

REACTIVITY OF DOUBLY CHARGED CATIONS IN THE GAS PHASE: INSIGHTS FROM CHEMICAL DYNAMICS AND STATISTICAL APPROACHES.

Molecular dications, ML^{2+} , formed by the association of neutral chemical compounds and doubly charged metal ions, were difficult to generate in the gas phase until the advent of electrospray ionization techniques, specially when the metal ion is a transition metal. However, this is not the case for alkaline-earth metals, such calcium or strontium, which yield easily detectable ML^{2+} dications and therefore allow the exploration of its unimolecular reactivity upon collision.

Two different kinds of fragmentations are observed in the experiments [1,2]: neutral loss fragmentation and Coulomb explosion. The first one corresponds to the loss of a neutral fragment L' , producing a lighter doubly charged molecular ion. The second one is a charge separation process yielding two pairs of singly charged fragments.

We have employed theoretical approaches at different time-scale levels [3] in order to have an almost complete picture and thus understand collision induced dissociation (CID) experiments for $[Ca(\text{formamide})]^{2+}$ and $[Sr(\text{formamide})]^{2+}$ species, formamide chosen as the simplest prototype of a peptide function.

QM+MM direct chemical dynamics was used to get ro-vibrational energy transfer after collision with inert atom (Ar) and reactivity in the pico-second time regime, providing with details on the mechanism of the different fragmentation pathways.

RRKM rate constants were used in conjunction with the obtained ro-vibration energy transfer probability distribution to elucidate the fragment formation as a function of time assuming complete IVR and statistical dynamics.

Finally, we emphasize how dynamics leads to a product distribution that might not be the one expected by a mere analysis of the potential energy surface.

References:

- [1] A. Eizaguirre, O. Mó, M. Yáñez, J.-Y. Salpin, *Phys. Chem. Chem. Phys.*, 13, 18409 (2011).
- [2] A. Eizaguirre, O. Mó, M. Yáñez, J.-Y. Salpin, J. Tortajada, *Org. Biomol. Chem.*, 10, 7552 (2012).
- [3] R. Spezia, A. Cimas, M.-P. Gageot, J.-Y. Salpin, K. Song, W. L. Hase, *Phys. Chem. Chem. Phys.*, 14, 11724 (2012).