



ELSEVIER

7 January 2000

Chemical Physics Letters 316 (2000) 129–134

**CHEMICAL
PHYSICS
LETTERS**

www.elsevier.nl/locate/cplett

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

D. Babikov^{a,*}, E.A. Gislason^a, M. Sizun^b, F. Aguillon^b, V. Sidis^b^a Department of Chemistry of University of Illinois at Chicago, SES (M/C 111), 845 West Taylor Street, Room 4500, Chicago, IL, USA^b Laboratoire des Collisions Atomiques et Moléculaires, Unité Mixte de Recherche CNRS-UPS 8625, Bât. 351, Université Paris-Sud, 91405 Orsay Cedex, France

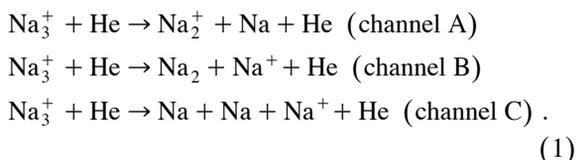
Received 27 September 1999; in final form 29 October 1999

Abstract

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.

1. Introduction

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.

2. Theory

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

* Corresponding author. Fax: +1-312-996-0431; E-mail: badim@uic.edu

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 include Na–He–Na three-centre-interaction terms [10,11]. The Na_3^+ is prepared with zero rotational energy and at a fixed classical vibrational energy with random phases. Next the He– Na_3^+ collision at a relative energy of 263 eV (the energy used in the experiments [3–5]) is treated using the classical path approximation for the He motion with the Na nuclei frozen (the sudden approximation). The instantaneous potential energy seen by the He is calculated using the semiclassical energy conserving trajectory method [13]. The He– Na_3^+ impact parameter and the orientation of the cluster plane are chosen randomly. In most cases the He interacts strongly with only one Na atom, but multiple hits do occur. After the He departs, the Na_3^+ is left with population in the three electronic states, and additional momentum has been transferred to each Na nuclei. The final step of the calculation is a trajectory surface hopping (TSH) study of the fragmentation of Na_3^+ with proper treatment of the conical intersection and avoided crossing [14,15].

3. Results and discussion

Two cuts of the three Na_3^+ PESs are shown in Figs. 1 and 2. Fig. 1 shows the three diatomic curves in the product region (with the third Na nucleus at infinity). The ground electronic state dissociates adiabatically to $\text{Na}_2^+ + \text{Na}$, and state 2 dissociates to

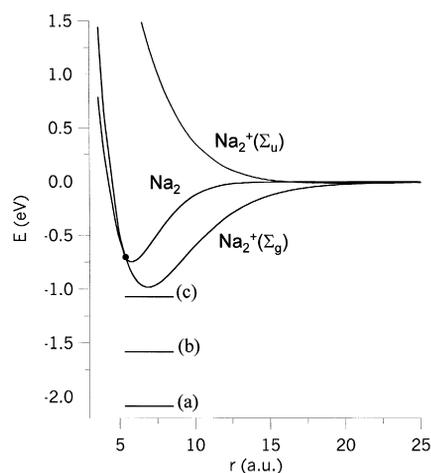


Fig. 1. A cut of the three Na_3^+ PESs. Shown are the three diatomic curves in the product region with the third Na nucleus at infinity. All three curves dissociate to $\text{Na} + \text{Na} + \text{Na}^+$. The crossing between the two lowest curves is shown as a solid circle. The short horizontal lines show the three initial energies of the Na_3^+ cluster ion studied in this work. The corresponding values of E_{int} are: (a) 0.02 eV – the ground vibrational state of Na_3^+ , (b) 0.5 eV, (c) 1 eV.

$\text{Na}_2 + \text{Na}^+$. By comparison, state 3 is repulsive in all configurations and dissociates adiabatically to three particles ($\text{Na} + \text{Na} + \text{Na}^+$). It is possible for a collision with He to transfer insufficient momentum to Na_3^+ in its ground electronic state so that no fragmentation occurs. (These collisions are not considered further.) Energy considerations show, however, that electronic excitation to either state 2 or 3 must result in fragmentation, even if the system subsequently hops to the ground electronic state. The diabatic crossing between states 1 and 2 is clearly seen in Fig. 1. The ground state of $\text{Na}_2^+ + \text{Na}$ lies about 0.24 eV below the $\text{Na}_2 + \text{Na}^+$ product, and it is seen that any $\text{Na}_2 (+\text{Na}^+)$ fragment with at least 0.04 eV vibrational energy can reach the diabatic crossing point. Of course, when the third nucleus comes to a finite distance from the other two the crossing becomes avoided.

Fig. 2 shows the PESs in a T-shape where one bond length (r) is fixed, and the Na on the perpendicular bisector is free to move. R is the distance of the third atom from the centre of mass of the fixed dimer. The conical intersection between the two upper states in the equilateral cluster shape is shown,

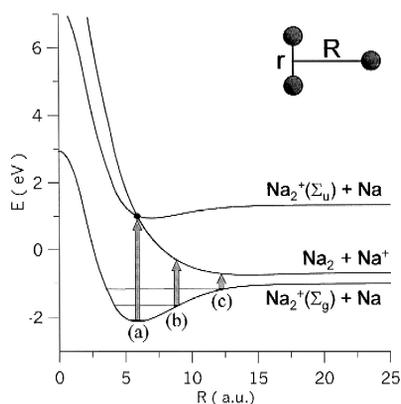


Fig. 2. A cut of the three Na_3^+ PESs for a T-shaped cluster with r fixed at 6.78 a.u. (the equilibrium internuclear distance of Na_3^+) and R free to vary. The conical intersection of the two excited states is shown as a solid circle. The three grey arrows show vertical excitation from the equilateral potential minimum of Na_3^+ (a), and from the outer turning points for R 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 fragmentation matrix. 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 after the collision with He but before fragmentation occurs means that the fragmentation is not adiabatic. Such a postcollisional transition leads to a mixing of the two mechanisms. For example, for pathway A2 the He

electronically excites Na_3^+ to state 2, but the trajectory then hops to the ground electronic state before the fragmentation is completed. In this case all the electronic energy is converted into rovibrational energy of Na_3^+ , and we argue that in this case both mechanisms contribute to the fragmentation. This ‘mixed’ mechanism for pathway A2 (and also A3) is analogous to dissociative photo-ionisation of a large molecule where the initial ionisation process produces the molecular ion in an excited electronic state. The molecular ion then quickly undergoes an internal conversion to the ground electronic state, converting electronic energy to rovibrational energy, and then dissociates. Pathway B1 also arises from a ‘mixed’ process. In this case some of the rovibrational energy imparted to state 1 is converted to electronic energy when the trajectory hops to the state 2 before fragmentation occur. Finally, pathway B3 also involves a transition between states 2 and 3, but because both are excited states, the transition does not change the EE nature of the process. The assignment of each of the nine pathways to the RVE, EE or MIXED mechanisms is summarised in Table 1. We conclude that the RVE and EE mechanisms are still useful ways to catalog most (but not all) fragmentation processes in Na_3^+ , but in larger systems where surface hops will be more prevalent this division will probably break down completely. Use of the fragmentation matrix implies that there is at most one hop between surfaces during the fragmentation process. (Pathway A3, however, requires two hops.) In fact, multiple hops do occur, but they are rare.

The total cross-sections for each pathway are shown in Table 1 for three values of the initial internal energy E_{int} of the Na_3^+ . The cross-sections summed over electronic states are given in the final column, and the results summed over product channels (for producing the electronic states) are given in the final row. The most striking feature of the table is the fact that the total cross-sections to produce electronic states 2 and 3 are always much smaller than for producing state 1. This attests to the importance of RVE in this system. Pathway A1 has in all cases the largest cross-section. All three electronic states make an important contribution to channel C, with the major contribution coming from RVE of state 1.

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 $E_{\text{int}} = 0.02, 0.5$ 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	E_{int}	Electronic state after He–Na ₃ ⁺ collision			Total values (observables)
		1	2	3	
A: Na ₂ ⁺ + Na		RVE	MIXED	MIXED	
	(a)	4.86	0.08	0.02	4.96
	(b)	5.60	0.14	0.00	5.74
B: Na ₂ + Na ⁺	(c)	8.05	1.28	0.00	9.33
		MIXED	EE	EE	
	(a)	0.04	0.15	0.03	0.22
C: Na + Na + Na ⁺	(b)	0.45	0.17	0.01	0.63
	(c)	0.65	0.94	0.00	1.59
		RVE	EE	EE	
Total: (A + B + C)	(a)	0.40	0.10	0.14	0.64
	(b)	0.48	0.10	0.11	0.69
	(c)	0.84	0.30	0.19	1.33
	(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 $E_{\text{int}} = 0$ 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 $E_{\text{int}} = 0.02$ eV the cross-section for state 2 is 75% larger than for state 3. This is due to the conjunction of two effects: (i) the flatness of the ground state PES, which allows the system to be significantly non-equilateral with a small amount of energy; and (ii) to the large difference in slopes of surfaces 2 and 3 near the equilateral shape (see Fig. 2), which is responsible for a strong sensitivity of the electronic transitions to the cluster geometry and favors state 2. The calculations at all three values of E_{int} show that there are transitions between states 2 and 3 during the fragmentation process, but in almost all cases the products are fully dissociated into atoms (channel C). Thus, transitions near the conical intersection have little effect on the product cross-sections. This fact, coupled with the small cross-section for producing state 3, ex-

plains why the cross-sections for pathways A3 and B3 are so small.

Hops between states 1 and 2 at the avoided crossing shown in Fig. 1 affect the 2×2 part of the fragmentation matrix composed from states 1 and 2 and channels A and B. This part is relevant when either of the two electronic states are produced but with insufficient energy to dissociate to three atoms. We see that when state 2 is produced, at least 24% of all trajectories undergo a transition to state 1 at the avoided crossing (see Fig. 1) and emerge in channel A. By comparison less than 7% of trajectories produced in state 1 undergo a transition to state 2 and appear in channel B. This is not surprising because channel A is less endothermic than channel B, so statistical considerations favour channel A. In addition, most Na₂ diatomics produced in state 2 can reach the avoided crossing (see Fig. 1) and hop to channel A. We conclude that non-adiabatic transitions between states 1 and 2 are facile and important to the final state distributions.

The dependence of the various cross-sections on the initial internal energy E_{int} in Table 1 is quite interesting. For all three values of E_{int} the cross-sections

tions for producing state 3 (and the three pathways that originate in state 3) are very small and do not increase with E_{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 E_{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 $E_{\text{int}} = 1$ 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 E_{int} is to lower the effective dissociation energy from 1.12 to 0.64 to 0.14 eV as E_{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 E_{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 $\text{Na}_2 + \text{Na}^+$. (This hop must occur before the third Na atom has moved too far away for the electron transfer to occur.) The fact that the cross-section for pathway B1 is so small at $E_{\text{int}} = 0.02$ eV indicates that the direct binary collision with the He does not produce much vibrational energy in the Na_2^+ dimer product. However, when $E_{\text{int}} = 0.5$ or 1.0 eV all of the modes of Na_3^+ are excited even before the He collision, and it is not surprising that a substantial fraction of the Na_2^+ products have vibrational energies of 0.27 eV or higher and can reach channel B.

One can note that at the lowest value of E_{int} the cross-section for pathway C1 greatly exceeds that for B1, even though the endothermicity is 0.75 eV greater. This surprising fact implies that the mechanisms for two and three body fragmentation must be different. Indeed, at the lowest internal energy considered here, the RVE three body fragmentation occurs after two successive collisions. The first one, just as in the A1 case, is a hard binary collision of He with a single Na nucleus; the second one is a Na–Na' collision. In principle, this 'sequential' mechanism could also give products in channel B, but our inspection of trajectories shows that this is rare.

Experiments can only determine the total cross-sections for producing channels A, B, and C; these are summarised in the final column of Table 1. We see that in going from $E_{\text{int}} = 0.02$ to 0.50 eV only the cross-section for channel B increases substantially. Raising E_{int} further to 1 eV then gives large increases in all three product channels, but again the relative increase is largest for channel B. This is due primarily to the large increase in the excitation cross-section for electronic state 2, which fragments extensively to channel B. The strong dependence on E_{int} of channel B coupled with the weaker dependences for channels A and C suggests that the ratio of cross-sections $[\text{Q(B)}/\text{Q(A)}]$ or $[\text{Q(B)}/\text{Q(C)}]$ might serve as a 'thermometer' for estimating the average internal energy of the Na_3^+ reactant cluster ions produced in a particular experimental ion source.

In summary, we have seen that the fragmentation of Na_3^+ by fast He atoms into different pathways is very sensitive to the initial vibrational excitation of the cluster, particularly when E_{int} is close to the lowest dissociation energy. This occurs because vibrational excitation both lowers the effective dissociation energy and makes electronic excitation of state 2 of Na_3^+ more likely. The results suggest that the temperature dependence of the fragmentation cross-sections might make a useful experimental 'thermometer' for the reactant clusters. The avoided crossing in the product region between states 1 and 2 plays a significant role in reducing the cross-section to make channel B, but the conical intersection between states 2 and 3 has little effect on the product distributions. The RVE and EE mechanisms remain useful concepts to characterise the fragmentation

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.

Acknowledgements

The authors would like to thank J.A. Fayeton, M. Barat and Y.J. Picard at LCAM (Orsay) for providing experimental information and for very fruitful discussions.

References

- [1] M. Barat, J.C. Brenot, H. Dunet, J.A. Fayeton, *Z. Phys. D.* 40 (1997) 323.
- [2] J.A. Fayeton, M. Barat, J.C. Brenot, H. Dunet, Y.J. Picard, U. Saalman, R. Schmidt, *Phys. Rev. A* 57 (1998) 1058.
- [3] M. Barat, J.C. Brenot, H. Dunet, J.A. Fayeton, Y.A. Picard, *Comm. At. Mol. Phys.* 34 (1999) 329.
- [4] M. Barat, J.C. Brenot, H. Dunet, J.A. Fayeton, Y.J. Picard, *J. Chem. Phys.* 110 (1999) 10758.
- [5] M. Barat, J.C. Brenot, H. Dunet, J.A. Fayeton, Y.J. Picard, D. Babikov, M. Sizun, *Chem. Phys. Lett.* 306 (1999) 233.
- [6] J. Durup, in: K. Ogata, T. Hayakawa (Eds.), *Recent Developments in Mass Spectrometry*, University of Tokyo Press, Tokyo, 1970, p. 921.
- [7] J. Los, T.R. Govers, in: R.G. Cooks (Ed.), *Collision Spectroscopy*, Plenum, New York, 1978, p. 289.
- [8] M. Sizun, E.A. Gislason, *J. Chem. Phys.* 91 (1989) 4603.
- [9] D. Babikov, F. Aguillon, M. Sizun, V. Sidis, *Phys. Rev. A* 59 (1999) 330.
- [10] D. Babikov, M. Sizun, F. Aguillon, V. Sidis, *Chem. Phys. Lett.* 306 (1999) 226.
- [11] D. Babikov, E.A. Gislason, M. Sizun, F. Aguillon, V. Sidis, (submitted).
- [12] P.J. Kuntz, *Mol. Phys.* 88 (1996) 693.
- [13] A.E. DePristo, *J. Chem. Phys.* 78 (1983) 1237.
- [14] G. Parlant, E.A. Gislason, *J. Chem. Phys.* 91 (1989) 4416.
- [15] M. Sizun, J.B. Song, E.A. Gislason, *J. Chem. Phys.* 109 (1998) 4815.