

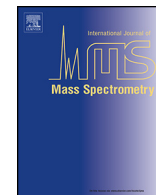


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Dynamics of ion–molecule reactions from beam experiments: A historical survey

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ABSTRACT

A historical survey of beam scattering studies of ion–molecule reactions from the sixties up to the present time is presented. The centers of research that developed key instrumentation for these studies and early achievements in characterizing basic collisional mechanisms in scattering experiments are reviewed. Important classes of cation–molecule reaction dynamics, impulsive atom–transfer, reaction complexes, electron transfer (charge transfer) dynamics and the dynamics of negative ion–molecule reactions are described. Selected specific examples of ion–molecule reaction dynamics, including multiply-charged and ion–surface collisions, are briefly presented.

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1. Introduction

Ion–molecule reactions were historically studied under single-collision conditions in ion sources of mass spectrometers and a large amount of data on reaction sequences and cross sections had been generated by the mid-sixties. An exciting new development in reaction kinetics—namely, beam scattering experiments and studies of neutral–neutral chemical reactions under single collision conditions—was introduced in the same time frame. Pioneering experiments of Datz and Taylor [1] initiated a new era of investigating the dynamics of chemical reactions of neutrals [2] and was the inspiration for extending analogous beam techniques to the investigation of chemical reactions of ions.

By physically separating ion formation and reaction chambers, beam techniques introduced significantly improved control of the translational energy of ion reactants. Mass, direction, and energy (and possibly internal state) of the ion reactant was fully defined prior to reaction. Tandem methods [3], guided-beam methods [4] and merged-beam methods [5] made it possible to determine total (integral) cross sections of ion–molecule processes and their dependence on collision energy. These powerful tools are reviewed elsewhere in this Special Issue and will not be described here; rather, we focus on techniques that specifically include scattering measurements of reactants and products and make it possible to obtain scattering diagrams and differential cross section of reaction products. A modification of the guided-beam method

using guided field variation as a way to obtain differential cross sections has also been described [6].

Beam scattering studies determine not only the identity of reaction products, but also their velocity and angular distribution, and often provide information on their internal state. The distinctive characteristic that ion reactions are readily investigated at collision energies from quasi-thermal up to many electron volts enabled a deeper general insight into the influence of translational energy on chemical processes. The sensitivity of mass spectrometric detection also enables detailed studies of low abundance products. More specifically, ion–neutral crossed beam experiments provide us with the following details of their reaction dynamics:

- Total and differential cross sections as a function of well-defined collision energy.
- Cross sections as a function of internal state of the ion reagents.
- Velocities and internal states of the products.
- Angular distribution of the products.

We also note that several reviews of beam scattering studies have been published that should be consulted for additional information [7–13].

2. The transition to molecular beam techniques

Fig. 1 illustrates schematically the components of an apparatus that enables this class of measurements. The required features are an appropriate ion source for preparation of a state-selected ion beam, its mass analysis and velocity selection, state and velocity selection of the neutral beam, and mass and velocity analysis of the

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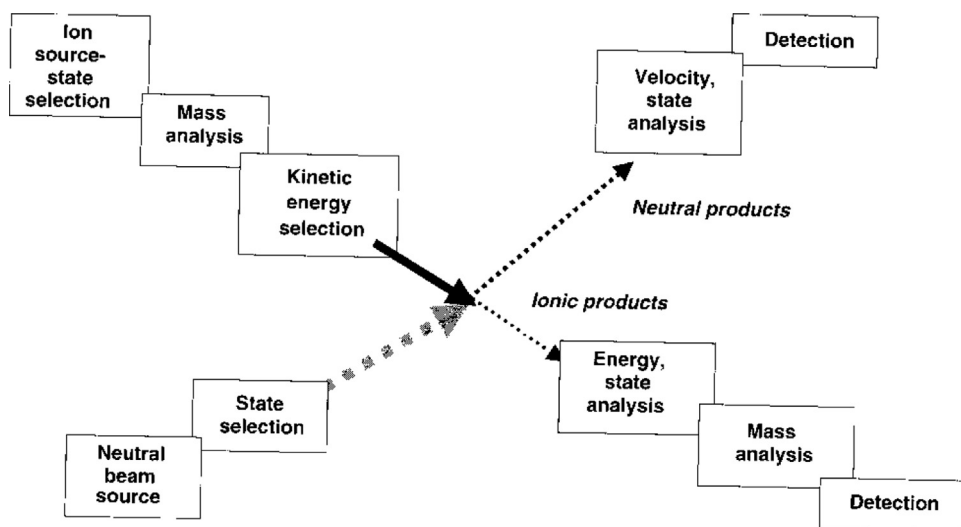


Fig. 1. Schematics of an ideal crossed beam experiment [13].

product ion and neutral product(s) along angular analysis of both. The actual development of instrumentation proceeded gradually to approach this ideal, starting from low-resolution crossed beam devices with mass analysis of the reagent ions beam and angular and velocity (energy) analysis of the product ion.

Because it was the standard technique utilized in mass spectrometry and provided high ion yields, electron impact ionization was used in the first generation crossed-beam instruments. Electronically and vibrationally excited states generated by electron impact could be removed by increasing pressure and by adding quenching gases. Mass selection utilized magnetic sectors or quadrupole mass analyzers. Deceleration of the reagent ions was achieved by multiple-element electrostatic lenses [14–16] and energy selection by cylindrical or hemispherical analyzers [17,18]. For preparation of neutral crossed beams, collimated multichannel effusive sources [14,19] were initially used; later versions utilized supersonic and seeded beams to achieve higher velocity and narrower angular distributions [15,16]. Product ion velocity (or energy analysis) was achieved by simple stopping-potential analyzers [14,20], by electrostatic deflection in cylindrical [16,21] or hemispherical [15,16,22] analyzers or by the time-of-flight method [23]. Mass analysis of product ions utilized magnetic or quadrupole mass analyzers and ions were detected utilizing various kinds of electron multipliers. The position-sensitive coincidence technique introduced early this century [24,25] added the unique capability to detect nascent velocities of product ion pairs originating from dissociation of multiply-charged ions.

Experiments are carried out in the laboratory systems of coordinates (LAB), while dynamical characteristics (angular distributions, relative translational energy distribution of products, comparison with trajectory calculations) are best analyzed in the center-of-mass (CM, barycentric) coordinate system [12,13]. This may be considered as the unique advantage of crossed-beam dynamics experiment. A particularly useful way of analyzing data from these experiments is the Newton velocity diagram [26] (Fig. 2). This figure depicts for a general chemical reaction $A+B \rightarrow C+D$ the relations between laboratory (v) and center-of-mass (u) velocities of reagents and products [12]. The utility of presenting product ion fluxes in the framework of these diagrams, and transformation relations between intensities in the polar laboratory and barycentric coordinate systems or as Cartesian probability units are thoroughly explained in the literature [12,13,27–29]. The utility of Newton diagrams for differentiating reaction mechanisms will become obvious in section 4.

3. Research leaders and key instrumental developments

Because mass spectrometers conventionally involve moderate to high kinetic energy ions, the first dynamics study involved hyperthermal energy ions colliding with neutrals at rest. In these pioneering studies only the translational energy [30,31] or the angular distribution of the ion products [32] was analyzed. Measurement of the translational energy distribution of products was much more informative than angular distributions. In particular, the relatively high velocity of reagent ions at electron volt collision energies impacting a neutral at rest restricts product ion angular distributions to such a narrow forward cone that different velocity components are not resolved. It was clear that the path forward would require measurement of both velocity and scattering angle of products in the next generation of scattering experiments.

Two approaches for measuring both energy (velocity) and angular distributions of product ions were soon developed. A simple scattering chamber was suitable for incident reactant ion energies in the eV range, where the random movement of neutral reagent particles could be neglected relative to the velocity of the ion reagent [17,20–22]. The other approach was the crossed beam technique, where the neutral reagent was formed into a collimated beam to react at the crossing point of this beam with the ion reagent beam [14,15]. With seeded neutral beams and improved

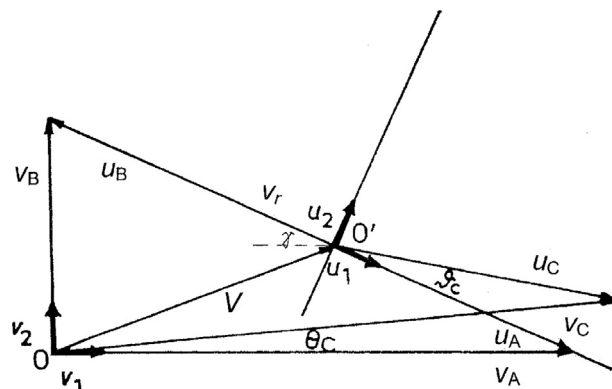


Fig. 2. Newton velocity vector diagram for a reaction $A+B \rightarrow C+D$, showing the relations between laboratory (LAB, v) and center-of-mass (CM, u) quantities [12].

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