Test of the spectator role of the Rydberg electron in the He(n) + CO reaction and effects of the CO dipole and quadrupole moments at low collision energies

Fernanda B. V. Martins, Valentina Zhelyazkova, Christian Seiler, and Frédéric Merkt

ETH Zurich, Laboratory of Physical Chemistry, Zurich 8093, Switzerland

Rydberg atoms have large electric dipole moments and therefore their translational motion can be easily manipulated by inhomogeneous electric fields [1–3]. We deflect a beam of He Rydberg atoms using a Rydberg-Stark surface deflector and accelerator and merge it with a beam of ground-state CO molecules to study the $He^+ + CO \rightarrow C^+ + O + He$ reaction. In the experiment, we exploit the facts that the Rydberg electron prevents the heating up of the ions by stray electric fields and that it hardly affects the ion-molecule reaction taking place within its orbit [4–8], in accordance with the independent particle model of Rydberg collisions [9,10]. We detect the C^+ product of the reaction as a function of the velocity of the He(n) atoms. In this way, we can adjust the collision energy of the reaction and probe the range between 0 and $\sim k_B \cdot 25$ K.

In the first part of our investigation, we tested the spectator role of the Rydberg electron by measuring the distribution of principal quantum numbers of the He(n) reactants and the C(n') products using pulsed-field ionization [11]. We find that the distributions are affected by spontaneous emission and blackbody-radiation-induced transitions, but not by the ion-molecule reaction, which in turn indicates that the Rydberg electron does not influence the ion-molecule reaction. In the second part, we carried out an investigation of the effect of the dipole and quadrupole moments of CO on the reaction rates at low collision energies. In particular, we observe a 30% decrease in the product formation at the lowest collision energies (below $\sim k_B \cdot 5$ K) and attribute it to the negative quadrupole moment of CO on the basis of calculated state-dependent capture-rate coefficients.

References

[1] Allmendinger P *et al.* 2014 *Phys. Rev. A* 90 043403
[2] Lancuba P and Hogan S D 2016 *J. Phys. B: At. Mol. Opt. Phys.* 49 074006
[3] Zhelyazkova V *et al.* 2019 *Mol. Phys.* 117 2980–9
[4] Pratt S T *et al.* 1994 *J. Chem. Phys.* 101 882–90
[5] Wrede E *et al.* 2005 *Phys. Chem. Chem. Phys.* 7 1577–82
[6] Matsuzawa M 2010 *Phys. Rev.* A 82 054701
[7] Allmendinger P *et al.* 2016 *ChemPhysChem* 17 3596–608
[8] Zhelyazkova V *et al.* 2020 *Phys. Rev. Lett.* 125 263401
[9] Stebbings R F and Dunning F B (ed) 1983 *Rydberg States of Atoms and Molecules* (Cambridge: Cambridge University Press)
[10] Gallagher T F 1994 *Rydberg Atoms* (Cambridge: Cambridge University Press)
[11] Martins F B V *et al.* 2021 *New J. Phys.* 23 095011