THE DYNAMICS OF THE $H_3O^+ + H_2$ INTERACTION: STATE-TO-STATE COLLISIONAL DATA WITH ASTROPHYSICAL APPLICATIONS

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***COLLEXISM* : Collisional excitation of interstellar molecules: towards reactive systems**

MOTIVATION

Hydronium (H_3O^+) has been observed both in dense and diffuse clouds of the ISM [1,2]. It is one of the backbones of interstellar oxygen and water chemistry and also a tracer of cosmic-ray ionization rates. For adequate interpretation of hydronium observations a complex, *non-LTE analysis* is required where both *radiative* and *collisional* properties are important. Among the collisional properties the *rate coefficients for collision with* H_2 are the most important.

The spectroscopy of H_3O^+ is well-studied [3], but *its collisional excitation is less-known* and limited to: rate coefficients for *ortho-* and *para*-H_3O^+ collisions with He (used as a template for H_2) [4] and scaled collisional data based on the interaction of the isoelectronic NH_3 with H_2 [5,6].

SCATTERING DYNAMICS MODEL AND METHOD

Rotational de-excitation cross sections are computed for the collision of *ortho-* and *para*-H_3O^+ with *ortho*-H_2 (up to 1700 cm^{-1} total energies) and *para*-H_2 (up to 1500 cm^{-1}). For the dynamical calculations we used the *coupled-channel* (close-coupling) method with the *HIBRIDON* scattering code [6]. The corresponding *thermal rate coefficients* are calculated up to 300 K by integrating over a Maxwell-Boltzmann distribution of relative velocities. The lowest 20 pure rotational states are taken into account in the case of *para*-H_3O^+ and the lowest 11 levels for *ortho*-H_3O^+ (both with internal energies up to 300 cm^{-1}, considering $j \leq 5$ states).

Radiative transfer calculations are performed based on the calculated rate coefficients, using the *RADEX non-LTE radiative transfer code* [7]

POTENTIAL ENERGY SURFACE (PES)

The PES is calculated in the rigid-rotor approximation (see [8] for details). The explicitly correlated CCSD(T)-F12 *ab initio* method is used with the aug-cc-pVTZ basis set applying BSSE correction. *99 000 single-point geometries* were computed in total. The PES was developed over an angular expansion using a *standard linear least-square-fit* procedure.

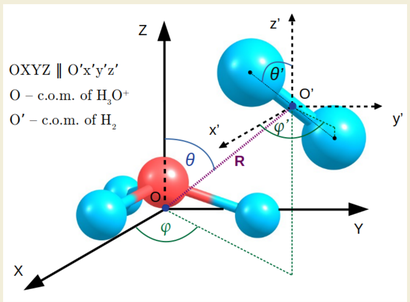
$$V(R,\theta,\phi,\theta_2,\phi_2) = \sum_{l_1,l_2=2} \sum_{m\, m_1=3n\geq 0, m_2} v_{l_1 l_2 m_1 m_2}(R)\bar{d}_{l_1 l_2 m_1 m_2}(\theta,\phi,\theta_2,\phi_2)$$

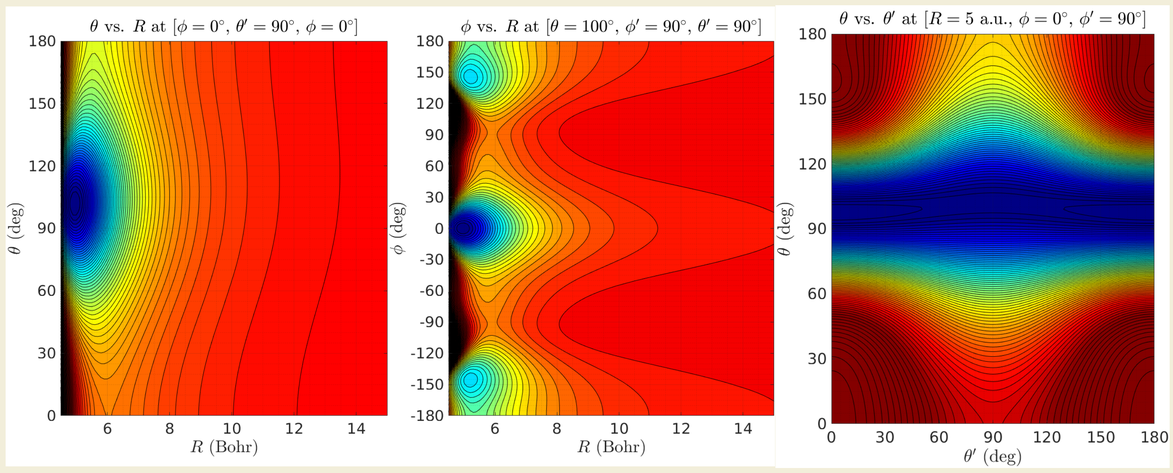
where $\bar{d}_{l_1 l_2 m_1 m_2}(\theta,\phi,\theta_2,\phi_2)$ is the normalized basis function:

$$\bar{d}_{l_1 l_2 m_1 m_2}(\theta,\phi,\theta_2,\phi_2) = \alpha_{l_1 l_2 m_1 m_2} d^{l_1}_{m_1 m_2}(\theta) d^{l_2}_{m_2 0}(\theta_2)\cos(m_1\phi + m_2\phi_2)$$

with the normalization factor

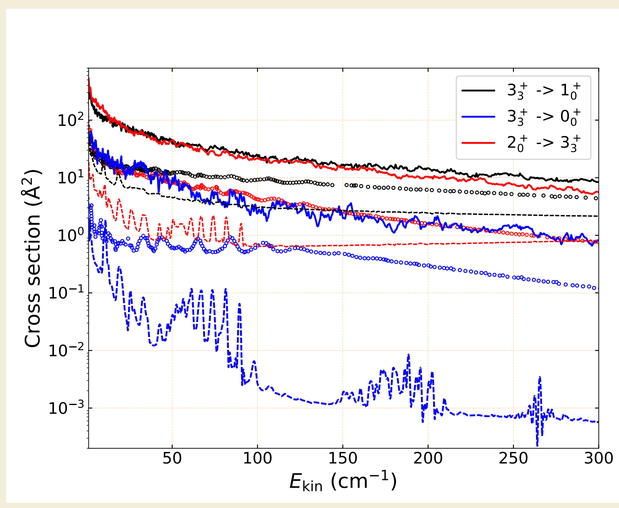
$$\alpha_{l_1 l_2 m_1 m_2} = \frac{1}{2\pi}\frac{1}{(1+\delta_{m_1 0}\delta_{m_2 0})^{1/2}}\left(\frac{(2l_1+1)(2l_2+1)}{2}\right)^{1/2}$$



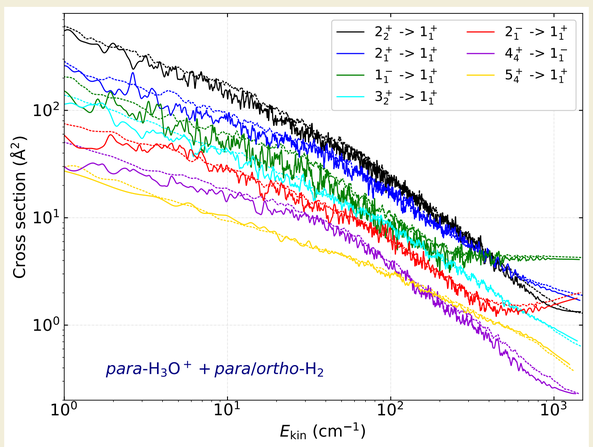


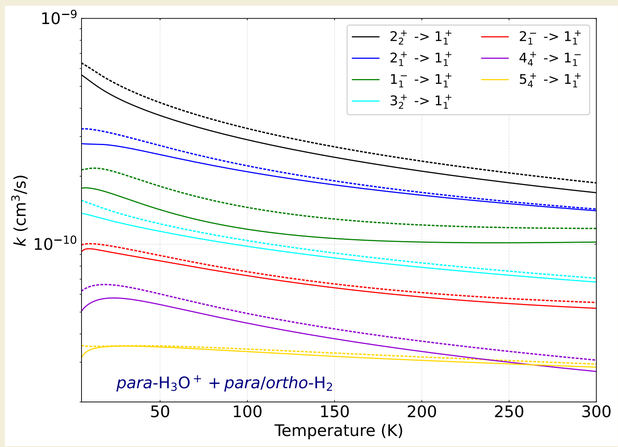
Contour plots showing some cuts of the 5-dimensional $H_3O^+ + H_2$ PES

CROSS SECTIONS AND RATE COEFFICIENTS



Rotational de-excitation cross sections for some selected transitions in collision of *o*-H_3O^+ + with *p*-H_2. Our results (solid lines) are compared with the corresponding for *o*-NH_3 + *p*-H_2 (dashed lines) and *o*-H_3O^+ + He (circles)

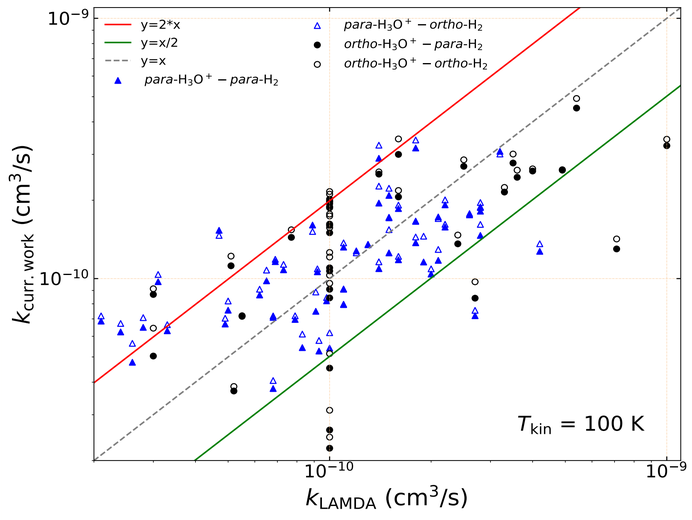




Rotational de-excitation cross sections (*left*) and thermal rate coefficients (*right*) for some randomly selected transitions of collision of *para*–H_3O^+ both with *para*–H_2 *(solid lines)* and *ortho*–H_2 *(dashed lines)*. The collisional data for the processes involving *ortho-* and *para*-H_2 are *qualitatively similar* for most of the transitions.

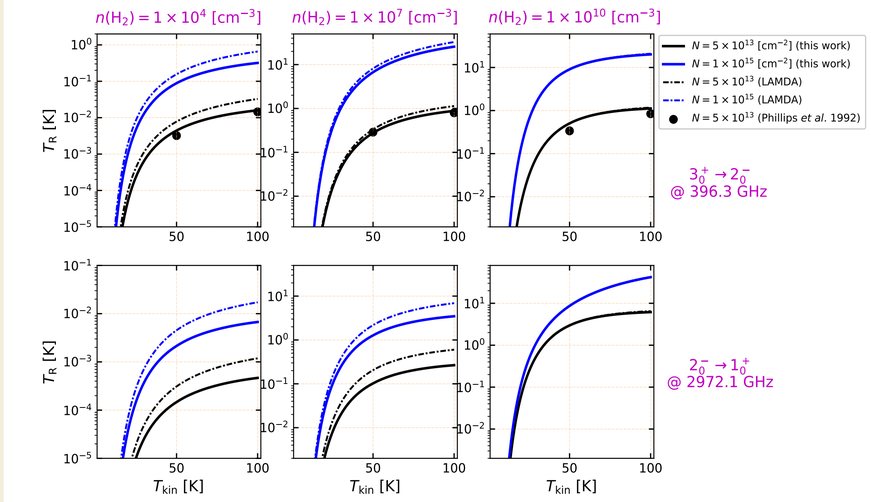
- The total number of rotational states considered is increased from 9 to 11 in the case of *ortho*–H_3O^+ and from 14 to 20 in the case of *para*–H_3O^+.
- No linear correlation could be found between the our data and those of from the LAMDA database [7]

For details, see Demes et al. (2022) [9]



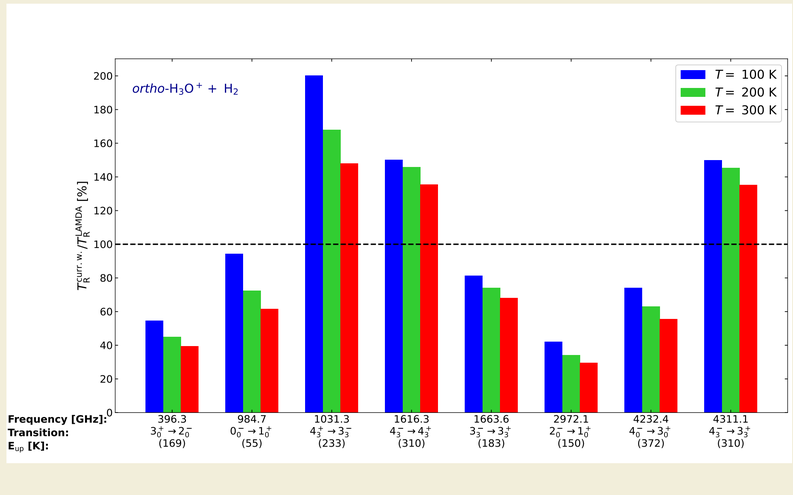
The ratios of our recent state-to-state thermal rate coefficients with respect to the reference data from the LAMDA database [7] at 100 K

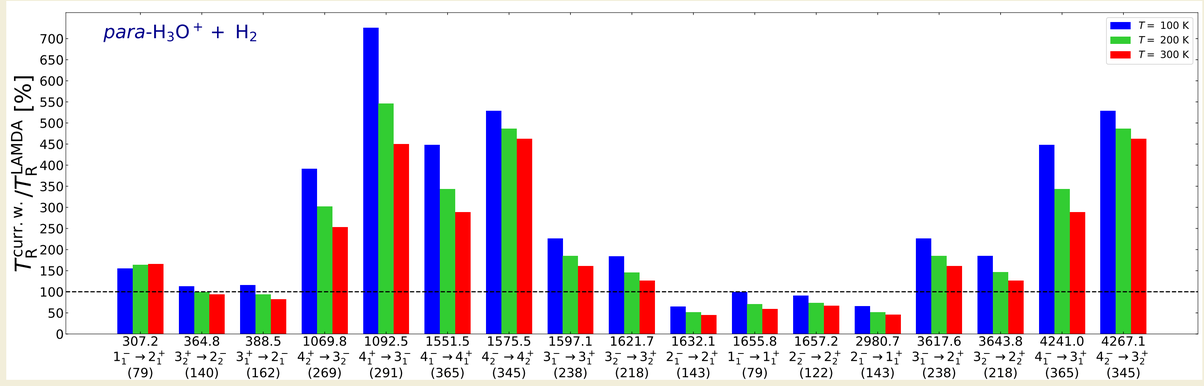
Astrophysical modelling



Radiance temperatures for the 396- and 2972-GHz emission lines of the *ortho*-H_3O^+ cation as a function of *kinetic temperature* (for different *para*-H_2 densities)

Ratio (percentage) of radiance temperatures computed by two sets of rate coefficients (our results vs. LAMDA data) for all radiative transitions of *ortho-* and *para*-H_3O^+ in collision with a statistical mixture of *ortho-* and *para*-molecular hydrogen





SUMMARY AND CONCLUSIONS

- An accurate *CCSD(T)-F12/AVTZ PES* is proposed for the $H_3O^+ + H_2$ collision
- The calculated *cross sections and rate coefficients* (< 300 K) are usually larger compared to the available data in the literature.
- The rate coefficients only *slightly depend on temperature* in general.
- The collisional data also *slightly depend on the nuclear spin* of the H_2 projectile.
- The *number of rotational states as well as the range of collision energies and kinetic temperatures have been significantly increased* in contrast with the earlier studies.
- The *new collisional data have a significant, non-negligible impact on the astrophysical observables* in radiative transfer modellings, especially at lower hydrogen densities and higher kinetic temperatures.
- *Reliable rate coefficients are obviously needed for precise astrophysical interpretations!*

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