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# Lifetime measurement of a collision complex using ion cyclotron double resonance. $\text{H}_2\text{C}_6\text{N}_2^+$

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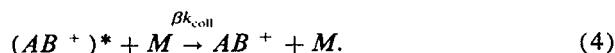
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In the ion-molecule reaction between  $\text{HC}_3\text{N}^+$  and  $\text{HC}_3\text{N}$ , the lifetime of the collision complex  $(\text{H}_2\text{C}_6\text{N}_2^+)^*$  was long enough that ion cyclotron double resonance techniques could be used to probe the distribution of the lifetimes of the collision complex. The mean lifetime of the collision complex at room temperature was measured as  $180\ \mu\text{s}$  with a distribution ranging from  $60$  to  $260\ \mu\text{s}$  as measured at the half-heights in the distribution. Lifetimes of this magnitude with respect to unimolecular dissociation allow for some stabilization of the collision complex by the slower process of infrared photon emission.

## INTRODUCTION

One of the crucial parameters required for an understanding of ion-molecule association [reactions (1)–(4)] is the lifetime of the collision complex  $(AB^+)^*$ :



The collision complex  $(AB^+)^*$ , is formed by the bimolecular reaction between  $A^+$  and  $B$  with a rate coefficient of  $k_f$ . It can dissociate back to reactants with a rate coefficient  $k_{-1}$ ; it can go on through exothermic channels to products with a rate coefficient  $k_2$ ; it can be stabilized by collision with a third body  $M$  with a rate coefficient  $\beta k_{\text{coll}}$ ; or it can be stabilized by photon emission with a rate coefficient  $k_r$ . The process of radiative association [reaction (3)], which occurs by way of infrared photon emission, is believed to have a rate coefficient on the order of  $10^{3 \pm 1}\ \text{s}^{-1}$ .<sup>1</sup> If the collision complex has a unimolecular dissociation lifetime that is very much shorter than the radiative lifetime, then stabilization by radiation cannot play an important role in the production of the stabilized  $AB^+$ . Radiative association has been invoked by modelers of interstellar cloud chemistry to account for the presence of several molecular species observed by radio astronomy techniques.<sup>2,3</sup>

We have made a number of laboratory studies from which we have been able to deduce lower limits to collision complex lifetimes ranging from  $1$  to  $50\ \mu\text{s}$ .<sup>4–8</sup> Although these lifetimes were lower limits only, they seem too small for direct measurement using the ion cyclotron resonance (ICR)

technique. The lifetime of the collision complex is defined as the inverse sum of the three unimolecular rates  $k_{-1}$ ,  $k_2$ , and  $k_r$ . In the model represented by Eqs. (1)–(4), there are five independent variables and it requires five independent pieces of information to determine all the variables uniquely. In most systems, we have been able to obtain only four independent pieces of data. Selected ion flow tube (SIFT) data generally gives  $k_f$  directly as long as the association is in the “saturated” regime; a low pressure ICR bimolecular rate constant, which is pressure independent and which determines the sum of  $k_2$  and  $k_r$ ; ICR data on the branching ratio between  $k_2$  and  $k_r$ ; and a higher pressure ICR result measuring the termolecular rate constant. Limits were able to be placed on the independent variables by setting the maximum value of  $\beta k_{\text{coll}}$  at the value of the collision rate constant, where  $\beta$  is the stabilization efficiency  $0 < \beta < 1$ . A fifth piece of independent data was needed to uniquely solve the system for the values of the microscopic rate constants. In this paper, we describe how the lifetime of  $(\text{H}_2\text{C}_6\text{N}_2^+)^*$  formed from the association of  $\text{HC}_3\text{N}^+$  and  $\text{HC}_3\text{N}$  can be measured in the ICR cell which thus allowed for a unique determination of the variables used in the model.

## EXPERIMENTAL

The Jet Propulsion Laboratory ICR spectrometer has been described previously.<sup>5,9</sup> The cyclotron frequency of the ions is utilized to monitor ion concentrations within the cell and detected using a bridge of the Wronka and Ridge design.<sup>10</sup> The ICR cell is of the trap/drift design after McMahon and Beauchamp,<sup>11</sup> and gas pressures within the cell are measured by an ion gauge calibrated against an MKS Baratron capacitance manometer. Drift times were measured by the method of McMahon and Beauchamp.<sup>12</sup> The experiments were conducted at  $298\ \text{K}$ . The second-order reaction rate constants have an estimated error of  $\pm 15\%$ .

The double resonance experiments were performed using the drift mode of operation of the spectrometer, in which ions were continuously drifted through the ICR cell. The ions typically require  $1$ – $3\ \text{ms}$  to transit both the reaction

<sup>a)</sup> NRC-NASA Research Associate at JPL 1989–1991.

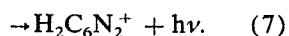
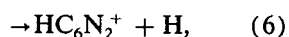
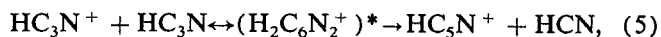
<sup>b)</sup> NRC-NASA Research Associate at JPL 1986.

region and the detection region. The double resonance experiment allows for the simultaneous observation of one ion and irradiation of another ion. Irradiation of an ion at its cyclotron frequency increases its translational energy in the plane perpendicular to the magnetic field and thus increases its cyclotron radius. When the orbit size reaches the dimensions of the cell, the ions collide with the metal plates and are neutralized. This process ejects the ion from the cell. If this ejected ion is connected chemically to the ion being observed, there will be a loss in the observed signal corresponding to the fraction of that ion being produced by the ejected ion.

The primary ion in this study  $\text{HC}_3\text{N}^+$ , was generated by electron impact on the parent gas  $\text{HC}_3\text{N}$  at an energy just above the ionization threshold. The cyanoacetylene gas was synthesized using standard procedure.<sup>13</sup>

## RESULTS AND DISCUSSION

There is an unusual property in the reaction between the cyanoacetylene radical cation and the cyanoacetylene neutral.<sup>8</sup> The radiative association channel is in competition with the usual exothermic ion-neutral pair products



While the collision complex  $(\text{H}_2\text{C}_6\text{N}_2^+)^*$ , has the same mass to charge ratio as the product of reaction (7), the major fraction of the branching ratio favors the product  $\text{HC}_5\text{N}^+$ . We were able to observe a reduction in the  $\text{HC}_5\text{N}^+$  ion signal while ejecting the  $\text{H}_2\text{C}_6\text{N}_2^+$  ion. This shows that the  $(\text{H}_2\text{C}_6\text{N}_2^+)^*$  ion is the precursor to the  $\text{HC}_5\text{N}^+$  ion. Thus the collision complex lives long enough to be probed by the double resonance technique.

Figure 1 shows the behavior of the double resonance signal with the power level of the double resonance oscillator. In this experiment, the  $\text{HC}_5\text{N}^+$  ion was observed and at the same time either the  $\text{HC}_3\text{N}^+$  ion or the  $\text{H}_2\text{C}_6\text{N}_2^+$  ion were irradiated using a second oscillator set to the appropri-

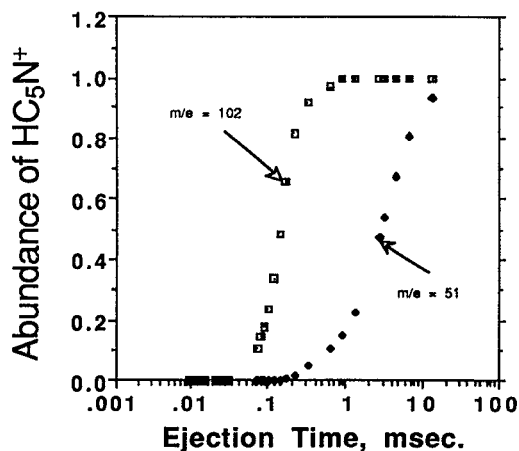


FIG. 1. Double resonance signal of the mass 75 ion for radiation of both the mass 51 and the mass 102 ions. The power levels have been converted to ejection times using the equation in the text.

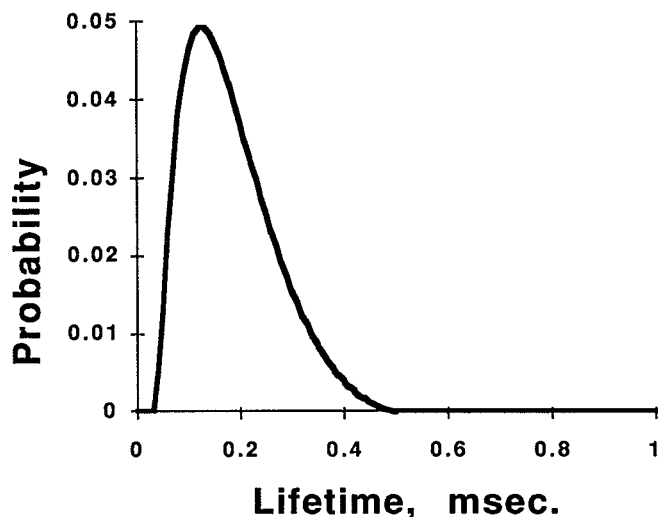


FIG. 2. Distribution of lifetimes for the collision complex.

ate resonant frequency. Both of these results are shown in Fig. 1. The rf power level has been converted into an ejection time by using the relationship, derived from the equations for power absorption,<sup>14</sup>

$$t = \frac{d^2 B}{V_{rf}},$$

where  $t$  is the ejection time,  $d$  is the cell dimension,  $B$  is the magnetic field, and  $V_{rf}$  is the base-to-peak voltage of the radio frequency. In our experiments,  $d$  was equal to 1.27 cm and  $B$  was equal to 1.5 Tesla.

The data set in Fig. 1 for  $\text{HC}_3\text{N}^+$  shows the normal low power ejection curve of a long-lived species. The data set in Fig. 1 for  $(\text{H}_2\text{C}_6\text{N}_2^+)^*$  shows the much higher power radio frequency needed to eject this short-lived species. The  $\text{HC}_3\text{N}^+$  curve does not rise as steeply as the curve for  $(\text{H}_2\text{C}_6\text{N}_2^+)^*$  because at the pressure used in the cell the time between collisions was about 1 ms and the ion, at this lower power level, had a chance to collide with the neutrals in the cell. The interruption of power makes the ejection process less efficient.

We believe that the data of Fig. 1 represent the sampling of the various lifetimes of the collision complex over its distribution. It takes a larger power level to observe the double resonance signal, because if the complex dissociates (either to products or reactants) before it can be ejected from the cell, there is no change in the product signal. Only after the power level is high enough and the shorter ejection times are being sampled can the change in the product signal be observed. It is seen that 90% of the  $\text{HC}_5\text{N}^+$  signal is lost when the ejection time is  $50 \mu\text{s}$ . It can be seen that the curve for the collision complex is symmetric in this semilogarithmic plot. The curve was extrapolated to the shortest times, fitted to a tenth-order polynomial, and then differentiated. Figure 2 shows this differential curve and the distribution of the lifetimes of the collision complex. The full width at half-height of the distribution ranges from 60 to  $260 \mu\text{s}$ . The most probable value of the lifetime is  $130 \mu\text{s}$ . The linear average of the distribution gives the mean lifetime of the collision complex

as  $180\ \mu\text{s}$ . The shape of the curve is similar to that expected for a Boltzmann distribution of energies.

As a check on this mean lifetime measurement, we performed an independent experiment to estimate the complex's lifetime using the "peak ratio" method described in an earlier paper.<sup>7</sup> We measured the peak heights of all four major ions in the spectra using the drift mode of operation and then analyzed this data for the rate constants. We modeled the kinetics using the mechanism above [Eqs. (1)–(4)], and by using the double resonance coupling between  $\text{HC}_5\text{N}^+$  and  $\text{H}_2\text{C}_6\text{N}^+$ , determined the fraction of  $\text{H}_2\text{C}_6\text{N}_2^+$  that was in the form of the collision complex  $(\text{H}_2\text{C}_6\text{N}_2^+)^*$  and the fraction in the form of the stabilized product  $\text{H}_2\text{C}_6\text{N}^+$ . This kinetic analysis showed that the lifetime  $1/k_2$  had a value of  $<310 \pm 80\ \mu\text{s}$  and that it was independent of pressure, in excellent agreement with the more direct experimental technique.

## CONCLUSION

Application of this double resonance technique in an ICR experiment can yield the distribution of lifetimes of a collision complex that is undergoing unimolecular decomposition, or is being stabilized by emission of photons, provided that certain conditions are fulfilled. The complex lifetime should be greater than  $100\ \mu\text{s}$  and the collision complex must also undergo unimolecular decomposition to products as well as reactants.

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