Very high critical energy fragmentations observed in CID

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Abstract

High energy CID fragmentations of triatomic alkali halide cluster ions were examined to estimate the energy transfer during the CID process. A detailed CID study using keV collisions revealed that M_2X^+ clusters yield not only the expected M^+ ions but practically all possible combinations of mono- and biatomic ions. In the case of Cs_2I^+, for example Cs^+, Cs_2^+, CsI^+, and even I^+ fragment ions are observed. The results suggest that collisional energy transfer in keV collisions has a monotonously decreasing shape (full width at half height is ~2 eV) and has a long high energy tail extending well over 10 eV (with at least 5% probability), the average collisional energy transfer being about 5 eV.
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1. Introduction

Study of cluster ions using mass spectrometry is a dynamically developing field. Salt clusters, especially positively charged halide clusters of the general formula $[M_{y+1}X_y]^+$ are particularly well studied and often occur in desorption ionization mass spectra [1–4]. In these spectra magic numbers are prominent, often corresponding to small nanoclusters of cubic structure [5]. Alkali halide clusters have been also used as probes to gain insight into the electrospray, nanospray and ionspray ionization mechanism [6,7]. Fragmentation of these clusters consists of consecutive losses of MX molecules observed in collision induced dissociation (CID) [8–13].

CID is the most important excitation method used in mass spectrometry. In a gas-phase collision a fraction of the kinetic energy is converted into internal energy of the ion. It is typically assumed that the kinetic energy is converted into vibrational energy (often called T to v or collisional energy transfer (CET)), although excited electronic states may also be involved. Determining this energy transfer usually requires

measurement of the internal energy of excited ions, which can be performed by a variety of methods like photoelectron photoion coincidence spectroscopy (PEPICO) [14], laser-induced fluorescence spectroscopy (LIF) [15], thermometer molecule method [16], deconvolution method [17] and the survival yield method [18]. So-called low energy collisions (laboratory frame collision energy in the ca. 0.1–200 eV range, accessible in ion trap and quadrupole instruments) are studied in most detail. Collisional energy transfer is described usually as a certain fraction of the center of mass (c.o.m.) collision energy, it is always characterized by a distribution, and depends on number of parameters. In these cases average CET values in the 2–20% range (of the c.o.m. collision energy) have been reported [19–26]. The CET distribution is often approximated by an exponential function [21]. Recently it was determined that (at least in some cases) the tail of this distribution extends up to the c.o.m. collision energy and the tail is significantly larger than that described by an exponential [27]. CET in high energy (keV) collisions, usually occurring on sector instruments, is less well understood [13,19,21]. Mean energy transfer is likely to be several eV and the CET distribution is thought to have a long high energy tail. Note that this high energy tail is responsible for

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most differences between low and high energy collisions, like charge transfer processes [28,29], peptide side chain cleavages [30–32], charge remote fragmentations [33,34] not observable on quadrupoles and ion traps.

The kinetic energy release (KER) and its distribution (KERD) of metastable and CID peaks contain important information on details of the dissociation process [35,36], including internal energy of the fragmenting ion. These can be determined from the width and shape of peaks observed in mass analyzed kinetic energy (MIKE) spectra. MIKE peaks most often have approximately Gaussian shape [35,36], corresponding to a Boltzmann-like KER distribution. This is the case when the reaction proceeds with no activation energy barrier, the internal energy is distributed statistically among various degrees of freedom, fragmentation may be described by the so-called 'prior to distribution' model [37] and the internal energy of the fragmenting species is either well-defined or is evenly distributed in a wider range. Although this is a long list of conditions (often termed simply as 'statistical' behavior), these are most usually approximately satisfied. When this is the case, the mean KER value can be used to characterize the internal energy of the fragmenting ion. This may be performed qualitatively or using reaction kinetic modeling or using the finite heat bath theory [38,39]. We have recently demonstrated that fragmentation of methanol clusters satisfy these conditions very well, and can be modeled accurately [40]. There are notable exceptions to statistical behavior resulting in e.g. dish-topped peaks (often observed in charge separation processes [28,35,36,41]. When the KER distribution is significantly different from statistical, the origin of this difference is well-worth studying.

Recently triatomic alkali halide clusters have been studied in detail [23,42]. Their fragmentation produces an alkali cation (by far the lowest energy process), as expected: In the case of e.g. the $CsRbCl^+$ cluster both Cs^+ and Rb^+ were observed. To some surprise relative product abundances of even so small clusters were determined by the energetics of the reactions and it was possible to use product abundances to derive thermochemical information. This implies that reaction rates can be described adequately by statistical reaction rate theories (like RRKM). This was used successfully to model CID fragmentation of these clusters in a triple quadrupole type instrument in the 20–50 eV range [23]. As an extension of these studies the same and various other triatomic systems were studied on a sector instrument using keV collisions. What seemed a simple routine extension of previous work turned out to produce unexpected results and could be used to characterize collisional energy transfer in the keV range in some detail.

2. Experimental

Mass spectrometric experiments were performed on a reverse-geometry VG ZAB2-SEQ (Micromass, Manchester, UK) hybrid instrument in positive ion mode. Alkali halide salts (purchased from Sigma–Aldrich) were dried on the stainless steel probe tip from aqueous solutions and cluster ions were generated in the secondary ion mass spectrometry (SIMS) ion source. Accelerating voltage was 8 kV, resolution of the instrument was set to 1000 (10% valley definition). CID of triatomic cluster ions were studied using Ar collision gas at a pressure corresponding to ca. 20% main ion beam attenuation, so predominantly single collisions are observed. In some experiments He collision gas was also used, the effect of varying the collision energy and gas pressure were also checked, as described in the text. Fragmentation of Cs_2I^+ has also been studied on a triple quadrupole type Sciex API 2000 instrument (using electrospray ionization and N_2 collision gas).

In order to determine KER values and the distributions (KERD) the shape of MIKE peaks was measured accurately (acquiring spectra over a long time, in some cases up to 1 h). MIKE peak profiles were analyzed using the 'META' computer program developed in our laboratory [41]. The algorithm applied by the program is based on a numerical approach and does not use pre-defined analytical functions for the KER distribution. This may make the determined KER profiles noisier but there is less danger of distorting the experimental results.

Various tests have been performed by theoretical calculations using the MassKinetics (Ver. 1.4) software (http://www.chemres.hu/ms/masskinetics). This reaction kinetics package, used to model reactions occurring in a mass spectrometer, was developed recently [43]. Reaction rates are calculated by RRKM [37,44–47] taking into account internal energy distributions and changes in this distribution as the ions are traveling from the ion source to the detector. Energy partitioning, necessary to describe consecutive reactions and to calculate KER, was assumed to follow a statistical behavior.

Critical energies of fragmentation processes, frequency sets and respective transition states have been determined using quantum chemical calculations. These were performed at the B3LYP/G2 (for molecules contain Cs, I and Rb atoms at the B3LYP/SDD) level of theory [48–52] using the Gaussian 98 program package [53]. The calculated results showed good agreement with experimental values in all cases when these were available. The loose transition states (TS) corresponding to an atom (or atomic ion) loss from a triatomic cluster were described by two low frequency vibrations (leading to translation) and a vibration corresponding to the vibrational frequency of the diatomic product.

3. Results and discussion

The first example discussed is the $CsRbI^+$ cluster studied by the mass analyzed kinetic energy (MIKE) technique in CID mode on a sector instrument (8 keV collision energy). The observed spectrum (Fig. 1) shows not only the expected Cs^+ and Rb^+ products (which were observed in low energy