PHYSICAL REVIEW A **82**, 040702(R) (2010)

Ab initio computation of the broadening of water rotational lines by molecular hydrogen

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(Received 8 July 2010; published 27 October 2010)

Theoretical cross sections for the pressure broadening by hydrogen of rotational transitions of water are compared to the latest available measurements in the temperature range 65–220 K. A high-accuracy interaction potential is employed in a full close-coupling calculation. A good agreement with experiment is observed above ~80 K, while the sharp drop observed experimentally at lower temperatures is not predicted by our calculations. Possible explanations for this discrepancy include the failure of the impact approximation and the possible role of ortho-to-para conversion of H_2.

DOI: 10.1103/PhysRevA.82.040702 PACS number(s): 34.50.Ez, 34.20.Gj, 98.38.Bn, 98.38.Am

Water is a prominent molecular component of interstellar matter. It has been observed in most astrophysical environments, in both the gas and the solid phases, as the most abundant polyatomic molecule [1]. Understanding water spectra is a key to the general thermodynamical budget of astrophysical objects, because of the many allowed spectral transitions, in millimeter, submillimeter, and infrared regions of the spectrum. Also, the chemical and even exobiological importance of water cannot be understated. A detailed comprehension of water physical chemistry in various environments is a major goal of the newly launched Herschel Space Observatory (HSO).

To extract information from a molecular rotational spectrum, it is essential to model its excitation scheme. Indeed, at low densities, some lines may appear in absorption, some others in emission, and there is no *a priori* reason for the molecule under scrutiny to be in thermodynamical equilibrium with the main neutral gas, H_2. Hence, retrieving physical information from spectral lines is only possible with a careful modeling of the interaction of the water molecule with its photonic and molecular environments. Obtaining such models has been a continuous effort in three directions: studies of radiative transfer mechanisms [2], scattering theory, and, very importantly, laboratory experiments capable of testing various theories and models pertaining to collisions. Many comparisons between experiments and theory are currently under way, to put the water-hydrogen interaction on a firm ground [3–6].

In this communication, we wish to show the results of a fully *ab initio* computation of pressure-broadening cross sections, $\sigma^{\text{p.b.}}(T)$, based on a high-precision potential energy surface (PES) for the water-hydrogen interaction (Refs. [7] and [8]; hereafter V08), as compared to the very recent experiments of pressure broadening at low temperatures by Dick *et al.* (Refs. [9] and [10]; hereafter DDP10). Other comparisons were very successful for simpler symmetries [11–15].

Water being an asymmetric rotor, the rotational levels are usually denoted $j_{\kappa_a\kappa_c}$ or (j,τ), where j is the rotational quantum number associated with the angular momentum, (κ_a,κ_c) (projections of j along the inertia axis) are pseudoquantum numbers, and $\tau = \kappa_a - \kappa_c$. The rotational constants of H_2O are taken as $A = 27.880\,631\,34$ cm^{-1}, $B = 14.521\,769\,59$ cm^{-1}, and $C = 9.277\,708\,381$ cm^{-1}. The rotational constant of H_2 is taken as $B = 60.853$ cm^{-1}.

Following the experiments of DDP10, here we compute the pressure broadening of the two spectral transitions connecting the ground states of water: the para 1113-GHz line ($1_{11} \leftarrow 0_{00}$) and the ortho 556-GHz line ($1_{10} \leftarrow 1_{01}$). All our calculations are based on the V08 water-hydrogen full-dimensional PES that was obtained by combining standard CCSD(T) calculations with elaborate explicitly correlated CCSD(T)-R12 calculations. Full details and references for these *ab initio* quantum chemical methods may be found in [8]. As did Dubernet *et al.* [16], we have employed the rigid-body version of the V08 PES obtained by averaging the full-dimensional PES over the ground vibrational states of the monomers. Full details are given in [8].

The broadening of a rotational spectral line because of collision with a buffer gas has been studied theoretically and experimentally for a long time, and theory is by now well established. The very general impact approximation states that collision times are much shorter than the time between collisions. Within that approximation, which we discuss later, it has been shown that the pressure-broadening cross section for the transition from initial state i to final state f, at temperature T, $\sigma^{\text{p.b.}}_{f\leftarrow i}(T)$, may be expressed by closed expressions based on the transition matrix $\mathbf{T}$ [17,18].

For a broadening coefficient $\Gamma_{f\leftarrow i}(T)$, in frequency per pressure units, Baranger [19] defined the pressure-broadening cross section at energy E, $\sigma^{\text{p.b.}}(E)$, as

$$\Gamma_{f\leftarrow i}(T) = 1/2\langle n v \sigma^{\text{p.b.}}_{f\leftarrow i}(E)\rangle_{T\ \text{Boltzmann av.}}, \tag{1}$$

where i and f are the initial and final states of the transition, n is the density of the observed molecule, and v is the relative velocity of water and hydrogen. E is the collision kinetic energy. Hence it is possible to define a Boltzmann averaged $\sigma^{\text{p.b.}}_{f\leftarrow i}(T)$:

$$\sigma^{\text{p.b.}}_{f\leftarrow i}(T) = \frac{1}{T^2}\int \sigma^{\text{p.b.}}_{f\leftarrow i}(E) e^{-E/T} E dE. \tag{2}$$

Two equivalent ways have been proposed to calculate $\sigma^{\text{p.b.}}_{f\leftarrow i}(E)$ and, consequently, the averaged $\sigma^{\text{p.b.}}_{f\leftarrow i}(T)$. Following Baranger [17], Schaefer and Monchik [20,21], and Green [22], we have, for a rotational transition of H_2O $(j_f,\tau_f \leftarrow j_i,\tau_i)$,

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assuming that H_2 remains in an unchanged j_2 state:

$$\begin{aligned}\sigma^{\text{p.b.}}&(j_f\tau_f j_2 \leftarrow j_i\tau_i j_2; E)\\ &= \frac{\pi}{k^2}\frac{1}{2j_2+1}\sum_{J_iJ_f}\sum_{l,l',j_{12}j'_{12},\bar{j}_{12}\bar{j}'_{12}}\\ &\quad\times X(J_i,J_f,j_i,j_f,l,l',j_{12}j'_{12},\bar{j}_{12}\bar{j}'_{12})\\ &\quad\times\langle j_2 l_0 j_{12} j_i\tau_i|\mathbf{T}^{J_i}(E_i)|j_2 l'_0 j'_{12} j_i\tau_i\rangle\\ &\quad\times\langle j_2 l_0 \bar{j}_{12} j_f\tau_f|\mathbf{T}^{J_f}(E_f)|j_2 l'_0 \bar{j}'_{12} j_f\tau_f\rangle^*. \qquad (3)\end{aligned}$$

In Eq. (3), j_{12} and j'_{12} are the angular quantum numbers resulting from the coupling of angular momenta j_2 and j_i/j_f [e.g., $|j_2 - j_i| \leqslant j_{12}$, $j'_{12} \leqslant (j_2 + j_i)$]. l_0 and l'_0 are the orbital quantum numbers. $\mathbf{T}^J(E) = 1 - \mathbf{S}^J(E)$ is the transition matrix, at total angular momentum J. The $X(\cdot)$ function groups all angular coupling coefficients and parity sign terms; this is explicit in [21]. E_i and E_f are the two initial and final *total* energies ($E_i \neq E_f$), corresponding to the same kinetic energy, $(\hbar k)^2/2\mu$, μ being the collision reduced mass and k the momentum. A similar equation relevant for H_2O- H_2 coupling is given by Monchik's Eq. (1) [21]. It should be noted that the $1/(2j_2+1)$ factor in front of Eq. (3), lacking in [22], is necessary, as emphasized, for example, in [23].

Baranger, followed by many other authors, proceeded to compute the $\sigma^{\text{p.b.}}(E)$ in a different, yet equivalent way, with the help of the optical theorem. We have, with nearly the same notations as [17],

$$\begin{aligned}\sigma^{\text{p.b.}}_{f\leftarrow i}(E) &= \frac{1}{2}\left[\sum_{f'}\sigma^{\text{inel.}}_{f'\leftarrow i}(E) + \sum_{i'}\sigma^{\text{inel.}}_{f\leftarrow i'}(E)\right]\\ &\quad + \int |f_i(\Omega;E) - f_f(\Omega;E)|^2 \mathrm{d}\Omega. \qquad (4)\end{aligned}$$

In Eq. (4), $\sigma^{\text{inel.}}(E)$ are ordinary *inelastic* cross sections, i' and f' being all levels connected to f or i at kinetic energy E. The $f_i(\Omega;E)$ and $f_f(\Omega;E)$ are the differential *elastic* scattering amplitudes for the initial and final states, respectively, which must be set to interfere before taking the modulus and integrating over all scattering angles Ω.

It must be strongly emphasized that both approaches are equivalent. Quite often, since inelastic cross sections or rate coefficients are made available in the literature, to get an estimate of $\sigma^{\text{p.b.}}_{f\leftarrow i}(E)$, Eq. (4) is truncated: only the first two terms, the inelastic cross sections, are used, sometimes yielding reliable results [24] and sometimes not [13], depending on the structure of the scattering amplitudes (see the following).

To calculate the **T**-matrix elements of Eq. (3), we performed a full quantum close-coupling scattering computation with the help of the MOLSCAT program [25]. The **T**-matrix elements were subsequently summed at each kinetic energy to get the relevant $\sigma(E)$ cross sections for inelastic and pressure broadening. We separately computed collisions of the four symmetry types: (para or ortho H_2O)-(para or ortho H_2). Parameters of the MOLSCAT calculations are similar to those used previously [6,16,26–28], with the following rotational basis sets: para-H_2, $j_2 = 0,2$; ortho-H_2, $j_2 = 1$; and ortho and para H_2O, $j_1 \leqslant 5,6,7$, for increasing collision energy. For $E < 20\ \text{cm}^{-1}$, the hybrid modified log-derivative (Airy) propagator of Manolopoulos and Alexander was used; above that energy, the diabatic modified log-derivative method of Manolopoulos was used [25]. We checked convergence with respect to basis set size, maximum range of radial integration, and size of step in the radial propagation. The collision energy range was $0.5 \leqslant E \leqslant 350\ \text{cm}^{-1}$, with increments ΔE small enough to roughly describe resonances. A decrease in the ΔE step did not change significantly the averaged $\sigma^{\text{p.b.}}_{f\leftarrow i}(T)$, which was obtained by a numerical integration of Eq. (2). At collision energies $E > 350\ \text{cm}^{-1}$, $\sigma^{\text{p.b.}}(E)$ remains essentially flat and was therefore extrapolated as a constant.

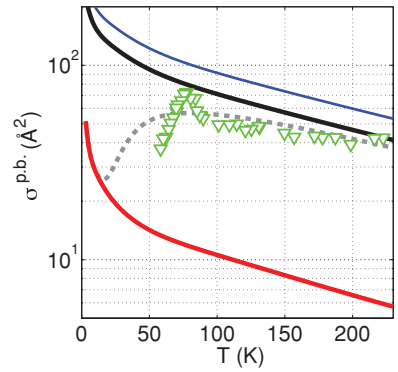

FIG. 1. (Color online) Pressure-broadening cross sections for the transition at 556 GHz, ortho-H_2O, $1_{10} \leftarrow 1_{01}$. Theory: lower solid (red) line, pure para-H_2 collisions; upper solid(blue) line, pure ortho-H_2 collisions; middle solid (black) line, OPR value, 3. Dashed (gray) line, OPR value at equilibrium for each T. Triangles (green), experimental values taken from [10].

Results are presented in Figs. 1 and 2. In addition to the pure ortho H_2 [upper (blue) lines] and para H_2 [lower (red lines)] cross sections, we added two possibilities for the ortho-to-para ratio (OPR) of H_2: solid (black) lines suppose a "normal" OPR value of 3, as expected in the DDP10 experiment. Dashed (gray) lines suppose that the thermodynamical equilibrium OPR value is reached at each temperature T, as if ortho-to-para transitions were possible. In both figures, the results of DDP10 are shown as open (green) symbols, with their exact values provided courtesy of B. Drouin.

Several points may be seen by inspection of Figs. 1 and 2. If we assume an OPR value of 3, we see that the theory vs. experiment agreement is very good (within 30%)

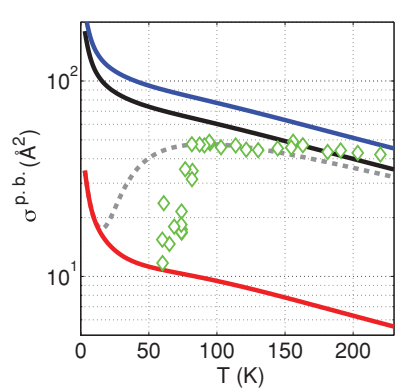

FIG. 2. (Color online) Pressure-broadening cross sections for the transition at 1113 GHz, para-H_2O, $1_{11} \leftarrow 0_{00}$. For details, see caption to Fig. 1.

for $T \gtrsim 80$ K. Let us recall that there are no adjustable parameters involved in the simulation, except for the OPR value. This agreement should come at no surprise, since recent analogous calculations on branches of Raman spectra show similar successes [11,23,29,30]. Both those calculations and ours make use of state-of-the-art *ab initio* PESs as well as fully converged close-coupling calculations. Within the impact approximation valid at these temperatures and moderate densities ($n \lesssim 1$ amagat), the Baranger formalism [17], Eq. (3), is essentially exact for nonoverlapping lines. The whole uncertainty that arises is due either to inadequacies of the impact approximation, which is to be ruled out here at $T > 80$ K (see, e.g., [18] or [31] for a discussion), or to imprecision of the PES. We thus see that we actually test the PES by comparing experimental pressure broadening with careful quantum calculations, in the relevant density and temperature ranges.

Pressure-broadening cross sections, at these intermediate temperatures, are sensitive to the overall shape of the PES, especially to the isotropic part. This may be understood in two ways. First, the **T**-matrix elements actually used in Eq. (3) are elastic in the rotational quantum numbers, thus nonzero also for an isotropic potential energy surface. Second, this is confirmed by the good quality of the pressure-broadening coefficients obtained by approximate semiclassical methods, where the impinging trajectory of the perturber is totally decoupled from the tensorial nature of the molecule-molecule electromagnetic interaction [31–33]. In retrospect, we understand that approximating the full Eq. (3) by the purely inelastic terms in Eq. (4) may be correct in certain cases, but this should at least be carefully checked. An analogous point has been made earlier; see [23].

We show in Fig. 3 the present results compared to estimates based on the inelastic sum, Eq. (4), but truncated to the first two terms, as in DDP10 (and corrected for an error of a factor of 2 for the Dubernet *et al.* data). We see that there is a strong disagreement between the two computational schemes. In particular, data computed from the inelastic

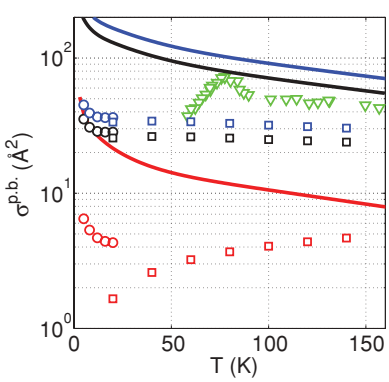

FIG. 3. (Color online) Pressure-broadening cross sections for the transition at 556 GHz, ortho-H_2O, $1_{10} \leftarrow 1_{01}$. Upper (blue), lower (red), and middle (black) solid lines represent present theories, as in Fig. 1. Open symbols: summation of inelastic scattering cross sections as in DDP10; color scheme identical to that for the solid lines. Circles, from Dubernet *et al.* [16]; squares, from Green *et al.* [24]; color scheme identical to that for the solid lines. Triangles: experimental values taken from DDP10.

rates of Dubernet *et al.* [16], which are based on the same PES as in the present work, are significantly lower than the present rigorous calculations. The observed differences are to be attributed to the approximation in applying the random phase approximation (neglect of the elastic scattering interference term) to Eq. (4). Furthermore, DDP10 made the further simplification of replacing the averaging procedure of Eq. (2) by using rate coefficients divided by the average thermal velocity. While this should not change the trend of the $\sigma^{p.b.}(T)$, it adds some further imprecision. For $T > 20$ K, the DDP10 points were extracted, via the same procedure, from the older values of Phillips *et al.* [34] based on a less accurate PES. We note that the same procedure was also applied by DDP10 to the case of H_2O-He, where it was found to be quite accurate, suggesting a very different structure of the scattering amplitudes. This is actually not surprising since (i) the H_2O-He and H_2O-H_2 PESs are very different (see, e.g., [3,4]), and (ii) additional coupling terms are introduced by the rotational angular momentum of H_2.

The low-temperature range of the theory vs. experiment comparison, $T \lesssim 80$ K, is more problematic. Experiments show a dramatic *decrease* in $\sigma^{p.b.}(T)$ as T goes below about 80 K, for both transitions examined here and, also, for higher transitions. An analogous, even if less pronounced, effect was also found for $\sigma^{p.b.}(T)$ in [12] and [13] for HCN-He and ^{13}CO-He, respectively, albeit at a much lower T, about 5 K. No definite explanation may be found in these preliminary calculations, but it must be noted that disagreement between computations and experiments arise at energies where the pressure-broadening and inelastic cross sections enter into a regime where narrow resonances become prominent (see, e.g., [28]). If resonances are sufficiently narrow, that is, if the complex H_2O-H_2 is sufficiently long-lived, the impact approximation may no longer be valid. According to the density in the DDP010 experiment ($n \sim 10^{20}$ cm^{-3}; B. Drouin, private communication), and with a cross section of about $\sigma^{p.b.}(E = 80\text{ K}) \simeq 50$ Å^2, an average speed of $v = \sqrt{2E/\mu} \simeq 1$ km/s, and a resonance width of about $\Gamma \simeq 1$ cm^{-1} [28], we have that the interaction volume U becomes comparable to the inverse density [19],

$$U = (hv\sigma^{p.b.}/\Gamma) \simeq 1.6 \times 10^{-20}\text{ cm}^3 \sim 1/n \simeq 10^{-20}\text{ cm}^3, \tag{5}$$

invalidating the impact approximation. It is also possible that, for yet unknown reasons, there is a dramatic conversion from ortho-H_2 to para-H_2 at low temperatures, through some paramagnetic impurities in the walls of the cell [35], even if there is no experimental hint that indicates this explanation at the moment. Further insight is obviously needed in those regimes. Measurements with para-$H_2(j = 0)$ would be particularly valuable both for comparison with theory and for applications to cold interstellar clouds, where H_2 is mostly in its para form [36].

In this communication, we have shown, using full quantum scattering methods combined with state-of-the-art PESs, that very good agreement is found between experimental pressure broadening and theoretical calculations at temperatures where the impact approximation is clearly valid, that is, $T \gtrsim 80$ K. We have found that the rigorous theory of Baranger is needed to make valuable predictions for the present system and that

simple approximations based on the manipulation of inelastic rates or cross sections are unreliable. We stress, in particular, that the sharp drop observed in the pressure-broadening measurements below ∼80 K, and not predicted by the present calculations, does not cast doubt on the inelastic rates computed by Dubernet *et al.* [6,16,26], since a rigorous quantum theory of broadening beyond the impact approximation seems necessary in this regime, as already discussed. As a result, in our opinion, the water-hydrogen V08 PES is once more successfully tested, with a special emphasis on the mid- to long-range region of the PES and the isotropic part. Thus, here we complement various tests performed recently on the water-hydrogen system, such as differential measurements [4] and molecular beam scattering experiments [5], which so far have all confirmed the high accuracy of the V08 PES. Another series of experiments, now under way, would aim at the spectroscopy of the bound H_2O-H_2 van der Waals molecule. With all these tests completed in the near future, the V08 PES will be thoroughly tested and extremely good confidence should be gained for all astrophysical applications.

We thank B. Drouin for communicating detailed experimental data, as well as F. Thibault for useful insights. This project was partly supported by the Institut National des Sciences de l'Univers, through its program Physico-Chimie de la Matière Interstellaire, and by the CNES. The Laboratoire d'Astrophysique is a joint CNRS/Université Joseph-Fourier Institute facility, under the name UMR 5585.

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