



FIG. 1. The ground state energy (K) of solid H<sub>2</sub> vs. molar volume (cm<sup>3</sup>).

Using the anisotropic interaction of equations (2) and (3) we find curve C of Fig. 1; A is experimental<sup>7</sup> and B is from reference 4, corresponding to  $V_{\text{ani}} \equiv 0$ . The dashed curve is the calculation of Krumhansl and Wu<sup>3</sup> also employing the  $E$ -6 potential. From the plot we see that the introduction of  $V_{\text{ani}}$  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  $\rho$  in equation (2). The value  $0.283 \text{ \AA}$  is theoretical; according to the empirical  $E$ -6 potential, however,  $\rho$  should be  $r_m/a = 3.339/14 = 0.239 \text{ \AA}$ . Since the exponential parts of  $V^{00}$  and  $V_{\text{ani}}$  should in principle have the same  $r$  dependence, we believe that the smaller  $\rho$  is preferred. Its use in  $V_{\text{ani}}$  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  $V_{\text{ani}}$ . It is straightforward but very tedious to include them; we expect that they will lead to values of  $\Delta E_a$  (the correction to  $E$  produced by

$V_{\text{ani}}$ ) about three or four times larger than those found here.<sup>15</sup> As a result, the calculated energy will be too low. However, the situation is rectified if we also decrease  $\beta_1$  in equation (2) by about a factor of 2 to  $\sim 1.3 \text{ K}$ ; there is considerable independent evidence that this is more nearly correct than  $\beta_1 = 2.6 \text{ K}$ . For example, the calculated volume dependence<sup>4</sup> of the  $\lambda$ -transition temperature agrees better with measurements when  $\beta_1$  is decreased by about a factor of two. Harris<sup>16</sup> gives a thorough discussion of further evidence supporting a smaller  $\beta_1$ .

An interesting feature of our calculation is that  $V^{20}$  and  $V^{02}$  make by far the most important contributions ( $\geq 90\%$ ) to  $\Delta E_a$  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 enhanced<sup>4</sup> 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 Eters<sup>11</sup> who find a vanishing contribution from  $V^{20}$  and  $V^{02}$ . This occurs because they treat the H<sub>2</sub> 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  $\phi_i^2 \rightarrow \delta(\mathbf{r}_1 - \mathbf{R}_i)$  as implicitly assumed in reference 11. We conclude that a quantum crystal formalism is essential in calculating  $\Delta E_a$  and leads to a much larger correction than would otherwise be found.

Another interesting result of our calculation is the amplitude  $\phi_{2i}$  for each molecule to be in the  $l = 2$  state. For  $V \geq 11 \text{ cm}^3$  it varies slowly, being 2–4% of the total amplitude. The amplitude rises to about 15% at  $V = 10 \text{ cm}^3$  in the case of curve D, indicating that our approach is not valid for much smaller  $V$ . Similarly, we note that  $\Delta E_a \sim 200 \text{ K}$  is large for curve D at  $V \sim 10 \text{ cm}^3$ ; however,

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

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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.