Dissociation dynamics of highly excited molecules produced by charge exchange: Two-body dynamics of CH$_5$ and three-body dynamics of sym-triazine

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Abstract. Translational spectroscopy and coincidence detection of the neutral photofragments have been used to observe the dissociation dynamics of highly excited neutrals produced by charge exchange between keV cation beams with Cs, and the results from two novel systems are presented. CH$_5$ is formed slightly above the 3s Rydberg level and dissociates into two possible fragmentation channels, H loss and H$_2$ loss. The kinetic energy release distributions of the two products are presented and the branching ratio between the two is found to be 11.4 ± 1.5 : 1 with the H loss being the dominant channel. Production of the highly symmetric azabenzene sym-triazine in its 3s Rydberg state has been shown to induce dissociation to 3HCN(X) + Σ. Examination of momentum correlation in the dissociation products shows that this dissociation occurs by two distinct mechanisms. Evidence from Monte Carlo simulations suggest a sequential mechanism occurs creating products accompanied by a kinetic energy release of ~1.5-5 eV. A symmetric concerted mechanism is also observed and is associated with products receiving a 2-4 eV kinetic energy release.

1. Introduction
Translational spectroscopy coupled with coincidence detection of neutral molecules allows a full kinematic description of many-body dissociation processes occurring from highly-excited neutral molecules to be obtained. This full kinematic description provides a complete measure of momentum correlation among dissociation products, bypassing many of the assumptions required by typical time-of-flight (TOF) techniques.[1] While momentum matching can be avoided when determining the kinetic energy release (KER) in the case of a two-body dissociation, the true strength of this technique lies in its ability to provide full three-dimensional information about higher-order dissociation processes. A prime example of the level of detail obtained in this type of experiment can be seen in recent studies of the three-body dissociation dynamics of H$_3$.[2, 3]

In the present experiments, charge exchange (CE) between a keV cation beam and Cs vapor is used to create excited neutral molecules which then dissociate. This is a well-studied technique and has been previously described in detail, so only key elements will be presented here.[4-6] The amount of internal energy deposited in the neutral upon CE is not discrete, and can occur via what has been described as resonant or near-resonant electron capture. Resonant CE excites the neutral to a state lying above the ground state by an energy equal to the adiabatic ionization potential of the neutral minus the ionization potential of Cs (3.89 eV). There exists a probability for populating neutral states

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that lie off resonance that has been shown to increase non-linearly with shorter interaction time (i.e. faster beam velocity). Reaction (1) illustrates several ways in which a polyatomic molecule (ABC) can dissociate following CE with Cs. In the absence of decay by fluorescence, excess energy is distributed to the fragments as internal and translational energy, the latter of which is measured in translational spectroscopy experiments. Product internal energies are inferred by translational (KER) measurements, and are often difficult to interpret in the case of molecular fragments.

\[
\text{ABC}^+ + \text{Cs} \rightarrow \text{ABC}^+ \rightarrow \text{A} + \text{BC} \\
\rightarrow \text{B} + \text{AC} \\
\rightarrow \text{C} + \text{AB} \\
\rightarrow \text{A} + \text{B} + \text{C}
\]  

The application of this technique to the examination of the product branching ratios in the dissociative CE of CH$_5^+$ and sym-triazine cation (H$_3$C$_3$N$_3^+$) is presented here. In the case of CH$_5^+$, the two low-lying product channels H + CH$_4$ and H$_2$ + CH$_3$ are observed, while in the case of sym-triazine, competing two- and three-body dissociation pathways are observed, with a focus in this manuscript on the three-body dissociation pathway H$_3$C$_3$N$_3$ → 3 HCN.

2. Experimental

The fast cation translational spectrometer used to carry out the current CE experiments is a modified version of an existing apparatus.[7] Cations are formed in an electric discharge on a pulsed (1 kHz) supersonic expansion of a gas mixture and then skimmed, accelerated, and focused using electrostatic optics. Cations of different mass-to-charge ratios are then separated by time-of-flight and the cation of interest is selected using a mass-gate prior to entering a Cs oven with a ~1 mm$^3$ interaction region. Any neutral fragments or stable neutrals created in the interaction region propagate 110 cm forward to the neutral particle detector. Unreacted cations are deflected out of the beam path and monitored using a time-sensitive microchannel plate detector. The time- and position-sensitive neutral particle detector consists of three microchannel plates in a z-stack arrangement above a four-quadrant crossed delay line anode.[8, 9] Each quadrant is capable of detecting two particles in coincidence, thus allowing coincidence detection of up to eight particles in a single event. Once empirical N(KER) distributions are obtained, Monte Carlo (MC) simulations of the detector’s geometric collection efficiency can be used to convert measured N(KER) distributions to true probability distributions, denoted by P(KER).[10]

3. Results and discussion

3.1 CH$_5$

CH$_5^+$ is the simplest non-classical carbonium ion.[11] It has importance in interstellar chemistry where it is formed via the radiative association of CH$_3^+$ and H$_2$.[12] There have been many studies, both theoretical and experimental of the cation, but very few of its corresponding neutral, due to its transient nature. CH$_5^+$ has a very small barrier to isomerization between C$_{s}$ (I), C$_{s}$ (II) and C$_{2v}$ geometries [13], resulting in free exchange of all H atoms within the molecule. Although the existence of CH$_5^+$ has been known since its discovery via mass spectrometry in the 1950s, it has only been within the last 10 years that a high resolution IR spectrum was taken.[14]

Neutralization reionization mass spectrometry (NRMS) experiments have studied the dissociative CE of this neutral using a variety of electron donors.[15-18] More recently, the dissociative recombination branching ratios have been measured using two methods, flowing afterglow[19] and ion storage rings.[20] These two methods have produced conflicting results; in the flowing afterglow, the H loss 2-body channel is dominant, whereas the ion storage rings have found the dominant channel to be the CH$_3$ + H + H channel. In the present experiment, fragments are detected in coincidence, and
translational KER distributions and branching ratios between different product channels are measured. Two possible dissociation channels are energetically accessible for dissociative CE with Cs.

\[
\text{CH}_3 \rightarrow \text{CH}_4 + \text{H} \quad (2)
\]

\[
\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2 \quad (3)
\]

Upon resonant CE of CH$_5^+$ with Cs, CH$_3$ is formed ~0.1 eV above the predicted energy of the 3s Rydberg state.[21] There are two dissociation channels that are energetically available, reactions (2) and (3) above and they are energetically nearly degenerate as shown in figure 1. Although H$_2$ is kinematically more favorable to detect, the dominant channel in the dissociation is the atomic H loss.

If CE with Cs were resonant, and CH$_5^+$ is assumed to be in its ground vibrational state, the maximum KER would be 4.2 eV for both channels, however, the experimentally observed maximum KER is ~5 eV. As shown in previous studies, near-resonant charge exchange (NRCE) can occur, increasing the probability of forming a neutral above the resonant level, resulting in a larger maximum KER.[2]

The P(KER) distribution for the dominant H-loss channel is shown in figure 2. It has a main peak with a shoulder at lower energy. The two Gaussians fit to the experimental data are also shown and peak at 2.0 eV and 3.1 eV. Both Gaussians extend to the maximum KER, indicating that the transient neutral for both features is formed in the same initial state. Most of the energy goes into internal excitation (vibration and rotation) of CH$_4$ as indicated by the low probability of products at the maximum KER.

The P(KER) distribution for the minor channel is shown in figure 3. Its distribution is bimodal with Gaussians peaking at 1.2 eV and 2.9 eV. The distribution of energy is more complicated for this channel because internal energy can go into both the CH$_3$ and H$_2$ products. Again, as in the case of the dominant channel, there is a low probability of products at the maximum KER, with most of the energy going into the internal excitation of the products. The branching ratios between the two channels can be calculated by integrating the P(KER) distributions over the given KER and dividing. The branching ratio for H loss to H$_2$ loss is 11.4 ± 1.5:1.

At first glance, it is surprising that the branching ratio shows a dominance for the H loss channel. The CH$_5^+$ cation is generally thought of as a CH$_3$ and H$_2^+$ moiety, and it would be expected that loss of the H$_2$ would have a more significant role in the dissociation. This may be a result of the fluxional nature of CH$_5^+$, with the protons essentially delocalized around the carbon center. Dynamical calculations on the ab initio potential energy surfaces of Bowman and co-workers may provide further insights into this phenomenon.[22]
3.2 Sym-triazine

Sym-triazine (1,3,5-triazine) is the most symmetric member of the azabenzene family and is a common backbone for a wide variety of organic compounds (e.g. RDX, melamine, atrazine). Sym-triazine is of particular interest in the present work as it has long been known to photodissociate to three HCN(X $^1\Sigma^+$) products by internal conversion from low-lying electronic states back to the $^1A'_1$ ground electronic state.[23-26] Early spectroscopic work probing infrared emission of HCN produced by photolysis of sym-triazine showed evidence for strong bending excitation and little evidence for the production of HNC fragments.[24] Previous photofragment translational spectroscopy (PTS) experiments have yielded several different interpretations of the three-body dynamics occurring from photoexcitation by 248 and 193 nm photons ($^1A'^*_{1}$ or $^1E'^* \leftarrow ^1A'_1$ and $^1A'_2 \leftarrow ^1A'_1$ respectively). Low-lying regions of the sym-triazine potential energy surface (PES) are densely populated by several electronic states which have been shown to have strong coupling, making the assignment of an exact mechanism extremely difficult.

While the first PTS experiment on the three-body dissociation of sym-triazine assumed HCN products were dissociating in a symmetric concerted manner, a similar experiment carried out later presented evidence for an asymmetric partitioning of momentum among the fragments.[23, 26] This asymmetric partitioning of momentum was described as being the result of a sequential process during which a short-lived (HCN)$_2$ intermediate is formed prior to complete dissociation to three HCN products, and is illustrated in reaction (4).

$$\text{H}_3\text{C}_3\text{N}_3^+ \rightarrow (\text{HCN})_2 + \text{HCN} \rightarrow 3\text{HCN} \quad (4)$$

A series of later ab initio studies found that a concerted mechanism with asymmetric partitioning of momentum among the products was a more likely reaction pathway.[27-29]

In the present experiment, the two- and three-body dynamics resulting from CE of the sym-triazine radical cation with Cs were examined using 12 and 16 keV cation beams. The adiabatic ionization potential for the lowest energy sym-triazine radical cation has been reported as 10.01 eV and corresponds to removal of an e' electron from a lone-pair orbital localized on a nitrogen atom in the

**Figure 2.** The P(KER) distribution for CH$_5$ → CH$_4$ + H. The dotted lines represent Gaussian fits to the data. The solid line represents the sum of the two Gaussians. The experimental P(KER) is shown by open circles.

**Figure 3.** The P(KER) distribution for CH$_5$ → CH$_3$ + H$_2$. The dotted lines represent Gaussian fits to the data. The solid line represents the sum of the two Gaussians. The experimental P(KER) is shown by open circles.
ring structure. The resulting doubly degenerate $^2E'$ state of the molecule is subject to the E⊗e Jahn-Teller effect and distorts from $D_{3h}$ to $C_{2v}$ equilibrium geometry. While no direct experiments have been carried out on this cation in the gas-phase, inference from an investigation into the corresponding 3s $^1E'$ Rydberg state ($\sigma^* e - n$) of the neutral suggests the ground vibronic state of the cation undergoes hindered pseudorotation along a single ring-breathing mode analogous to $\nu_6$ in benzene. Upon resonant CE, neutral sym-triazine is expected to be formed 6.12 eV above its ground state (4.26 eV above the ground state 3 HCN limit). The competing two-body dissociation channel forming (HCN)$_2$ + HCN products will not be further discussed in this work.

The empirically measured N(KER) distributions and corrected P(KER) probability distributions for the three-body dissociation at both beam energies are presented in figure 4. The resulting P(KER) distributions at both beam energies are extremely broad and exhibit two features, one peaked at ~2.6 eV (Feature I) and another peaked at ~0.5 eV (Feature II). The 12 and 16 keV distributions are very similar, varying only slightly on the rising edge of Feature I. The maximum observed KER in the P(KER) distributions extends ~0.75 eV past the theoretical limit for resonant CE and indicates the initially populated state of the neutral lies ~6.9 eV above the ground state. Based on these energetics, it is likely that the neutral is being formed initially in the 3s Rydberg state which has favorable Franck-Condon (FC) overlap with the cation and preserves the cation core (i.e. requires no electronic rearrangement). The peak of Feature I at 2.6 eV suggests that on average ~48% of the available energy is distributed to internal modes of HCN, the majority of which is presumably deposited in the HCN bending mode.

In order to illustrate momentum correlation dynamics among the fragments, Dalitz representations of the momentum partitioning in each event were constructed over small P(KER) intervals. The Dalitz plot is a histogram with each axis corresponding to a single fragment's fractional square of the total momentum ($f_i=p_i^2/\Sigma p_i^2$). In practical use a single point on the Dalitz plot represents the partitioning of momentum between the three fragments in a single event, as illustrated in figure 5.

The intervals over which Dalitz plots were constructed, labeled in figure 4, correspond to the following KER ranges: A(1.69 – 1.86 eV), B(2.70 – 2.87 eV), and C(3.38 – 3.54 eV). Figure 6 shows the resulting Dalitz plots over these intervals. In the 12 keV distributions, a feature corresponding to two slow and one fast fragment is apparent in intervals A-C and will be referred to as the ‘acute’ feature. This acute feature is also present in the corresponding 16 keV Dalitz distributions, although a symmetric (equal momentum partitioning) feature is also prevalent for intervals B and C. This velocity-dependent change suggests that dissociation proceeds from two different initial neutral states. Examination of the momentum correlation over small KER ranges reveals the KER range over which
each feature is present, and is not readily apparent from P(KER) distributions alone. The acute feature occurs over a KER range of ∼1.5-5 eV while the symmetric feature occurs from ∼2-4 eV.

The observed acute feature shows a nearly two-fold symmetry in the slow HCN products when interpreted as being the result of a concerted process. Nuclear motion on the lower sheet of the 3s 'E' surface is largely dictated by motion along the ν₆ coordinate.[32, 33] A simple model using ab initio predicted ν₆ displacement vectors for the D₃h ground state of sym-triazine shows that while distortion along ν₆ preserves a two-fold (C₂v) symmetry in the molecule as a whole, the geometry never passes through a configuration with two identical HCN fragments constructed from adjacent atoms.[27] Investigations employing MC techniques show that interpretation of the Dalitz plot is not intuitive in the case of a sequential dissociation. If the (HCN)₂ intermediate is assumed to have a lifetime greater than one rotational period (represented by random rotation of the intermediate), the simulations are dependent on only one parameter describing the partitioning of the total (measured) KER into each step of the sequential process. Simulations with a small primary KER (25%) and a larger secondary KER from the intermediate (75%) result in Dalitz distributions that are notably similar to the acute feature observed in the present experiment (figure 7).

Symmetry correlation predicts that the three-body dissociation of sym-triazine must ultimately occur by coupling of the initial excited state to the 1A'_g ground state.[23] The observed energetics suggest that the acute mechanism is occurring from an initial neutral state ∼6.9 eV above the ground state, most likely in the 3s Rydberg manifold which is then coupled to the ground state. The symmetric mechanism is presumably the result of a near-concerted process from a three-fold symmetric geometry, although the origin is somewhat ambiguous due to uncertainty in the energetics of near-resonant CE processes. The velocity dependent nature of this feature’s intensity relative to the acute feature qualitatively suggest that it arises from a state lying further off resonant excitation. The following two mechanisms are proposed, and would benefit greatly from further theoretical investigation. The splitting between the
zero-point level on the lower sheet and the conical intersection on the 3s 'E' surface has been reported as 0.13 eV, and states lying above the conical intersection are expected to have D$_{3h}$ geometries.[32, 33] Based on the approximate maximum KER observed for this feature (~4 eV), it is possible that population of a vibronic state on the upper sheet of the 3s surface followed by non-radiative decay to a dissociative state is giving rise to this feature. Alternatively, the lower-lying valence state of sym-triazine (π$^*$$\rightarrow$n) has D$_{3h}$ equilibrium geometry and excitation of the neutral to this highly symmetric region of the PES could lead directly to the dissociation mechanism.

4. Conclusion

The study presented here reveals some of the insights studies of dissociative charge exchange can provide to understanding the structure and dynamics of energized neutral species. The dissociative CE of CH$_5^+$ is particularly interesting as the H + CH$_4$ product channel is found to be strongly favored in spite of the fact that the CH$_5^+$ equilibrium geometry is more easily classified as a CH$_3$-H$_2^+$ molecule. In the case of the three-body dissociation of sym-triazine following CE we see a beautiful example of competing two- and three-body dissociation with both symmetric and asymmetric momentum partitioning occurring in the dissociation.

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Figure 7. Dalitz distribution resulting from MC simulations of a sequential dissociation over interval A with 25% of the total KER partitioned to the first step and 75% to the second step, classified as a CH$_3$-H$_2^+$ molecule. In the case of the three-body dissociation of sym-triazine following CE we see a beautiful example of competing two- and three-body dissociation with both symmetric and asymmetric momentum partitioning occurring in the dissociation.
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