

RAPID COMMUNICATION | DECEMBER 20 2010

## Communication: Rotational excitation of interstellar heavy water by hydrogen molecules **FREE**

Yohann Scribano; Alexandre Faure; Laurent Wiesenfeld



*J. Chem. Phys.* 133, 231105 (2010)

<https://doi.org/10.1063/1.3507877>



View  
Online



Export  
Citation

CrossMark



## The Journal of Chemical Physics

### Special Topic: Algorithms and Software for Open Quantum System Dynamics

**Submit Today**



## Communication: Rotational excitation of interstellar heavy water by hydrogen molecules

Yohann Scribano,<sup>1,a)</sup> Alexandre Faure,<sup>2,b)</sup> and Laurent Wiesenfeld<sup>2,c)</sup>

<sup>1</sup>Laboratoire Interdisciplinaire Carnot de Bourgogne-UMR 5209, CNRS-Université de Bourgogne, 9 Av. Alain Savary, B.P. 47870, F-21078 Dijon Cedex, France

<sup>2</sup>Laboratoire d'Astrophysique, Observatoire de Grenoble-UMR 5571, CNRS-Université Joseph Fourier, B.P. 53, 38041 Grenoble Cedex 09, France

(Received 28 September 2010; accepted 12 October 2010; published online 20 December 2010)

Cross sections and rate coefficients for low lying rotational transitions in D<sub>2</sub>O induced by *para*-H<sub>2</sub> collisions are presented for the first time. Calculations have been performed at the close-coupling level with the deuterated variant of the H<sub>2</sub>O–H<sub>2</sub> interaction potential of Valiron *et al.* [J. Chem. Phys. **129**, 134306 (2008)]. Rate coefficients are presented for temperatures between 1 and 30 K and are compared to the corresponding rate coefficients for H<sub>2</sub>O. Significant differences caused by the isotopic substitution are observed and are attributed to both kinematics and intramolecular geometry effects. Astrophysical implications are briefly discussed in view of the very recent detection of D<sub>2</sub>O by the Herschel Space Observatory. © 2010 American Institute of Physics. [doi:10.1063/1.3507877]

Despite the low elemental deuterium abundance in the Galaxy, D/H~10<sup>-5</sup>, a spectacular deuterium enrichment of many interstellar molecules has been discovered in star forming regions.<sup>1</sup> Among these molecules, the deuterated water isotopologues HDO and D<sub>2</sub>O are of special importance because they can help to understand the origin of water in the interstellar medium and its possible link with the D/H ratios observed in comets, and in the oceans on the Earth. While interstellar HDO was detected a few years after the discovery of H<sub>2</sub>O in the interstellar medium,<sup>2</sup> D<sub>2</sub>O (in the *para* form) has been identified only recently toward the protostar IRAS 16293-2422.<sup>3</sup> In order to interpret the observed spectra in terms of local physical conditions and relative abundances, radiative transfer modeling is necessary which, in turns, requires the knowledge of rates for collisional (de)excitation. In contrast to H<sub>2</sub>O and HDO for which collisional rates with He and/or H<sub>2</sub> are available (see Refs. 4–6 and references therein), there is to the best of our knowledge no collisional data for D<sub>2</sub>O except those of Faure *et al.*<sup>7</sup> for electron-impact excitation.

Here we report calculations of rates for the rotational (de)excitation of D<sub>2</sub>O by *para*-H<sub>2</sub> molecules, the dominant collision partners in cold interstellar molecular clouds.<sup>8</sup> Our main objective is to assess the importance and magnitude of the isotopic substitution on the water excitation. Our work is particularly motivated by the mission of Herschel Space Observatory, which was launched in May 2009, and especially by the very recent detection of the *ortho* form of D<sub>2</sub>O, which has allowed for the first time to derive the *ortho*-to-*para* ratio of D<sub>2</sub>O in the cold and diluted envelope of the protostar IRAS 16293-2422.<sup>9</sup>

All scattering calculations below are based on the full nine-dimensional (9D) H<sub>2</sub>O–H<sub>2</sub> Potential Energy Surface

(PES) of Valiron *et al.*<sup>10</sup> (see also Ref. 11). This PES is independent of nuclear masses and can be employed for any water isotopologues. Its high accuracy has been spectacularly confirmed very recently by differential cross sections measurements,<sup>12</sup> pressure broadening<sup>13</sup> and molecular beam experiments,<sup>14</sup> and bound state calculations.<sup>15,16</sup> Valiron *et al.* were able to establish that employing state-averaged geometries is a reliable approximation for including zero-point vibrational effects within a rigid-rotor PES. Indeed, the explicit average of the full-dimensional PES over the ground state vibrational wavefunctions was found in very good agreement with the rigid-rotor PES at the vibrationally averaged ground state geometries. The corresponding effects on scattering cross sections are examined below. We note that other authors have investigated these effects in the calculation of rovibrational spectra, e.g., recently for the water dimer.<sup>17</sup>

Averaged intramolecular geometries can be determined either theoretically, by computing the integral of the coordinate operator on the vibrational wave function of the monomers, or from some experimental data. In this study, we have chosen the latter approach to determine the ground state averaged geometry of D<sub>2</sub>O, starting from the equilibrium geometry of H<sub>2</sub>O which is the reference for all water isotopologues within the Born–Oppenheimer approximation. The averaged intramolecular geometry  $\bar{\mathbf{q}}$  of D<sub>2</sub>O (i.e.,  $\bar{r}_{\text{OD}}$  and  $\bar{\alpha}_{\text{DOD}}$ ) was obtained from the theoretical equilibrium value,  $\mathbf{q}_{\text{eq}}^{(1)}$ ,<sup>18</sup> and a correction term derived from experimental data using the relation below,

$$\bar{\mathbf{q}}_{\text{D}_2\text{O}} = \mathbf{q}_{\text{eq}}^{(1)} \left( 1 + \frac{\Delta\mathbf{q}^{(2)}}{\mathbf{q}_{\text{eq}}^{(2)}} \right), \quad (1)$$

where  $\mathbf{q}_{\text{eq}}^{(2)}$  is the experimental equilibrium value<sup>20</sup> and  $\Delta\mathbf{q}^{(2)}$  is the deviation of the averaged geometry with respect to the equilibrium one.<sup>19</sup> This way of determining averaged geometries can be seen as a combination of *ab initio* and experimental approaches. The D<sub>2</sub>O averaged geometry is reported

<sup>a)</sup>Electronic mail: Yohann.Scribano@u-bourgogne.fr.

<sup>b)</sup>Electronic mail: Alexandre.Faure@obs.ujf-grenoble.fr.

<sup>c)</sup>Electronic mail: Laurent.Wiesenfeld@obs.ujf-grenoble.fr.

TABLE I. Averaged geometries of H<sub>2</sub>O, D<sub>2</sub>O, and H<sub>2</sub> in their ground vibrational state (distances in angstroms and angles in degrees). The present values for H<sub>2</sub>O and H<sub>2</sub> were taken from Ref. 11 while those for D<sub>2</sub>O were computed from the nuclear correction formula, Eq. (1). The theoretical equilibrium geometry was taken as  $r_{\text{OH}}^{\text{eq}} = 0.9578$  and  $\alpha_{\text{HOH}}^{\text{eq}} = 104.48$  (Ref. 18).

	H <sub>2</sub> O		D <sub>2</sub> O		H <sub>2</sub>
	$\bar{r}_{\text{OH}}$	$\bar{\alpha}_{\text{HOH}}$	$\bar{r}_{\text{OD}}$	$\bar{\alpha}_{\text{DOD}}$	$\bar{r}_{\text{HH}}$
Present	0.9753	104.41	0.9685	104.37	0.7668
Ref. 21	0.9756	104.43	0.9707	104.41	–

in Table I and we observe a very good agreement (better than 1%) with the purely theoretical estimate.<sup>21</sup>

The rigid-rotor D<sub>2</sub>O–H<sub>2</sub> PES was obtained from the full flexible potential energy function of H<sub>2</sub>O–H<sub>2</sub>,  $V_{\text{H}_2\text{O}-\text{H}_2}^{(9D)}$ , but in the center of mass frame of D<sub>2</sub>O and fixing the internal coordinates  $\mathbf{q} \equiv \{\mathbf{q}_{\text{D}_2\text{O}}, \mathbf{q}_{\text{H}_2}\}$  at their vibrationally averaged values (Table I). The water center of mass is shifted by the distance  $\delta\mathbf{r}_{\text{CM}}$  toward the D atoms (along the C<sub>2v</sub> symmetry axis of water). The D<sub>2</sub>O–H<sub>2</sub> intermolecular energies,  $V_{\text{D}_2\text{O}-\text{H}_2}$ , were then generated on a grid  $(R, \theta, \phi, \theta', \phi')$  using the relation:

$$V_{\text{D}_2\text{O}-\text{H}_2}(R, \theta, \phi, \theta', \phi') = V_{\text{H}_2\text{O}-\text{H}_2}^{(9D)}(R^*, \theta^*, \phi, \theta', \phi'; \bar{\mathbf{q}}), \quad (2)$$

where

$$R^* = R(1 + t^2 + 2t \cos \theta)^{1/2} \quad (3)$$

$$\cos \theta^* = (\cos \theta + t) \frac{R}{R^*} \quad (4)$$

with  $t = \delta\mathbf{r}_{\text{CM}}/R$ . The grid points  $(\theta, \phi, \theta', \phi')$  describing the angular coordinates of H<sub>2</sub> relative to D<sub>2</sub>O (see Ref. 10 for conventions) were chosen via random sampling for 28 fixed intermolecular distances  $R$  in the range 3–14  $a_0$ . At each intermolecular distance, the interaction potential  $V_{\text{D}_2\text{O}-\text{H}_2}$  was then least-square fitted using the 149-term angular expansion optimized for H<sub>2</sub>O–H<sub>2</sub> by Valiron *et al.* Full details on the fitting procedure can be found in Ref. 10.

The quantal theory for scattering of an asymmetric top with a linear molecule can be found in Ref. 22. In the present work, calculations were performed using the (non reactive) scattering code MOLSCAT.<sup>23</sup> All calculations were performed at the close-coupling level. In order to properly compare D<sub>2</sub>O and H<sub>2</sub>O cross sections, calculations were performed for both targets. The rotational energy levels of water are labeled by three numbers: the angular momentum  $j_1$  and the pseudo quantum numbers  $k_a$  and  $k_c$ , which correspond to the projection of  $j_1$  along the inertia  $a$  and  $c$  axis. Owing to the nuclear spins of the H and D atoms, H<sub>2</sub>O and D<sub>2</sub>O present two spin modifications: para and ortho. The para-form corresponds to  $k_a + k_c$  even (odd) for H<sub>2</sub>O (D<sub>2</sub>O) and the ortho-form corresponds to  $k_a + k_c$  odd (even). As the ortho and para levels do not interconvert in inelastic collisions, these were treated separately. We adopted the following rotational constants:  $A = 27.88063134$ ,  $B = 14.52176959$ , and  $C = 9.277708381$  cm<sup>-1</sup> for H<sub>2</sub>O and  $A = 15.41998452$ ,  $B = 7.272989273$ , and  $C = 4.845292736$  cm<sup>-1</sup> for D<sub>2</sub>O, as given in the Jet Propulsion Laboratory (JPL) catalog.<sup>24</sup> The projectile H<sub>2</sub> was restricted to its lowest para level ( $j_2 = 0$ )

with a rotational constant of 59.322 cm<sup>-1</sup>.<sup>25</sup> The reduced mass is 1.81277373 amu for H<sub>2</sub>O–H<sub>2</sub> and 1.831300100 amu for D<sub>2</sub>O–H<sub>2</sub>.

The coupled-channel equations were integrated using the diabatic modified log-derivative airy propagator of Alexander and Manolopoulos.<sup>26</sup> The radial propagation used a step size parameter STEPS=10 except at collision energies below 10 cm<sup>-1</sup> where STEPS was increased up to 200 to constrain the step length of the integrator below  $\sim 0.1a_0$ . Other propagation parameters were taken as the MOLSCAT default values. Calculations were performed for collision energies between 0.01 and 500 cm<sup>-1</sup>. The energy grid was adjusted to reproduce all the details of the resonances. For *ortho*- and *para*-D<sub>2</sub>O, 800 energy grid points were sampled with an adapted energy step (0.25 cm<sup>-1</sup> for a total energy inferior to 200 cm<sup>-1</sup> and 1 cm<sup>-1</sup> beyond). All calculations also included several energetically closed channels to ensure that cross sections were converged to within a few per cent for all transitions involving  $j_1 \leq 3$ . Thus, the basis set incorporated all target states with  $j_1 \leq 6$ . The inclusion of the  $j_2 = 2$  level of H<sub>2</sub> was also necessary, even at collision energy where this channel is closed. Finally, rate coefficients were obtained up to 100 K by integrating the cross sections over Maxwell–Boltzmann distributions of relative velocities. We will restrict the discussion below to the low temperature regime ( $T \leq 30$  K) and the low lying transitions ( $j_1 \leq 2$ ) relevant to the cold protostar envelope where D<sub>2</sub>O has been detected in absorption.<sup>9</sup> Results for larger temperatures and higher transitions will be published elsewhere.

Preliminary scattering calculations for H<sub>2</sub>O–H<sub>2</sub> were performed in order to test the approximation of using state-averaged geometries in a rigid-rotor PES. It should be noted that Dubernet *et al.*<sup>27</sup> have shown that using equilibrium geometries is inaccurate and that the inclusion of zero-point vibrational effects (through the explicit average of the full-dimensional PES over the ground state vibrational wave functions) has a significant impact on the rotational cross sections. In the present work, calculations were performed with two different H<sub>2</sub>O–H<sub>2</sub> PES constructed from the flexible PES of Valiron *et al.*: (i) the vibrationally averaged PES (VAP) obtained by integrating the full PES over the ground state vibrational wave functions and (ii) the rigid-rotor PES at the vibrational ground state (VGS) geometries obtained by fixing the H<sub>2</sub>O and H<sub>2</sub> internal coordinates at their vibrationally averaged values (Table I). Cross sections and rate coefficients are presented for both PES in Fig. 1 for the fundamental transition  $1_{10} \rightarrow 1_{01}$  of *ortho*-H<sub>2</sub>O. It can be observed that both PES give very similar cross sections, with differences that do not exceed 10%, even at the lowest collision energies. At very low energies ( $\lesssim 2 \times 10^{-2}$  cm<sup>-1</sup>) the cross sections were found to vary inversely as the relative velocity as expected from the Wigner’s threshold law.<sup>28</sup> Above this regime, prominent open channel (orbiting) and closed channel (Feshbach) resonances are observed and the resonance structure (amplitude and position) is found to be very similar for the two PES. As a result, at temperatures above  $\sim 5$  K (i.e., relevant for astrophysical applications), differences in rate coefficients are below  $\sim 4\%$ . The agreement with the results of Dubernet *et al.* is also shown to be excellent, as expected since the same

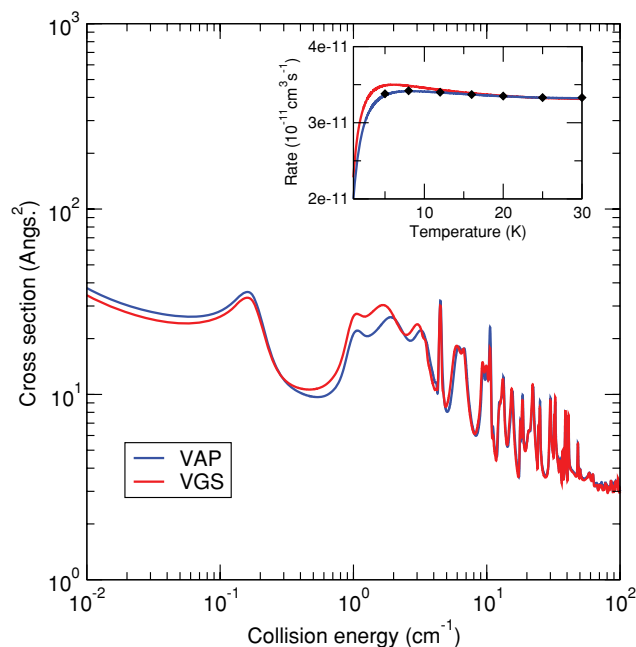


FIG. 1. Cross sections for the fundamental transition  $1_{10} \rightarrow 1_{01}$  of *ortho*- $\text{H}_2\text{O}$  quenched by  $\text{H}_2(j_2 = 0)$  as a function of collision energy. The VAP and VGS  $\text{H}_2\text{O}-\text{H}_2$  PES (see text) are employed. The inset shows the corresponding rate coefficients. Diamonds give the results of Dubernet *et al.* (Ref. 27).

PES was employed. A similar agreement was observed for other transitions. We conclude that employing state-averaged geometries within a rigid-rotor PES is indeed a reliable approximation for the computation of scattering cross sections.

Scattering calculations for  $\text{D}_2\text{O}$  were performed with the rigid-rotor  $\text{D}_2\text{O}-\text{H}_2$  PES, as defined in Eq. (2). Results are presented in Fig. 2 for the fundamental transition  $1_{10} \rightarrow 1_{01}$

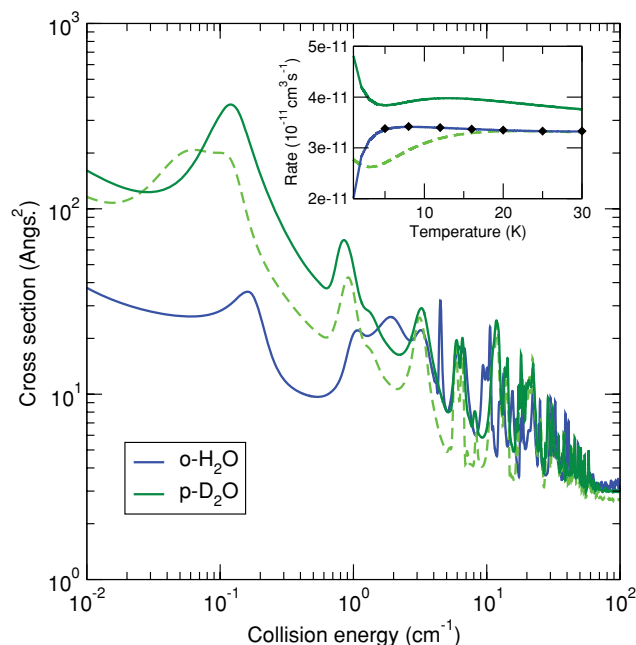


FIG. 2. Cross sections for the fundamental transition  $1_{10} \rightarrow 1_{01}$  of *para*- $\text{D}_2\text{O}$  (*ortho*- $\text{H}_2\text{O}$ ) quenched by  $\text{H}_2(j_2 = 0)$  as a function of collision energy. The inset shows the corresponding rate coefficients. The dashed-line corresponds to the hybrid  $\text{D}_2\text{O}-\text{H}_2$  PES (see text). Diamonds give the *ortho*- $\text{H}_2\text{O}$  results of Dubernet *et al.* (Ref. 27).

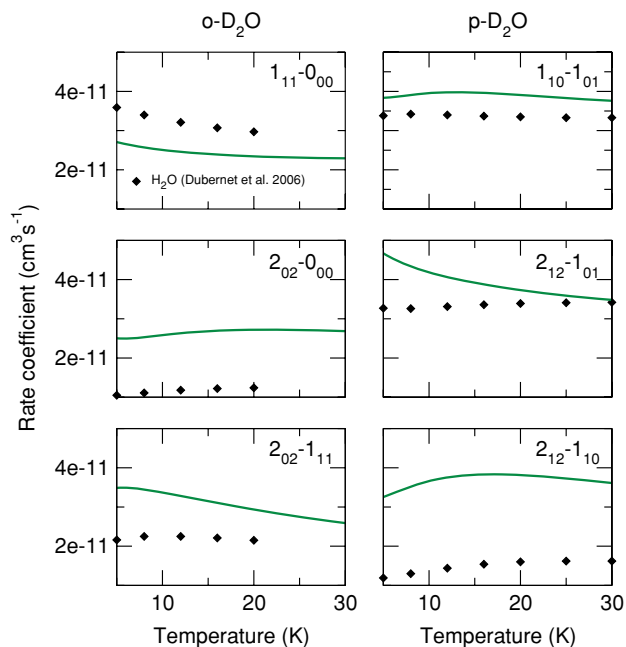


FIG. 3. Rate coefficients for the rotational deexcitation of  $\text{D}_2\text{O}$  by *para*- $\text{H}_2$  as a function of temperature. Diamonds give the corresponding  $\text{H}_2\text{O}$  results of Dubernet *et al.* (Ref. 27).

of *para*- $\text{D}_2\text{O}$  and *ortho*- $\text{H}_2\text{O}$ . For the latter, the cross sections based on the VAP model only are reported. We can first notice significant differences between the two water isotopologues in the whole energy range, and especially below  $\sim 1 \text{ cm}^{-1}$  where differences up to a factor of 10 are observed. We have also added to the plot the *para*- $\text{D}_2\text{O}$  cross sections obtained using a second “hybrid”  $\text{D}_2\text{O}-\text{H}_2$  PES: in Eq. (2), the  $\text{D}_2\text{O}$  internal coordinates were fixed at the  $\text{H}_2\text{O}$  averaged values, thus neglecting the internal geometry effects (but obviously keeping the  $\text{D}_2\text{O}$  rotational constants and reduced mass). We can observe that the corresponding cross sections are significantly different from the “full” *para*- $\text{D}_2\text{O}$  cross section, although the resonance structure is similar. We also checked that the shift of centre of mass ( $\sim 0.1a_0$ ) had only a minor effect on the cross sections. As a result, both kinematics (i.e., mass and velocities) and PES effects are found to be important, the main PES effect being caused by the change in intramolecular geometries. This is further illustrated at the rate coefficient level. Note that the good agreement between the hybrid *para*- $\text{D}_2\text{O}$  and the *ortho*- $\text{H}_2\text{O}$  rate coefficients above  $\sim 15 \text{ K}$  is accidental and that the two curves diverge above  $30 \text{ K}$ .

We compare in Fig. 3 the rate coefficients of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  for the lowest six deexcitation transitions.<sup>29</sup> Significant differences are observed, especially for the dipole forbidden  $2_{12} \rightarrow 1_{10}$  transition where the  $\text{D}_2\text{O}$  rate is about a factor of 3 larger than the  $\text{H}_2\text{O}$  one. Even larger differences were observed for higher (dipole forbidden) transitions. For dipole allowed transitions, however,  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  rate coefficients were found to agree within a factor of 2. This result suggests that the dipolar interaction terms (e.g., dipole quadrupole) are not much affected by the isotopic substitution, as expected from the negligible difference between the  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  ground state dipole values (1.8546 and 1.8545 D, respectively<sup>24</sup>).

Finally, we note that only the lowest fundamental transitions of *para*- and *ortho*-D<sub>2</sub>O have been observed in space so far. The *ortho*-D<sub>2</sub>O column density in the cold ( $T < 30\text{K}$ ) and diluted envelope of the protostar IRAS 16293-2422 was estimated by Vastel *et al.*<sup>9</sup> by using preliminary approximate rate coefficients and assuming that only the first two levels are significantly populated. The present results are crucial to check this approximation and to derive a more accurate total column density and *ortho*-to-*para* ratio for D<sub>2</sub>O.

In summary, we have computed the first cross sections and rate coefficients for low lying rotational transitions in D<sub>2</sub>O induced by *para*-H<sub>2</sub> collisions. The full 9D PES of Valiron *et al.* was employed with the internal coordinates of D<sub>2</sub>O and H<sub>2</sub> fixed at their vibrationally averaged values. Significant differences with H<sub>2</sub>O rate coefficients (up to a factor of 3) were observed and attributed to both kinematics and PES effects. To our knowledge, this study is the first devoted to the PES effects caused by isotopic substitution in scattering calculations. The present rate coefficients will lead to a significantly improved determination of the heavy water abundance in cold interstellar environments. Similar calculations are underway on the HDO–H<sub>2</sub> system. In this case, additional effects are caused by the rotation of the principal axes of inertia which, in particular, induces different collisional selection rules. In contrast, isotopic effects for the oxygen isotopologues of water (H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O) can be safely ignored (except for obvious kinematics ratios) since the change in internal geometries is essentially negligible.

All calculations presented in this paper were performed at the Service Commun de Calcul Intensif de l'Observatoire de Grenoble (SCCI). This work was supported by the CNRS national programme Physique et Chimie du Milieu Interstellaire.

<sup>1</sup>C. Ceccarelli, P. Caselli, E. Herbst, A. G. G. M. Tielens, and E. Caux, in *Protostars and Planets V*, edited by B. Reipurth, D. Jewitt, and K. Keil (University of Arizona, Tucson, 2007), pp. 47–62.

<sup>2</sup>B. E. Turner, N. Fourikis, M. Morris, P. Palmer, and B. Zuckerman, *Astrophys. J.* **198**, L125 (1975).

<sup>3</sup>H. M. Butner, S. B. Charnley, C. Ceccarelli, S. D. Rodgers, J. R. Pardo, B. Parise, J. Cernicharo, and G. R. Davis, *Astrophys. J.* **659**, L137 (2007).

<sup>4</sup>A. Faure, N. Crimier, C. Ceccarelli, P. Valiron, L. Wiesenfeld, and M.-L. Dubernet, *Astron. Astrophys.* **472**, 1029 (2007).

<sup>5</sup>S. Green, *Astrophys. J., Suppl. Ser.* **70**, 813 (1989).

<sup>6</sup>F. Daniel, M.-L. Dubernet, F. Pacaud, and A. Grosjean, *Astron. Astrophys.* **517**, A13 (2010).

<sup>7</sup>A. Faure, J. D. Gorfinkiel, and J. Tennyson, *Mon. Not. R. Astron. Soc.* **347**, 323 (2004).

<sup>8</sup>N. Troscompt, A. Faure, S. Maret, C. Ceccarelli, P. Hily-Blant, and L. Wiesenfeld, *Astron. Astrophys.* **506**, 1243 (2009).

<sup>9</sup>C. Vastel, C. Ceccarelli, E. Caux, A. Coutens, J. Cernicharo, S. Bottinelli, K. Demyk, A. Faure, L. Wiesenfeld, Y. Scribano, P. Hily-Blant, S. Maret, A. Walters, E. A. Bergin, G. A. Blake, A. Castets, N. Crimier, C. Dominik, P. Encrenaz, M. Gerin, P. Hennebelle, C. Kahane, A. Klotz, G. Melnick, L. Palgani, B. Parise, P. Schilke, V. Wakelam, A. Baudry, T. Bell, M. Benedettini, A. Boogert, S. Cabrit, P. Caselli, C. Codella, C. Comito, E. Falgarone, A. Fuente, P. F. Goldsmith, A. Lorenzani, D. Neufeld, B. Nisini, S. Pacheco, J. Pearson, T. Phillips, M. Salez, P. Saraceno, K. Schuster, X. Tielens, F. van der Tak, M. H. D. van der Wiel, S. Viti, F. Wyrowski, H. Yorke, P. Cais, J. M. Krieg, M. Olberg, and L. Ravera, *Astron. Astrophys.* **521**, L38 (2010).

<sup>10</sup>P. Valiron, M. Wernli, A. Faure, L. Wiesenfeld, C. Rist, S. Kedzuch, and J. Noga, *J. Chem. Phys.* **129**, 134306 (2008).

<sup>11</sup>A. Faure, L. Wiesenfeld, M. Wernli, and P. Valiron, *J. Chem. Phys.* **123**, 104309 (2005).

<sup>12</sup>C.-H. Yang, G. Sarma, J. J. ter Meulen, D. Parker, G. C. McBane, L. Wiesenfeld, A. Faure, Y. Scribano, and N. Feautrier, *J. Chem. Phys.* **133**, 131103 (2010).

<sup>13</sup>L. Wiesenfeld and A. Faure, *Phys. Rev. A* **82**, 040702 (2010).

<sup>14</sup>F. Belpassi, M. L. Recca, F. Tarantelli, L. F. Roncaratti, F. Pirani, D. Cappelletti, A. Faure, and Y. Scribano, *J. Am. Chem. Soc.* **132**, 13046 (2010).

<sup>15</sup>A. van der Avoird and D. Nesbitt, "Rovibrational states of the H<sub>2</sub>O-H<sub>2</sub> complex; an ab initio calculation" submitted to *J. Chem. Phys.*

<sup>16</sup>X.-G. Wang and T. Carrington, "Theoretical study of rovibrational spectra of H<sub>2</sub>O-H<sub>2</sub>" submitted to *J. Chem. Phys.*

<sup>17</sup>R. E. A. Kelly, J. Tennyson, G. C. Groenenboom, and A. van der Avoird, *J. Quant. Spectrosc. Radiat. Transf.* **111**, 1262 (2009).

<sup>18</sup>A. G. Császár, G. Czakó, T. Furtenbacher, J. Tennyson, V. Szalay, S. V. Shirin, N. F. Zobov, and O. L. Polyansky, *J. Chem. Phys.* **122**, 214305 (2005).

<sup>19</sup>C. W. Kern and R. L. Matcha, *J. Chem. Phys.* **49**, 2081 (1968).

<sup>20</sup>W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.* **24**, 1139 (1956).

<sup>21</sup>G. Czakó, E. Mátyus, and A. G. Császár, *J. Phys. Chem. A* **1113**, 11665 (2009).

<sup>22</sup>T. R. Phillips, S. Maluendes, and S. Green, *J. Chem. Phys.* **102**, 6024 (1995).

<sup>23</sup>J. M. Hutson and S. Green, computer code, MOLSCAT, version 14, CCP6, Daresbury, 1994.

<sup>24</sup>H. M. Pickett, I. R. L. Poynter, E. A. Cohen, M. L. Delitsky, J. C. Pearson, and H. S. P. Muller, *J. Quant. Spectrosc. Radiat. Transf.* **60**, 883 (1998).

<sup>25</sup>K. P. Huber, and G. Herzberg, *Constants of diatomic molecules* (Van Nostrand Reinhold, New York, 1979).

<sup>26</sup>M. H. Alexander and D. E. Manolopoulos, *J. Chem. Phys.* **86**, 2044 (1987).

<sup>27</sup>M.-L. Dubernet, F. Daniel, A. Grosjean, A. Faure, P. Valiron, M. Wernli, L. Wiesenfeld, C. Rist, J. Noga, and J. Tennyson, *Astron. Astrophys.* **460**, 323 (2006).

<sup>28</sup>E. P. Wigner, *Phys. Rev.* **73**, 1002 (1948).

<sup>29</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3507877> for the values of rate coefficients of deexcitation of D<sub>2</sub>O by hydrogen as a function of temperature.