

Cluster Growth from the Gas Phase: Associative Collisions of Small Alkali Halide Aggregates

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Dedicated to Prof. Dr. H. Baumgärtel on the occasion of his 60th birthday

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Growth of clusters and eventually particles from free molecules in the gas phase lends itself to simulation. This report discusses classical molecular dynamics simulations of collisions of KCl molecules with small KCl clusters and of small KCl clusters with each other. Particular attention is given to long-lived collision complexes, especially those that endure long enough to be models for association and growth. Mechanisms of breakup are examined, as to structures through which the complexes go and the exchange processes that appear.

Der vorliegende Artikel behandelt Computersimulationen des Wachstums von Clustern aus freien Molekülen in der Gasphase. Es werden molekulardynamische Studien von Stößen von KCl-Molekülen mit kleinen KCl-Clustern und von kleinen KCl-Clustern untereinander diskutiert. Unser besonderes Interesse gilt dabei der Ausbildung langlebiger Stoßkomplexe, die, wenn sie genügend lange Zeit überdauern, als Modelle für Assoziation und Clusterwachstum dienen können. Mechanismen des Zerfalls und Strukturen des Übergangszustandes werden ebenso wie auftretende Austauschprozesse diskutiert.

I. Introduction

Alkali halide clusters have been attractive candidates for studying the growth of clusters [1–3], particularly by experiment [4–10] and simulation [11–36]. This is due at least in part to the supposition that rather simple

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interparticle interactions yield reliable models of their behavior [37]. Much of the attention in this field has devoted itself to structures of these clusters [11–21] and to the problem of isomerization and melting [22–29]; some has dealt with excess electrons and excess holes, particularly work concerning nonstoichiometric clusters [20, 30–33]. A few explorations have treated collisions of alkali halide clusters with surfaces [34, 35]. However, apart from one study of ion-ion recombination in atom-cluster collisions [36] virtually no efforts have dealt yet with collisions of molecules with clusters or of clusters with clusters, the processes that presumably lead to growth of alkali halide particles in the gase phase. Also for other chemical systems the process of cluster growth has rarely been investigated theoretically. Notable exceptions are studies of fusion of Na_n ($n = 8,9$) clusters [38] and of C_{60} fullerenes [39].

This work is a study, by classical molecular dynamics simulation, of some examples of such collisions of small neutral clusters of potassium chloride. We consider collisions of KCl molecules with other molecules and with clusters of two through four molecules, and also collisions of like-size clusters with each other, including dimer-dimer, trimer-trimer and tetramer-tetramer collisions. We consider collision energies up to 0.5 eV/ion.

The ultimate goal of this work is studying cluster growth, so we examine the lifetimes of compound states formed in relatively slow collisions, and compute cross sections for collisions which have lifetimes long enough to be considered associated into a relatively stable aggregate, i.e. clusters which remain bound long enough that if a thermalizing gas were present, the cluster would have had a high probability of stabilizing and coming to thermal equilibrium during its lifetime as a compound system. We also examine, but not exhaustively or systematically, the mechanisms by which such compound systems break up.

II. Computational details

A. Model

In the present study we describe the collisions of small KCl clusters using classical trajectory methods. The clusters are assumed to consist of K^+ and of Cl^- ions which are modelled as particles interacting through Born-Mayer potentials. In the framework of the Born-Oppenheimer approximation the particles are restricted to the ionic potential only. This can be rationalized because the collision energies considered here ($E < 0.5$ eV/ion) are well below the energy of the neutral KCl interaction.

For a system of closed-shell particles such as alkali halides the total potential energy of an aggregate can be well described as a sum of pair interactions which are independent of cluster size and shape [3]. Here a simple interionic pair potential of the form

Table 1. Parameters of the Born-Mayer potential as defined in Eq. (1) for pair interactions of K^+ and Cl^- ions [37].

	A [eV]	ϱ [nm]
K^+K^+	1555.21	0.0337
K^+Cl^-	1786.91	0.0337
Cl^-Cl^-	1924.80	0.0337

$$V_{ij}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left(-\frac{r_{ij}}{\varrho}\right) \quad (1)$$

is used where the first term of the right hand side gives the Coulomb interaction of two ions i and j at an internuclear separation of r_{ij} . The charges are $+e$ and $-e$ for K^+ and Cl^- , respectively. The exponential contribution to the potential function given in the second term represents the mutual repulsion due to the overlap of the electron shells and consequent shielding of the nuclear repulsion according to the Pauli principle. The values of the parameters A_{ij} and ϱ are given in Table 1. They were determined by Tosi and Fumi on the basis of crystal data [37]. A more realistic model would also have to include polarization effects which are omitted here for reasons of simplicity, see our discussion in Section IV.

B. Trajectories

In order to simulate reactive collisions of small clusters, we first have to specify the initial conditions of an impact. The initial distance of the collision partners has to be chosen large enough (≈ 5 nm) that their mutual interaction is negligibly small ($\ll 1$ meV). The impact parameter b is defined as usual as the component of this vector perpendicular to the direction of the relative velocity which is given by

$$v_{\text{rel}} = \sqrt{2E_{\text{rel}}/\mu} \quad (2)$$

where μ is the reduced mass of the two clusters. It is noted that in the following the relative impact energy E_{rel} is given in units of eV/ion to facilitate the comparison of the different collision pairs. The clusters are assumed to be initially in their minimum energy configurations discussed in Section III. This is a reasonable assumption for simulations of “cold” molecular beam experiments. Thus, the spatial orientation can be specified by Euler rotations which are described by the angles ϕ , θ , and ψ [40]. Furthermore, initial rotations of the reactants are neglected because they typically are much slower than the collisions.

Starting from the initial conditions specified above, trajectories of the colliding KCl clusters are obtained from Newton’s equations of motion. The

second-order equations are integrated numerically with the help of a six-point predictor-corrector scheme introduced by Gear [41]. In order to reach a stability of the energy of ± 1 meV throughout the course of each trajectory a timestep between 1 fs and 3 fs is chosen for the highest and lowest values of the impact energy, respectively.

C. Associative cross sections

Trajectories yielding associative collisions are detected in the following way. The start of the collision is defined as the time at which the separation of the two centers of mass falls short of a certain value chosen as the sum of the cluster radii. The end of the lifetime of the collisional complex by evaporation occurs if the distance between any of the ions and the center of mass of the rest of the ions exceeds a certain value. A trajectory is termed associative if its lifetime surpasses an arbitrarily chosen relatively low value (see below). The probability P_{ass} for the occurrence of such reactive events is calculated from averaging over N trajectories by counting the number N_{ass} of trajectories leading to the desired association reaction

$$P_{\text{ass}} = \frac{N_{\text{ass}}}{N}. \quad (3)$$

In general, this probability is a function of all the variables characterizing the initial conditions of a trajectory as defined previously. An orientationally averaged probability is obtained by statistical averaging over the three orientational angles of each of the aggregates

$$\begin{aligned} \bar{P}_{\text{ass}}(v_{\text{rel}}; b) &= \int_0^{2\pi} \frac{1}{2\pi} d\phi_1 \int_0^{\pi} \frac{1}{2} \sin\theta_1 d\theta_1 \int_0^{2\pi} \frac{1}{2\pi} d\psi_1 \\ &\times \int_0^{2\pi} \frac{1}{2\pi} d\phi_2 \int_0^{\pi} \frac{1}{2} \sin\theta_2 d\theta_2 \int_0^{2\pi} \frac{1}{2\pi} d\psi_2 \\ &\times P_{\text{ass}}(v_{\text{rel}}; b, \phi_1, \theta_1, \psi_1, \phi_2, \theta_2, \psi_2). \end{aligned} \quad (4)$$

Then the cross section for association processes is defined as the integral over the impact parameter b of the collision [42]

$$\sigma_{\text{ass}}(v_{\text{rel}}) = \int_0^{\infty} 2\pi b db \bar{P}_{\text{ass}}(v_{\text{rel}}; b). \quad (5)$$

Because the association probability P_{ass} is known to approach zero for large impact parameters the integration over b is truncated. To obtain fully converged results, we choose a maximum value of b between 1 nm and 2 nm. To circumvent the difficulties inherent to multidimensional integration using standard techniques, the 7-dimensional integrals are calculated by a Monte-Carlo procedure [42, 43]. This method has the advantage of converging at a rate that is approximately independent of the dimensionality. The statisti-

Table 2. Structure and energetics of small KCl clusters. The table gives structures, point groups, binding energies ΔE , and bond lengths ℓ of small KCl clusters of size n and of the crystalline KCl ($n = \infty$).

n	Structure	Symmetry	ΔE [eV/ion]	ℓ [nm]
1	linear	$C_{\infty v}$	-2.3733	0.265
2	rhombic	D_{2h}	-2.8809	0.285
3	hexagon	D_{3h}	-3.0189	0.283
4	rectangle	C_{2h}	-3.0614	0.281 ... 0.321
	octagon	D_{4h}	-3.0655	0.282
	cube	T_d	-3.1208	0.289
∞^a	crystal	fcc	-3.5142	0.319

^a Adapted from References [13, 48].

cal error scales as $N^{-1/2}$ with N being the number of Monte Carlo points. In the present study a typical number of $10^4 \dots 10^5$ trajectories had to be evaluated to achieve an accuracy of better than 1% for the cross sections.

III. Formulation of initial conditions

In this section we want to discuss the configurations of the dimer, trimer, and tetramer used as initial geometries in the study of reactive collisions. Based on the pair potentials of Eq. (1) we calculate minimum energy configurations in the following way. Starting from a set of randomly chosen initial structures we perform constant energy molecular dynamics simulations. By slowly scaling down the velocities of the ions the energy of the cluster is reduced. It becomes trapped in one of the various catchment areas of the potential energy hypersurface until finally a minimum energy structure is reached.

Our results are summarized in Table 2. The most stable structure of the dimer is a near square rhombic arrangement of the four ions. As for the case of the KCl monomer, the calculated bond lengths are in the order of 3% lower than the corresponding experimental values [4]. As a consequence of the long range of the Coulomb forces, close packing structures are not necessarily the most stable ones for small alkali halide systems. This shows up first for the trimer where due to the repulsion between second nearest neighbours the energetically most favored structure is a regular hexagon. Chain-like isomers are only slightly less stable. As was shown for the dimer and trimer of sodium chloride, these structures are only 7% higher in energy than the most stable species [3].

For the KCl tetramer we find three structures. As predicted earlier in a study of various alkali halide compounds, the most stable structures of systems with approximately equal size of cation and anion are cube-like [14].

It is followed by a regular octagon and a rectangular structure which are nearly degenerate in energy. The preference of the cuboidal geometry which can be considered as a fragment of the crystalline rocksalt structure is in agreement with recent *ab initio* calculations [21]. However, with increasing temperature planar isomers become preferred over cubic structures for entropic reasons. This transition was characterized previously in the literature. For the tetramer of potassium chloride it was found to occur between 600 K and 700 K [27]. Similar results were also obtained for $(\text{NaCl})_4$ [3, 25].

IV. Results

A. Lifetimes of collision complexes

In the following we study two groups of collision complexes. The first one will be the cluster growth by addition of a single molecule to a small cluster



This class of reactions will be termed $(n + 1)$. The second class of systems studied here involves associative reactions of small clusters of equal size



which we refer to as $(n + n)$ associations. In principle the reaction products are unstable due to the excess energy of the impact and the lack of an additional cooling mechanism. This question will be elucidated in the discussion in Section IV.

The distribution of lifetimes of the collision complexes for both types of reactions is shown in Fig. 1. After the first three or four picoseconds all the curves are roughly linear in the semi-logarithmic plots. This corresponds to an exponential decay of the collision complexes with mean lifetimes in the regime of a few picoseconds. It can be seen from Fig. 1a that the KCl dimers decay faster than the larger clusters formed in $(n + 1)$ reactions. This is in accord with statistical theories like the RRK or RRKM theory which predict the probability that more than a certain energy can be found in a critical mode leading to decay. This probability decreases drastically with the number of internal degrees of freedom among which the excess energy may be distributed [44]. This trend, however, does not apply for the larger clusters formed by monomer addition $(n + 1)$ which are equal within the statistical error. For the symmetrical cluster growth in $(n + n)$ reactions this tendency seems even to be reversed. As is evident from Fig. 1b the lifetime of the association product formed in the collision of two dimers is considerably larger than that formed in the reaction of monomers, trimers, or tetramers.

To investigate the lifetime of association products more in detail, we want to distinguish between short-lived collision complexes which decay

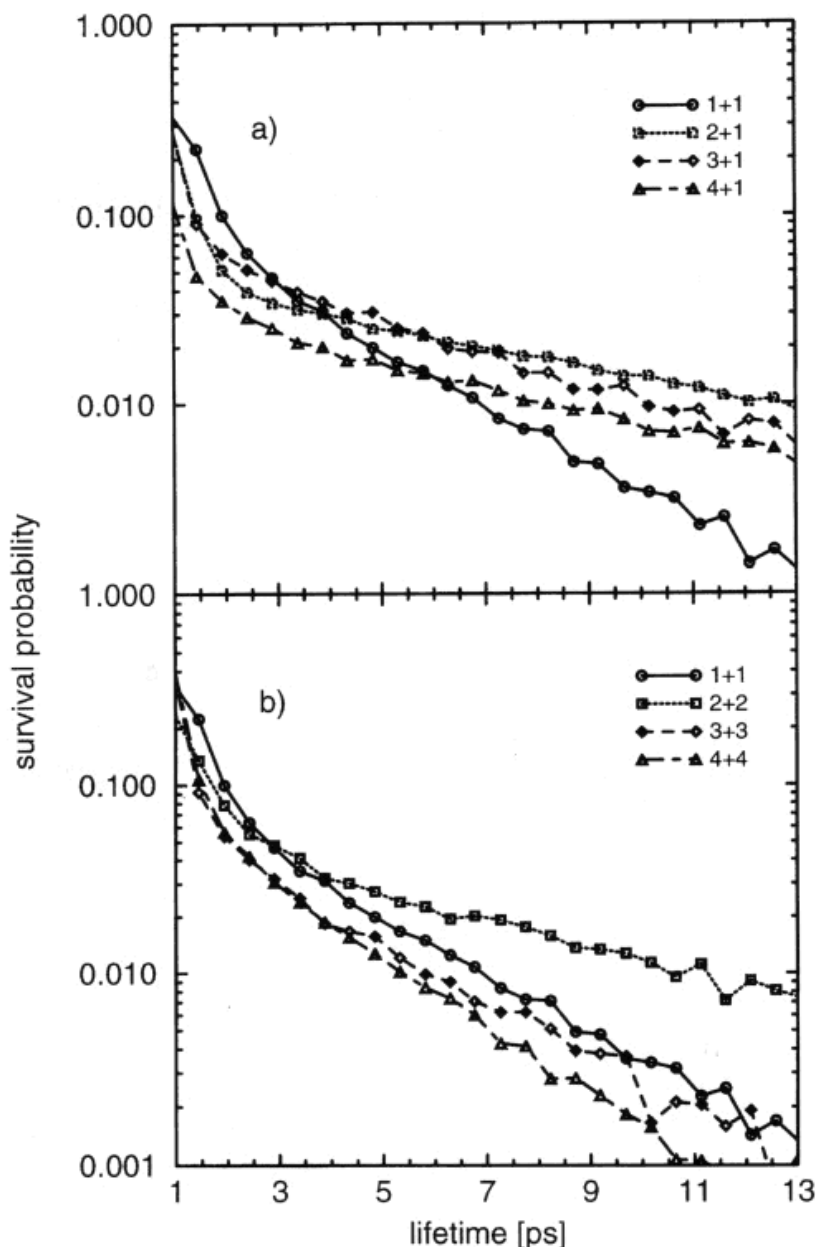


Fig. 1. Distribution of lifetimes of collisional complexes of small KCl clusters for $E_{\text{rel}} = 0.3$ eV/ion for $(n+1)$ (upper panel) and for $(n+n)$ reactions (lower panel) as defined in Eqs. (6) and (7), respectively.

within the first few periods of rotations and long-lived ones. As a somewhat arbitrary criterion we choose a lifetime of 17 ps. This choice of a time scale is motivated by the previous observation that only between 10^{-3} and 10^{-2} of the trajectories do not redissociate within this time. Fig. 2 shows the dependence of the orientationally averaged reaction probability \bar{P}_{ass} defined in Eq. (4) on the impact parameter b and on the relative energy of collision E_{rel} for associations of a dimer and a bare molecule ($2+1$). It shows that long-lived products are formed preferentially for low values of both the

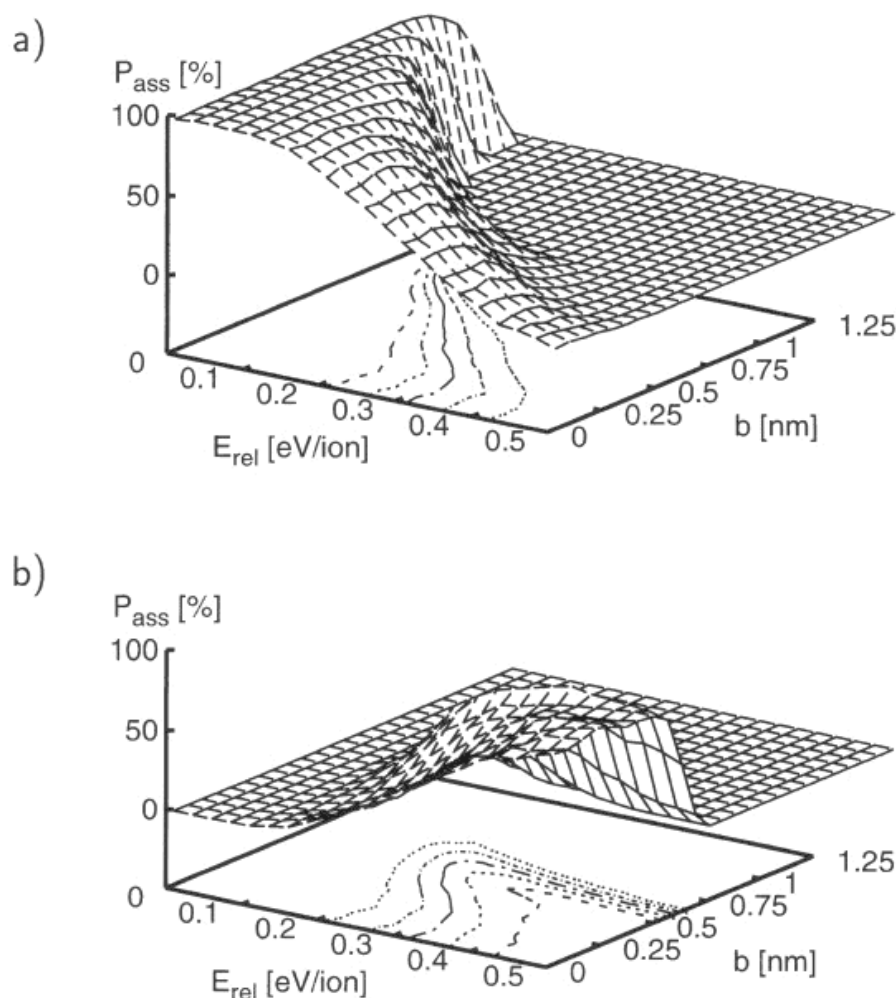


Fig. 2. Reaction probabilities for the formation of KCl trimers in a (2 + 1) collision. The upper and the lower panels give the probabilities for formation of long-lived and of short-lived complexes, respectively, with 17 ps the lifetime that divides them.

impact parameter and the collision energy. For a given energy the probability decreases drastically in an almost stepwise manner with increasing b which is due to centrifugal dissociation. In contrast, shortlived complexes are formed at higher energies ($E_{\text{rel}} > 0.2 \text{ eV/ion}$) and for all impact parameters below a certain value ($b < 0.6 \text{ nm}$).

Both the sudden fall-off of the probability with increasing b and the “ridge” in the perspective view along $b \approx 0.5 \text{ nm}$ extending towards lower energies indicate the importance of collisions with grazing incidence for the formation of complexes. An example for such a (classical) orbiting is illustrated by the trajectory of Fig. 3. It shows the formation of a complex in a planar (2 + 1) collision. The complex is formed by attaching the molecule sideways to the rhombic dimer. Due to the high angular momentum of the collision the complex starts rotating and as a consequence of the centrifugal force it stretches out and becomes quasi-linear. After about 4 ps or 1.5 per-

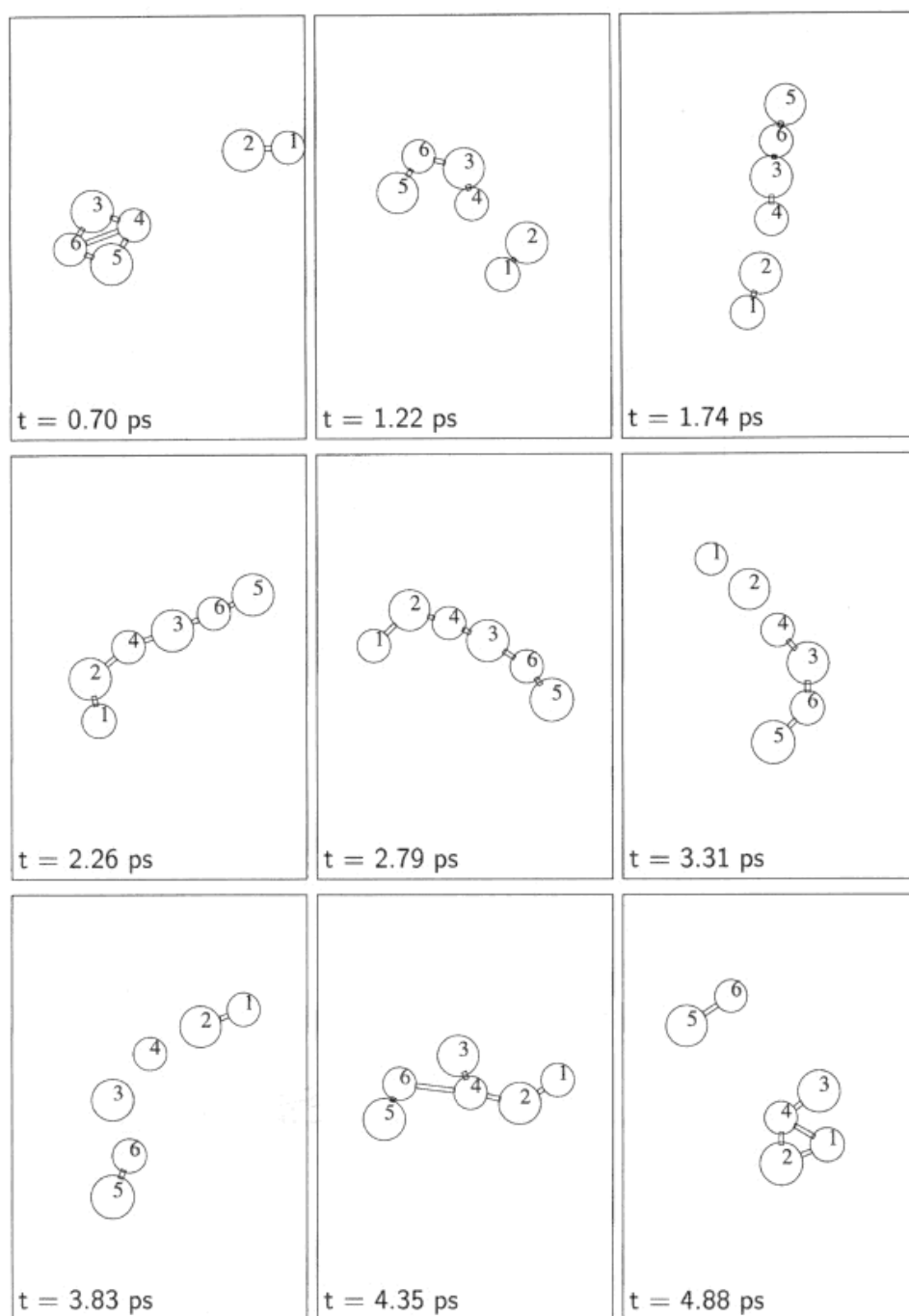


Fig. 3. Example trajectory for the formation of a short-lived KCl trimer in a (2 + 1) collision for $b = 0.58$ nm and $E_{\text{rel}} = 0.42$ eV/ion. The initial velocity of the KCl monomer is from top to bottom.

ions of rotation it redissociates again. The final snapshot shows that the remaining dimer is again a rhombic structure which is slowly rotating. Thus the evaporated monomer unit serves to release both energy and angular momentum. The numbering of the ions reveals yet another interesting aspect of the example trajectory. While the complex is formed of the reactants

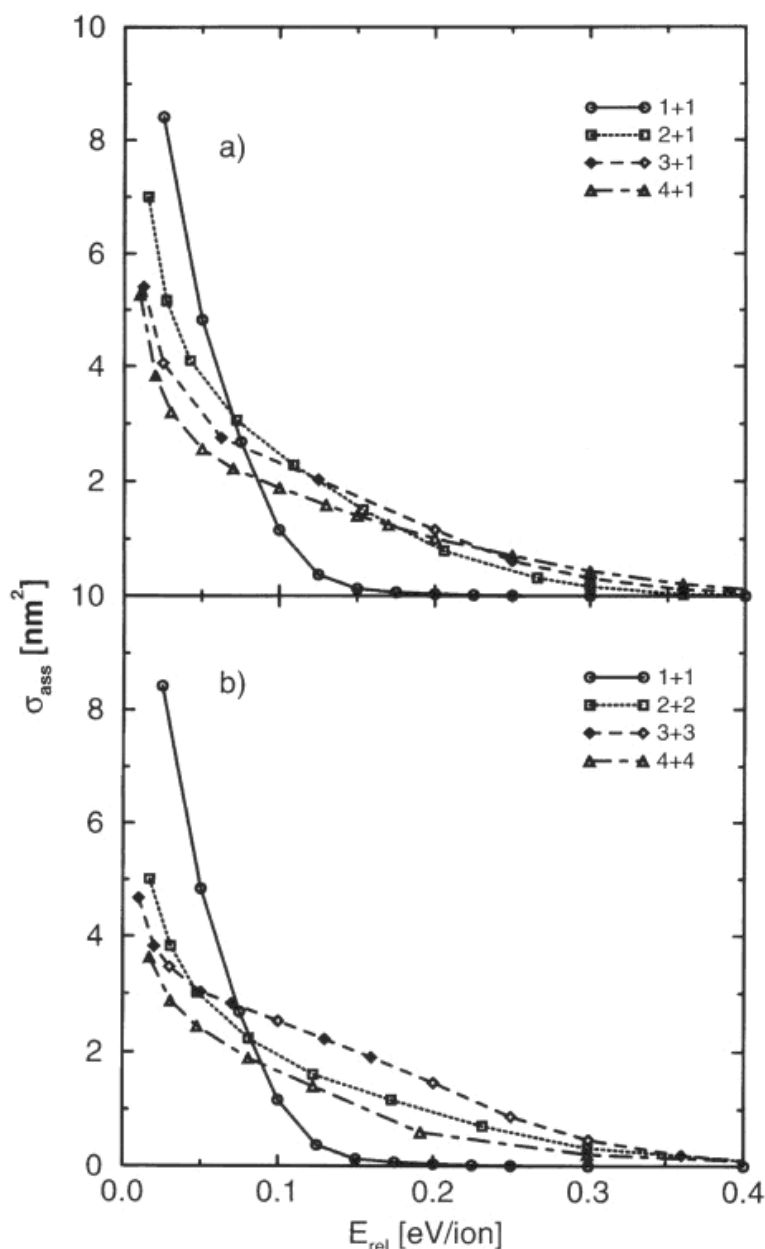


Fig. 4. Energy dependent cross sections for the formation of long-lived KCl associations for $(n + 1)$ (upper panel) and for $(n + n)$ reactions (lower panel).

with atoms labelled 1–2 and 3–4–5–6 it dissociates into 1–2–3–4 and 5–6. In other words, the rotating complex has lost its “memory” of the identity of the constituting reactants after less than two periods of rotation.

B. Associative cross sections

In this section we want to focus on the cross sections for formation of long-lived associations only. Fig. 4 shows these values for a variety of collision pairs as a function of the relative energy of impact. In each case the clusters

are assumed to be initially in their most stable configuration (see Table 2). All of the curves exhibit a monotonically decreasing behavior from values of a few nm^2 at $E_{\text{rel}} < 0.1$ eV/ion down to values below the sensitivity limit of our Monte Carlo method of approximately 10^{-3} nm^2 at $E_{\text{rel}} = 0.5$ eV/ion. This is typical for reactions that take place on a purely attractive potential surface and that are controlled by the centrifugal barrier only [45]. Thus it can be concluded that although the orientationally averaged Coulomb interaction of the neutral clusters vanishes the associative reactions occur preferentially for orientations where this interaction is attractive.

The cross sections for both the $(n + 1)$ and $(n + n)$ reactions can be characterized by two opposite trends. (1) For low impact energies ($E_{\text{rel}} < 0.1$ eV/ion) the cross sections for association of small clusters are much higher than those for the larger clusters. This can be explained by the different ranges of the electrostatic forces between the reactants. For example, for not too small distances r the $(1 + 1)$ potential can be approximated very well by a pure dipole-dipole interaction which falls off as $1/r^3$. This has to be compared to the dipole-octupole interaction for the $(4 + 1)$ system or the octupole-octupole interaction for the $(4 + 4)$ system which decrease as $1/r^5$ or $1/r^7$, respectively.

(2) For higher impact energies this trend is reversed. The cross sections for monomer addition to a dimer, trimer, and tetramer are much higher than those for the monomer-monomer association. Also the cross sections for combination of $(n + n)$ with $n = 2 \dots 4$ clearly exceed those for the $(1 + 1)$ system. Apparently the different lifetime of the complexes as discussed previously rules the behavior of the cross sections here. Due to the larger kinetic energy of the reactants the distribution of excess energy of the reaction product to its internal degrees of freedom gains more importance than the range of the attractive potential. For larger products there is a higher number of internal vibrations and consequently the rate of redissociation is lower [44]. Hence, the probability of surviving a given time is larger. However, as was seen before in the discussion of the lifetimes, there are exceptions to this general tendency. First of all, the cross sections for the $(2 + 1)$, $(3 + 1)$, and $(4 + 1)$ systems are equal within statistical errors although the number of degrees of freedom differs appreciably (see Fig. 4a). Furthermore, the cross section of the association of tetramers is smaller than that of dimers or trimers (see Fig. 4b).

Another interesting question is the dependence of the associative cross section on the isomeric structure of the reactants. As an example we study here collisions of a single molecule with the three most stable structures of the tetramer as discussed in Section III. Fig. 5 shows our results for the energy dependent cross sections. The overall picture is the same as discussed above. For low impact energies ($E < 0.1$ eV/ion) the cross sections are basically dictated by the attractive forces. Due to the relatively long range of the dipole-quadrupole interaction the cross section for the rec-

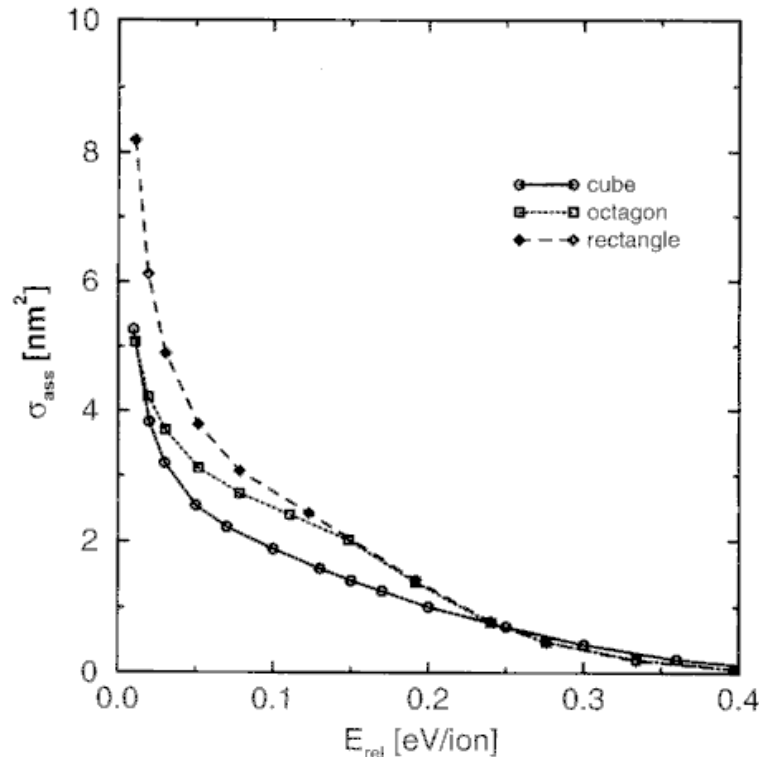


Fig. 5. Energy dependent cross sections for the formation of long-lived KCl associations for (4 + 1) reaction. The three curves show the cross section for the various isomers of the KCl tetramer.

tangular isomer of $(\text{KCl})_4$ is larger than those for the ring-like (octagon) or for the cube-like structure. For larger impact energies ($E > 0.25$ eV/ion) the values for the three systems are practically equal.

V. Discussion: Future questions and summary

The potential functions used in this work are not the most sophisticated ones for the alkali halides, by any means. It would be desirable to test our findings with a potential that includes at least polarization of the ions and induced-dipole induced-dipole interactions. However, on the basis of previous studies, we expect any changes from our findings to be relatively small quantitative differences, not large changes [27]. Another aspect of growth by collision that needs exploration is the process of intra-cluster vibrational relaxation, which can also be expressed as the dissipation of the heat of condensation. Accompanying that issue are the questions of the extent to which accretion can induce some kind of local melting, followed by recrystallization via a process of growth from the remaining, solid-like cluster – or by fresh nucleation and growth [46]. Competition between cooling by evaporation and by radiation is also an issue to be

studied (for examples of molecular dynamics studies of two processes see Refs. [36] and [47], respectively); alkali halides have very high binding energies and very large transition dipole moments, so it might be that accreting alkali halide clusters could be one class of systems that could effect a non-negligible part of their cooling by radiation rather than by the far more usual particle loss. Of course this also raises the ubiquitous problem of rates of relaxation by third-body collision. Last in this list is the question, readily addressable with further computations, of the size of system for which a statistical treatment such as the Rice-Ramsperger-Kassel-Marcus (RRKM) formulation is valid.

This work has begun the examination of how ionic molecules and clusters collide and respond to those collisions. Collisions occurring with impact parameters comparable to the sizes of the collision partners frequently lead to long-lived complexes and, even if not such extreme situation, to rearrangements and exchanges: the particles comprising the colliding species scramble in the process of forming the separating products. A particularly striking morphology of the separating products, at least in the small systems studied here, is a sort of string-of-beads, a structure which minimizes the potential energy but also the binding energy that the departing fragments must overcome. It is striking that even long-lived monomer-monomer collisions decay by something approaching RRKM statistics, and that collision complexes of all the larger systems we studied show characteristic exponential decays in concentration.

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A collection of typical trajectories such as shown in Fig. 3 can be viewed as MPEG movies in the World Wide Web at location <http://www.chemie.fu-berlin.de/manz>.

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