Comment on "Collisional cooling investigation of THz rotational transitions of water"

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A possible experimental explanation for the unusual temperature dependence of water line broadening by molecular hydrogen recently observed by Dick *et al.* [Phys. Rev. A **81**, 022706 (2010)] is proposed. This temperature dependence differs radically from both theoretical predictions and the higher temperature behavior, but remains unexplained. It is suggested that the cause is a change in sample composition due to preferential adsorption of orthohydrogen onto the cell walls at low temperature. As parahydrogen has collision cross sections with water molecules up to an order of magnitude smaller than those with orthohydrogen, an enrichment of the gas sample by parahydrogen would lead to a decrease in broadening parameters at low temperatures, as observed in the experiment.

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In their investigation of collisional broadening of some THz lines of H_2O by He and H_2, Dick *et al.* [1] observed dependence of H_2 broadening on temperature which deviates strongly from both theoretical predictions and extrapolations from higher temperature measurements at the lower end of the temperature range they studied. Specifically, instead of the expected increase in the broadening parameters with lowering of the temperature, they found a sharp decrease starting from about 70–80 K. In contrast, the temperature dependence of broadening by He followed both theoretical predictions and extrapolation from higher temperatures. Dick *et al.* [1] state that this sharp decrease in broadening was not predicted by the most recent theoretical calculations and discuss the impact of their new broadening measurements on the interpretation of results of the interstellar medium studies and models of star formation. Thus, confirmation of the temperature dependence found in [1] may lead to important consequences such as, for example, revision of the abundance of the important molecule water in cold dense clouds. This Comment suggests a possible mechanism, not discussed by Dick *et al.* [1], which could lead to the unexpected temperature dependencies observed.

Dick *et al.* [1] do not discuss their H_2 sample composition and their analysis appears to assume that it is normal (25% para, 75% ortho). It is reasonable to assume that, on the time scale of the experiment, no significant orthohydrogen-parahydrogen conversion can occur. The mechanism proposed here is connected to another possible change of the H_2 sample composition not controlled in [1]. The change of a fixed amount of the H_2 sample [2] can be produced through orthohydrogen-parahydrogen separation by preferential adsorption at low temperatures. As first observed by Sandler [3], and summarized by White *et al.* in an International Union of Pure and Applied Chemistry publication [4], the effect of preferential adsorption showed that hydrogen molecules in their $J = 1$ rotational state (ortho-H_2) are more strongly adsorbed than molecules in the $J = 0$ ground state (para-H_2). The ortho-para separation factor increases with decreasing temperature; it was measured as rising from 1.6 at 90 K [3] to 16 at 20.4 K

by Cunningham and Johnston [5]. Characteristic evidence for the preferential adsorption of orthohydrogen was given by the experiments of Cunningham *et al.* [6], who prepared nearly pure orthohydrogen by successive adsorption and desorption of hydrogen. The theory of this effect is given by White and Lassettre [7]. Calculations by Phillips *et al.* [8] and Dubernet *et al.* [9] give cross sections for ortho-H_2 and para-H_2 collisions with water which differ by up to an order of magnitude with the cross section for parahydrogen being smaller and close to the cross section for He-H_2O collisions. This means that an excess of parahydrogen and a lack of orthohydrogen in the gas sample at low temperatures as a result of orthohydrogen-parahydrogen separation by preferential adsorption would lead to a decrease in the broadening parameter measured, as was observed in experiment [1].

Dick *et al.* [1] found that the temperatures of the walls in their spectrometer absorption cell, as measured by a thermometer, were significantly lower than the gas in their cell, as given by the kinetic temperature measured through Doppler line broadening. Strong deviation of the observed broadening from the expected one begins at a gas temperature of 70–80 K, what corresponds by their formula in Fig. 3 to 43–32 K wall temperature, and increases for lower temperatures. So the wall temperatures in the range of measurements are low enough for the ortho-para separation coefficient to be large. The effect of modification of the cell surface by a loose deposit of frozen water on the cold walls produced by water vapor continuously entering the cell may play a significant role. Preferential adsorption of orthohydrogen onto amorphous ice exposed to normal H_2 at 12 K was observed by Buch and Devlin [10], who found that only the ortho-H_2 infrared band was visible in their spectrum of a newly formed adsorbate layer; they identified the para-H_2 content of the layer as less than 10%. Of course, 100% adsorption is unlikely (even at 12 K). Work by Buch and Devlin [10] was done at a lower temperature than the Dick *et al.* work [1], and, as was pointed out earlier, the efficiency of the separation process decreases at higher temperatures. It is difficult to find a study in which all conditions of the experiment exactly matched those of the Dick *et al.* work [1], and Buch and Devlin [10] studied preferential adsorption of ortho-H_2 with respect to para-H_2 on amorphous ice surface which is most relevant to the Dick

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et al. [1] study. Buch and Devlin comment that amorphous ice is a form of ice obtained by slow deposition of gaseous H_2O on a cold surface. This description corresponds to the conditions in which an ice deposit is formed in experiment [1]. Furthermore, low-temperature amorphous ice deposits are microporous and have a very high surface area with respect to gas adsorption [10] (of the order of 400 m^2/g [11]).

Support for the proposed mechanism comes from the observation that all the line broadening parameters measured by Dick *et al.* [1] show a qualitative change in their temperature dependence at about the same temperature. This is not what one would expect if this phenomenon was due to low-energy, quantum-mechanical effects. In addition, similar experiments on H_2-CO line-broadening parameters by Mengal *et al.* [12] show excellent agreement with calculations based on

broadening by para-H_2 only at temperatures below 20 K; this behavior can also be seen at low temperature for the $J = 5$–4 CO transition measurements by Dick *et al.* [13].

At present it is difficult to give a precise quantitative estimate of the effect proposed here. However, Dick *et al.* [1] propose exploring the individual roles of para- and orthohydrogen in collision with water. Such experiments would clearly be a major step in resolving this issue.

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