PHYSICAL REVIEW A **82**, 036704 (2010)

Reply to “Comment on ‘Collisional cooling investigation of THz rotational transitions of water’ ”

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(Received 3 August 2010; published 29 September 2010)

This response describes the authors’ reaction to a critique of recent work on the ultracold physics of water. The possibility of spin-selective adsorption occurring in the context of the collisional cooling experiment is discussed.

DOI: 10.1103/PhysRevA.82.036704 PACS number(s): 34.10.+x, 33.70.−w, 34.80.Gs

“Comment on Collisional cooling investigation of THz rotational transitions of water,” by A. F. Krupnov, is a reasonable and thought-provoking critique of recent literature published in Physics Review A. At first glance the premise of the comment (that the experiment in Dick *et al.* [1] had preferential adsorption of hydrogen spin isomers) appears probable, but several issues lead to some doubt of that premise.

The first issue relates to the temperature regime at which the adsorption process has been documented by Buch and Devlin [2]. In that study the adsorption was performed at 12 K, where n-H_2 (as well as p-H_2 and o-H_2) exists in a liquid phase with a small vapor pressure. Choice of a condensible temperature dramatically increases adsorption of a gas onto any surface, and based on vapor pressures reported in Leachman *et al.* [3] the vapor pressure of n,p and o-H_2 all increase by orders of magnitude above 20 K, where the experiment in Dick *et al.* was performed. Increased vapor pressure would imply a similar reduction in adsorption, but there is currently no source of temperature-dependent adsorption potential for any type of H_2 over amorphous ice. There are some interesting studies of temperature-dependent desorption [4,5] of ices prepared in a similar fashion to Buch and Devlin [2]. In these studies the amorphous ice seems capable of holding onto the adsorbed H_2 until the ice is heated to about 26 K, and the authors specifically state “. . .most of the [H_2] molecules are released before 30 K.” The most direct argument for preferential adsorption at temperatures above 12 K seems to follow from the direct measurement of the adsorption energy difference between o- and p-D_2 (over amorphous water ice) [5], which was determined to be 1.4 ± 0.3 meV (16 K). This would indicate that temperatures below 16 K are efficient for fractionation and that temperatures above 16 K are considerably less efficient. A direct measurement of the o- and p-H_2 adsorption energy difference is not available, but even an isotope effect as large as a factor of 2 ($\sqrt{2}$ is expected for the pre-exponential factor) would not make preferential adsorption likely above 30 K. Therefore, the difference in temperatures is difficult to ignore in the present comparison, and Krupnov’s suggestion that spin-selective adsorption can occur above condensible temperatures seems highly speculative in this regard.

The second issue regards the statement that low-energy quantum mechanical effects are not expected to qualitatively modify the temperature dependence of pressure-broadening coefficients. In support of this statement the similar (but less pronounced) behavior in the CO-H_2 [6] is also brought into question. There are two problems with this reasoning. The first one is that quantum-mechanical “resonances” are actually expected [7] to cause major qualitative, even unpredictable, changes in the collision cross sections and therefore pressure broadening. Secondly, indeed structure is apparent in the CO-H_2 data, however, a very similar structure is also apparent in the CO-He data. It is not clear how the logic flows through this argument since there is no expectation of significant amounts of amorphous water ice in the system; amorphous CO ice does form below 40 K but, as far as we are aware, it is not expected to capture H_2. Furthermore, the He-CO system does not have any components that could fractionate.

Nevertheless, there is a need to experimentally prove or disprove the adsorption hypothesis, and we intend to fully explore the possibility of the o-H_2 adsorption effect occurring in our system. If the amorphous ice developed during the experiment is pumped “clean” and then used in a controlled fashion, we might expect to perform measurements through the o-H_2 vapor-pressure maximal point, that is, below a certain pressure at a given temperature (the vapor pressure of o-H_2 over amorphous ice) we would observe the broadening of a mixed sample of o- and p-H_2, but pressures above this point (and below the ice saturation threshold) would exhibit a different pressure-broadening curve (indicative of p-H_2) since the added o-H_2 would be actively condensed. Observation of this piece-wise linear pressure dependence was not observed in our previous experiments, perhaps because no effort was made to clean the amorphous ice, which was likely always saturated with o-H_2. If this behavior can be observed it may allow us to measure the vapor pressure of o-H_2 over amorphous ice. As the work of Amiaud *et al.* [4,5] as well as Buch and Devlin [2] have stated, the adsorption process (as well as preferential spin adsorption) must be considered in astrophysical models, therefore, any evidence for its effect in our apparatus will need to be fully exploited.

This paper presents research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

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