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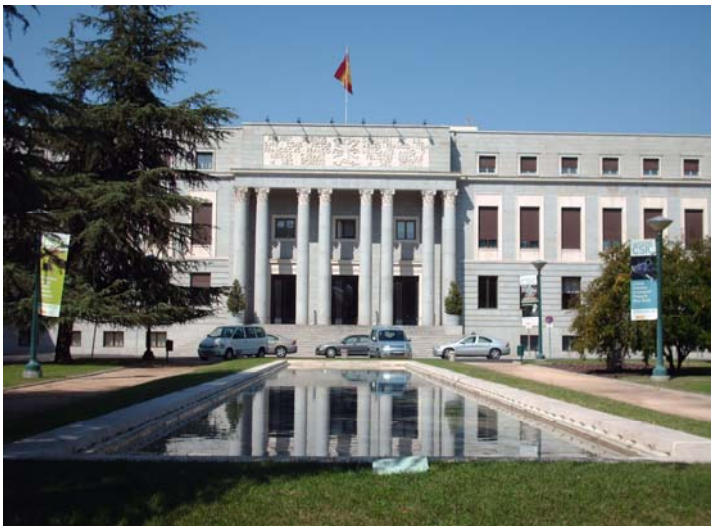

Book of Abstracts

Nonadiabatic dynamics in O_2+O_2 collisions

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The energy transfer by collisions involving the ground and excited species of molecular oxygen plays a crucial role in the chemistry of the upper Earth's atmosphere. The specificities of molecular oxygen (a stable radical in its ground $X\ ^3\Sigma_g^-$ state, with two low-lying excited states $a\ ^1\Delta_g$ and $b\ ^1\Sigma_g^+$) provide appropriate conditions for a rich variety of collision-induced energy transfer mechanisms. Experimentally, the rate coefficients measured for the collisional removal of $O_2(X\ ^3\Sigma_g^-$, high-v),$O_2(a\ ^1\Delta_g$, low-v) and $O_2(b\ ^1\Sigma_g^+$, low-v) by O_2 are fast and show peculiar features which cannot be explained by simple vibrational cascadings. The strong changes observed in the rate coefficients between adjacent vibrational levels suggest that near-resonant processes, involving electronic energy transfers, should dominate the removal processes. However, the final state distribution could not be probed experimentally, and theoretical studies are needed to unveil the underlying mechanisms. By resorting to a reduced dimensionality model of the dimer, together with *ab initio* methods and quantum dynamics calculations, we have shown[1] that i*ntra*-molecular electronic energy transfers,

$$O_2(X\ ^3\Sigma_g^-, v) + O_2 \rightarrow O_2(a\ ^1\Delta_g, v') + O_2,$$

$$O_2(X\ ^3\Sigma_g^-, v) + O_2 \rightarrow O_2(b\ ^1\Sigma_g^+, v'') + O_2,$$

mediated by spin-orbit couplings between the dimer states, were able to mimic the sharp changes observed in the measured collisional removal rate coefficients for $O_2(X\ ^3\Sigma_g^-, v \geq 26)$. In a recent study[2], we have also addressed the problem of *inter*-molecular electronic energy transfer,

$$O_2(b\ ^1\Sigma_g^+, v) + O_2(X\ ^3\Sigma_g^-, v=0) \rightarrow O_2(X\ ^3\Sigma_g^-, v') + O_2(b\ ^1\Sigma_g^+, v=0),$$

mediated by nonadiabatic radial couplings between the dimer states. It is found that the multidimensional nonadiabatic couplings can be predicted with high accuracy, compared to the *ab initio* results, by using analytical forms only depending on a reduced set of adiabatic energy terms. The results of quantum dynamics calculations for the removal of $O_2(b\ ^1\Sigma_g^+, v \leq 3)$ are found qualitatively consistent with the experimental observations.

[1] F. Dayou, M.I. Hernández, J. Campos-Martínez and R. Hernández-Lamoneda, *J. Chem. Phys.* 1**26**, 194309 (2007)

[2] F. Dayou, M.I. Hernández, J. Campos-Martínez and R. Hernández-Lamoneda, *J. Chem. Phys.* **132**, 044313 (2010)