

Intramolecular charge migration in betaine by impact of fast atomic ions

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Electron dynamics governs the fragmentation dynamics occurring at long timescales. Experimentally, it is possible to observe this can be observed using different experimental schemes: On the one hand, it is possible to obtain the time-resolved dynamics by using pump-probe schemes, for example with high harmonic generation or free electron lasers [1]. Alternatively it is possible to clock the electronic dynamics using Coulomb explosion or electron emission after photoionization. On the other hand, electronic dynamics can also be induced with low-energy ion collisions that are characterized by a sub-fs interaction time where one can expect a "sudden" ionization. In this regime, resonant electron captures dominate and are associated with large cross sections, thus low target excitation are expected. The main disadvantage is that currently it is not possible to perform pump-probe experiments at the fs timescale with ion beams and ion collisions are not selective.

Betaine is a zwitterion molecule, i.e. with one end positively charged (N(CD₃)₃ group) and the other one negatively charged (CO₂ group) while the whole molecular system remains neutral. During the collision with 3 keV/amu O₆⁺, two electrons are removed from the CO₂ side leading to the formation of a dication with two holes localized at both sides. We observe two main dissociation channels as depicted in Figure 0. Beside the expected direct Coulomb explosion giving the pair CO+2

=(CD₂)N(CD₃)₂⁺, we observe a competitive channel following intramolecular charge migration (ICM) and giving the pair CD₃⁺=(CD₂)N(CD₃)₂⁺. These two channels are rationalized by simulating the dynamics with surface hopping semiclassical methodology where the electronic states are represented via perturbation theory based in multireference wavefunctions [2].

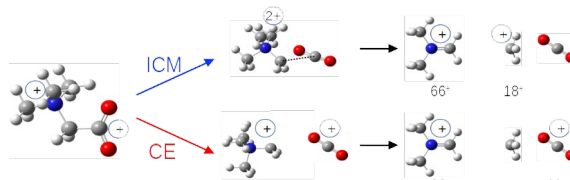


Figure 0: Ion pair coincidences in the dissociation of betaine dication following collisions with 48 keV O₆⁺ ions and associated fragmentation schemes.

Index Terms: molecular dynamics, surface hopping, potential energy surface.

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