Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 243 (2005) 41–47

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Very high critical energy fragmentations observed in CID

Ferenc Pollreisz[a], Ágnes Gömöry[a], Judit Sztáray[a], Péter Végh[a,b], László Drahos[a], András Kiss[a], Károly Vékey[a,*]

[a] *Institute of Chemistry, Chemical Research Center of the Hungarian Academy of Sciences, Pusztaszeri ut 59-67, H-1025 Budapest, Hungary*
[b] *National Institute for Research and Development of Isotopic and Molecular Technologies, R-3400 Cluj-Napolca, PO Box 700, Romania*

Received 24 August 2004; accepted 16 December 2004
Available online 18 January 2005

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.

Keywords: Collision induced decomposition (CID); Salt-cluster; Collision energy transfer; Internal energy

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

---

[*] Corresponding author. Tel.: +36 1 438 0481; fax: +36 1 325 9105.
E-mail address: vekey@chemres.hu (K. Vékey).

1387-3806/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.12.026

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

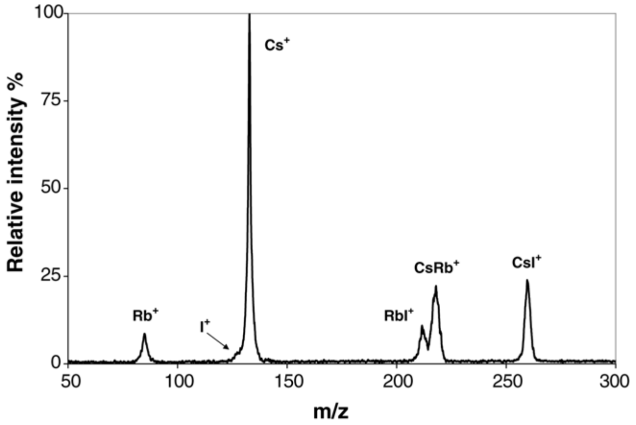

Fig. 1. High energy CID spectrum of $CsRbI^+$ cluster.

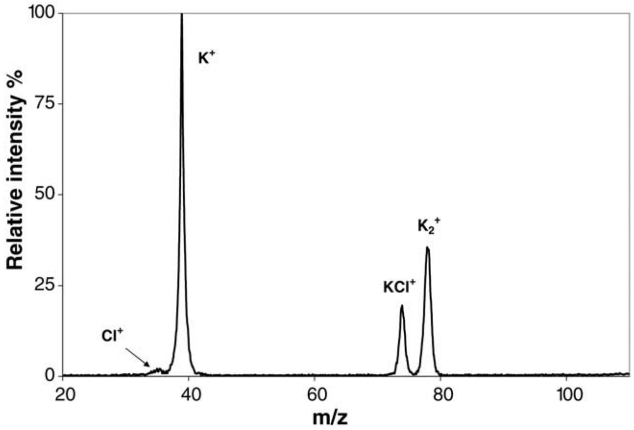

Fig. 3. High energy CID spectrum of K_2Cl^+ cluster.

CID) but all possible combinations of singly charged mono- and diatomic positive ions, $CsRb^+$, CsI^+, RbI^+ including even I^+. Formation of the diatomic fragment ions require 4.0, 4.4 and 4.7 eV, respectively, that of I^+ 10.9 eV critical energy. Various other triatomic alkali halide clusters were studied, all yielding analogous results. Fig. 2 shows the somewhat simpler case of Cs_2I^+. The MIKE spectra of Cs_2I^+ were studied under a variety of experimental conditions, changing the collision gas (to He), the collision energy (4–8 kV) and the collision gas pressure (by ca. one order of magnitude). The resulting spectra were all very similar, relative fragment abundances varied only within a factor of two. These suggest that the observed high energy fragmentation is a general feature of keV collisions and depends only relatively little on the experimental conditions. In a control experiment fragmentation of Cs_2I^+ was checked in a triple quadrupole instrument, varying the collision energy in the 10–130 eV range (the maximum values on this instrument). Under these conditions only the Cs^+ ion was seen, no traces of high energy fragments were observed even at 130 eV. Figs. 3 and 4 show further examples of K_2Cl^+ and $NaKCl^+$. The spectra show close analogy with those discussed above. The positively charged chlorine atom is well resolved from other peaks in the spectrum, so can be identified unequivocally. Note that formation of Cl^+ requires 14 eV internal energy, even more than that of I^+. We believe Figs. 1–4 are excellent demonstrations that keV CID produces a significant amount of high energy fragments.

Before discussing implications on energy transfer in detail, some details need to be discussed. These will be explained in case of the Cs_2I^+ cluster, but many similar experiments were performed on other clusters as well. Note that, in so small clusters the kinetic shift is negligible (less than 0.01 eV, as calculated by MassKinetics), so all ions above the dissociation limit will fragment in less than 1 μs. This means that although during ionization clusters are likely to be formed with a significant amount of internal energy [18], only those Cs_2I^+ ions will get into the fragmentation (second field free) region, which have internal energy below the critical energy (1.55 eV). To support this theoretical suggestion and to exclude the possibility of long-lived excited states which might be responsible for the high energy processes observed, the metastable MIKE spectra were also measured, but no fragments were observed (detection limit was 0.001% that of the main ion beam). This is in good agreement with theoretical expectations, which suggest that metastable fragments should have abundance less than 10^{-10} that of the main

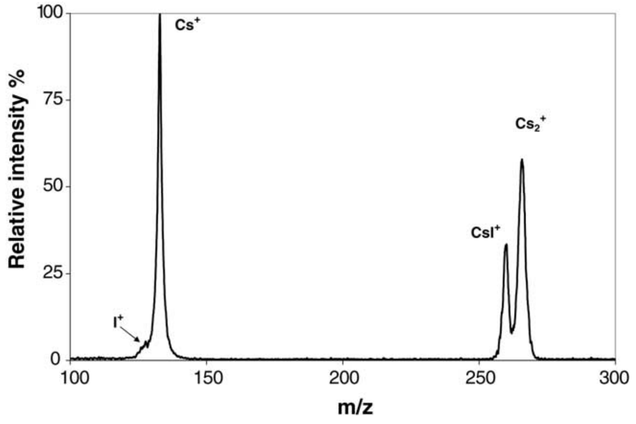

Fig. 2. High energy CID spectrum of Cs_2I^+ cluster.

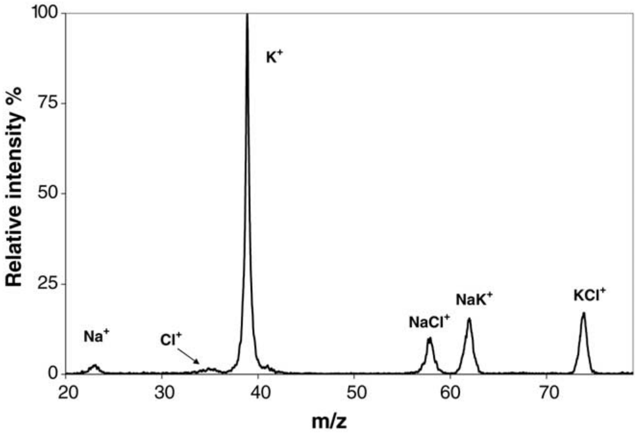

Fig. 4. High energy CID spectrum of $NaKCl^+$ cluster.

beam. (Note that it is a consequence of small kinetic shift.) The absence of spontaneous fragmentation also rules out the possibility that some of the CID fragments are due to long-lived excited states of the triatomic parent ion produced in the SIMS ion source.

Another important point to check if the spectra shown in Figs. 1–4 are indeed due to single collisions. To ascertain that formation of these CID spectra is indeed the consequence of single collisions, pressure dependence of the spectra was studied. If double collisions would play a significant role in determining the spectra relative peak abundances would change as a function of collision gas pressure. The spectra (in particular the abundance ratio of the high and low energy I^+ and Cs^+ ions) did not show any variation in the 1–35% main beam attenuation range. Note that this is equivalent to a 35-fold increase in the probability of double, compared to single collisions. In a second set of experiments, the abundance of fragment ions (compared to that of the main ion beam) was measured as a function of collision gas pressure (in the same 1–35% attenuation range). The results show a linear increase of fragment abundance with collision gas pressure, which is consistent with the idea that fragmentation is due to single collisions and ruling out any significant contribution from double collisions.

The observed spectra can be evaluated in terms of ion energetics in a qualitative manner. Note that in CID there are significant discrimination effects (discussed below in connection with KER), so the measured ion abundances do not accurately reflect branching ratios, so only qualitative evaluation is attempted. For Cs_2I^+ the energetics of fragmentation is given schematically in Fig. 5, including possible consecutive processes. Critical energies were determined using quantum chemical methods as discussed in the experimental section in greater details. Critical energy of Cs^+ formation is 1.55 eV. The kinetic shift in these small systems is negligible, so all ions above the dissociation limit will fragment practically instantaneously. For this reason the internal energy of Cs_2I^+ ions getting into the fragmentation region must be between 0 and 1.55 eV therefore its mean internal energy may be estimated to be ca. 0.5–1.0 eV. Although the mean internal energy is not known exactly, it has only a very little effect on the evaluation of ion energetics. Formation of $Cs_2{}^+$ and CsI^+ requires similar, 4.0 and 4.5 eV critical energy, respectively. To form these ions CID has to increase internal energy of Cs_2I^+ by at least 3–4 eV. Abundance of these ions is comparable to that of Cs^+, so collisional energy transfer will exceed 3–4 eV with at least 50% probability. Formation of I^+ becomes possible only above 11.1 eV critical energy, but reaction rate calculations show that it will compete effectively with Cs^+ formation only above 15 eV internal energy. Relative abundance of I^+ is ∼2.5% compared to that of Cs^+, so the probability of collisional energy transfer exceeding 10–15 eV will have ca. 5% probability. This assumes that above this energy I^+ and Cs^+ would be formed in equal proportion. (Note also that I^+ is on the tail of the Cs^+ peak, so its abundance can be measured only with high uncertainty, $2.5\% \pm 1$.) Qualitatively a very similar result is observed for the K_2Cl^+ cluster: In this case Cl^+ formation requires higher, 14.1 eV critical energy, the observed Cl^+/K^+ abundance ratio is slightly lower $1.6\% \pm 0.2$. Although this is only a qualitative or semi-quantitative description of CET, this clearly indicates that (a) collisional energy transfer is very similar for various salt clusters, (b) the degree of excitation is quite large and (c) energy transfer has a high energy tail well exceeding 10 eV. From these data it is not possible to obtain the exact shape of energy transfer, but e.g. an exponential or half-Gaussian CET distributions with at least 4–6 eV mean energy transfer would explain the results.

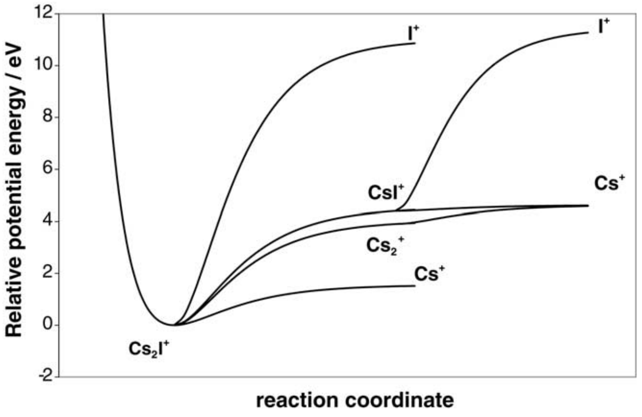

Fig. 5. Schematic potential energy diagram of Cs_2I^+ fragmentation.

Kinetic energy release was also studied to get information on energy transfer. The MIKE peak shapes (for fragmentation of Cs_2I^+) are shown in Fig. 6a and b. Note that the shape of Cs^+ is significantly different from those of CsI^+ and $Cs_2{}^+$, which have approximately Gaussian shapes. First these two will be discussed, but as they very similar in all respects, the results will be detailed only for CsI^+. The KERD has been calculated from the peak shape and shows an approximately statistical distribution, as illustrated in Fig. 7a. This indicates that the KER is derived from statistical energy distribution considering three degrees of freedom, as found before for fragmentation of protonated amine and methanol clusters [40,54]. The peak shapes have been analyzed by MassKinetics modeling, methodology is similar to that used to study protonated amin and methanol clusters [40,54]. Although the initial internal energy distribution of Cs_2I^+ in the ion source is unknown, it was found that it has a negligible influence on kinetic energy release. Several CET distribution types have been used (exponential, half-Gausian, Gaussian and composites between two different exponentials), all resulted in nearly indistinguishable KER distributions for CsI^+. Neither was the mean KER value of CsI^+ and $Cs_2{}^+$ sensitive to the amount of energy transfer: Varying the mean energy transfer tenfold (from 1 to 10 eV), the resulting ⟨KER⟩ changed varied only by ca. 20%. The theoretically calculated result using on average 2 eV energy transfer with an exponential distribution is shown in Fig. 7a. Although the experimentally found and the modeled mean KER values differ by about 30%, the shape

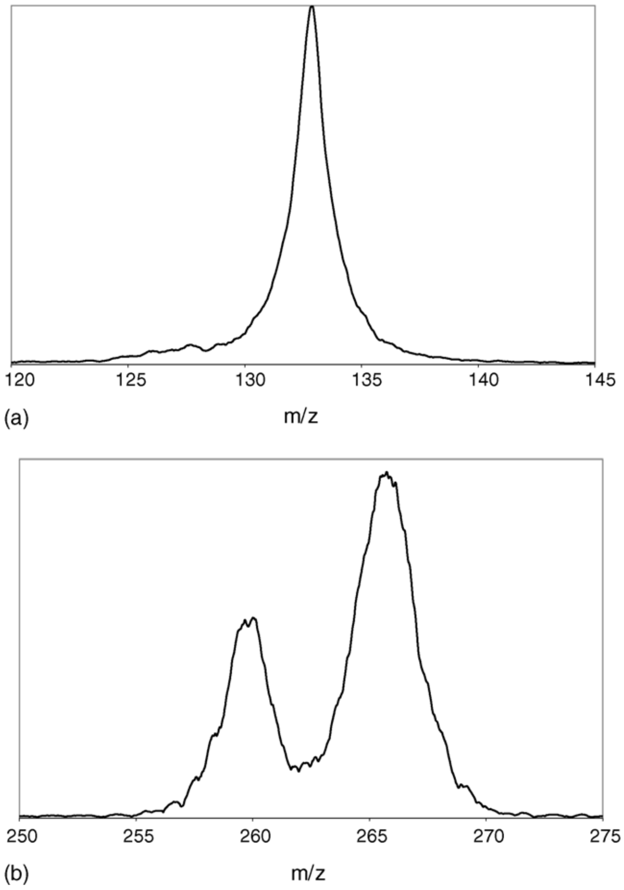

Fig. 6. CID-MIKE peak shape of (a) Cs^+ ions and (b) CsI^+ and $Cs_2{}^+$ ions formed from Cs_2I^+.

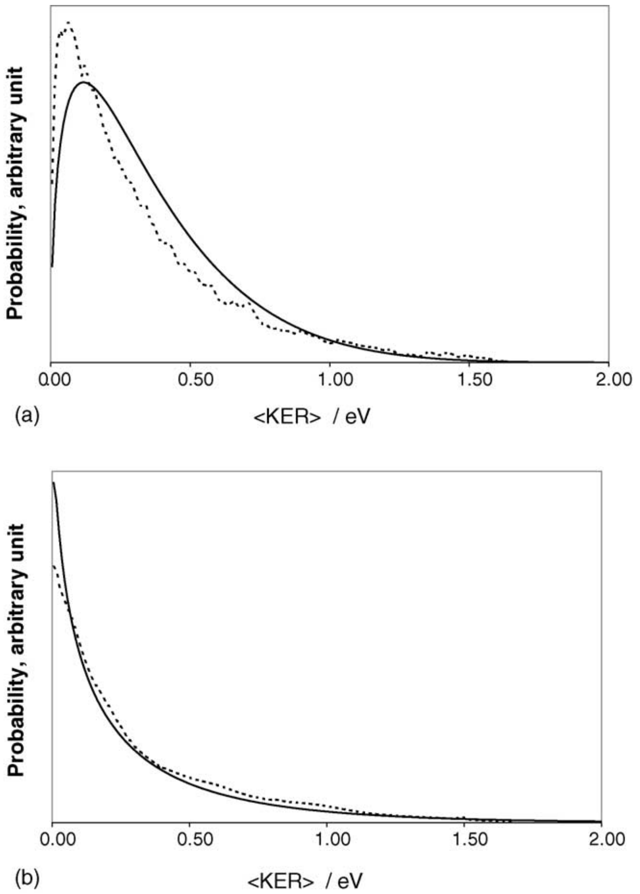

Fig. 7. Experimentally obtained (dashed lines) and calculated (MassKinetics modeling, solid lines) KER distributions of (a) CsI^+ and (b) Cs^+ ions formed from Cs_2I^+.

of the two curves indicate a fair agreement between experiment and theory. (Note that secondary fragmentation of CsI^+ to Cs^+ distorts the observed distribution somewhat, making accurate modeling difficult.)

The shapes of MIKE and KERD peaks of the Cs^+ fragment is significantly different from those discussed above. The mean KER value is 0.67 eV, its distribution shows a fast, approximately exponential decrease (Fig. 7b). Note that the only difference between the $Cs_2I^+ \rightarrow Cs^+ + CsI$ and $Cs_2I^+ \rightarrow Cs + CsI^+$ reactions is the position of an electron and the critical energy. These are among the smallest possible differences between two reactions, so they are expected to be governed by a similar type of energy partitioning. This suggests that the unusual KER distribution of Cs^+ is due to the internal energy distribution after CID, which should have a sharply decreasing shape above 1.55 eV internal energy. The KER distribution of Cs^+ has also been studied by MassKinetics modeling, using the same parameters as above. Modeling shows a good agreement with the experimentally observed KER shape when exponential or half-Gaussian CET distributions were used. The mean KER value in this case (and in contrast to $Cs_2{}^+$ and CsI^+) depends significantly of the mean energy transfer. Best agreement was found using on average 2 eV energy transfer with exponential distribution (Fig. 7b). This is a very satisfactory agreement, but there is an experimental limitation related to high KER values: When the KER is large, discrimination (products hitting the slits or colliding with the walls of the mass spectrometer) becomes a major problem. The META program does take discrimination into account, but at 1 eV KER only 20%, at 2 eV KER only 10% of the products will get to the detector. This, coupled to the experimental difficulty of measuring the tail of a CID peak accurately, makes it practically impossible to obtain reliable information on the high energy tail of collision energy transfer (over ca. 5 eV excitation) from kinetic energy release measurements.

Combining information based on high energy fragments and KER indicates that collisional energy transfer in keV collisions has a monotonously decreasing shape starting with a narrow, ca. 2 eV wide peak, has a long high energy tail extending well over 10 eV with ca. 5% probability and the average collisional energy transfer being about 5 eV. Such an energy transfer distribution is shown in Fig. 8. This shape, qualitatively at least, resembles those determined recently for low energy collisions [27].

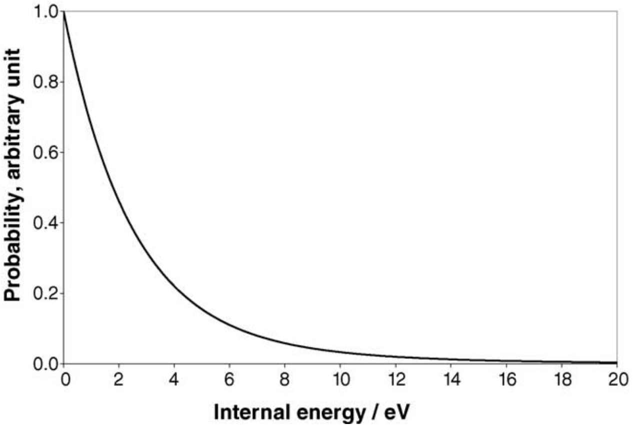

Fig. 8. Shape of a collisional energy transfer (CET) explaining the experimentally observed results for salt clusters.

4. Conclusions

In the present paper high energy collision induced dissociation of triatomic alkali halide clusters is discussed. In the CID spectrum of the Cs_2I^+ cluster ion unexpected fragments were detected, which require over 10 eV critical energy. It was shown that formation of these ions are not due excitation in the ion source, but is the consequence of a single keV collision. The same behavior was observed in the case of other triatomic alkali halide clusters as well. These include both heavy (like Cs, Rb, I) and relatively light atoms (like Na, K, Cl) colliding on He and Ar gases so this phenomenon is not due to a special electronic structure or high polarizability, but seems quite general.

Observation of high energy fragments (I^+ and Cl^+, but also the diatomic fragments) clearly shows that very large amounts of energy may be transferred in a single keV collision. To account for these ions, collisional energy transfer must have a long high energy tail extending well over 10 eV, probably even higher that 20 eV. Kinetic energy release, on the other hand, indicates that the probability of energy transfer decreases quite fast with the amount of energy transferred. Such an energy transfer curve is shown in Fig. 8. Getting accurate information on energy transfer, especially for large molecules, is quite elusive. For this reason it is tempting to consider implications for large molecules and the energy transfer curves determined for triatomic clusters might be applicable for proteins and peptides as well. It is known that in high energy collisions peptides do pick up sufficient energy for side-chain cleavages to take place, so keV collision probably will continue to play an important role in the structure elucidation of proteins and peptides.

Acknowledgements

This work was supported by the Hungarian Research Fund (OTKA) No. T 043538, the QLK2-CT-2002-90436 European Union project for Center of Excellence in Biomolecular Chemistry.

References

[1] K.L. Busch, R.G. Cooks, Science 218 (1982) 247.
[2] T.M. Barlak, J.R. Wyatt, R.J. Colton, J.J. Decorpo, J.E. Campana, J. Am. Chem. Soc. 104 (1982) 1212.
[3] M.A. Baldwin, C.J. Proctor, I.J. Amster, F.W. McLafferty, Int. J. Mass Spectrom. Ion Process. 54 (1983) 97.
[4] J.E. Campana, B.N. Green, J. Am. Chem. Soc. 106 (1984) 531.
[5] E.C. Honea, M.L. Homer, R.L. Whetten, Phys. Rev. B 47 (1993) 7480.
[6] G.D. Wang, R.B. Cole, Anal. Chim. Acta 406 (2000) 53.
[7] R. Juraschek, T. Dulcks, M. Karas, J. Am. Soc. Mass Spectrom. 10 (1999) 300.
[8] T.G. Morgan, M. Rabrenovic, F.M. Harris, J.H. Beynon, Org. Mass Spectrom. 19 (1984) 315.
[9] T. Drewello, R. Herzschuh, J. Stach, Z. Phys. D: Atoms Mol. Clusters 28 (1993) 339.
[10] P.J. Derrick, A.W. Colburn, M.M. Sheil, E. Uggerud, J. Chem. Soc., Faraday Trans. 86 (1990) 2533.
[11] K. Vekey, G. Czira, Org. Mass Spectrom. 28 (1993) 546.
[12] K. Vékey, K. Ludányi, Org. Mass Spectrom. 29 (1994) 615.
[13] K. Ludányi, K. Vékey, Rapid Commun. Mass Spectrom. 10 (1996) 1115.
[14] D.H. Aue, M.T. Bowers, Gas Phase Ion Chemistry, Academic Press, New York, 1979.
[15] M.J. Pilling, P.W. Seakins, Reaction Kinetics, Oxford University Press, New York, 1995.
[16] V.H. Wysocki, H.I. Kenttamaa, R.G. Cooks, Int. J. Mass Spectrom. Ion Process. 75 (1987) 181.
[17] K. Vekey, A. Somogyi, V.H. Wysocki, J. Mass Spectrom. 30 (1995) 212.
[18] F. Derwa, E. Depauw, P. Natalis, Org. Mass Spectrom. 26 (1991) 117.
[19] R.G. Cooks, Collision Spectroscopy, Plenum Press, New York, 1978.
[20] M.S. Kim, F.W. McLafferty, J. Am. Chem. Soc. 100 (1978) 3279.
[21] A.K. Shukla, J.H. Futrell, Mass Spectrom. Rev. 12 (1993) 211.
[22] R.M.A. Heeren, K. Vekey, Rapid Commun. Mass Spectrom. 12 (1998) 1175.
[23] L.M. Wu, J.W. Denault, R.G. Cooks, L. Drahos, K. Vekey, J. Am. Soc. Mass Spectrom. 13 (2002) 1388.
[24] O. Meroueh, W.L. Hase, Int. J. Mass Spectrom. 201 (2000) 233.
[25] E.R. Lovejoy, R. Bianco, J. Phys. Chem. A 104 (2000) 10280.
[26] C. Basic, R.A. Yost, Int. J. Mass Spectrom. 194 (2000) 121.
[27] F. Muntean, P.B. Armentrout, J. Chem. Phys. 115 (2001) 1213.
[28] K. Vekey, Mass Spectrom. Rev. 14 (1995) 195.
[29] J.K. Beynon, R.K. Boyd, A.G. Brenton, Adv. Mass Spectrom. 10 (1986) 437.
[30] R.S. Johnson, S.A. Martin, K. Biemann, J.T. Stults, J.T. Watson, Anal. Chem. 59 (1987) 2621.
[31] K.F. Medzihradszky, G.W. Adams, A.L. Burlingame, J. Am. Soc. Mass Spectrom. 7 (1996) 1.
[32] C.G. Gu, A. Somogyi, V.H. Wysocki, K.F. Medzihradszky, Anal. Chim. Acta 397 (1999) 247.
[33] M. Claeys, L. Nizigiyimana, H. VandenHeuvel, P.J. Derrick, Rapid Commun. Mass Spectrom. 10 (1996) 770.
[34] M. Claeys, H. VandenHeuvel, S. Chen, P.J. Derrick, F.A. Mellon, K.R. Price, J. Am. Soc. Mass Spectrom. 7 (1996) 173.
[35] J.L. Holmes, J.K. Terlouw, Org. Mass Spectrom. 15 (1980) 383.
[36] R.G. Cooks, J.H. Beynon, R.M. Caprioli, G.R. Lester, Metastable Ions, Elsevier, Amsterdam, 1973.
[37] T. Baer, W.L. Hase, Theory and Experiments, Oxford University Press, New York, 1996.

[38] C.E. Klots, J. Chem. Phys. 90 (1989) 4470.

[39] J. Laskin, J. Futrell, J. Phys. Chem. A 104 (2000) 8829.

[40] A. Gomory, P. Vegh, J. Sztaray, L. Drahos, K. Vekey, Eur. J. Mass Spectrom. 10 (2004) 213.

[41] Z. Szilagyi, K. Vekey, Eur. Mass Spectrom. 1 (1995) 507.

[42] G.D. Chen, R.G. Cooks, J. Mass Spectrom. 32 (1997) 1258.

[43] L. Drahos, K. Vekey, J. Mass Spectrom. 36 (2001) 237.

[44] P.J. Robinson, K.A. Holbrook, Unimolecular Reactions, John Wiley & Sons Ltd., Bristol, 1972.

[45] J. Steinfeld, J. Francisco, W. Hase, Chemical Kinetics and Dynamics, Prentice-Hall, New Jersey, 1989.

[46] R.A. Marcus, O.K. Rice, J. Phys. Colloid Chem. 55 (1951) 894.

[47] R.A. Marcus, J. Chem. Phys. 20 (1952) 359.

[48] A.D. Becke, Phys. Rev. A 38 (1988) 3098.

[49] C.T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[50] A.D. Becke, J. Chem. Phys. 97 (1992) 9173.

[51] T.H. Dunning Jr., P.J. Hay, Modern Theoretical Chemistry, Plenum Press, New York, 1976.

[52] L.A. Curtiss, K. Raghavachari, G.W. Trucks, J.A. Pople, J. Chem. Phys. 94 (1991) 7221.

[53] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98 (Revision A), Gaussian Inc., Pittsburgh, PA, 1998.

[54] L. Drahos, J. Sztaray, K. Vekey, Int. J. Mass Spectrom. 225 (2003) 233.