Quantum calculations of the O(^{3}P)+CO scattering

Marko Gacesa[*1], **David Schwenke**[*2]

[*] NASA Ames Research Center, Moffett Field, CA 94035, USA

Synopsis We theoretically investigate O(^{3}P)+CO reactive scattering at collision energies from 0.1 eV to 5 eV using quantum multi-channel formalism with newly constructed $^3A'$ and 2x$^3A''$ potential energy surfaces. We construct the elastic, inelastic, and momentum transfer cross sections, as well as the reaction rate coefficient for O(^{3}P)+CO $\rightarrow$ C+O$_2$ exchange reaction. The results are directly relevant for physical processes in upper atmospheres of planets rich in CO and CO$_2$.

Upper layers of planetary atmospheres interact with solar radiation and interplanetary plasma. These interactions determine atmospheric escape rates of light neutrals capable of escaping by different physical mechanisms including thermal (Jeans) escape, and various non-thermal processes. Atmospheric escape to space is of particular interest on Mars, where it has likely contributed to the loss of primordial surface water oceans [1]. Mars' present-day atmosphere is composed of 96% CO$_2$, 1.9% Ar, and about 1.9 % N$_2$, with CO being the second most abundant molecular species above 310 km. Hot (suprathermal) O atoms produced in photodissociative recombination of O_2^+ with electrons are sufficiently energetic to directly escape to space through the upper atmosphere and form hot O corona. Therefore, a good model of O escape requires accurate knowledge of O+CO cross sections, which will determine the attenuation of hot O flux in the upper atmosphere as well as heating of background CO layer and its deviation from the thermal equilibrium conditions. In addition, under typical conditions, the temperature of a bowshock layer forming in front of a spacecraft entering martian atmosphere at 5-8 km/s will reach up to 10,000 K and dissociate CO$_2$ into hot O and CO. Under these conditions, non-equilibrium collisions of O with excited CO will determine the heating of the spacecraft.

In the present work, we perform quantum mechanical time-independent coupled-channel calculations of the cross sections for O(^{3}P)+CO reactive scattering at collision energies from 0.1 eV to 5 eV. The elastic and inelastic cross sections were calculated using MOLSCAT code [2], and the reactive channels were resolved using a modified version of ABC [3]. Three newly constructed potential energy surfaces (PES) correlating to O(^{3}P), namely $^3A'$ and two $^3A''$, are used to describe the interaction. The *ab-initio* PESs were calculated using MRCI+Q and CCSD(T) methods as implemented in MOLPRO [4] with aug-cc-pVQZ basis. Scalar relativistic effects were included using second order Douglas-Kroll-Hess method. Our methods resemble the ones used in the similar context for O+H$_2$ process [5].

The cross sections were calculated for the three PESs. The elastic cross sections calculated using different methods [2, 5] (coupled states (CS) approximation, infinite-order sudden (IOS) approximation, and full coupled-channel with 40 states) for $^3A'$ PES are given in Fig. 1, while the cumulative reaction probability (CRP) is given in the inset. Our results will help constrain the escape rates observed by the NASA MAVEN orbiter [1] and ongoing experiments at NASA Ames Electric Arc Shock Tube facility.

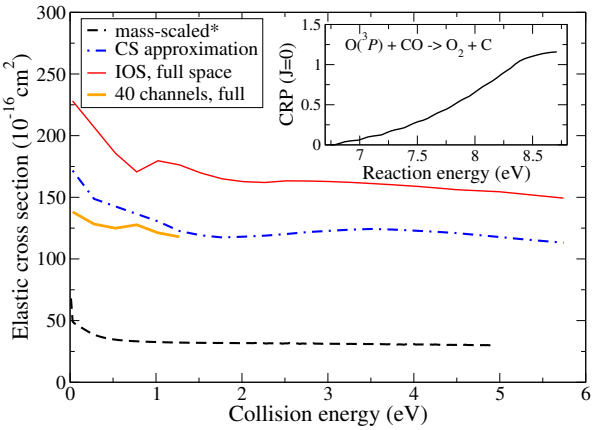

Figure 1. Average elastic O(^{3}P)+CO cross sections at a different level of theory: IOS (red), CS (blue), full CC (40 channels) (orange). The results are compared to the cross sections mass-scaled from O+H$_2$ [5].

References

[1] Lillis, R. J. *et al.* 2015 *Space Sci. Rev.* **195** 357.

[2] Hutson J. M., Green S. 2012 *MOLSCAT Version 14, CRC*; www.giss.nasa.gov/tools/molscat

[3] Skouteris, D. *et al.* 2000 *Comp. Phys. Com.* **133** 128

[4] Werner, K. *et al.* 2012 *MOLPRO v2012.1, a package of ab initio programs*, see www.molpro.net

[5] Gacesa, M. and Zhang, P. and Kharchenko, V. 2012, *Geophys. Res. Lett.* **39** L10203; Gacesa, M. and Kharchenko, V. 2014, *J. Chem. Phys.* **141** 164324.

[1]E-mail: marko.gacesa@nasa.gov
[2]E-mail: david.w.schwenke@nasa.gov