SUPPLEMENTARY INFORMATION

Experimental and Theoretical Studies of the N(^{2}D) + H_2 and D_2 Reactions

Dianailys Nuñez-Reyes,[a,b] Cédric Bray,[a,b] Kevin M. Hickson,[a,b] Pascal Larrégaray,[a,b] Laurent Bonnet[a,b] and Tomás González-Lezana[c]

[a]*Université de Bordeaux, Institut des Sciences Moléculaires, F-33400 Talence, France*

[b]*CNRS, Institut des Sciences Moléculaires, F-33400 Talence, France*

[c]*Instituto de Física Fundamental, CSIC, IFF-CSIC Serrano 123, 28006 Madrid*

We illustrate here, for the N+H_2 process, the origin of the quantitative differences between SQM and SC-Capture rate constants as well as the effect of including tunneling in the capture model.

Figure S1 displays the integrand E.$\sigma_{vj}(E).e^{-\beta E}$ of the rate constant formula (eq. 4) as a function of collision energy E for the three temperatures 127, 177 and 296 K, and the three theoretical approaches SQM, SC-Capture and standard classical Capture (C-Capture) where tunneling is not accounted for. Left and right figures correspond respectively to j=0 and 1, the most populated rotational levels in the experiment.

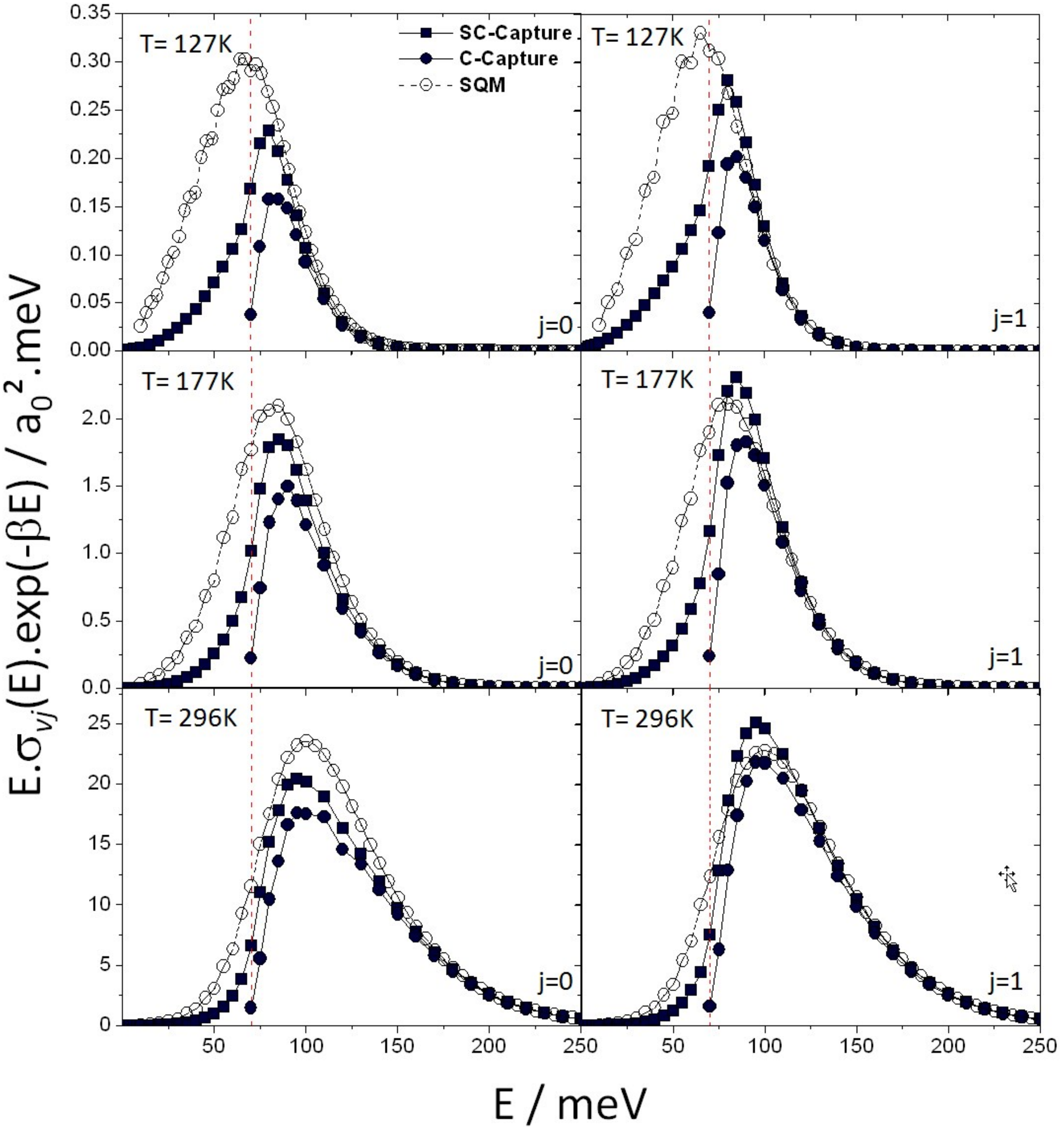

Figure S1: Integrand of eq. 4, for the N+H_2 process, as a function of collision energy at 127 K (upper), 177 K (middle) and 296 K (lower) for j=0 (left) and j=1 (right) for SQM (open circles), SC-Capture (black squares) and C-Capture models (black circles). The vertical red dashed line is at 70 meV, approx. the classical threshold for reaction.

For both H_2 rotational states, reactivity is significantly higher with the SQM approach, below the classical threshold for reaction (approx. 70 meV, red dashed line). Consequently, significant differences appear between the SQM and SC-Capture rate constants when this low energy domain largely contributes, which is the case at 127 K. As the reactivity of both models is similar above threshold, the relative difference between rate constants then decreases as temperature increases. The ratios of SQM to SC-Capture rate constants, $k_{SQM} / k_{SC\text{-}Capture}$ are respectively, 1.82, 1.39 and 1.11 for 127, 177 and 296 K. (see Table 2 for rate values) Due to the absence of tunneling, C-Capture rate constants are the lowest of the three theoretical models, being respectively 0.245×10^{-13}, 2×10^{-13} and 19.8×10^{-13} $cm^3 s^{-1}$ for 127, 177 and 296 K. The ratios of SC-Capture to classical Capture rate constants, $k_{SC\text{-}Capture} / k_{C\text{-}Capture}$, are respectively 2.94, 2 and 1.45. The comparison of the SC-Capture and classical Capture models from Figure S1 highlights that tunneling, within the semi-classical approximation, leads to an increase of reactivity up to approximately 100 meV collision energy at the lowest temperature and approximately 120 meV at the highest one. Above the classical threshold, SQM reactivity is somewhat higher than the SC-Capture one at j=0 but this difference is less pronounced for j=1 (see Figure S1).

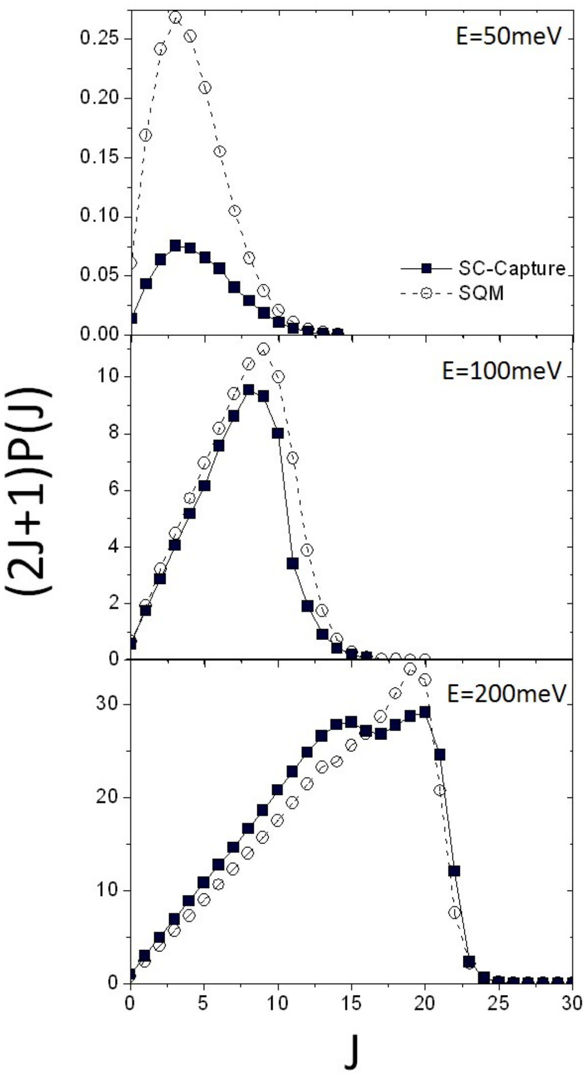

Figure S2: Opacity functions, including the degeneracy factor, for the N+H_2(j=0) process at 50, 100 and 200 meV. SQM and SC-Capture are displayed as open circles and black squares respectively.

Figure S2 displays the opacity functions, multiplied by the degeneracy factor, for the N+H_2 (j=0) process, at 50, 100 and 200 meV collision energies, relevant for this study. It appears that, even though the maximum values of the maximum orbital angular momentum (here equal to the total angular momentum) seems to be similar within the SQM and SC-Capture model, the reaction probability is much higher for all J with the SQM approach at 50 meV (below the classical threshold) and at the highest J at 100meV.

All the above features suggest that the tunneling probability is significantly higher within the SQM model, at least in this CS version, than within SC-capture model. A detailed study on tunneling should be performed to understand this issue better.