

# A Comparative Study of the DR Reactions of $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$ : Preliminary Theoretical Studies

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**Abstract.** Preliminary calculations related to the dissociative recombination (DR) of electrons with  $\text{C}_3\text{H}_3^+$  have been carried out. Both the linear and cyclic isomers of this ion exist in the interstellar medium, and accurate DR rate constants for both isomers are needed for astrophysical models. The electronic structure calculations reported here yield quasi-diabatic potential energy curves that can be used to assess the efficiency of dissociation of a CH bond. The calculations confirm a favorable position of a dissociative state for the cyclic isomer and suggest that dissociation of the linear isomer is less probable. More detailed dynamical studies are planned, and a normal mode analysis of the vibrational modes of  $\text{C}_3\text{H}_3^+$  is reported as the first step in that direction.

## 1. Introduction

The three-membered ring molecule cyclopropenylidene ( $c\text{-C}_3\text{H}_2$ ), discovered in the interstellar medium (ISM) in 1985 [1], has gained attention very rapidly because of its ubiquity in space. It is not a common molecule on Earth, and it is not used in the laboratory for any synthesis. However, it is a stable interstellar species surviving even in UV exposed regions. Its linear counterpart  $l\text{-C}_3\text{H}_2$  was detected in 1991 [2] and appears to coexist in the ISM with  $c\text{-C}_3\text{H}_2$ . It is considered in the astrochemical models that both are formed from the dissociative recombination of the corresponding ions:



In 1993, Abouelaziz *et al* [3] attempted an experimental determination of the rate coefficient for the DR of  $\text{C}_3\text{H}_3^+$ . At 300K, they measured this coefficient to be  $(7 \pm 2) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ . This value, indicating an efficient DR process, is in agreement with the  $1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  determined earlier at 2000K [4]. However, there are two uncertainties related to the Abouelaziz *et al* experiment. These are the state of excitation and the isomeric form of the recombining ion including whether or not  $\text{C}_3\text{H}_3^+$  was in its cyclic form.

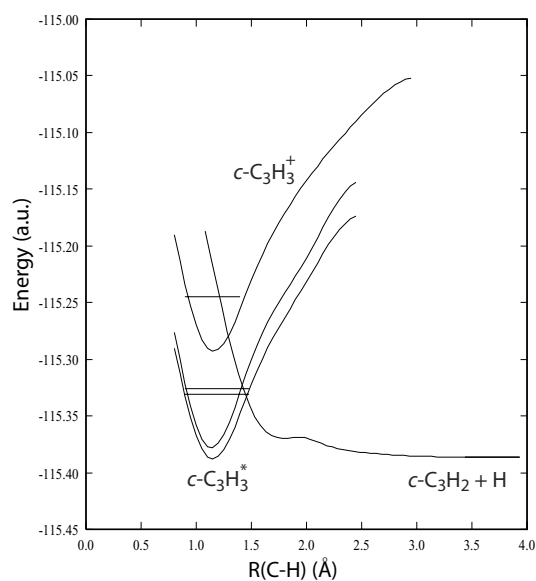
In the ISM, the  $c\text{-C}_3\text{H}_2/l\text{-C}_3\text{H}_2$  abundance ratio, observed to be varying from the dense molecular clouds to the diffuse ones [5, 6], has been proposed to serve as a tool to probe the electronic abundances in the ISM [7]. However, in order to deduce accurate values of the fractional ionization of astrophysical objects from the  $c\text{-C}_3\text{H}_2$  and the  $l\text{-C}_3\text{H}_2$  abundances, the branching ratios and kinetic rates used in the related chemical networks must be more accurately known. Among the uncertainties concerning the interstellar chemistry of  $\text{C}_3\text{H}_2$ : the efficiency of the DR of the  $c\text{-C}_3\text{H}_3^+$  and  $l\text{-C}_3\text{H}_3^+$  ions. For the cyclic isomer, the above experimental rate constant [3] determined at 300K is used in the astrochemical models. For the linear isomer, the rate constant of the cyclic one is assumed. Since it is difficult to get experimentally a rate constant for each of these isomers at the low temperature of the ISM, a quantum chemical study of the two DR processes appears to be a good alternative. Indeed, quantum chemical calculations have proven to be extremely useful for understanding these recombining processes. Such processes may occur by direct and/or indirect mechanisms. While the former involves a direct transition from the ionic state to the final neutral dissociative state, the second one is a two-step process involving the formation of a rovibrationally excited state of the neutral molecule (mainly a Rydberg state). For this last case, either autoionization takes place or the state formed after binding the electron predissociates. Understanding the DR of an ion requires knowledge of the potential energy surfaces of the ionic, Rydberg and dissociative states of the corresponding neutral molecule. This is not a trivial task because, very often, the nature of the states changes along the reaction coordinate. Carefully designed wave functions are needed to accurately follow those transformations. But the difficulty is also in the even handed treatment required for all the states involved in the mechanism. Moreover in the present case, where we are interested by the relative efficiency of the formation of  $c\text{-C}_3\text{H}_2$  and  $l\text{-C}_3\text{H}_2$  from the DR of the corresponding ionic isomers, potential energy surfaces involved in both DR of  $c\text{-C}_3\text{H}_3^+$  and  $l\text{-C}_3\text{H}_3^+$  has to be treated at the same theoretical level.

To ensure an even-handed treatment of both the ionic, Rydberg and dissociative states of  $c\text{-C}_3\text{H}_3$  as well as of  $l\text{-C}_3\text{H}_3^+$ , the correlation energy must be treated through the same CI (Configuration Interaction) procedure so as not to favor one state over another. In order to fulfill this requirement, we have adopted a methodology, already defined [8, 9], that is based on the use of orbitals of strong localized character to build the CI wave functions. It is then possible to separate, valence bonding from antibonding orbitals and antibonding from Rydberg orbitals, each of them having a well-defined spatial expansion and a clear physicochemical meaning. The advantage of such a method is that the CI  $n$ -particle space is defined in terms of orbitals whose chemical significance is clearly identified. Configurations can be selected according to chemical evidence and the type of arbitrariness associated with energy related selection processes can be avoided. More important, the CI expansion is directly obtained in a configuration space that contains the approximate diabatic representation of the problem [10]. It is therefore possible to extract an approximate diabatic representation of the states (hereafter referred to as quasi-diabatic) according to the weights of their relevant configurations in the CI wave function.

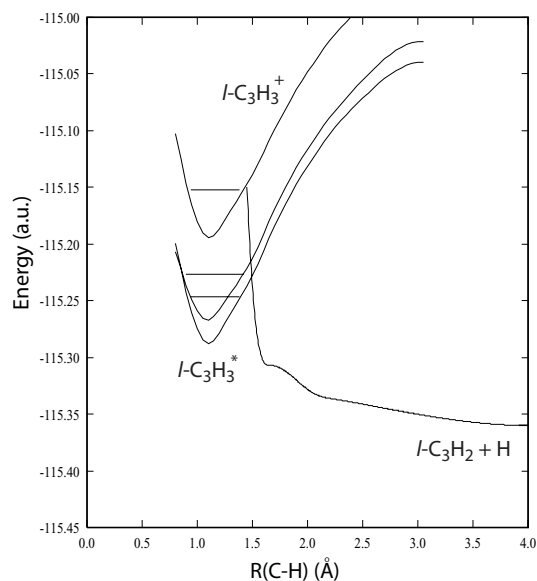
The methodology used to study the DR of  $c\text{-C}_3\text{H}_3^+$  is presented elsewhere [11] and therefore will not be repeated again here. The same one has been applied to build the potential energy surfaces involved in the DR of  $l\text{-C}_3\text{H}_3^+$ , including the size and nature of the atomic basis set, the procedure to get the localized orbitals and the CI partitioning. The dissociation path has been chosen so as to preserve the  $C_{2v}$  symmetry of the molecule. The Alchemy program [12] has been used for the calculations.

## 2. The Potential Energy Curves

Thanks to the use of orbitals with a strong localized character to build the electronic states configurations for the  $c\text{-C}_3\text{H}_3$  and  $l\text{-C}_3\text{H}_3$  systems, it has been possible to extract quasi-diabatic potential energy curves from their CI adiabatic wave functions according to the weights of the



**Figure 1.** Quasi-diabatic potential energy surfaces for the lowest Rydberg and lowest repulsive states of  $c\text{-C}_3\text{H}_3$  and for the lowest state of the ion. The  $v = 0$  levels are shown.



**Figure 2.** Quasi-diabatic potential energy surfaces for the lowest Rydberg and lowest repulsive states of  $l\text{-C}_3\text{H}_3$  and for the lowest state of the ion. The  $v = 0$  levels are shown.

relevant configurations in these CI wave function. The quasi-diabatic potential energy surfaces for the cyclic and linear isomers of  $\text{C}_3\text{H}_3$  are reported in Figures 1 and 2, respectively. For more clearness, we have only reported the curves of interest for the present DR mechanisms (the ion, the two lowest bound Rydberg and the lowest repulsive states) but the reader has to keep in mind that there exist plenty of valence excited states of  $c\text{-C}_3\text{H}_3$  and  $l\text{-C}_3\text{H}_3$  not of interest for the present mechanism showing up at the energies of the figures and that have been omitted and that there exist a series of Rydberg states converging to the ion that has not been calculated.

### 2.1. $c\text{-C}_3\text{H}_3^+ + e \rightarrow c\text{-C}_3\text{H}_2 + \text{H}$

The quasi-diabatic potential energy surfaces of the lowest repulsive and of the two lowest Rydberg states of  $c\text{-C}_3\text{H}_3$ , all of  ${}^2A_1$  symmetry, are reported as a function of the CH linear dissociation coordinate in Figure 1 together with the potential energy curve of the corresponding ion. The next higher repulsive state of  $c\text{-C}_3\text{H}_3$  is of  ${}^2A_2$  symmetry. It crosses the ion at very high energies and has therefore not be reported here since it is not of interest for the present study. As can be seen the lowest  ${}^2A_1$  repulsive state of  $c\text{-C}_3\text{H}_3$  dissociating to ground state fragments  $c\text{-C}_3\text{H}_2$  and H, intersects the  ${}^1A_1$  curve of the ion at its minimum energy below the  $v = 0$  energy level. The position of the crossing argues for an efficient DR mechanism for  $c\text{-C}_3\text{H}_3^+(v = 0)$  to dissociate through the direct mechanism to  $c\text{-C}_3\text{H}_2$  and H.

### 2.2. $l\text{-C}_3\text{H}_3^+ + e \rightarrow l\text{-C}_3\text{H}_2 + \text{H}$

The quasi-diabatic potential energy surfaces for the lowest  ${}^2A_1$  repulsive state of  $l\text{-C}_3\text{H}_3$  as well as those of the two lowest  ${}^2A_1$  Rydberg states and of the  ${}^1A_1$  corresponding ionic state are reported Figure 2 as a function of the CH linear dissociation coordinate. A second repulsive state (of  ${}^2B_1$  symmetry) is much higher in energy and is not shown. Figure 2 shows that the crossing between the lowest repulsive state of  $l\text{-C}_3\text{H}_3$  (which dissociates to ground state  $l\text{-C}_3\text{H}_2$ ) and the  $l\text{-C}_3\text{H}_3^+$  ion is located above the  $v = 0$  ground vibrational energy level of the ion. Contrary to

the cyclic isomers, there does not exist for  $l\text{-C}_3\text{H}_3^+(v=0)$  an efficient curve crossing with the repulsive state leading to ground state  $l\text{-C}_3\text{H}_2$ .

Even if preliminary, these theoretical studies show that the formation of  $c\text{-C}_3\text{H}_2$  from the DR of  $c\text{-C}_3\text{H}_3^+$  should be more efficient than the formation of  $l\text{-C}_3\text{H}_2$  from the DR of  $l\text{-C}_3\text{H}_3^+$ . This theoretical conclusion corroborates the DR experiments of Adams *et al* [13], who determined using afterglow techniques that the cyclic ion recombines more rapidly than the linear isomer at 300K. This agreement should encourage further studies on these two DR processes, including calculations of the corresponding rate coefficients and the investigation of other dissociation paths such as the C-C bond breaking. The experimental results of Mitchell *et al* [14] provide relevant branching ratios for the  $c\text{-C}_3\text{H}_3^+ + e^-$  reaction.

Our discussion so far has considered dissociation of  $c\text{-C}_3\text{H}_3^+$  into  $\text{C}_3\text{H}_2$  along one of the C-H bonds; we implicitly assume that the initial CH vibration in  $c\text{-C}_3\text{H}_3^+$  is governed by a single ionic potential curve. We can improve the analysis by including the energy redistribution among the three equivalent CH stretching modes (and other modes as well) by considering normal coordinates. This analysis is described next.

### 3. Vibrational Analysis of $c\text{-C}_3\text{H}_3^+$

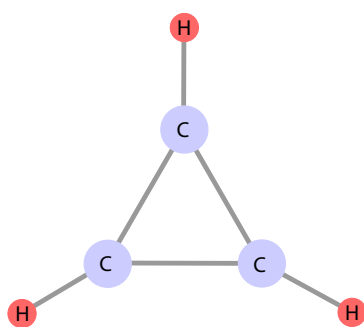
As a preliminary step in the treatment of the dynamics, we have calculated the normal modes of  $c\text{-C}_3\text{H}_3^+$ . The normal mode analysis will enable us to formulate a realistic initial vibrational wave function for the molecular ion.

#### 3.1. Structure, Force Constants, and Classical Dynamics

As shown in Figure 3,  $\text{C}_3\text{H}_3^+$  is a planar molecule whose symmetry group is  $D_{3h}$ . An analysis using group theory shows that the molecule has 12 nontrivial vibrational modes: four are degenerate and eight come from four degenerate pairs. We set up a secular equation in terms of spring constants  $k_{\text{CH}}$ ,  $k_{\text{CC}}$ ,  $k_{\text{p}}$  and  $k_{\text{z}}$  (defined in Figure 3) and factored it into two identical  $3 \times 3$  blocks ( $E'$ ), one  $2 \times 2$  block ( $A'_1$ ) and several uncoupled ( $1 \times 1$ ) roots.

The spring constants were determined using the GAMESS code [15]. Figure 3 shows the results of our preliminary CI calculations, which were carried out at the level of single and double excitations (CISD). Table 1 compares these results with others available in the literature.

The key feature in the dynamics of  $\text{C}_3\text{H}_3^+$  that may influence the dissociative recombination is the flow of energy into and out of the vibration of a single CH bond. Even if we neglect anharmonic effects and assume the energy in each normal mode is constant, then the amplitude of the CH bond vibration will not be a constant of the motion. Instead, the amplitude will fluctuate. The quasi-adiabatic potential curves shown in Figure 1 show that the dissociating



force constant	definition	value ( $E_{\text{h}}/\text{\AA}^2$ )
$k_{\text{CH}}$	CH stretch	1.439
$k_{\text{CC}}$	CC stretch	1.816
$k_{\text{p}}$	H wagging (in plane)	0.109
$k_{\text{z}}$	H flapping (out of plane)	0.078

**Figure 3.** Structure and force constants of  $\text{C}_3\text{H}_3^+$ . We set up a secular equation in terms of the spring constants  $k_{\text{CH}}$ ,  $k_{\text{CC}}$ ,  $k_{\text{p}}$  and  $k_{\text{z}}$ , and the values of these constants were calculated.

**Table 1.** Fundamental vibrational frequencies of  $C_3H_3^+$  in  $cm^{-1}$ .

		present calculation	observed (Craig <i>et al</i> ) [16]	MP2 calculation (Forney <i>et al</i> ) [17]
$A'_1$	(breathing)	3519	3183	3333
		1810	1626	1646
$A'_2$	(pinwheel)	1160	(1030)	1037
$E'$	(in plane)	3476	3138	3283
		1460	1290	1328
		884	927	948
$A''_2$	(drumhead)	842	758	768
$E''$	(out of plane)	980	(990)	1009

curve for the cyclic isomer does cross the ionic curve. The details of the overlap between the initial state and the dissociating curve would therefore determine the magnitude of the DR rate. Speaking classically, one would expect that at those times when the energy in a particular CH bond is large, the probability of dissociation along that bond would be large, and that at other times the probability might be weaker. This analysis supports the idea that a careful determination of the distribution of CH bond lengths should be incorporated into the theory.

### 3.2. Quantum Mechanical Analysis and Comparison with Classical Model

The ground state harmonic oscillator wave function for a mass-weighted normal coordinate is

$$\psi(Q) = \left(\frac{\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{\hbar}{2\omega}Q^2\right).$$

where  $Q$  is a normal coordinate and  $\omega$  is the corresponding frequency. If a variable  $z$  can be expressed as a linear combination of normal coordinates,

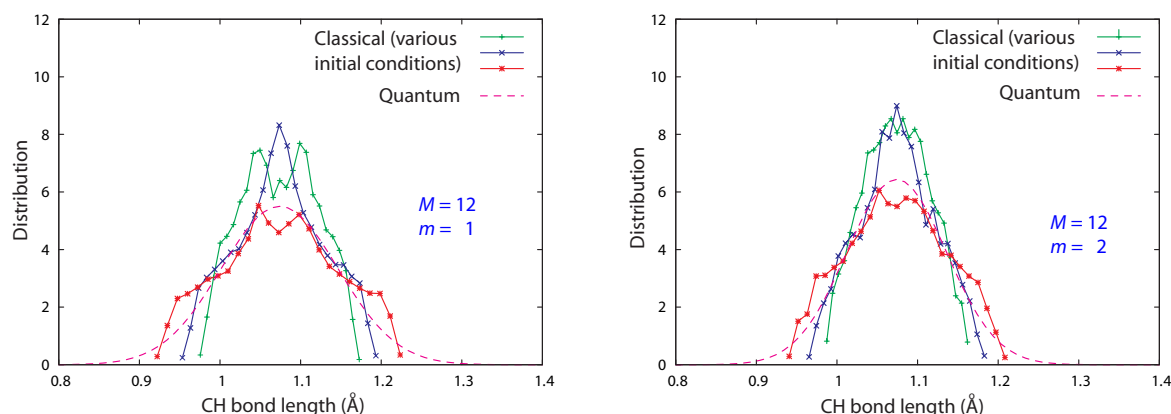
$$z = \sum_{i=1}^N c_i Q_i,$$

one can calculate analytically the distribution of values of  $z$ :

$$P(z) = \int dQ_1 \psi_1(Q_1)^2 \cdots \int dQ_N \psi_N(Q_N)^2 \delta\left(z - \sum_{i=1}^N c_i Q_i\right).$$

We can interpret  $P(z)$  as the quantum mechanical probability density for the distribution of values of  $z$ . By letting  $z$  be the CH internuclear distance, we can thereby obtain the range of CH distances that may occur in ground state  $C_3H_3^+$ . In this case, we can regard  $P(z)$  as the square of the quantum mechanical wave function of the variable  $z = R_{CH}$ . There is no closed form expression for  $P(z)$ , but we wrote a simple recursive algorithm to evaluate it.

In order to explore the classical motion of the  $C_3H_3^+$  we performed classical simulations using the normal coordinate analysis. We randomly selected initial conditions for which the energy in each normal mode was the quantum mechanical zero point energy and then monitored the evolution of the CH bond length over a long period of time. The results are shown in Figure 4.



**Figure 4.** Distribution of CH bond lengths using the quantized normal mode formula (dashed line) and a classical simulation based on putting the zero point energy into each normal mode.  $M$  and  $m$  denote the masses of C and H in amu, respectively.

#### 4. Concluding Remarks

The *ab initio* calculations reported here confirm the existence of a direct mechanism for the DR of electrons with  $c\text{-C}_3\text{H}_3^+$  and show how a normal mode analysis of the ion can provide an appropriate initial vibrational wave function. Further work will involve the application of the block diagonalization method [18] to obtain more quantitative diabatic potential curves and coupling terms. Detailed dynamical calculation are also planned.

#### Acknowledgments

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