High-resolution scattering imaging reveals vibrational-state-specific mechanisms in paradigmatic ion-molecule reaction

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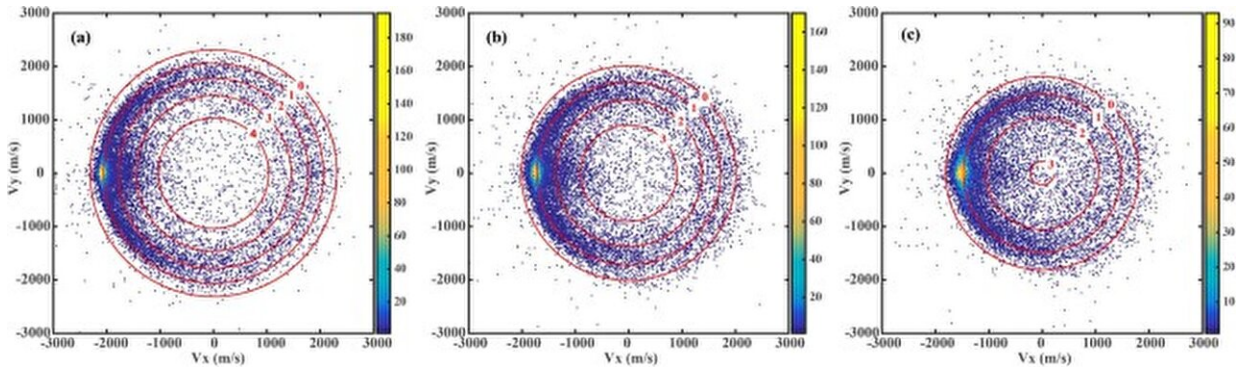

Product imaging at lower collision energies. Credit: *Nature Chemistry* (2023).
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Charged atomic and molecular species are ubiquitous in environments such as planetary atmospheres, interstellar medium and plasma. The collisions between charged ions and neutral molecules play vital roles in determining the chemical evolution and energy transfer in these complex gaseous environments.

$Ar^+ + N_2 \rightarrow Ar + N_2^+$ is a paradigmatic ion-molecule reaction, which has been intensively studied both experimentally and theoretically during the last half century. However, the underlying microscopic charge-transfer

dynamics have not been fully understood mainly due to the relatively low energy resolution achievable and the coexistence of both the spin-orbit ground $Ar^+(^2P_{3/2})$ and excited $Ar^+(^2P_{1/2})$ in the reactant ion beams in most previous experiments.

In a study published in *Nature Chemistry*, Prof. Gao Hong's group from the Institute of Chemistry of the Chinese Academy of Sciences (ICCAS) reinvestigated the charge-transfer reaction $Ar^+(^2P_{3/2}) + N_2 \rightarrow Ar + N_2^+(v', J')$ by using a home-made quantum-state-selected ion-molecule crossed-beam setup.

Full-dimensional trajectory surface-hopping (TSH) calculations were also carried out by Prof. Guo Hua's group at the University of New Mexico, U.S. The synergistic experimental and theoretical work identified two distinct charge-transfer mechanisms in the model reaction $Ar^+ + N_2 \rightarrow Ar + N_2^+$.

To gain deeper insights into ion-molecule reaction dynamics, the researchers at ICCAS designed and constructed a new ion-molecule crossed-beam scattering apparatus with a well-focused photoionization-based quantum-state-selected ion beam source and high-resolution three-dimensional (3D) velocity-map imaging (VMI) for detecting reaction products.

The product velocity can be measured with a resolution better than 1.5%. The Ar^+ ion was prepared exclusively in the spin-orbit ground state $^2P_{3/2}$ by using the resonance-enhanced multiphoton ionization (REMPI) method. The ion beam was carefully focused into the reaction center where it crossed with a supersonic N_2 beam. The velocities of the charge-transfer product N_2^+ were measured by the 3D VMI system.

The relatively high resolution achieved in the experiment enables the product vibrational and rotational distributions and their correlations

with the scattering angles to be measured accurately for the first time. The full-dimensional TSH calculation semi-quantitatively reproduces the experimental measurements.

Additionally, novel vibrational-state-specific charge-transfer mechanisms were clearly revealed. For the v′=1 vibrational level of N_2^+, the well-known long-distance harpooning mechanism dominates, resulting in strong forward scattering with low rotational excitation.

For v′=2, strong rotational excitation is found in the forward scattering region, contradicting the well-known hard sphere scattering model. The TSH calculation showed that it is due to the hard-collision glory scattering (HCGS) mechanism, which results from the delicate balance between the long-range attraction and short-range repulsion of the collisional partners.

This study demonstrated that the same level of quantum state-to-state understanding reached for neutral-neutral scattering in crossed-beam experiments is also achievable for ion-molecule scattering.

More information: Guodong Zhang et al, Imaging of the charge-transfer reaction of spin–orbit state-selected Ar+(2P3/2) with N2 reveals vibrational-state-specific mechanisms, *Nature Chemistry* (2023). DOI: 10.1038/s41557-023-01278-y

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