

Revised results for the pressureinduced rotationlibration transition in molecular solid hydrogen

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Keeping in mind the spread in collision energy, the high energy tail of the distribution at the highest energy point may well be due to a small contribution from the $N(^2D)$ channel.

The vibrational and rotational distribution in the product molecules have been determined by the analysis of the observed $NH(A-X)$ band spectrum. We consider here vibrational levels $v' = 0$ and $v' = 1$ below the predissociation limit which is due to intersection with the repulsive $^5\Sigma^-$ state. Because of near unity Franck-Condon factors for (0,0) and (1,1) bands, the relative peak height of each Q branch reflects the relative vibrational population of the $v' = 0$ and $v' = 1$ levels. Throughout the collision energy range we found the $v' = 1/v' = 0$ population ratio to be 0.60 ± 0.12 for the $N^* + HI$ system; that ratio was 0.41 ± 0.05 for the $N^* + HBr$ system. The weak collision energy dependence observed may be due to the large width in the energy distribution. Figure 1(b) is a computer generated spectrum⁷ for the run represented in Fig. 1(a). The rotational populations for $v' = 0$ and $v' = 1$ were assumed to follow a Boltzmann distribution. The best fit rotational temperatures obtained corresponding to $v' = 0$ and $v' = 1$ levels were 4000 ± 250 and 2000 ± 250 K, respectively. The ratios $v' = 1/v' = 0$ for the

product $NH(A)$ are close to the statistical distributions [0.69 and 0.44 at $\bar{E} = 1.12$ eV for processes (1) and (3)] predicted by prior calculation by Levine *et al.*⁸; however, cooler rotational distributions than the statistical predictions were observed for these processes.

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NOTES

Revised results for the pressure-induced rotation-libration transition in molecular solid hydrogen

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The pressure-induced rotation-libration transition in solid molecular para- H_2 and ortho- D_2 was recently calculated by Monte Carlo simulation¹ using anisotropic nearest-neighbors interaction potentials of the form

$$V_{ij} = \sum_m C_m(r_{ij}) Y_{2m}(\Omega_i) Y_{2-m}(\Omega_j), \quad (1)$$

where Ω_i is the orientation of molecule i , with respect to the i - j intermolecular axis, and $r_{ij} = R_{ij}/R_0$ is the distance between molecular centers in units of the nearest-neighbor distance at zero pressure. The coefficients $C_m(r)$ were determined from the Ree-Bender potential.² For the fcc lattice in question, the expectation of the potential energy can be written in the form¹

$$\left\langle \frac{1}{2} \sum_{ij} V_{ij} \right\rangle = \frac{4\pi}{5} \left[A(r) C^2(r) + \frac{4}{9} D(r) \right] \left\langle \frac{1}{2} \sum_{ij} Y_{20}(\Omega_i) Y_{20}(\Omega_j) \right\rangle, \quad (2)$$

where $A(r)$, $C(r)$, $D(r)$ are functions of the intermolecular distance determined from *ab initio* calculations in Ref. 2. The ground state energy was calculated in Ref. 1 by a variational procedure using a trial wave function of Jastrow type. This is expressed in terms of the orientational vectors ω_i , where each ω_i specifies the orientation of molecule i with respect to its own symmetry axis (one of the four threefold axes of the fcc structure). The form of the wave function is

TABLE I. The transition parameters.

Isotope	Transition volume cm ³ /mol	Transition pressure (Kbar)		
		Experiment ^a	SG	YR
H ₂	3.00	Above 900	1500	1170
D ₂	4.37	278	500	390

^a Reference 5.

$$\psi(\omega_1, \dots, \omega_N) = \prod_{i=1}^N \phi(\omega_i) \prod_{j < k}^N F(\omega_j, \omega_k), \quad (3)$$

where

$$\phi(\omega) = Y_{00}(\omega) + \gamma Y_{20}(\omega), \quad (4)$$

$$f(\omega_j, \omega_k) = \exp[\lambda w_{jk} b(\omega_j) b(\omega_k)], \quad (5)$$

where λ , γ are variational parameters, and $w_{jk} = 1$ if j, k are nearest neighbors, and zero otherwise. The function b is defined by $b(\omega_j) = \cos^2 \xi_j$, where ξ_j is the polar angle of the direction ω_j , with respect to the symmetry axis of molecule j . The multiple integrals appearing in the expectation of the potential energy [Eq. (2)], as well as in the rotational kinetic energy, were evaluated by a Monte Carlo simulation procedure. The search for the transition density was carried out by mapping the total energy as a function of the variational parameters λ , γ , and of the density (or specific volume), and

by looking for a jump in the location of the minimum. The transition pressure was determined in Ref. 1 with the help of the equation of state proposed by Silvera and Goldman.³ The values are given in Table I, column SG. In the high density region where the transitions occur for both para-H₂, and ortho-D₂, their (PV) curves are almost indistinguishable.

The equation of state recently discussed by Ross, Ree, and Young (YR in Ref. 4), gives significantly lower values for the transition pressure (see Table I, column YR), bringing them closer to the experimental values.⁵ While in the case of the SG equation of state the agreement for D₂ with experiment was relatively better than for H₂, suggesting the fact that this equation was not well suited for the high density region, the YR equation of state seems to agree with the experiment to a comparable extent for both isotopes.

Although YR do not give an equation of state for D₂, we have assumed in analogy with the SG equation of state, that the (PV) curves of both isotopes are almost indistinguishable in the high density region of the transition.

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Femtosecond study of the recovery dynamics of malachite green in solution

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Interest has developed in the absorption dynamics of the triphenyl methane dyes in solution, especially in their nonradiative ground state recovery process. The characteristic time for this internal conversion process exhibits a sub-linear dependence on viscosity which has been attributed to a conformational change in the excited state to a new structure characterized by enhanced rates of nonradiative decay.¹ Since this conformational change is thought to involve the rotation of a phenyl ring about the central carbon atom, it should be hindered by the viscous drag introduced by the solvent molecules, resulting in a ground state recovery time which increases with solvent viscosity. For low viscosity ($\eta \approx 0.01$ P) solvents, such as water, this relaxation process is very fast, ~ 1 ps. Previous measurements of the relaxation time in this low viscosity regime have either been in the frequency domain,²⁻⁴ or in the time domain with a temporal resolution comparable to the decay times being measured.⁵ We present here the first time-domain study of the triphenyl methane dye malachite green (MG) in both water and ethylene glycol (EG) using the recently developed equal-pulse

correlation technique⁶ and using a time resolution significantly better than previous time-domain studies.

Our measurement is based upon the saturation effect in the transmission characteristics of a thin jet of MG in solution. The sample is excited by two ~ 90 fs, 612 nm laser pulses of equal powers and orthogonal polarizations, which are collinearly propagating and have a delay τ between the pulses. The time-averaged combined transmitted flux of both pulses is measured as a function of τ . Because of rapid population relaxations, both out of the excited and into the ground state, reducing the degree of saturable absorption, the time-averaged transmitted power reaches a peak when $\tau = 0$ and decreases to a background value for large τ . The shape of this peak is related to the convolution between the laser pulse autocorrelation and the relaxation processes that govern the population difference between ground and excited states.

To interpret our data, we model the vibrational-rotational manifolds of the ground (S_0) and electronically excited (S_1) states of MG in solution as a four-level system (see inset