Measurement of the Adsorption Energy Difference between *Ortho*- and *Para*-D_2 on an Amorphous Ice Surface

L. Amiaud,[*] A. Momeni, F. Dulieu,[†] J. H. Fillion,[‡] E. Matar, and J.-L. Lemaire
LERMA, UMR8112 du CNRS, de l'Observatoire de Paris et de l'Université de Cergy Pontoise,
5 mail Gay Lussac, 95031 Cergy Pontoise Cedex, France

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Molecular hydrogen interaction on water ice surfaces is a major process taking place in interstellar dense clouds. By coupling laser detection and classical thermal desorption spectroscopy, it is possible to study the effect of rotation of D_2 on adsorption on amorphous solid water ice surfaces. The desorption profiles of ortho- and para-D_2 are different. This difference is due to a shift in the adsorption energy distribution of the two lowest rotational states. Molecules in $J'' = 1$ rotational state are on average more strongly bound to the ice surface than those in $J'' = 0$ rotational state. This energy difference is estimated to be 1.4 ± 0.3 meV. This value is in agreement with previous calculation and interpretation. The nonspherical wave function $J'' = 1$ has an interaction with the asymmetric part of the adsorption potential and contributes positively in the binding energy.

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Because of the nuclear spin of its atomic constituents, two states of H_2 exist in the lowest electronic state: *para*-H_2 with even J rotational numbers, and *ortho*-H_2 with odd J rotational numbers. In the dark clouds of the interstellar medium, the dust grains are covered with ice, mainly composed of water, which is the most abundant molecule in the solid phase [1]. In these environments, molecular hydrogen is the most abundant species. The interaction between molecular hydrogen and a water ice surface is therefore a major process [2–5] in these dense interstellar regions. The ortho- to para- (o/p) ratio of the hydrogen molecules has great consequences on the subsequent chemistry, particularly on the deuteration of species [6]. The o/p conversion on interstellar grains has been discussed in the context of photodissociation regions [7]. The adsorption energy of the molecules, and therefore of the ortho- and para- states, can play an important role in the coverage of the interstellar dust grains [8].

The difference in adsorption energy on some cold surfaces (TiO_2 ...) of ortho- and para-H_2 states has been known for a long time ([9] and references within). This is the basis for experimental procedures that allow separating ortho-H_2 from normal H_2. In the case of a water surface, infrared spectroscopy has demonstrated the adsorption of ortho-H_2 in preference to para-H_2, by observing change in the spectra in time [10]. Computations have been carried out to explain this behavior using H_2 water ice cluster interactions [11]. The calculated average difference in the adsorption energy is found to be ~30 K (~2.6 meV). These authors [11] explain this energy difference from a physical point of view as follows: the wave function of para-H_2 ($J = 0$) is approximately spherically symmetric, while the wave function of ortho-H_2 ($J = 1$) is similar to the nonspherical hydrogen atom's p function. Therefore para-H_2, does not "feel" the anisotropic part of the potential, while ortho-H_2, has extra binding energy with respect to para-H_2 due to the anisotropic part. Even if in the astrophysical context H_2 is much more relevant than D_2, this experimental study deals with D_2 only, which has been chosen to avoid complications due to the presence on H_2 as a main pollutant of UHV chambers. In the case of deuterium, the ortho-D_2 has even J rotational numbers, whereas para-D_2 has odd ones. At 300 K, the normal D_2 o/p ratio is statistically equal to 2/1. To our knowledge, there is no experimental measurement of such difference in the adsorption energies for molecular hydrogen adsorbed on water ice surfaces despite its high importance for astrophysics. In this Letter we present a new technique coupled to an original analysis in order to measure directly the difference in adsorption energies of the two lowest states of D_2. In the first part we present briefly the experimental setup and the technique used (thermal desorption spectroscopy of selected quantum state TDS-SQS). In order to explain the method that will be used to analyze the TDS-SQS profiles, the second part shows the change of the classical TDS profiles when two hydrogen isotopes are present on the surface. We briefly recall the model that has been used to describe this isotopic segregation, based only on an energy shift between two populations. The last part presents the experimental D_2 desorption study from amorphous solid water (ASW) ice surface of the $J = 0$, 1, 2 rotational states and the analysis that concludes to an average adsorption energy difference between para- and ortho- states of 1.4 ± 0.3 meV.

Our experiments were performed using the FORMOLISM setup. The precise experimental procedures and more details are described in [12]. The setup contains a main UHV chamber. A copper sample thermally controlled between 8 and 800 K, with 0.2 K precision and 1 K absolute accuracy, is covered with the ASW ice sample. The sample is composed of 250 layers of nonporous ASW deposited at 120 K [13] in order to isolate subsequent depositions from the copper sample [14]. On top of this first ice substrate, 10 layers of porous ASW are deposited at 10 K using water vapor pressure at 2.0×10^{-8} mbar. The overall sample (nonporous substrate and porous thin layer) has the property of a porous amorphous ice, at least for the interaction with D_2 [8]. The sample is annealed at 32 K in order to avoid any further change during the next experiments done with thermal ramps ranging from 10 to 30 K. A constant dose (1.5×10^{15} mol cm^{-2}) of normal mixture of ortho- and para-D_2 at room temperature is exposed to the surface held at 10 K. The sample is heated with a 10 K/ min linear ramp. The TDS-SQS signal is recorded simultaneously using a quadrupole mass spectrometer (QMS), located at 15 cm above the surface, and laser ionization coupled to a time of flight (TOF) detection. The laser beam, focused at 8 mm away from the surface, ionizes the molecules during the deposition as well as during the heating phase. To selectively ionize a rotational level, we have used a well-investigated (2 + 1) resonance enhanced multiphoton ionization (REMPI) scheme [15–17] via the E, $F\ {}^1\Sigma^+g$ resonant electronic state. Photons are produced by a tunable dye laser (Quantel-TDL50) pumped with the second harmonic of a ND:YAG Laser (Quantel-YG981E) pulsing at 20 Hz. The visible light of the dye laser is frequency-tripled (via a mixing after doubling scheme using potassium dihydrogen phosphate and beta barium borate crystals) in order to produce photons of 0.5 mJ/pulse in the 200–206 nm wavelength range. The wavelength is tunable to the maximum of a specific $Q(J'')$ transition of the (2 + 1) REMPI $E, F\ {}^1\Sigma^+g\ (v' = 0, J' = J'')$-$X\ {}^1\Sigma^+g\ (v'' = 0, J'')$ spectrum giving therefore the possibility to probe a specific rotational level of the ground state during the heating phase of the sample. During the deposition phase, the ionization signal for each line is recorded at fixed wavelength. It allows us to calibrate the detection efficiency for each line.

The TDS profiles of D_2 on ASW ice surfaces are highly molecular coverage dependent [12]. The disordered morphological nature of the porous structure changes the adsorption energy from one site to another, as calculated in detail [18], leading to an adsorption energy distribution. This broad energy distribution $g(E)$ can be analytically described by a simple polynomial law: $g(E) = a(E_0 - E)^b$, where E is the adsorption energy, E_0, a, and b are physical parameters fitted to the TDS curves. The assumption underlying this analysis includes a site coverage following Fermi-Dirac statistics with only one molecule occupying each site. Figure 1 shows the desorption profile of pure H_2 adsorbed on ASW ice and the same desorption profile in presence of HD. The desorption profile of H_2 is modified by the presence of the other isotope. This behavior is well reproduced by our model, as can be seen in Fig. 1. This analysis has been previously presented with D_2/H_2 segregation [19] and is fully described for a 3 isotopes mixture (H_2, HD, and D_2) [8]. An important conclusion of this previous study is that a small difference in the adsorption energy between two isotopes leads to a large change in the desorption profiles. In other words, distortion of the desorption profiles is due to the energy shift in the energy distribution of the isotopes. By using the energy difference as a free parameter in our model, we reproduced the distortion of the desorption profiles.

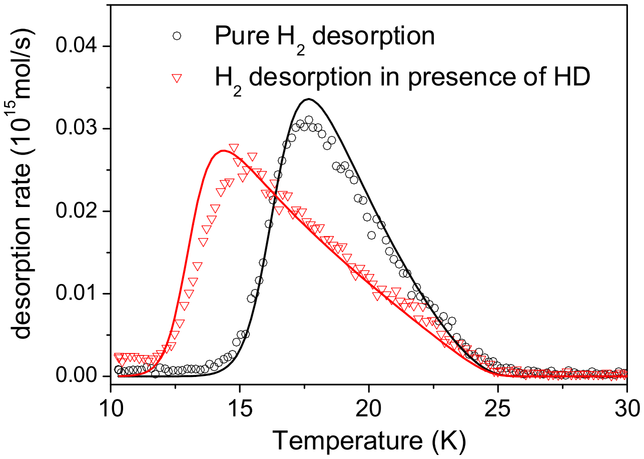

FIG. 1 (color online). H_2 Desorption after deposition of 0.7 ML (1 ML = 1×10^{15} mol/cm^2) on 10 ML porous ASW ice at 10 K. Desorption without any other adsorbate (circles), and in presence of 0.5 ML of HD (triangles). Solid lines: result of our model fitting simultaneously several isotopic mixtures at various doses.

The relative population of $J'' = 1$ to $J'' = 0$ depends on the para-ortho (p-o) conversion. At 10 K, if p-o conversion occurs, more than 99.9% of the molecules should be detected in the $J'' = 0$ state. If conversion does not occur, molecules that reach the surface in even rotational states relax in the $J'' = 0$ state, whereas molecules in odd rotational states relax and are detected in the $J'' = 1$ state. Thus in this case at 10 K, 66.6% of the population should be in the $J'' = 0$ state and 33.3% in the $J'' = 1$ state. Figure 2 shows D_2 desorption profiles of the individual $J'' = 0$, 1, and 2 rotational states. At 300 K, the temperature of the incident beam, the $J'' = 2$ state is the most populated state. Its desorption, that could occur between 15 and 27 K, is very weak. Below 30 K, only the $J'' = 0$ and $J'' = 1$ states are populated because the molecules are desorbing in thermal equilibrium with the surface. At this temperature the $J'' = 2$ state is not populated (<1%). We found within the error bar that no conversion occurs. In a separate experiment, we waited for 30 min after deposition and did not see any changes (within error bars). In our experimental conditions, there is no p-o conversion on a time scale of 10^3 s, on the contrary to what has been observed with other substrates [20]. On porous ASW ice, the conversion to the lowest state has been observed by Hixson *et al.* [10] with a half-life of 116 min [21]. But as mentioned, there remains some exchange between H_2 in the gas phase and the porous network, which is not the case

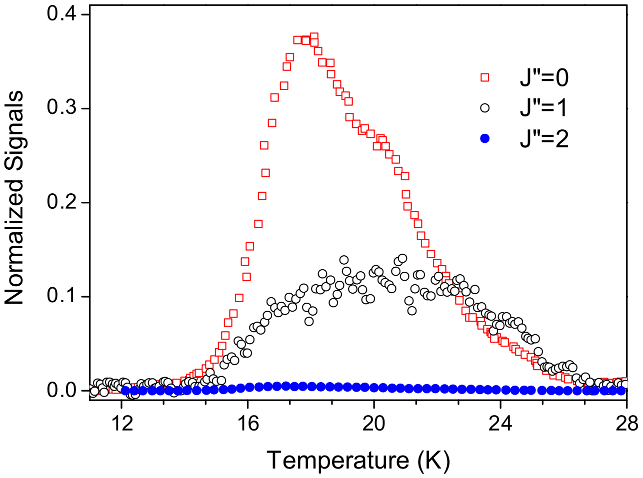

FIG. 2 (color online). D_2 desorption after deposition of 1.5 ML of D_2 on 10 ML porous ASW ice at 10 K. Square: $J'' = 0$ rotational state (average of 5 measurements); empty circles: $J'' = 1$ rotational state, full circles: $J'' = 2$ rotational state (average of 3 measurements). The data have been averaged with 20 points (each point in the figure represents 1 s).

under our UHV conditions. Therefore the results of the two experiments are not in contradiction because experimental conditions are not identical. The desorption profiles of the D_2 molecules in the $J'' = 0$ and $J'' = 1$ states are not similar. The $J'' = 0$ desorption signal is dissymmetric and starts with a sharp edge at 15 K, whereas the $J'' = 1$ desorption signal is much more symmetric and on average, desorption occurs at higher temperature than for $J'' = 0$. This kind of modification of the profiles is rather similar to what is observed for isotopic mixtures and without any rotational selection. Analogously we can conclude that molecules in the $J'' = 1$ rotational state have a slightly higher adsorption energy than the molecules in the $J'' = 0$ state because they desorb at higher temperature. Figure 3 shows the QMS profile that has been normalized to 1, and the sum of the $J'' = 0$ and $J'' = 1$ desorption profiles (normalized, respectively, to 2/3 and 1/3). We can see that the two curves are identical within the experimental error bars. This is what is expected because the QMS signal integrates the contribution of every quantum rotational state. The chosen normalization conditions are based upon the assumption that no *p*-*o* conversion occurs. The fact that the normalized QMS signal and the normalized rotational signal match together, reinforces the hypothesis that no conversion occurs. On Fig. 3 is also reproduced the result of our modeling which fits correctly all the curves. The following assumption has been used: the adsorption energy distributions of the molecules in the $J'' = 1$ and $J'' = 0$ states are simply shifted by a constant value E_s. This energy shift represents the contribution of the asymmetric part of the $J'' = 1$ wave function to adsorption energy. The results presented in Fig. 3 correspond to $E_s = 1.4$ meV. Other parameter values are similar to those adopted in Ref. [12]. Meanwhile, parameter a, which is a normalization parameter, can be slightly readjusted, and a moderately better fit can be obtained. We have used this degree of freedom in order to estimate the uncertainty of the fitting procedure and we have determined that the shift in adsorption energy between the two D_2 states is $E_s = 1.4 \pm 0.3$ meV. This adsorption energy shift is an average value over all the adsorption sites. It is around half the value calculated for H_2 interaction (2.6 meV) [21], and this result therefore confirms the pertinence of both calculation and analysis. Of course the inversion of the o/p energy shift between D_2 and H_2 is not significant because the effect is only linked to the difference between the $J'' = 0$ and $J'' = 1$ symmetry of the wave function. The very small energy difference between ortho- and para- species could appear as a minor effect in the context of astrophysical media. But if we consider here a typical dark cloud with a density of 10^4 hydrogen molecules per cubic centimeter and a medium (gas and grains covered with ice) at 10 K, using our measured value of 1.4 meV and our model to estimate the behavior of absorbed molecules, the o/p ratio of adsorbed deuterium is enhanced by a factor of 5. For hydrogen, if we use the 2.6 meV value [11], that has been estimated but never measured so far, the o/p ratio is reduced by a factor of 20. In the next attempts to observe H_2 adsorbed on ice, this should be taken into consideration. Moreover as the o/p ratio is surface temperature dependent, it might be possible to determine the grain temperature by measuring the two contributions of the infrared lines (4141 and 4131 cm^{-1}). These lines correspond, respectively, to the $Q(0)$ and $Q(1)$ transitions of adsorbed para- and ortho-H_2.

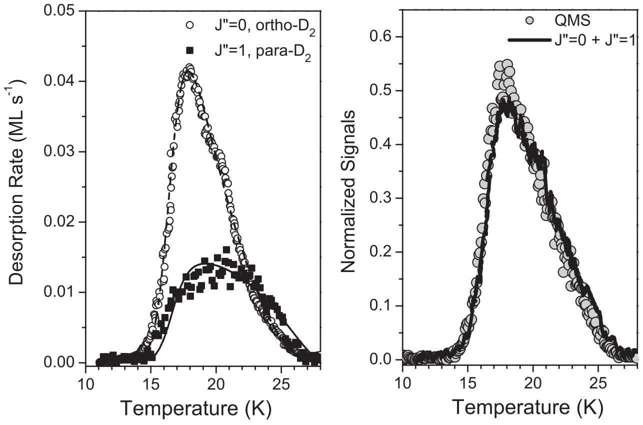

FIG. 3. D_2 desorption after deposition of 1.5 ML of D_2 on 10 ML porous ASW ice at 10 K. Right side; filled gray circles: QMS signal, dotted line: normalized sum with coefficient (see text) of the $J'' = 0$ and $J'' = 1$ desorption. Left side; circles $J'' = 0$ desorption signal; full squares: $J'' = 1$ desorption signal, solid lines: modeling.

We have applied a new experimental procedure (TDS-SQS) in order to address the problem of the rotational energy dependence of the D_2 adsorbed on porous ASW ice. By coupling classical TDS and REMPI-TOF detection it is possible to obtain information about the rotational states behavior, during the adsorption-desorption process. D_2 molecules at room temperature deposited on a surface at 10 K, relax in the lowest ortho- and para- states without *p-o* conversion on a 10^3 s time scale. When a temperature ramp is applied, D_2 desorbs in the $J'' = 0$ and $J'' = 1$ rotational states. The desorption profiles have different shapes, suggesting that the broad adsorption energy distribution of D_2 on porous ASW ice is dependent on the rotational state of the adsorbed molecules. By using a Fermi-Dirac distribution over the adsorption sites, and by assuming an average energy shift $E_s = 1.4 \pm 0.3$ meV between the adsorption energy distribution of the $J'' = 1$ and $J'' = 0$ states, it is possible to reproduce the shape of the observed TDS—SQS. This first experimental measurement is in agreement with the value previously calculated for H_2-water cluster interaction. We plan to apply this new technique to the study of H_2 adsorption on ASW ice. Even if the analysis is complicated by the constant background signal due to residual pressure in UHV chambers, knowledge of the difference between ortho- an para- hydrogen during the adsorption—desorption process is of paramount interest in an astrophysical context.

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*Present address: Université Paris-Sud, LCAM, UMR 8625 du CNRS, Bât. 351, 91405 Orsay cedex, France.
†Corresponding author.
francois.dulieu@u-cergy.fr
‡Present address: Université Pierre et Marie Curie–Paris 6, LPMAA, UMR 7092 du CNRS, France.

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