

# Distribution of final electronic states following three-body fragmentation of $\text{Na}_3^+$ excited by He impact

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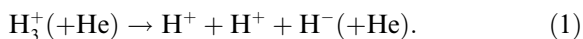
Received 28 February 2001; in final form 27 April 2001

## Abstract

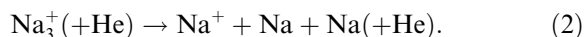
Three-body fragmentation of  $\text{Na}_3^+$  ions to  $\text{Na}^+ + \text{Na}(1s) + \text{Na}(1s)$  is studied experimentally and theoretically. A procedure is developed for distinguishing the three adiabatic electronic  $1A'$  states in the product region, even though these states are degenerate at the detector. The procedure requires knowledge only of the three atom–atom and ion–atom relative velocities, and this information is obtained in our coincidence experiments. This paper reports the first experimental determination of the populations of the three-product adiabatic states in a three-body fragmentation process. The results, which are different for each state (despite of degeneracy), are compared with theoretical calculations. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

A number of laboratories have demonstrated that it is now possible to carry out collision-induced dissociation (CID) experiments where three-body fragmentation occurs and all three particles are detected in coincidence. One such process is the polar fragmentation of  $\text{H}_3^+$  following a collision with He studied by Jaecks and co-workers [1]



A related study of the same system was carried out by Hinojosa et al. [2]. A second example is the one studied in our laboratories both experimentally [3–5] and theoretically [6–9]



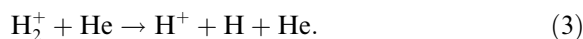
A third is collision less fragmentation of a photo-excited  $\text{H}_3$  molecule to three ground state H atoms [10–12]. In processes (1) and (2) it is clear that at the end there are three degenerate singlet electronic product states. (For example, in (1) the negative charge can be on any of three H nuclei; each possibility corresponds to a different electronic state.) It is also clear that early in the fragmentation process the three states are not degenerate and, presumably, the population of the three states is not the same. Thus, at the end the three

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degenerate states may or may not have equal populations, and it would be quite interesting to determine the asymptotic population distribution. In this paper we describe for the first time a procedure to make this determination from data obtained in a coincidence experiment.

The analysis that permits the determination of the asymptotic product distribution is an extension of earlier work [13,14] by Gislason and Guyon for the CID process



Here there are two degenerate product electronic states. They showed that at all distances the He atom breaks the degeneracy of these two states and that it is possible to determine the final electronic state by knowing the final relative velocity vectors between the three atoms. A number of experiments of this type have been considered in the light of this rule [13–19].

This paper extends the analysis of Gislason and Guyon to process (2). We show that the product electronic state at the detector can be determined from the three relative velocities of two neutral Na atoms and one  $\text{Na}^+$  ion measured in the experiments. The experimental product distribution for 10 512 three-body fragmentation events is presented. In addition we have carried out calculations for process (2) and obtained the theoretical distribution of product electronic states. Thus, in this paper we are able to report and compare the first experimental and theoretical determinations for a three-body fragmentation process; namely for process (2).

## 2. Theory

The analysis of process (2) is analogous to that of Gislason and Guyon [13,14]. The electronic state of the  $\text{Na}_3^+$  cluster ion has symmetry  $1A'$ . The fast  $\text{Na}_3^+$  collides with a He target that excites the ion electronically and/or rovibrationally above the three-body dissociation limit. The He quickly leaves the scattering region, and then the excited  $\text{Na}_3^+$  fragments into three particles. We assume that the electronic symmetry of  $\text{Na}_3^+$  is preserved in the collision with He; in this case there are three

low-lying  $1A'$  product electronic states involved in process (2). The three Na nuclei form a triangle. We label the nuclei a, b, and c and denote the length of the triangle side opposite nucleus  $k$  as  $R_k$ . Once the particles are far apart they fly in straight lines, and the relative distances  $R_k$  are given by

$$R_k = v_k t + R_k^0. \quad (4)$$

Here the atom–atom relative speed is given by  $v_k = dR_k/dt$ , and  $R_k^0$  is on the order of a few Angstroms. At sufficiently large  $t$  the  $R_k$  values are ordered in the same way as the  $v_k$ . Thus, for example, if  $v_a < v_b < v_c$ , then  $R_a < R_b < R_c$ , and this ordering is maintained until the particles reach the detector.

The goal of this work is to determine the adiabatic electronic state of the system at the detector for each three-body fragmentation event of reaction (2) from the available experimental coincidence data. This requires knowledge of the relationship between the diabatic and adiabatic states of  $\text{Na}^+ + \text{Na} + \text{Na}$ . (The general relationship between diabatic and adiabatic states is discussed in [20]). A *diabatic* state (a, b, or c with energy  $E_a$ ,  $E_b$ , or  $E_c$ ) is identified by which nucleus (a, b, or c) has the positive charge, and this state is determined experimentally in each fragmentation event. The *adiabatic* states (1, 2, or 3), on the other hand, are determined by the energy ordering with  $E_1 < E_2 < E_3$ . The general relationship between diabatic and adiabatic states is well known. The simplest diabatic picture uses zero-order states that are single-configuration wavefunctions with the positive charge being located on one of the three Na nuclei. Thus, if nucleus a has the positive charge, the diabatic wavefunction would be  $\phi_a$ , and similarly for  $\phi_b$  and  $\phi_c$ . One can then set up the  $3 \times 3$  diabatic electronic Hamiltonian with matrix elements  $H_{ij} = \langle \phi_i | H | \phi_j \rangle$ . The off-diagonal elements such as  $H_{ab}$  are nonzero whenever there is appreciable electronic overlap between nuclei a and b. At large a–b separations (i.e.,  $R_c$  large),  $H_{ab}$  falls off exponentially with  $R_c$ . If the diabatic Hamiltonian matrix is diagonalized, one obtains the adiabatic energies and wave functions. The adiabatic states are identified by their energy ordering, with state 1 corresponding to the lowest energy and states 2 and 3 corresponding to the first and second excited states. In general the positive

charge is delocalized over all three Na nuclei for each adiabatic state, and there is no one–one mapping between diabatic and adiabatic states.

However, if all three atom–atom distances are sufficiently large (greater than 12 Å for the  $\text{Na}_3^+$  system), the relationship between diabatic and adiabatic states is greatly simplified. In this case the positive charge is fixed on one of the three nuclei. This guarantees that the diabatic off-diagonal matrix elements are all zero, and the diabatic Hamiltonian matrix is diagonal. (The diagonal elements are in general all different, however). In this case the three diabatic energies and the three adiabatic energies are the same, but we still need to determine the one–one mapping between the diabatic and adiabatic states and their energies. (As an example, one possible mapping would be  $E_1 = E_a < E_2 = E_b < E_3 = E_c$ ).

We define the asymptotic region as the region where all three  $R_c$  values are sufficiently large that two conditions are simultaneously satisfied: first, the positive charge is permanently localized on one nucleus (i.e., the diabatic state is known) and, second, the  $R_c$  values are ordered in the same way as the  $v_k$  values (see Eq. (4)). It is straightforward to determine the one–one mapping between diabatic and adiabatic states in this region. We first calculate the total energies of the three diabatic states in the asymptotic region. Since all interatomic distances are large, we can neglect three-body contributions to the interaction potential, and we can use perturbation theory to estimate each pair of atom–atom interactions. The longest-ranged interaction between the  $\text{Na}^+$  ion and either Na atom is given by the attractive ion-induced dipole potential

$$V(R) = -\alpha e^2 / 2R^4, \quad (5)$$

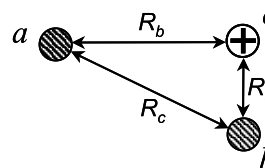
where  $e$  is the electronic charge and  $\alpha$  is the dipole polarizability of Na. By comparison, the longest-ranged interaction between two Na neutrals is proportional to  $1/R^6$  and can be neglected compared to the terms in Eq. (5). As discussed earlier, the electron exchange term between  $\text{Na}^+$  and each Na atom falls off exponentially and also can be neglected. Thus, the total diabatic energy for each of the three possible  $\text{Na}^+ - \text{Na} - \text{Na}$  configurations consists of the sum of two ion-induced dipole

terms. The result can be written in the following useful form:

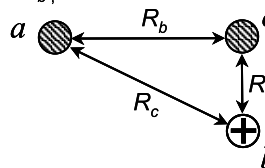
$$E_k = -(\alpha e^2 / 2)[1/R_a^4 + 1/R_b^4 + 1/R_c^4] + (\alpha e^2 / 2)/R_k^4, \quad (6)$$

where  $k = a, b$  or  $c$  is the vertex that contains the  $\text{Na}^+$  ion. The first term is the same for all three possible configurations and the second, positive-definite term depends only on the length of the side opposite vertex  $k$ . Once the three diabatic energies are known, it is straightforward to order them and obtain the adiabatic energies. Suppose for definiteness that  $R_a < R_b < R_c$ . This example is shown in Fig. 1. Then Eq. (6) gives  $E_c < E_b < E_a$ . Thus, the ground adiabatic state corresponds to the case that

a)  $E = E_c$ , ground electronic state:



b)  $E = E_b$ , first excited state:



c)  $E = E_a$ , second excited state:

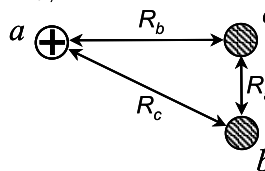


Fig. 1. Examples of the three possible triangular configurations of the particles Na, Na, and  $\text{Na}^+$  at the detector. The nuclei are labeled a, b, and c, and the sides opposite the nuclei are  $R_a, R_b$ , and  $R_c$ , respectively. Here  $R_a < R_b < R_c$ . The location of the  $\text{Na}^+$  ion is indicated by a '+'. The triangles are identical except for the location of the charge. (a)  $\text{Na}^+$  ion at c. As indicated in Eq. (6) this configuration has the lowest energy and corresponds to the ground electronic state; (b)  $\text{Na}^+$  ion at b. This configuration has the second lowest energy and corresponds to the first excited electronic state; (c)  $\text{Na}^+$  ion at a. This configuration has the highest energy and corresponds to the second excited state.

the  $\text{Na}^+$  ion is located opposite the longest side of the triangle ( $R_c$ ). Put in another way, state 1 corresponds to the ion being at the vertex formed by the two shortest sides ( $R_a$  and  $R_b$ ). Similarly, adiabatic state 2 (state 3) corresponds to the case that the  $\text{Na}^+$  ion is located opposite the second longest (the shortest) side of the triangle. For this case the one–one mapping is given by  $E_1 = E_c$ ,  $E_2 = E_b$ , and  $E_3 = E_a$ . Since the conditions that define the asymptotic region persist to the detector, this is the mapping at the detector as well.

Based upon the analysis given above, the experimental determination of the final adiabatic state for each fragmentation event is straightforward. The detector determines the final laboratory velocities of the two neutral Na atoms as well as the  $\text{Na}^+$  ion. From these the three atom–atom relative speeds  $v_k$  can be calculated. Consider the triangle with vertices corresponding to the three nuclei a, b, and c with the sides opposite the vertices equal to  $v_a$ ,  $v_b$ , and  $v_c$ . Assume for definiteness that  $v_a < v_b < v_c$ . Then if nucleus c has the positive charge, the system is in the ground adiabatic state (state 1). Similarly if nucleus b (nucleus a) has the positive charge, the system is in state 2 (state 3).

It is instructive to consider two limiting cases for the relative population of states 1, 2, and 3. The first would be where all three-body fragmentation occurs in a single adiabatic electronic state. This exciting possibility is very unlikely for  $\text{Na}_3^+$  because earlier studies of CID on a wide range of systems [3–5,21–23] have shown that fragmentation is caused by two general mechanisms when He hits a molecular ion like  $\text{Na}_3^+$ . The first is rovibrational excitation (RVE) in the ground electronic state sufficient to give fragmentation, and the second is electronic excitation (EE) to repulsive states that quickly fragment. At the energy considered here, the RVE mechanism dominates EE, so state 1 will most likely be favoured in the three-body fragmentation of  $\text{Na}_3^+$  but all electronic states should have appreciable populations. The second limiting case would be that the positive charge is distributed statistically among the Na atoms in the product triangle; thus adiabatic states 1–3 would have equal populations. This case is consistent with the fact that the three states are degenerate in energy at the detector, but it ignores

the reality that at finite separation there are three low-lying  $1A'$  electronic states of  $\text{Na}_3^+$  that have different energies and are not equally populated by the collision with He. Nevertheless, the statistical result could be realized if there were a strong coupling region as the  $\text{Na}_3^+$  fragmented, where transitions among the three adiabatic states were facile so that the positive charge was redistributed statistically. This redistribution is analogous to the mixing of fine structure states during photo fragmentation [24]. Clearly the result where all three adiabatic states are equally populated would be the least interesting possibility.

### 3. Experimental

Our experimental procedure has been described in detail elsewhere [3–5] and only a brief summary is given here. A beam of mass-selected  $\text{Na}_3^+$  ions is accelerated to 4800 eV and is crossed by a supersonic He beam. (The relative collision energy is 263 eV.) For fragmentation into three particles, the two neutral atoms fly in a straight line and are detected on a two-dimensional position sensitive detector (PSD). The particles must arrive at least 40 ns apart, since the detector has a dead time of 40 ns. The loss of events due to the detection dead time is estimated to be 10% [5]. The ionic fragment  $\text{Na}^+$  is mass selected in a parallel plate energy analyzer and detected in coincidence in a second PSD. The incident beam is chopped, allowing the time-of-flight (TOF) of all three fragments to be measured. From the arrival times and the positions on the PSDs, the velocities of all three particles can be determined and then the three relative velocities needed in this work. For each three-body fragmentation event we determine the relative velocities between the  $\text{Na}^+$  ion and each Na neutral as well as between the two neutrals. Then the rule described earlier is used to determine the final adiabatic electronic state.

### 4. Results and discussion

The experimental results for 10 512 three-body fragmentation events are shown in Table 1. We see

Table 1  
Experimental and theoretical distribution of product states

| State | Experimental results |                   | Theoretical results, contributions (%) |                          |   |
|-------|----------------------|-------------------|--|--------------------------|---|
|       | Number of events     | Contributions (%) | Giving three-body <sup>a</sup>         | At detector <sup>b</sup> | After dead-time adjustment <sup>c</sup> |
| 1     | 4457                 | 42.4              | 62.1                                   | 39.9                     | 44.1                                    |
| 2     | 3480                 | 33.1              | 23.4                                   | 34.0                     | 35.8                                    |
| 3     | 2575                 | 24.5              | 14.5                                   | 26.1                     | 20.1                                    |

<sup>a</sup> The calculated percentage of three-body events that originate in each of the three states of  $\text{Na}_3^+$  immediately after the collision with He.

<sup>b</sup> The calculated percentage of final three-body adiabatic states of  $\text{Na}_3^+$  at the detector.

<sup>c</sup> For comparison with experiment the theoretical results have been adjusted to account for the dead time of 40 ns of the experimental detector (see text for further details).

that product state 1, which corresponds to the ground adiabatic electronic state, has the largest number of products, but states 2 and 3 also have significant populations. A straightforward statistical analysis allows us to claim that with 99% confidence the true result for state 1 is larger than for state 2 or 3. These results are the first determination of the relative population of product states for three-body fragmentation, and it is quite exciting that the three populations are different. This suggests that other three-body fragmentation processes such as (1) could give similar results, and the experiments should be carried out to test this possibility.

We have also carried out a series of calculations for reaction (2). The calculations have been described in detail elsewhere [6–9] and only a brief summary is given here. The three lowest singlet states of  $\text{Na}_3^+$  have been calculated using the diatomics-in-molecule (DIM) procedure of [25]. The interaction of  $\text{Na}_3^+$  with He is obtained by extending the DIM basis to include certain Na–He and  $\text{Na}^+$ –He interactions and, in addition, three centre interactions of the type  $\text{Na}^+$ –He–Na are included. In addition, we have made small modifications in the Kuntz diatomic potentials when the bond lengths are long to ensure they have the proper asymptotic behavior using [26].

The theoretical calculation is carried out in three steps. First, the  $\text{Na}_3^+$  cluster ion classical reactant state is prepared for a fixed initial vibrational energy. The displacements of each Na nucleus from equilibrium and the momenta are chosen randomly as described in [4] with the con-

straints of zero rotational energy and a fixed vibrational energy. Second, the  $\text{Na}_3^+$ –He collision is treated assuming a random impact parameter for the He atom and a random orientation of the  $\text{Na}_3^+$  ion. The classical path approximation is used for the fast He atom and the vibrationally sudden approximation for the  $\text{Na}_3^+$ . The  $\text{Na}_3^+$ –He interaction introduces couplings between the three adiabatic states of  $\text{Na}_3^+$ , and, in addition, gives an impulse to each Na nucleus. The Schrodinger equation gives a system of time-dependent coupled equations for the three states that is solved numerically as the He passes by the cluster with fixed nuclei. Solution of these equations gives us the populations of all three electronic states just after the collision as well as the new momenta of each Na nucleus. Third, the fragmentation of the  $\text{Na}_3^+$  after the collision with He is treated using the trajectory surface hopping (TSH) procedure. The initial conditions for the trajectories are the populations of the adiabatic electronic states as well as the momenta of the cluster nuclei immediately after the  $\text{Na}_3^+$ –He collision. There is a conical intersection between states 2 and 3 in the equilateral configuration, and there is an avoided crossing between states 1 and 2 in the product region. The TSH properly treats transitions between two electronic states near these crossings. Our method describes both RVE and EE, and their features have been studied and reported earlier [6–9]. The calculations give two-body fragmentation to  $\text{Na}_2^+ + \text{Na}$  or  $\text{Na}_2 + \text{Na}^+$  as well as three-body fragmentation to  $\text{Na}^+ + \text{Na} + \text{Na}$ . In this Letter we consider only the last process. Earlier works

[6–8] have shown that the initial vibrational energy of the  $\text{Na}_3^+$  in the experiment is about 1 eV. Accordingly, this amount of initial vibrational energy was used in the present work.

The TSH calculations are carried out until all three values of  $R_k$  exceed 23 a.u. Our calculations show that at this point the positive charge is fixed on one nucleus. We check that three-body fragmentation is occurring. If it is, the calculation gives the three values of  $R_k$  and  $v_k$  (see Eq. (4)) and the identity of the nucleus with the positive charge. Thus, the diabatic state of the system is known at the end of the TSH calculation, and it remains the same until the detector. The determination of the theoretical adiabatic electronic state at the detector is straightforward and is the same as the experimental determination described earlier in Section 2. The calculated distribution of adiabatic states can be directly compared with the experimental results.

The theoretical results are also shown in Table 1 and compared with the experimental results. It is interesting to examine both the initial distributions of adiabatic states of  $\text{Na}_3^+$  following the collision with He and the final distribution once the fragmentation is completed. We consider only those trajectories that lead to three-body fragmentation. In that case, immediately after the collision with He 62% of the  $\text{Na}_3^+$  cluster ions are in adiabatic state 1, 23% in state 2, and 15% in state 3. Thus the ground electronic state is heavily favoured. If all fragmentations took place adiabatically, then the above percentages would be the final-state distribution at the detector. In reality the TSH calculations show that transitions between adiabatic states can occur until the particles reach the asymptotic region. These transitions, as expected, tend to equalize the product populations in the three states, but in the end adiabatic state 1 is still favoured with 39.9% of the products compared to 34%, and 26.1% for the states 2 and 3, respectively. Finally, to compare with experiment, we have eliminated all trajectories where the two neutral particles would arrive at the detector within 40 ns of each other. Accounting for the dead time of the detector reduces the population of all three states, but the effect is biggest for state 3 followed by state 2. Contributions from the remaining fragmentation events are given in the last column of the Table 1 (44.1%, 35.8% and 20.1%);

they should be directly compared with experimental contributions. The comparison between theory and experiment in Table 1 shows that, overall, the agreement is quite good.

There are no other comparable experimental results to compare with our work. As discussed earlier, in the past few years a few studies of three-body fragmentation have been made. Two studies have been made of process (1) [1,2]. No analysis of the electronic state distribution of the product ions of the type given here was carried out, but they did determine that in most cases the  $\text{H}^-$  was located between the two  $\text{H}^+$  fragments. This obviously corresponds to the ground electronic state of the three products. Further theoretical studies of process (2) are ongoing in our laboratories.

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