

Collisional excitation of OH⁺ by molecular hydrogen

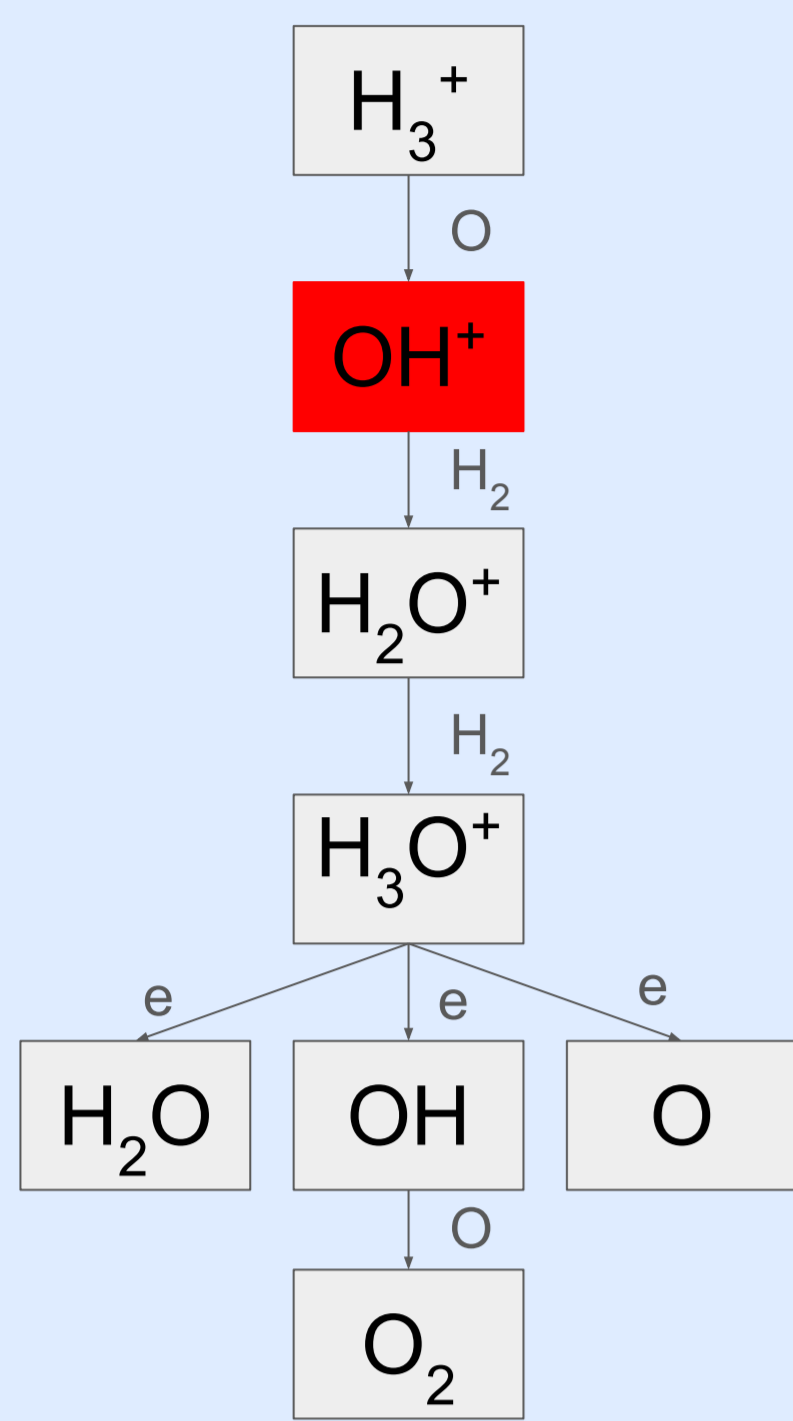
Toward a new statistical approach for treating reactive systems

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Introduction

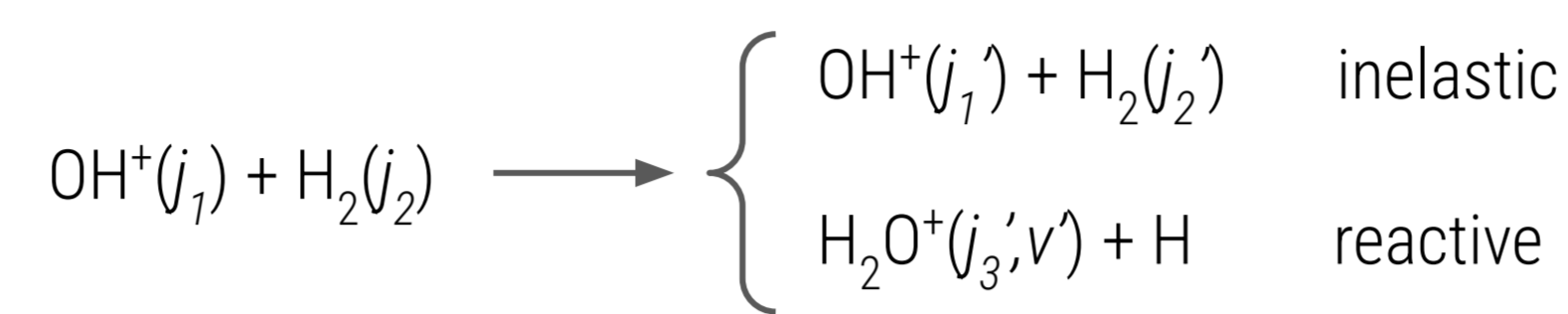


In the gas-phase interstellar medium (ISM), ion-neutral reactions play a crucial role in the formation of complex molecular species. These reactions occur without activation energy barriers [1]. Understanding the mechanisms driving these processes at low temperatures (below 100 K) is essential for interpreting the chemical diversity of the ISM and infer the physical conditions.

The hydroxyl ion OH⁺ radical is one of the most simple oxygen-bearing molecules and serves as a key precursor in the formation of more complex species such as H₂O.

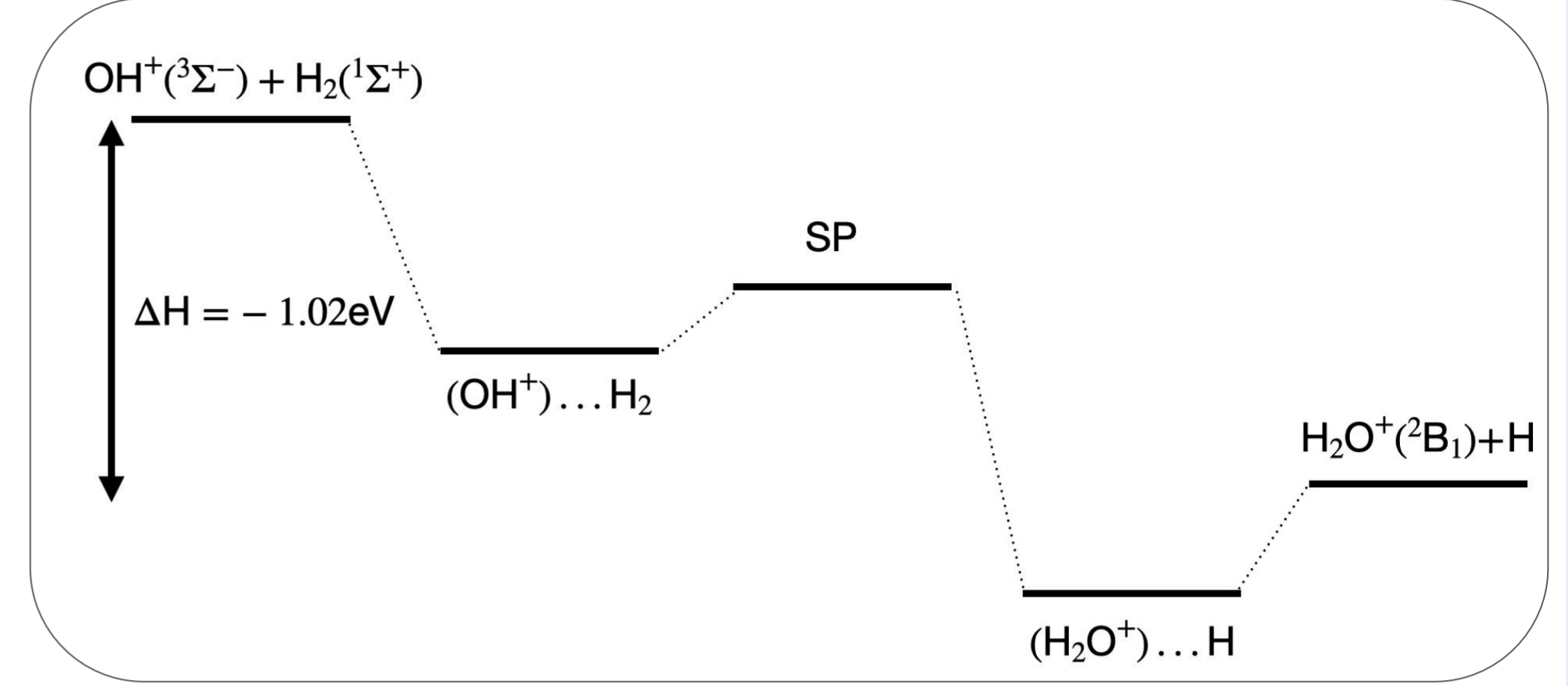
1. The OH⁺ + H₂ → H₂O⁺ + H reaction

At low temperatures, collisions of OH⁺ induced by H₂, the most abundant projectile in the ISM, can result in the two following possibilities:



Reactants can either exchange energy through inelastic collisions or undergo reactions to form new products. Given the significant exothermicity of the reaction ($\Delta H = -1.02$ eV, approximately 8000 cm⁻¹) [2], products can be generated in excited rotational states (j), including those with high vibrational motion (v).

As a result, there is a **complex interplay between inelastic and reactive processes**. However, no current methodology simultaneously accounts for these processes at the **state-to-state level for low temperatures**. **This work seeks to address this theoretical challenge by quantifying the collisional excitation of OH⁺ by H₂, including reactive channels.**



At low energies, the titled reaction processes adiabatically through the lowest triplet potential energy surface (PES). In this work, we use the full-dimensional PES computed by Li & Guo with the MRCI+Q/AVQZ method and fitted with the PIP-NN method [3].

2. Statistical method

Based on the close-coupled (CC) equations, the use of the statistical adiabatic channel model (SACM) [4] relies on diagonalizing the molecular Hamiltonian, excluding the kinetic term for each total angular momentum J , and resulting in **adiabatic curves**:

$$\langle \alpha' | H_{nuc} + V + \frac{\hat{L}^2}{2\mu R^2} | \alpha \rangle$$

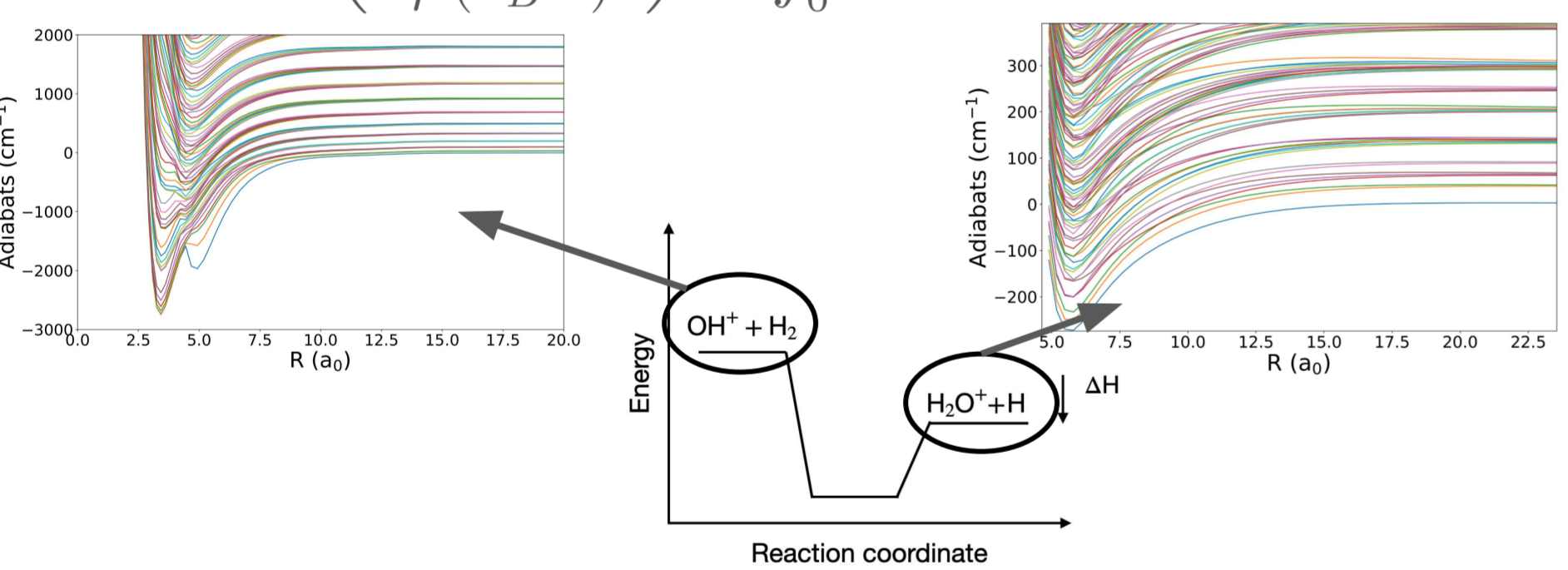
- α : angular functions
- L : orbital angular momentum
- V : potential energy surface
- R : intermolecular distance

In this approach, we assume an **equal distribution of the probability for all open channels** $N(E, J)$, and the scattering-matrix elements are computed as:

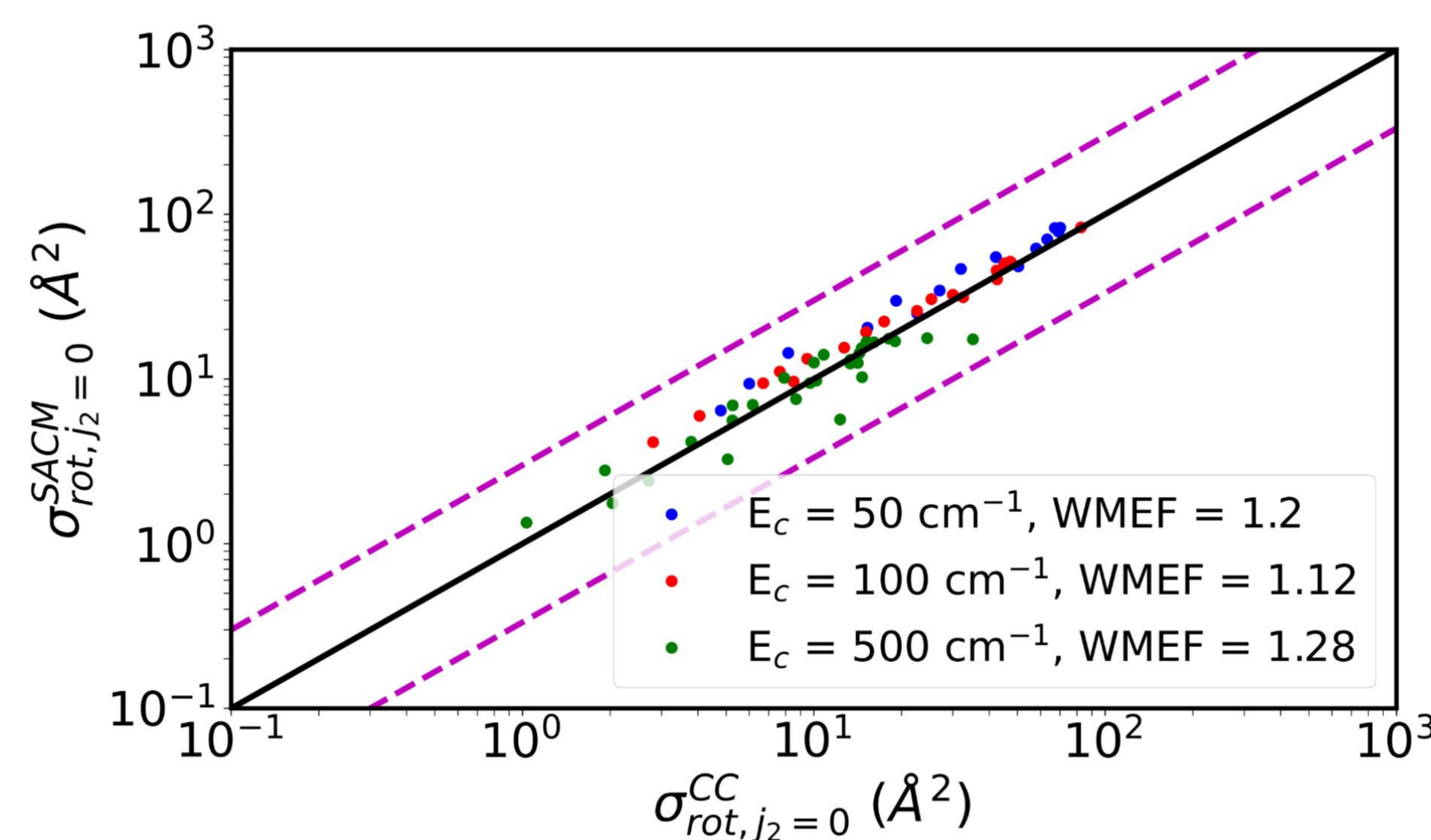
$$|S_{if}^{\text{SACM}}(E, J)|^2 = \begin{cases} 1/N_{\text{tot}}(E, J) & \text{for open channels} \\ 0 & \text{for closed channels} \end{cases}$$

$$\sigma_{i \rightarrow f}^{\text{SACM}}(E) = \frac{\pi}{k_i^2 [j_1 j_2]} \sum_J [J] \frac{N_i(E, J) N_f(E, J)}{N_{\text{tot}}(E, J)}$$

$$k_{i \rightarrow f}(T) = \left(\frac{8}{\pi \mu (k_B T)^3} \right)^{1/2} \int_0^\infty \sigma_{i \rightarrow f}(E_c) E_c e^{-E_c/(k_B T)} dE_c$$



3. Validation of the approach



The first step of validation has been done considering **pure inelastic calculations**. Scattering calculations have been performed for OH⁺ collisions with both *ortho*- and *para*-H₂ forms for three samples of collisional energies (E_c). The dark line represent a perfect agreement between CC and SACM, whereas dashed lines represent deviations by a factor of 3. We can also quantify differences by computing the Weighted Mean Error Factor (WMEF):

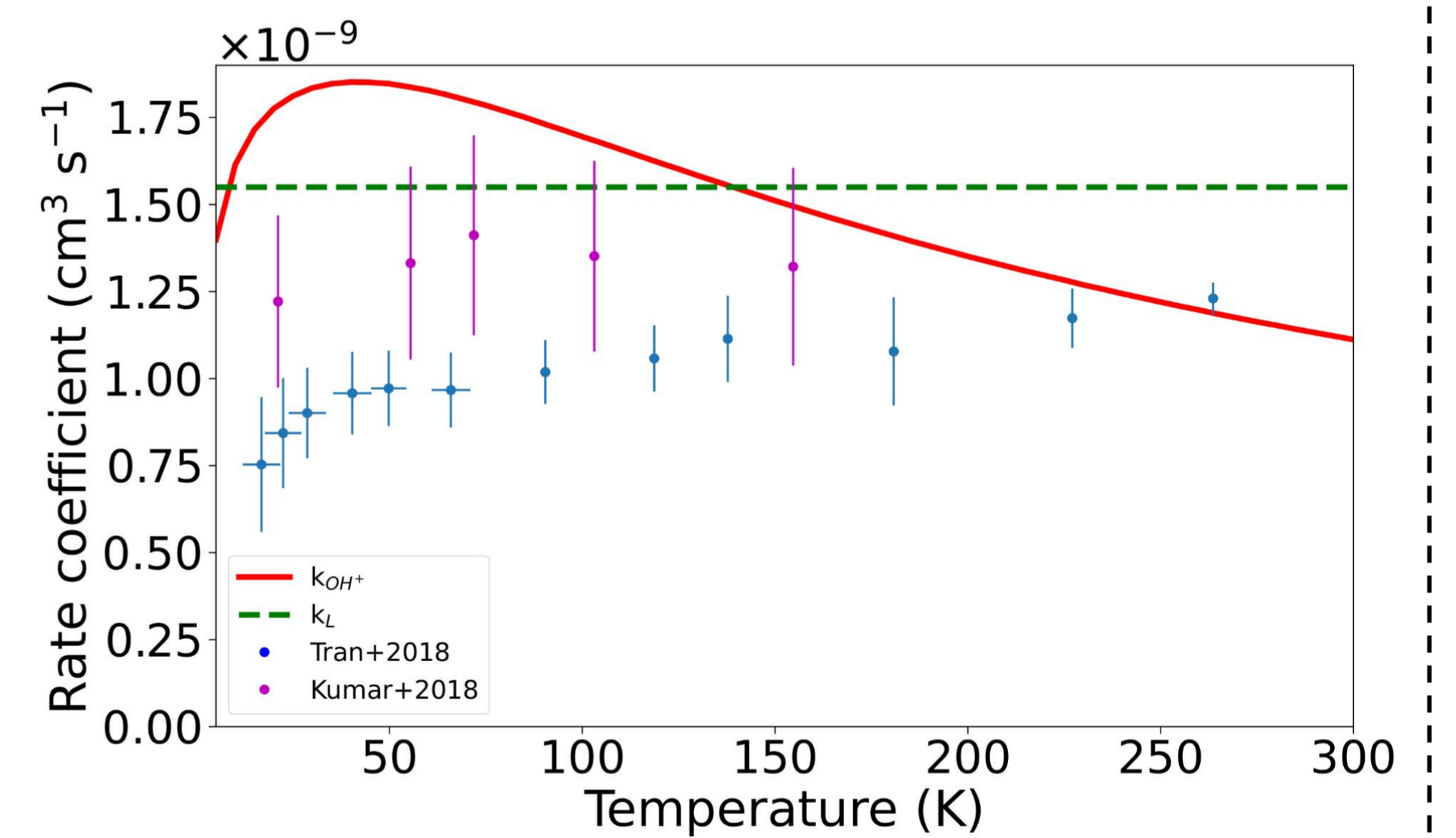
$$\text{WMEF} = \frac{\sum_{i,f} \sigma_{i \rightarrow f}^{\text{CC}} r_i}{\sum_i \sigma_i^{\text{CC}}}$$

$$r_i = \max(\sigma_i^{\text{CC}} / \sigma_i^{\text{SACM}}, \sigma_i^{\text{SACM}} / \sigma_i^{\text{CC}})$$

The second step of validation is done for the **reactive path of the system**. We compared the total reactive rate coefficient k_{OH^+} with the available experimental measurements done by Tran *et al.* [5] and Kumar *et al.* [6] and to the typical Langevin rate coefficient k_L . The total rate coefficient was computed as follow, including a 300 K statistical distribution of the population for molecular hydrogen:

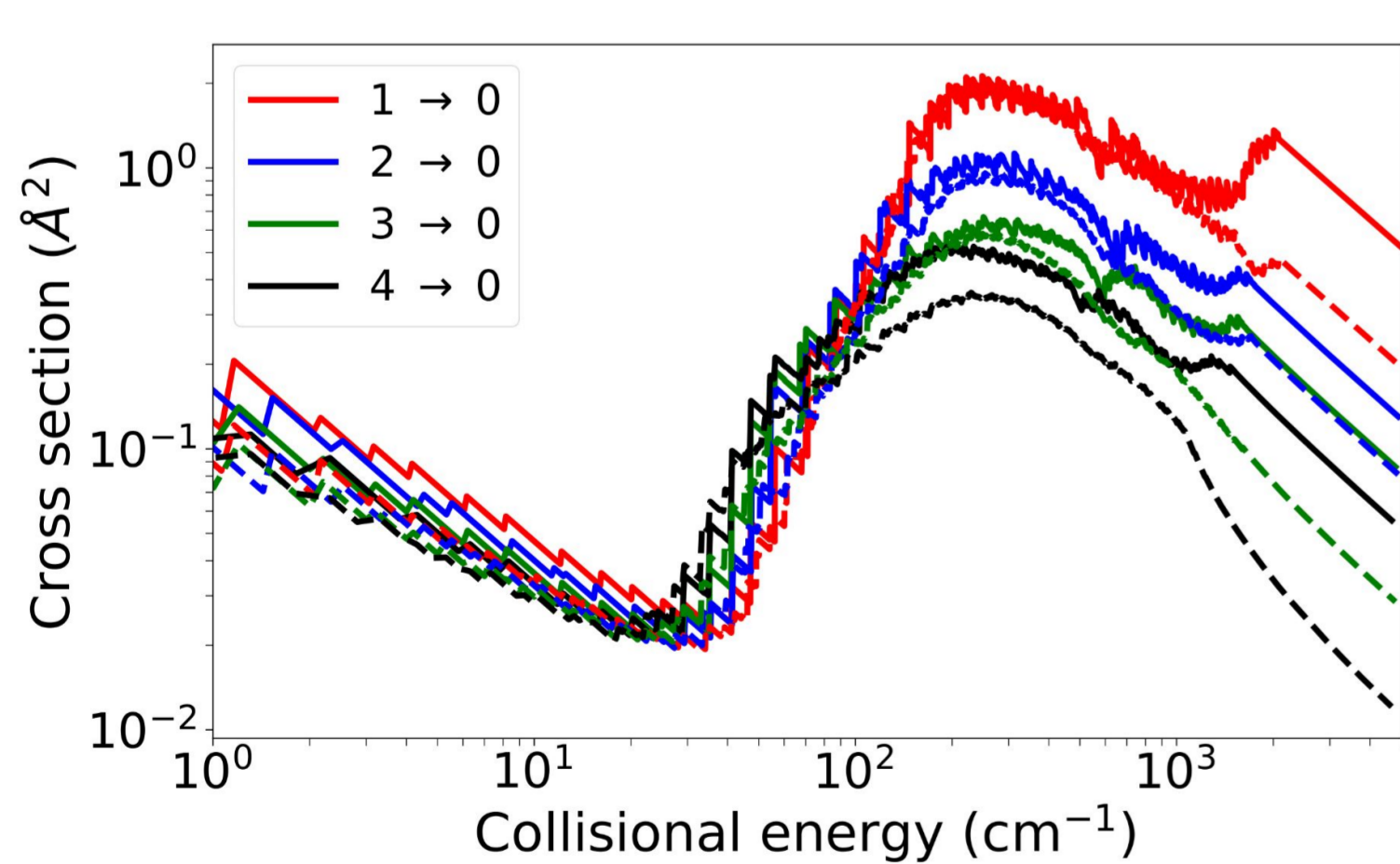
$$k_{\text{OH}^+}(T) = \sum_{j_1} n_{j_1}(T) \sum_{j_2} n_{j_2}(T) \sum_{\beta'} k_{j_1 j_2 \rightarrow \beta'}(T)$$

$$\beta' \equiv j_3', v', \nu_i'$$

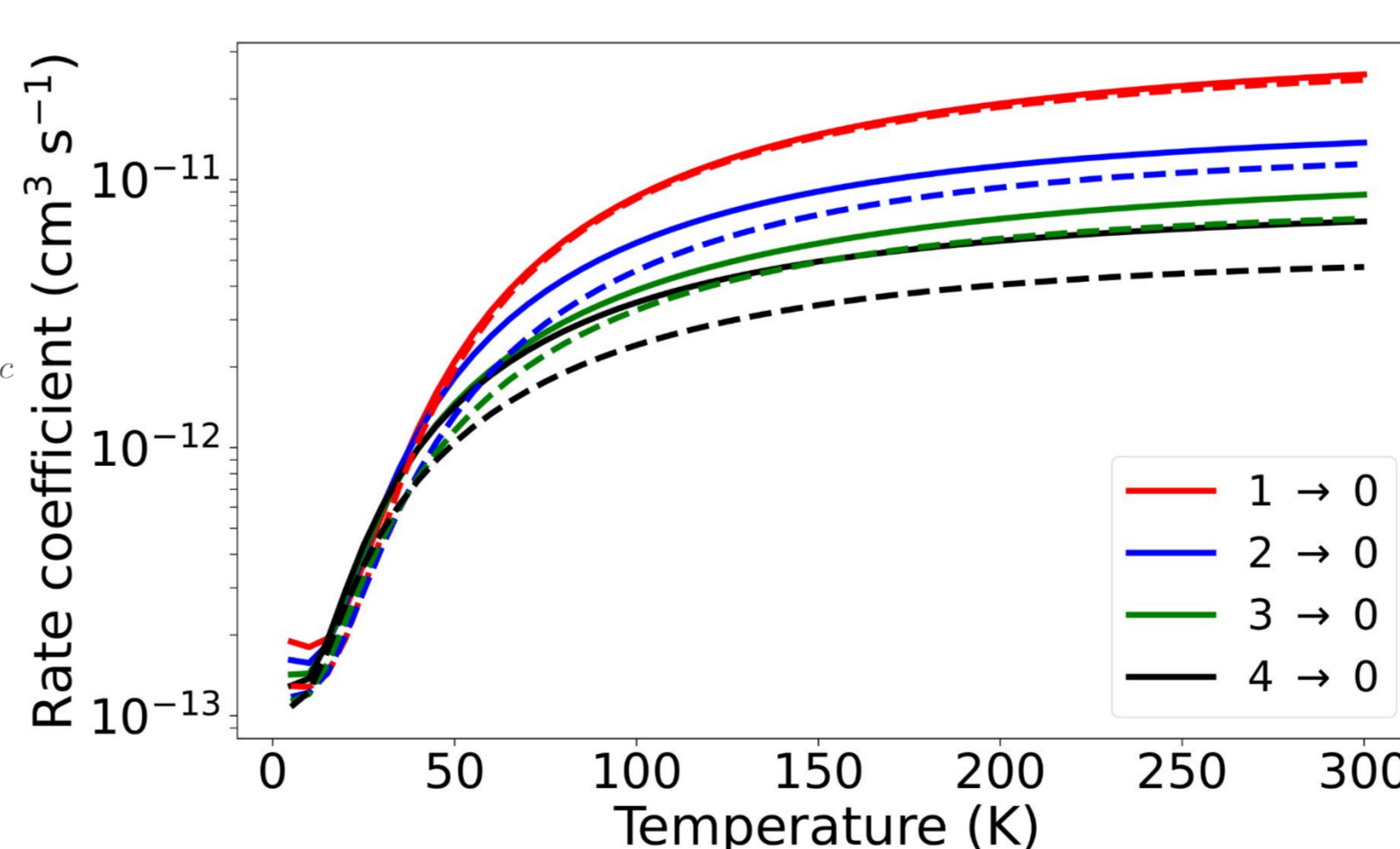


SACM shows good agreement with CC calculations and experiments and is validated for data production.

4. Rotational excitation of OH⁺ by H₂



$$\sim \int_0^\infty \sigma_{i \rightarrow f}(E_c) E_c e^{-E_c/(k_B T)} dE_c$$

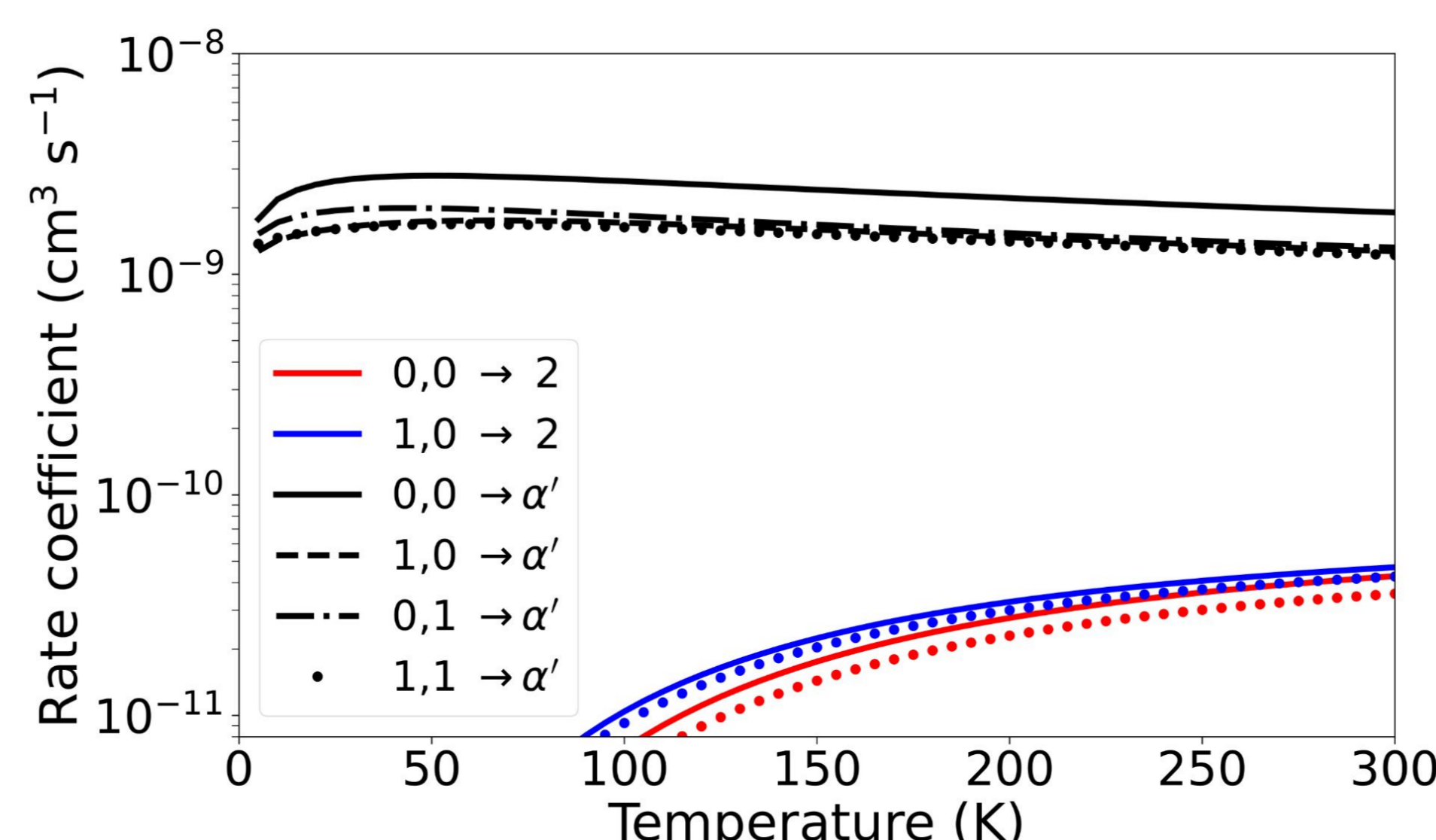


We present the **first** cross sections and rate coefficients for rotational excitation of OH⁺ by *para*- (solid lines) and *ortho*-H₂ (dashed lines) **including inelastic and reactive channels** at low temperatures at a state-to-state level.

The intensity of the OH⁺-H₂ rate coefficients are **lower by two orders of magnitude** compared to the collisional data considering He and atomic hydrogen, usually used as a proxy for H₂ [7].

State-specific reactive rate coefficients (dark lines) are **dominating collisional excitation** (coloured lines) by at least two orders of magnitude for temperatures from 5 to 300 K.

Due to the high exothermicity of the reaction, OH⁺ reacts with H₂ more rapidly than for collisional excitation. This suggests that OH⁺ excitation may predominantly occur in **astrophysical environments with a low fraction of H₂**. In such conditions, collisional excitation would be more likely to be driven by helium and atomic hydrogen, particularly in **regions where OH⁺ is observed in emission** [8].



Conclusions

We presented the first set of collisional data for the OH⁺-H₂ collisional system, accounting for both inelastic and reactive processes simultaneously at low temperatures and at a state-to-state level. The full-dimensional lowest triplet potential energy surface (PES) for the H₃O⁺ complex was used. Both reactants and products were considered as rigid rotors.

The statistical adiabatic channel model (SACM) was validated, showing strong agreement with the coupled-channel (CC) approach for pure inelastic collisions; and with experimental measurements when including the reactivity.

As a result, reactive rate coefficients are dominating by far inelastic ones due to the large exothermicity of the system. Additionally, the computed rotational rate coefficients are two orders of magnitude lower than those determined for collisions involving H and He, which have served as templates for excitation by H₂ in astrophysical modeling. These differences suggest that the collisional excitation of OH⁺ by molecular hydrogen is less likely compared to atomic hydrogen and helium, indicating that astrophysical modeling may need revision.

References

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