

Fragmentation of Na_3^+ clusters by He impact: effect of initial cluster temperature on non-adiabatic phenomena

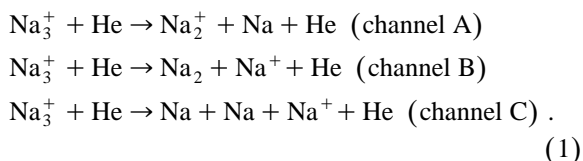
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A theoretical study has been carried out of the fragmentation of Na_3^+ ions following a collision with He. The collision leaves Na_3^+ in any of three electronic states, and each of these can fragment into three product channels ($\text{Na}_2^+ + \text{Na}$, $\text{Na}_2 + \text{Na}^+$ and $\text{Na} + \text{Na} + \text{Na}^+$). The Na_3^+ system has a conical intersection and an avoided crossing; these permit transitions between the different states. Cross-sections for each of the nine fragmentation pathways are presented for three different values of the initial vibrational excitation of Na_3^+ . The cross-sections are very sensitive to this vibrational energy. © 2000 Elsevier Science B.V. All rights reserved.

Recently, the fragmentation of Na_n^+ ($2 \leq n \leq 9$) in fast collision with He atoms has been studied experimentally [1–5]. For $n = 3$ the processes studied were [3–5]



In general, the experimental internal energy of Na_3^+ before the collision is unknown, but it is expected to be a significant fraction of the lowest dissociation energy (to channel A) of 1.14 eV. Earlier studies of

the dissociation of diatomic clusters by rare gases show that there are two general mechanisms of energy deposition in the cluster that can lead to fragmentation [1,2,6–9]. The first is rovibrational excitation (RVE mechanism) of the cluster in its ground (bound) electronic state. The second is electronic excitation (EE mechanism) of the cluster to a repulsive state that rapidly dissociates to two particles. It will be interesting to determine how useful these two simple mechanisms will be for large clusters, where the fragmentation process can be complicated by the presence of conical intersections and avoided crossings between different electronic states that allow transitions between them.

In this paper we report results from a theoretical study of the processes shown in (1). The procedure

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allows us to identify the contributions of the RVE and EE mechanisms as well as surface hops to the various product channels. The calculations were carried out at three different values of the Na_3^+ internal energy (0.02, 0.5 and 1 eV) to see how the mechanism of the process changes with internal energy. The theoretical procedure is described in detail elsewhere [10,11] and is briefly summarised here. The three lowest singlet adiabatic potential energy surfaces (PESs) of Na_3^+ are computed from Kuntz's DIM treatment of this system [12]. We identify the ground state as state 1, and the first and second excited states as states 2 and 3, respectively. States 1 and 2 have an avoided crossing in the product region and states 2 and 3 exhibit a conical intersection in the equilateral configuration. The couplings between electronic states of Na_3^+ in the presence of He are calculated in the DIM formalism, but they also in-
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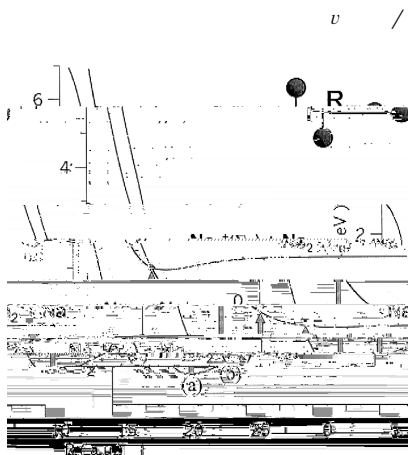


Fig. 2. A cut of the three Na_3^+ PESs for a T-shaped cluster with fixed at 6.78 a.u. (the equilibrium internuclear distance of Na_3^+) and free to vary. The conical intersection of the two excited states is shown as a solid circle. The three grey arrows show vertical excitation from the equilateral potential minimum of Na_3^+ (a), and from the outer turning points with 0.5 eV (b) and 1.0 eV (c) vibrational energy.

and it is also seen that as the Na nucleus moves away from the other two the energy of state 2 drops and the ground state energy rises. Because electronic excitation is more facile when two surfaces are close together, we expect that vibrational excitation of the reactant Na_3^+ will lead to more population of state 2 in the collision with He.

Any collision with He that leads to fragmentation of Na_3^+ can be uniquely assigned to a particular pathway by specifying the intermediate electronic state of Na_3^+ (1, 2 or 3) and the final product channel (A, B or C). We can then present any results calculated for the nine pathways in a 3×3

. As discussed earlier the RVE and EE mechanisms are useful ways to describe the fragmentation of diatomic ionic clusters. After excitation by He the diatomic (for example, Na_2^+) dissociates adiabatically [6,7,9]. A number of the Na_3^+ pathways follow a similar pattern where rovibrational or electronic excitation of the cluster by He is followed by adiabatic fragmentation. For RVE these pathways are A1 and C1, and for EE they are B2, C2 and C3. A transition between two electronic states

Table 1

Fragmentation matrix

The columns labelled 1, 2 and 3 indicate the electronic states immediately after the He–Na₃⁺ collision, and the rows labelled A, B and C denote the three possible product channels. Each numerical entry is a total cross section in Å². Results for $\epsilon_{\text{int}} = 0.02, 0.5$ and 1.0 eV are identified by (a), (b) and (c), respectively. The final column gives the cross-section for each row summed over states 1, 2 and 3; this is the total product cross-section for each channel. Similarly, the final row gives the cross-sections for each column summed over channels A, B and C; these are the total cross-sections for populating states 1, 2 and 3 in the collision with He. Each pathway, identified by electronic state and product channel, has been assigned to a particular fragmentation mechanism (see text for explanation).

Product channel	ϵ_{int}	Electronic state after He–Na ₃ ⁺ collision			Total values (observables)
		1	2	3	
A: $2^+ +$	(a)	RVE 4.86	MIXED 0.08	MIXED 0.02	4.96
	(b)	5.60	0.14	0.00	5.74
	(c)	8.05	1.28	0.00	9.33
B: $2^+ +$	(a)	MIXED 0.04	EE 0.15	EE 0.03	0.22
	(b)	0.45	0.17	0.01	0.63
	(c)	0.65	0.94	0.00	1.59
C: $+ + +$	(a)	RVE 0.40	EE 0.10	EE 0.14	0.64
	(b)	0.48	0.10	0.11	0.69
	(c)	0.84	0.30	0.19	1.33
Total: (A + B + C)	(a)	5.30	0.33	0.19	5.82
	(b)	6.53	0.41	0.12	7.06
	(c)	9.54	2.52	0.19	12.25

Table 1 also shows that the cross-section for producing state 3 is always less than for state 2. In the limiting case of $\epsilon_{\text{int}} = 0$ the Na₃⁺ configuration is equilateral, the excited states are degenerate, and vertical excitation should make an equal amount of states 2 and 3 at the conical intersection (see Fig. 2). (We have confirmed this in a separate calculation.) It is therefore remarkable that when $\epsilon_{\text{int}} = 0.02$ eV the cross-section for state 210144.23472.44Tm / F32 (It) TjEre

tions for producing state 3 (and the three pathways that originate in state 3) are very small and do not increase with ϵ_{int} . This can be understood from Fig. 2, which shows that the PES for state 3 is flat in the Franck–Condon region, and the excitation energy is always large. For state 2 increasing ϵ_{int} from 0.02 to 0.5 eV leads to only a small increase in the cross-sections that arise from state 2, even though Fig. 2 shows that the excitation energy to state 2 is considerably smaller. A further increase to $\epsilon_{\text{int}} = 1$ eV greatly increases the cross-sections for all three pathways that originate in state 2. This is due in part to the very small electronic energy gap between states 1 and 2 at the outer turning point (see Fig. 2). We have also determined that the magnitude of the coupling between the ground and first excited state, which is primarily due to the three-centre-interaction, greatly increases when the molecular configuration changes from equilateral to an elongated T-shape with $r \sim 11$ a.u. This also plays a role in increasing the production of state 2 when the Na_3^+ is vibrationally excited.

For the ground electronic state the main effect of increasing ϵ_{int} is to lower the effective dissociation energy from 1.12 to 0.64 to 0.14 eV as ϵ_{int} increases from 0.02 to 0.5 and 1 eV. The increasing cross-sections for pathways A1 and C1 (RVE mechanism) are consistent with this analysis. The most remarkable result in Table 1 is the dramatic jump in the cross-section for the mixed pathway B1 when ϵ_{int} increase from 0.02 to 0.5 eV. Our analysis of individual trajectories shows that pathways A1 and B1 arise predominantly from a hard binary collision of He with a single sodium nucleus that is rapidly ejected leaving behind an Na_2^+ dimer. Fig. 1 shows that if the Na_2^+ has at least 0.27 eV vibrational energy it can reach the avoided crossing and possibly hop to state 2 producing $\text{Na} + \text{Na}^+$ (

processes, but the fact that several pathways involve both mechanisms limits their applicability. Finally, the method used here is general and can be extended to larger Na_n^+ systems.

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