy. We believe that an important point in this connection is the value of ρ in equation (2). The value 0.283 Å is theoretical; according to the empirical *E*-6 potential, however, ρ should be $r_m/\alpha = 3.339/14 = 0.239$ Å. Since the exponential parts of V^{00} and V_{ani} should in principle have the same r dependence, we believe that the smaller ρ is preferred. Its use in V_{ani} leads to curve D of Fig. 1 which agrees quite well with Stewart's measurements, especially at high pressures where our general formalism is most reliable.

The good agreement is, of course, conditional depending on the validity of the approximations. We believe the only questionable point is that some terms proportional to Y_{2m} , $m \neq 0$, are ignored in V_{ani} . It is straightforward but very tedious to include them; we expect that they will lead to values of ΔE_a (the correction to E produced by

V_{ani}) about three or four times larger than those found here.¹⁵ As a result, the calculated energy will be too low. However, the situation is rectified if we also decrease β_1 in equation (2) by about a factor of 2 to ~ 1.3 K; there is considerable independent evidence that this is more nearly correct than $\beta_1 = 2.6$ K. For example, the calculated volume dependence⁴ of the λ -transition temperature agrees better with measurements when β_1 is decreased by about a factor of two. Harris¹⁶ gives a thorough discussion of further evidence supporting a smaller β_1 .

An interesting feature of our calculation is that V^{20} and V^{02} make by far the most important contributions ($\geq 90\%$) to ΔE_a at all molar volumes investigated, even though V^{22} is larger at large V . The reason is that zero-point motion and correlations are important in modulating the strength of the interactions; V^{02} and V^{20} are strongly enhanced⁴ by these quantum crystal effects at large volume. At smaller volume, they are larger than V^{22} .

These results are in conflict with the work of Raich and Eters¹¹ who find a vanishing contribution from V^{20} and V^{02} . This occurs because they treat the H₂ molecules as quantum mechanical rigid rotators pinned to the lattice sites with no zero-point motion and, naturally, no correlated motions. Consequently, V^{20} and V^{02} give zero net contribution to u_i when summed over nearest neighbors of a given molecule in an h.c.p. or cubic crystal. Because we have zero-point motion and find the field u_i according to equation (6), we find a non-vanishing and in fact large contribution from these potentials. It vanishes only in the classical limit of $\phi_i^2 \rightarrow \delta(r_1 - R_i)$ as implicitly assumed in reference 11. We conclude that a quantum crystal formalism is essential in calculating ΔE_a and leads to a much larger correction than would otherwise be found.

Another interesting result of our calculation is the amplitude ϕ_{2i} for each molecule to be in the $l = 2$ state. For $V \geq 11$ cm³ it varies slowly, being 2–4% of the total amplitude. The amplitude rises to about 15% at $V = 10$ cm³ in the case of curve D, indicating that our approach is not valid for much smaller V . Similarly, we note that $\Delta E_a \sim 200$ K is large for curve D at $V \sim 10$ cm³; however,

the energy shift for a given pair of molecules is ~ 30 K, still considerably smaller than the energy ~ 200 K required to produce a rotational or translational excited state.

Acknowledgements – The authors wish to thank Professor J.R. Korringa for his helpful comments and criticism. They also thank Professor J.A. Krumhansl for bringing this problem to their attention.

REFERENCES

1. POLLOCK E.L., BRUCE T.A., CHESTER G.V. and KRUMHANSL J.A., *Phys. Rev. B*, April 15 (1972).
2. BRUCE T.A., *Phys. Rev. B*, April 15 (1972).
3. KRUMHANSL J.A. and WU S.Y., *Phys. Letters* **28A**, 263 (1968); *Phys. Rev. B*, April 15 (1972).
4. EBNER C. and SUNG C.C., *Phys. Rev.* **B4**, 2638 (1971).
5. Some early work was done by KRONIG R., DE BOER J. and KORRINGA J., *Physica* **12**, 245 (1946). For recent developments see NEECE G.A., ROGERS F.J. and HOOVER W.G., *J. Computational Phys.* **7**, 621 (1971).
6. *Proc. Lunar Science Inst. meeting on High Pressure Phys. and Planetary Interiors.*, North-Holland, Amsterdam (to be published).
7. STEWART J.W., *J. Phys. Chem. Solids* **1**, 146 (1956).
8. For a review of the various potentials see reference 3.
9. NAKAMURA T., *Progr. theor. Phys. (Kyoto)* **14**, 135 (1955). It is an approximation of the theoretical calculation by DE BOER J., *Physica* **9**, 363 (1942), neglecting terms in P_l with $l \geq 4$. The neglected terms are about 10% of V^{20} at all volumes.
10. HIRSCHFELDER J.O., CURTISS C.F. and BIRD R.B., *Molecular Theory of Gases and Liquids* p. 1083. Wiley, New York (1954).
11. RAICH J.C. and ETTERS R.D., *J. Low Temp. Phys.* **6**, 229 (1972).
12. We assume 100% parahydrogen.
13. SRIVASTAVA I.B. and BARUA A.K., *Indian J. Phys.* **35**, 320 (1961), find that this *E-6* potential fits the measured second virial coefficients of H₂ better than the more common Lennard-Jones potential.
14. Units $\hbar = k = 1$ are used.
15. A detailed calculation including the effect of ortho-H₂ will be published elsewhere.
16. HARRIS A.B., *Phys. Rev.* **B1**, 1881 (1970).

On étudie l'équation d'état d'Hydrogène solide à haute pression. Il existe une contradiction importante entre théorie et expérience. On attribue cette contradiction à une anisotropie faible de l'interaction moléculaire. On montre que la théorie de 'quantum crystal' utilisée avec le potentiel intermoléculaire conventionnel peut résoudre complètement cette dilemme.