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A theoretical description of multi-channel fragmentation of the Na_3^+ cluster-ion in collision with a He target

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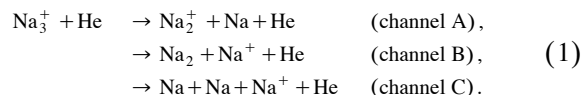
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Abstract

Fragmentation of the Na_3^+ cluster-ion in collision with He in the 100 eV (centre of mass) energy range is investigated theoretically. The dynamics study is split into two stages: the He– Na_3^+ encounter itself and the post-collisional motion of the Na_3^+ cluster-ion. The first stage is treated semiclassically and involves a ‘frozen cluster approximation’. The second stage is treated by a trajectory surface hopping procedure. The two stages make use of diabatic and adiabatic representations, respectively and involve diatomics-in-molecules calculations. For the He– Na_3^+ system, an adaptation of the DIM approach incorporating three-centre integrals is employed. Different fragmentation mechanisms are discussed and comparison with experiment is made. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The fragmentation of sodium cluster-ions, Na_n^+ ($2 < n < 9$), in collisions with He in the 100 eV centre-of-mass energy range has recently been investigated experimentally [1–4]. This has been a strong incentive for undertaking the present work after an earlier one on the simpler Na_2^+ –He system [5]. Here we are concerned with the Na_3^+ –He collision and especially with the following fragmentation processes:



This system has been the subject of a detailed experimental study which is reported in a companion Letter in this issue [6]. In general, the experimental results of Refs. [1–4,6] show evidence for essentially two different fragmentation pathways. The first one involves an *impulsive mechanism* whereby momentum is transferred elastically from the He atom to the atoms in the cluster. The second one involves an *electronic excitation mechanism* which brings the cluster in a dissociative state and thereby leads to cluster breakup.

In a previous work on the Na_2^+ –He collision [5,7], ab initio calculations were used to determine the relevant potential energy surfaces (PESs) and couplings, and a semiclassical coupled wavepacket method [8] was explored in the treatment of the dynamics. The latter treats both the electronic motions and the vibrational motion of the Na_2^+ dimer quantumly and the other degrees of freedom classi-

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cally. For the $\text{Na}_3^+ - \text{He}$ collision, such an approach would be unworkable for two main reasons: (1) the ab-initio determination of the PES and couplings becomes an awkward task; and (2) the wavepacket treatment of the three internal degrees of freedom of the Na_3^+ cluster during and after the collision far exceeds current computational possibilities.

Concerning the determination of the PES, one has to use an approach which is light enough while being able to account for a peculiarity of metal clusters, namely: the property of their electrons to be delocalised, and thus to participate somehow in the cluster dynamics. In general, it is not possible to describe interactions with and within a metal cluster(-ion) using mere binary additive potentials as is the case of van der Waals clusters. On the other hand, standard ab initio or density functional theory (DFT) calculations are much too computationally demanding when interfaced with non-adiabatic dynamics calculations [9–11]. The more so when they require a knowledge of several PESs and the corresponding couplings as the nuclei evolve along thousands of trajectories. These considerations have led us to use a diatomics-in-molecules (DIM) approach [12]. It has already been shown in the literature that hole hopping in the charge transfer dynamics of molecule-ions and rare gas cluster-ions can efficiently be studied using such a formalism [13]. It also turns out that the DIM formalism contains intrinsically electron (or hole) delocalisation represented as superpositions of valence bond configuration states in which the electrons (or holes) are localised. This is a particularly appealing feature for the problem at hand. We have used this method as described in Section 2 with an adaptation to the $\text{Na}_3^+ - \text{He}$ system which includes three-centre integrals.

Concerning the treatment of the dynamics, a considerable reduction in computational effort may be achieved by resorting to a sudden approximation also used in $\text{Na}_2^+ - \text{He}$ collision [5]. It rests on the comparison of a characteristic vibration time of the cluster ($t_{\text{vib}} \approx 10^{-13}$ s) with the typical atom–cluster interaction time for a collision ($t_{\text{coll}} \approx 10^{-15}$ s) in the considered energy range. Accordingly, the whole phenomenon (1) has been subdivided into two consecutive stages:

(i) The cluster–atom collision itself, during which the Na nuclei are considered as clamped while the

fast He atom passes by. In this stage, it is justifiable to use a semi-classical energy conserving trajectory (SCECT) method [14];

(ii) The post-collisional evolution of the Na_3^+ cluster, which has to account for non-adiabatic transitions as a result of the movement of the Na nuclei. It is adequately handled using the trajectory surface hopping (TSH) scheme developed by Gislason and co-workers [15,16].

2. DIM potential energy surfaces and couplings

The PESs and couplings required to investigate the non-adiabatic dynamics of the $\text{Na}_3^+ - \text{He}$ system in the above discussed framework have been obtained using the DIMZO method [12]. The DIM treatment lends itself to a facile determination of the adiabatic PES of the cluster [17] and offers the opportunity for easily incorporating the interaction of the helium atom with the cluster.

For the Na_3^+ cluster-ion, we followed Kuntz [17], namely: a DIM basis composed exclusively of Σ states of the diatomic fragments is chosen. In the corresponding valence-bond configuration-state functions one sodium atom at most can be excited. The adiabatic states of the cluster-ion are obtained as eigenvalues of the Hamiltonian matrix \mathbf{H}_0 in the DIM basis. We call \mathbf{C} the corresponding unitary transformation from the DIM basis to the adiabatic basis. When the non-adiabatic coupling between the Na_3^+ adiabatic states is needed in the post-collisional stage of the dynamics it is determined as described in Ref. [18].

Consistently, the DIM Hamiltonian for the $\text{Na}_3^+ - \text{He}$ system ($\mathbf{H} = \mathbf{H}_0 + \mathbf{U}$) requires Σ adiabatic potential curves of the Na–He, $\text{Na}^+ - \text{He}$ and $\text{Na}^* - \text{He}$ diatomics (to build the \mathbf{U} matrix). These are calculated using the GAMESS [19] code and employ the same basis set and l -dependent effective-core potential for Na as in Ref. [5]. The interaction between the cluster-ion in its different electronic states and the helium atom is described by the potential matrix $\mathbf{C}^{-1} \mathbf{H} \mathbf{C}$ (with the above definition of the \mathbf{C} matrix). The $\text{Na}_3^+ - \text{He}$ states obtained from this procedure are diabatic [20] with respect to the motion of the He atom relative to the cluster. Transitions between

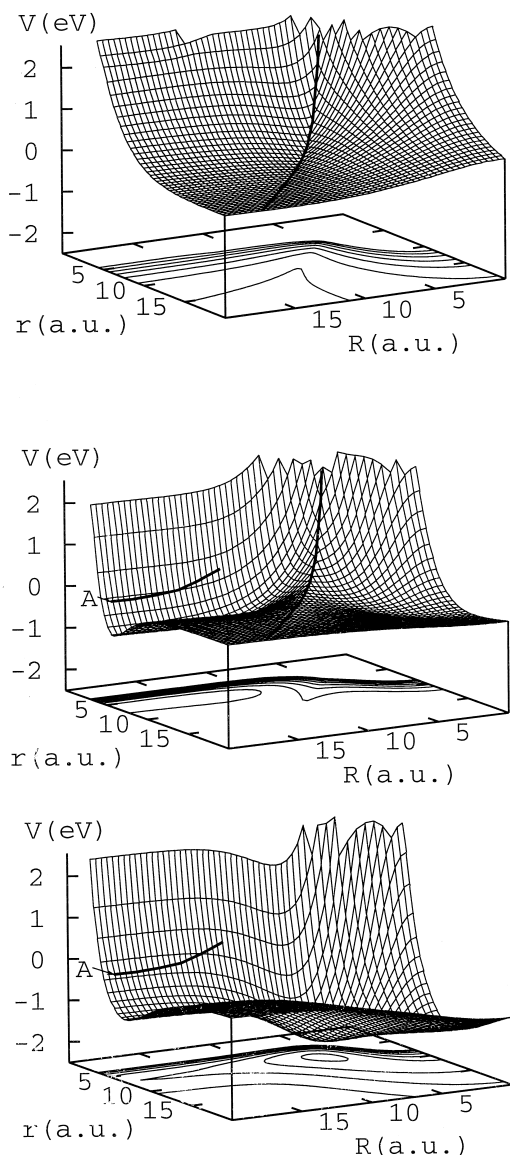


Fig. 1. 1A_1 potential energy surfaces for Na_3^+ in T-shape geometry (C_{2v}) as a function of the Jacobi coordinates (r, R). The ground state PES (lowest view) exhibits a well of -2.12 eV in equilateral geometry. For large R , it displays a valley leading to the $\text{Na}_2^+ + \text{Na}$ products (-0.98 eV below the 3-body dissociation limit). The avoided crossing between the ground state and the first excited state is labelled A. The second surface (intermediate view) has a valley, at large R , leading to the $\text{Na}_2 + \text{Na}^+$ products (-0.74 eV below the 3-body dissociation limit); it exhibits a conical intersection with the upper state in equilateral geometry. The third state (upper view) is completely dissociative until the 3-body dissociation limit.

electronic states of the cluster in the above described *frozen cluster approximation* (stage i) arise from off-diagonal matrix elements of the $\mathbf{C}^{-1} \mathbf{U} \mathbf{C}$ matrix.

The above procedure has first been applied to the $\text{Na}_2^+ - \text{He}$ system for which an ab initio calculation [5] was available and could be used as a reference. The latter calculation showed that electronic transitions in an Na_2^+ dimer are favoured when the helium atom passes in between the two nuclei. To obtain the same results with the DIM approach, it was necessary to incorporate to the DIM formalism *three-centre integrals* related to interactions of the type $\langle a | V(\text{He}) | b \rangle$, where a and b are Na_A and Na_B orbitals. These short-range three-centre interactions are expressed in the form $\alpha R_{\text{He}-A}^n \exp\{-\lambda R_{\text{He}-A}\} \cdot R_{\text{He}-B}^n \exp\{-\lambda R_{\text{He}-B}\}$ which assumes a non-local separable potential for He [21]. The values of the parameters have been chosen to reproduce at best the crossing of the $\text{Na}_2^+({}^2\Sigma_g)$ and $\text{Na}_2^+({}^2\Sigma_u)$ states and their coupling in the presence of the He [5].

The size of the DIM matrix considered for the Na_3^+ system is 9×9 [17]. Only the three lowest eigenstates of this matrix, which correlate with the limit $\text{Na}(3s) + \text{Na}(3s) + \text{Na}^+$ and directly pertain to reactions A–C in Eq. (1), have been retained in the dynamics. They merge into their common 3-body dissociation limit and display avoided crossings seams (Fig. 1). These features are of relevance for the non-adiabatic dynamics of the Na_3^+ system in the post-collision stage (ii).

3. Dynamics of the process

As mentioned in Section 1, the first stage of the dynamics study consists of a description of the encounter of the frozen Na_3^+ cluster-ion with the He atom. This is done using a single trajectory semiclassical method [5,14] where the relative cluster–atom motion is handled classically while the populations of the electronic states of the cluster along the trajectory are described quantally. This method has been preferred to a more conventional TSH method because at the high collision energy studied here, the classical trajectory does not practically depend on the electronic state of the system. Although the nuclei are held frozen, they acquire momenta during their collision with helium. These momenta are de-

terminated by solving the Hamilton's equations with the constraint of fixed positions for the nuclei of the cluster.

Such a classical calculation requires a sampling of the initial conditions. In the experiment [1–4,6], the Na_3^+ cluster-ions are in the ground electronic state, and probably [22] vibrationally excited and rotationally cold. Accordingly, the initial classical conditions were obtained by uniformly sampling the classical phase-space available when the system is in its ground state, with some vibration energy and no rotation energy. Each calculation in the first stage determines both the electronic state populations and the momenta gained by the Na atoms of the cluster. The scattering angle χ is obtained from the latter momentum transfers.

Each trajectory of the first stage calculation gives rise to three branches for the post-collisional treatment. Each branch is associated with a given adiabatic electronic state, and is weighted by the corresponding state population. As the dissociation motion of the cluster-ion is very sensitive to the specific PES it moves on, and as these PESs exhibit crossing seams (see Fig. 1), we use the 'ant' version of the Gislason TSH procedure [15,16]. Its advantage is its ability to describe motions on different PESs while accounting for non-adiabatic transitions.

The analysis of the trajectories provides the probability of finding the system in a given electronic state with given positions and momenta of the nuclei. From these data, one can decide whether or not reaction A, B, or C (Eq. (1)) has occurred, and obtain various differential cross-sections. It is also possible to analyse the time evolution of the system to extract physical information on the fragmentation mechanism.

4. Results and discussion

The $\text{Na}_3^+ + \text{He}$ collision at a centre-of-mass kinetic energy $E_{\text{cm}} = 263$ eV has been studied by sampling 50 000 $\text{Na}_3^+ + \text{He}$ collisions with randomly chosen initial conditions subject to the ro-vibrational energy specification ($E_{\text{vib}} = 1$ eV, $E_{\text{rot}} = 0$). Table 1, to be referred to as 'the fragmentation matrix', displays the contribution of the different electronic states populated by the $\text{Na}_3^+ - \text{He}$ encounter to the fragmen-

Table 1

Total cross-sections (\AA^2) for Na_3^+ fragmentation induced by collision with He at $E_{\text{cm}} = 263$ eV

Fragmentation channel		Electronic state after the He- Na_3^+ encounter		
		1	2	3
A	$\text{Na}_2^+ + \text{Na}$	7.2764	0.7329	0.0008
B	$\text{Na}_2 + \text{Na}^+$	0.4614	1.6611	0.0060
C	$\text{Na} + \text{Na} + \text{Na}^+$	0.7763	0.2645	0.2130

Columns correspond to the electronic state of the cluster just after the $\text{Na}_3^+ - \text{He}$ encounter *stricto sensu*. Rows correspond to the final fragmentation channels, as obtained after the post-collisional non-adiabatic dynamics of the cluster dissociation.

tation channels of Eq. (1). Elements of this matrix will be denoted as XY ($X = \text{A, B, C}$; $Y = 1, 2, 3$). One of the main features displayed by this fragmentation matrix is that channel A (respectively B) is mainly obtained from the ground (respectively first excited) state of the cluster. This is actually related to the fact that at the equilibrium distance of Na_2^+ (respectively Na_2), the electronic state 1 (respectively 2) is correlated with channel A (respectively B). In other words, when the diatomic fragment is vibrationally cold, the system evolves in the bottom of the corresponding valleys of the adiabatic PES (see Fig. 1). More generally, one can note that post-collisional non-adiabatic effects (A2, B1, A3, B3) are relatively weak as illustrated by the ratios: B1/A1 , A2/B2 , B3/C3 ; this is even more spectacular on the A3/C3 ratio, which reflects the probability of two non-adiabatic transitions during the dissociation. Another important feature revealed by the fragmentation matrix is that complete fragmentation (channel C) is possible via different paths.

The experimental measurements of Ref. [6], limited to the range $\varepsilon < 3.5$ eV, $\chi < 30^\circ$ of relative fragment energy and scattering angle respectively, yield the values: 90%, 4% and 6% for channels A, B and C, respectively. Restricting our results to the same window gives: 73%, 21% and 6% for channels A, B and C, respectively. This comparison is judged satisfactory given the lack of information concerning the initial internal energy of the cluster-ion.

Fig. 2 presents doubly differential (ε, χ) fragmentation cross-sections for all elements of the fragmentation matrix. As in Ref. [5] we find that electronic excitation takes place when the He atom passes

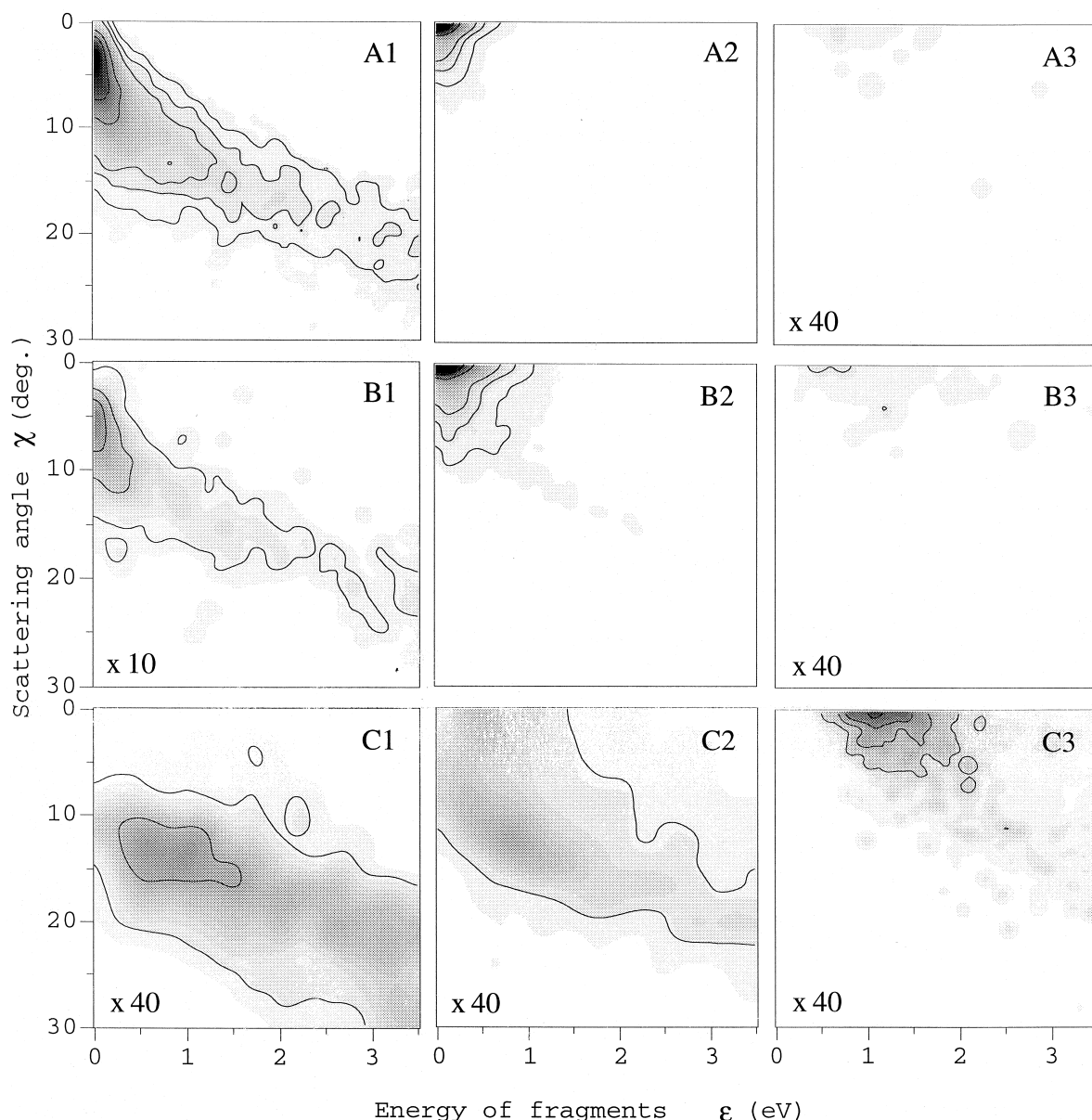


Fig. 2. Doubly differential cross-sections for fragmentation of Na_3^+ as a result of its collision with He at $E_{\text{cm}} = 263$ eV. χ is the He- Na_3^+ centre-of-mass scattering angle, ϵ is the kinetic energy of the fragments in the centre-of-mass frame of the Na_3^+ cluster. The different panels correspond to the processes defined in the fragmentation matrix Table 1 and are labelled accordingly.

through the cluster far enough from the Na cores. This is the reason that the purely electronic mechanisms (A2, B2 and C3) occur at small scattering angles. Their appearance in concentrated ranges of fragment energies is associated with Franck–Condon

type considerations [5]. In contrast, all the processes involving momentum transfer (A1, B1, C1, C2) show a strong ϵ dependence on χ .

One should emphasise the similarity between frames A1 and A2 on one hand, and between B1 and

B2 on the other hand. This similarity shows that electronic transitions between states 1 and 2, in the post-collisional stage, only affect the final fragmentation channel but have no influence on the relative energy of the fragments (nor, of course, on the deflection angle).

Analysis of the trajectories provides abundant information on the fragmentation mechanisms. We present here only two examples of such an analysis for the ground state processes A1 and C1; a more comprehensive study will be presented elsewhere. For process A1, two typical mechanisms are actually identified (see also Ref. [6]):

- a *direct* binary mechanism (referred to as IM1 in Ref. [4]) where one of the Na atoms is knocked out from the cluster by a violent binary collision with the He atom;
- a *complex* mechanism (referred to as IM2 in Ref. [4]) whereby the collision with He excites the cluster into a ro-vibrational state above the dissociation limit. In the latter mechanism, one of the cluster atoms is ejected after typically 5–10 periods of cluster vibrations.

Although an actual trajectory can barely be considered as purely binary or purely collective, we can estimate that the contribution of the collective mechanism to the A1 process is $\sim 25\text{--}35\%$. It preferentially produces low-energy fragments. On the other hand, the binary mechanism is responsible for the tail of the structure in the (ε, χ) A1 diagram.

For the complete fragmentation in the ground electronic state (C1) we have also identified two typical mechanisms:

- A *sequential* mechanism, in which one of the Na atoms gains large momentum during the collision with He and then shares this momentum in the post-collisional stage with the other atoms of the cluster;
- A *multi-collision* mechanism, in which the He atom gives momentum to more than one Na atom during the encounter.

About 20% of the C1 events can be attributed to multi-collision type trajectories.

Finally, Fig. 3 displays the differential cross-section, summed over all electronic states, for each of the three channels in Eq. (1). An overall satisfactory agreement with the experimental data of Ref. [6] is obtained. Still some differences are observed be-

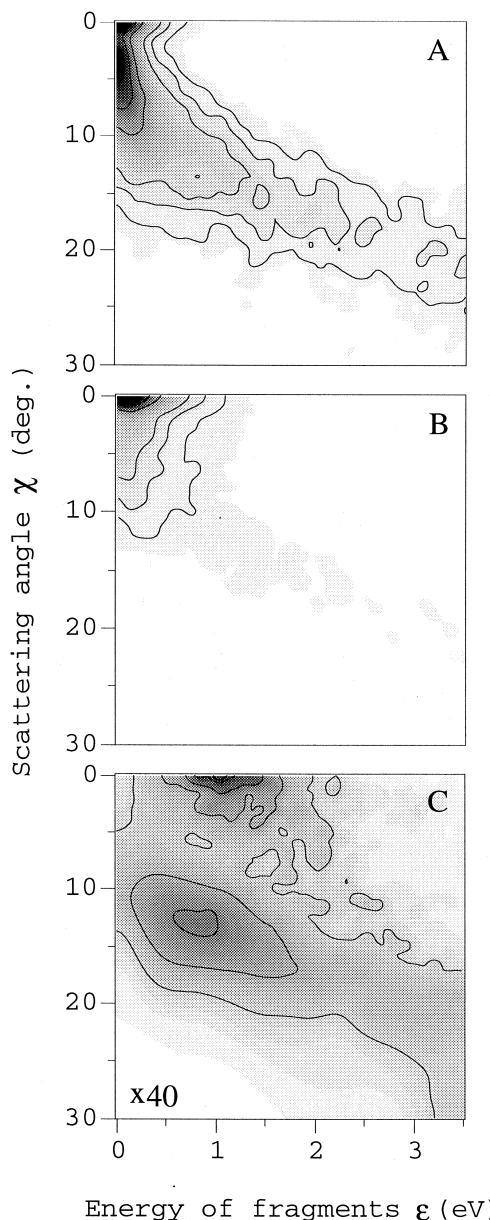


Fig. 3. Doubly differential cross-sections for fragmentation Na_3^+ into: (A) $\text{Na}_2^+ + \text{Na}$, (B) $\text{Na}_2 + \text{Na}^+$ and (C) $\text{Na} + \text{Na} + \text{Na}^+$.

tween experiment and theory for the 3-body channel C. They are tentatively attributed to the influence of the initial internal energy of the cluster, which is thought to affect the balance between purely impulsive and electronic processes significantly.

5. Conclusions

The three steps of the theoretical method described in this Letter: the DIM method, the frozen cluster approximation during the collision and the post collisional relaxation of the cluster together with the semi-classical and trajectory surface hopping approaches used in the latter two, are proving to provide an efficient computational scheme. It opens promising perspectives for the theoretical study of non-adiabatic collisions involving metal clusters. The application of this scheme to larger Na_n^+ clusters ($n = 5-9$) is within reach and is planned for the near future.

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