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Hybridization of the rotational state of HD adsorbed on porous Vycor glass

T. E. Huber*
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

J. A. Perez
Department of Physics, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

C. A. Huber†
Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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We present measurements of the infrared absorption corresponding to the rovibrational transitions of adsorbed HD. The absorption-line bandwidths at low coverages of HD on porous Vycor glass are more than two times larger than those of adsorbed H_2 and D_2. Also, we observe the transitions corresponding to $\delta J=3$ and 5, whereas only the allowed $\delta J=0,\pm 2$ are observed for the pure isotopes. Our observations strongly suggest hindrance of the rotational states of HD, which may be attributed to the hybridization of rotations and adsorbed HD phonons resulting from the molecule's mass asymmetry.

In a typical molecular condensed state the rotational angular momentum is quenched when the strength of the anisotropic interactions is larger than the spacing between molecular rotational levels. The rotational spacings are very large for molecular hydrogen, and, as a result, it is a unique example of a free rotor. In this regard, recently published results of nuclear magnetic resonance (NMR) studies of HD and D_2 in amorphous silicon are most interesting.[1] In these studies deuteron multiple echoes have been detected. Such observations, made at low temperatures, are believed to indicate that the rotational ground state $J=0$ is mixed with higher J states. Reportedly, the mixing is due to the strong crystal fields in the voids of the amorphous silicon. Clearly, it is important to study the prospects that this molecular behavior could occur in other restricted geometries, which can potentially hinder the rotational motion. Porous Vycor glass (PVG) is attractive in this respect, especially in view of current research on the state of aggregation of the hydrogens in such a system.[2]

HD is a simple molecule, and many of its properties are well known. The electron density around the proton and deuteron is approximately spherical. The center of interaction (CI), defined as the center of the electron density, is located halfway between the proton and the deuteron. The center of mass (CM) and the CI do not coincide as they do in H_2 and D_2. A rotation about the CM of HD therefore results in a translation of the CI. As a result of the rotation-vibration coupling, the ground-state energy is higher for an assembly of heteronuclear molecules than for homonuclear ones.[3] Because of this, the equation of state of HD is different from that of H_2 and D_2, and vapor pressure and molar volume anomalies are observed for HD as compared to H_2 and D_2. These effects can also be observed spectroscopically. Raman scattering of solid HD reveals that the $J=0$ to $J=2$ transition is quite broad, 5 cm^{-1}, in comparison with that in the pure isotopes for which the bandwidths are less than 0.5 cm^{-1}.[4] The rotational-translational coupling also manifests itself as an additional structure in the phonon replicas in the infrared absorption spectra of bulk, solid, and liquid, HD for phonon energies about $2B_0$, where B_0 is the rotational constant ($B_0=44.7\text{cm}^{-1}$) for the isolated molecule.[5,6] Such energy corresponds to the excitation of the molecule from the $J=0$ to the $J=1$ rotational state.

Given the paramount importance of rotational-translational coupling in the bulk, we can expect that such effects will also be important for HD on surfaces. Considering that hydrogen is the simplest molecular system, surprisingly few experimental studies of hydrogen in the adsorbed state exist. Since few spectroscopic techniques achieve the necessary resolution of a few cm^{-1},[7] most of these studies do not have a bearing on the molecular state. One exception is the measurement of rotational Feshbach resonances in the surface scattering of H_2.[8] Our work was also partially motivated by previous studies of photodesorption processes in PVG,[9] which suggest that HD may photodesorb more readily than the pure isotopes. We have previously reported on the fundamental and overtone infrared absorption of H_2 and D_2 on porous Vycor glass and silica gels.[10,11] We found that the vibrational absorption spectrum of the pure isotopes is enhanced by the presence of the surface, which can be attributed in a general manner to surface electric fields. It was also found that the rotational state of adsorbed H_2 and D_2 remains essentially like that of the free molecule and that the corresponding absorption features are well defined, with a typical FWHM of 50 cm^{-1}. If quantum effects are considered, HD stands as an intermediate between H_2 and D_2 and one would anticipate the state of surface HD to be like that of H_2 and D_2. Instead, we find the width of the rovibrational resonances of surface HD to be 120 cm^{-1}, more than twice those of the pure isotopes. We also observe lines corresponding to $\delta J=3$ and $\delta J=5$ transitions, which are not allowed for the pure isotopes. Since surface effects are not sufficiently strong to change the HD molecular parameters significantly, we argue that the underlying basis for the observed broadening and breakdown of selection rules is the hybridization of the rotational states and phonons.

The Vycor sample (Corning 7930) was a disk 3.6 mm in diameter and 4 mm thick. The Vycor pore radius was 3.5 nm. From adsorption isotherms of HD a surface-layer coverage of $n_0=3.5\times10^{-3}$ mol/cm^3 was obtained at 20 K. The high-purity HD (nominally 99.5%) was obtained from a commercial supplier. The sample preparation and apparatus and procedures for measuring the infrared absorption spectra have been described previously.[11] Figure 1 (lower part) shows the absorbance $A=\log_{10}(I_0/I)$ measured for various HD coverages at 20 K. The reference intensity I_0 is that which is transmitted through the bare Vycor at the same temperature. The large feature at 3750 cm^{-1}, as well as the features between 4450 cm^{-1} and 4600 cm^{-1}, arise from a shift upon HD adsorption of the broad absorption from the surface hydroxyls (OH) present in Vycor. The dispersive shape results from the effect of the frequency shift on the absorbance.[11] This frequency shift is essentially the same for the three isotopes at the same coverage. The strong absorption from the hydroxyl prevents the observation of the HD fundamental vibrational feature that appears at $\Omega(Q_1)=3632$ cm^{-1} for the isolated HD molecule. The absorption spectrum for full pores, curve *d*, is dominated by the lines characteristic of bulk HD. The spectrum of bulk liquid HD is also shown in Fig. 1 for comparison purposes. The strongest absorption features in the rovibrational part of the spectrum of bulk liquid HD are the $Q_1(0)+S_0(0)$ and $S_1(0)+S_0(0)$ lines, which correspond to two-molecule transitions resulting from intermolecular interactions.[5,6] Here the number in parentheses indicates the rotational quantum number J of the initial state and the subindex indicates the change in the intramolecular vibrational quantum number. These lines are also present in the absorption spectrum of HD on PVG for high coverages. This indicates that the liquid in the pores, far from the surface, is not significantly affected by the confinement of the Vycor. Some features in the absorption spectrum of liquid HD mark the presence of H_2 impurities. The most prominent of these features in the spectral region investigated is the double transition $Q_1(0)+S_0(0)[H_2]$ at 3980 cm^{-1}, a combination of the HD fundamental vibrational Q_1 and the $J=0\rightarrow2$ rotational transition of H_2, $S_0(0)$. Comparison with the absorption spectrum of HD with H_2 impurities in Ref. 6 indicates that the concentration of H_2 in our samples is around 0.7%. This small amount may be attributed to impurities in the HD gas supply.

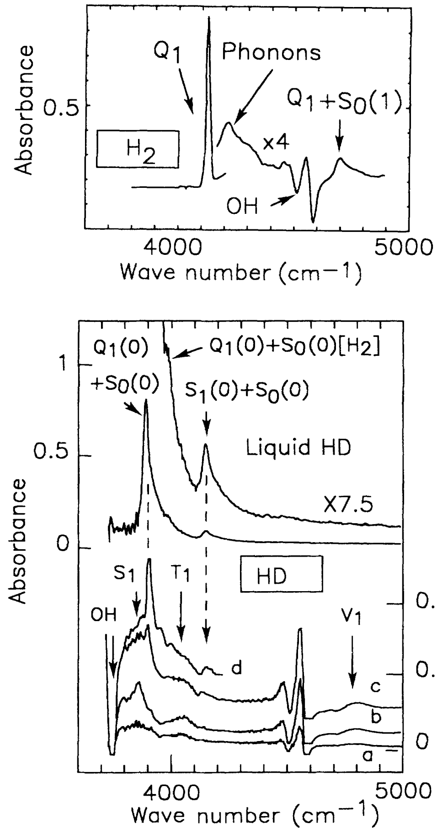

FIG. 1. Top: Infrared absorption spectrum of H_2 on porous Vycor glass for a coverage $n_s=0.6n_0$, with $n_0=3.5\times10^{-3}$ mol/cm^3 the surface layer coverage. Bottom: Infrared absorption spectra of HD on porous Vycor glass. Curves *a*, *b*, and *c*, taken at 20 K, correspond to coverages $n_s=0.3n_0$, $0.7n_0$, and $1.2n_0$, respectively. Curve *d* corresponds to full pores. The two uppermost curves show the spectrum of bulk liquid HD at two magnifications. The curves have been displaced vertically by arbitrary amounts for clarity.

The peaks at 3850 cm^{-1} (S_1), 4040 cm^{-1} (T_1), and 4780 cm^{-1} (V_1), observed in curves *a*, *b*, and *c* of Fig. 1, appear at low coverages of HD. Their intensities saturate for coverages above that of a monolayer. These absorption lines are not observed for adsorbed H_2 (upper part of Fig. 1), nor in bulk HD. With a FWHM of 120 cm^{-1}, the S_1, T_1 and V_1 surface lines of HD are broader than the Q_1 vibrational line (FWHM=20 cm^{-1}) and the $Q_1+S_0(1)$ rovibrational line (50 cm^{-1}) of adsorbed H_2 and D_2 (Fig. 1, top part). The absorption features at 3850 cm^{-1}, 4040 cm^{-1}, and 4780 cm^{-1} are identified as the double transitions $\delta v=1$, with v the vibrational quantum number, and $\delta J=2$, $\delta J=3$, and $\delta J=5$, respectively, of adsorbed HD. The observed frequencies correspond closely to the transition frequencies calculated from the parameters of the HD molecule. The energy levels of the isolated molecule are well known, the transition energies can be calculated from the cubic polynomial given by Stoicheff[12] and are presented in Table I. The $\delta J=0$ and $\delta J=1$ transitions are outside the experimental frequency range. The $\delta J=4$ transition is masked by the strong hydroxyl feature and could not be observed either. A simple comparison indicates that although the observed frequencies, considering the large bandwidth of the absorption lines, nearly match the transition frequencies calcu-

TABLE I. Vibrational-rotational transitions observed for HD in porous Vycor glass. The calculated values correspond to the isolated molecule.

	Calculated frequency (cm^{-1})[a]	Experimental frequency (cm^{-1})
$Q_1(0)+S_0(0)$	3890	3890
$Q_1(0)+S_0(0)[\mathrm{H}_2]$	3980	3980
$S_1(0)+S_0(0)$	4150	4140
$S_1(J=0\rightarrow J=2)$	3888	3850
$T_1(J=0\rightarrow J=3)$	4141	4040
$U_1(J=0\rightarrow J=4)$	4477	not observed
$V_1(J=0\rightarrow J=5)$	4891	4780

[a]Reference 12.

lated from the parameters of the isolated molecule, an important redshift is noticed. The vibrational and rovibrational lines of adsorbed HD are indeed expected to be shifted towards lower energies reflecting a weakening of the intra-molecular bonds in the presence of an attractive external potential. These shifts upon adsorption have been observed for H_2 and D_2. The frequency shift for adsorbed HD can be calculated from the parameters of the HD molecule. For a typical adsorption potential of hydrogen on porous Vycor glass, redshifts of 25 cm^{-1}, 27 cm^{-1}, and 31 cm^{-1} of the S_1, T_1, and V_1 lines, respectively, are obtained.[13] These values are not inconsistent with the observed frequency shifts of 38 cm^{-1}, 101 cm^{-1}, and 111 cm^{-1}, as deduced from Table I, considering the approximations involved in the calculation.

In analogy with liquid and solid HD, rotation-phonon coupling effects on the molecular levels of adsorbed HD can be expected to be significant. The selection rule $\delta J=0,\pm 2$, resulting from the symmetry under rotations of the hydrogen molecule, is applicable to the one-molecule and two-molecule absorption lines of the pure isotopes in the bulk.[14] Liquid HD exhibits, in addition to the $\delta J=0,\pm 2$ lines, a $R_1(0)$ $(\delta J=1)$ absorption line. This transition is forbidden in H_2 and D_2 but not in heteronuclear HD. In this case, since the CM and the CI do not coincide, the dipole moment induced by intermolecular quadrupolar interactions is modulated at the frequency of rotation of the molecule. Another special property of HD in the condensed phases is the coupling of molecular rotations and phonons. Babloyanz[3] studied, in second order of perturbations, the resonance between the state $|1\rangle=|J=1\rangle|n_{\mathrm{ph}}=0\rangle$, where $|n_{\mathrm{ph}}=0\rangle$ is the zero-phonon state, and the state $|2\rangle=|J=0\rangle|n_{\mathrm{ph}}=1\rangle$ of energies ε_1 and ε_2, respectively. Here $\varepsilon_1=2B_0$ is the energy of the $J=0$ to $J=1$ transition and $\varepsilon_2=\varepsilon_{\mathrm{phonon}}$ is the characteristic phonon energy, where energies are measured with respect to the ground state $|G\rangle=|J=0\rangle|n_{\mathrm{ph}}=0\rangle$. The hybridization interaction, which couples rotations and phonons, has a strength $\Delta\approx\langle 1|H_I|2\rangle$. For $|\varepsilon_1-\varepsilon_2|\ll\Delta$, the hybridized states are, approximately, $|I_\pm\rangle=|1\rangle\pm|2\rangle$ with energies $\varepsilon_\pm=2B_0\pm\Delta$.[15] Clearly, the extent of hybridization effects is determined by the strength of the rotation-phonon coupling Δ, as compared to B_0. An estimate for Δ can be obtained from the following argument. Consider the case of solid HD where the effects of hybridization between the $J=1$ rotational state and the bulk phonons are known to be important. The rotational-translational coupling manifests itself as a structure consisting of a sharp dip, FWHM=10 cm^{-1}, in the high-energy side of the broad phonon replica of the fundamental vibrational line Q_1. This dip appears at an energy $2B_0$ away from Q_1, corresponding to a $J=0$ to $J=1$ molecular transition. The sharp dip reflects a reduction of the phonon density of states resulting from hybridization, and one can then estimate Δ to be about 10 cm^{-1} for solid HD. For adsorbed HD we expect a stronger rotation-phonon coupling since the surface adsorption energy is approximately 300 cm^{-1}, more than five times larger than the depth of the potential well of the molecule in the solid[16] (53 cm^{-1}). Also, the surface is very asymmetric, while the hcp solid is only slightly noncentrosymmetric.[14] An increase in Δ by one order of magnitude would presumably be enough to bring the antisymmetric hybridized state $|I_-\rangle$ close to the ground state $|G\rangle$, which would indicate strong coupling.

The rotation-phonon coupling is important if the phonon energy is enough to change the rotational state of the molecule, that is $\omega_D\approx 2B_0$, where ω_D is the high-frequency cutoff of the phonon density of states of adsorbed HD. From the phonon sidebands of the Q_1 vibrational line of adsorbed H_2 the characteristic phonon energies of hydrogen adsorbed in porous Vycor glass are found to be between 70 and 110 cm^{-1} at low coverage.[10] On going from H_2 to D_2 the change in phonon frequencies from decreasing quantum effects and from increasing mass would tend to compensate and we may assume ω_D to be the same for all the isotopes. Since $B_0=45$ cm^{-1}, the condition for resonance $\omega_D\approx 2B_0$ is approximately satisfied. Therefore, the conditions that would result in hybridization are satisfied in this case. Furthermore, since the transitions involve a phonon it would be reasonable to expect broadening with a bandwidth assimilating that of the phonon distribution of states. Further, if the rotational eigenstates have mixed J, there is no basis for $\delta J=0,\pm 2$ selection rules.

The phenomena described here need not be restricted to HD on surfaces. HD in other restricted geometries is equally likely to exhibit rotational anomalies. The infrared absorption spectra of HD isolated in Ar matrices show large frequency shifts, breakdown of selection rules, and large bandwidths.[17,18] The results of our study also indicate that adsorbed HD presents a path for energy transfer from the infrared light into adsorbate phonons not present for adsorbed H_2 and D_2

In summary, the use of a porous substrate has enabled us to measure the characteristic absorption spectrum of HD on surfaces. The observation of fairly broad absorption lines resulting from rovibrational transitions, which are normally forbidden by selection rules, is attributed to coupling between molecular rotations and adsorbate phonons. A precondition for this coupling to be significant is for the rotational frequencies to lie below the adsorbate phonon energies, a condition that is facilitated by strongly adsorbing substrates and by small rotationally constant molecules, and especially by mass-asymmetric molecules.

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[*] Permanent address: Polytechnic University, Brooklyn, NY 11201.

[†] Present address: Naval Surface Warfare Center-White Oak, Silver Spring, MD 20903.

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