



The cross-section and branching fractions for dissociative recombination of the diacetylene cation $C_4D_2^+$

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ABSTRACT

In this paper we report the results of a study on the dissociative recombination (DR) of the diacetylene cation, $C_4D_2^+$, which has been carried out at the ion storage ring CRYRING in Stockholm, Sweden. The energy-dependent absolute DR cross-section as well as the branching fractions at ~ 0 eV collision energy were measured. The DR cross-section was best fitted using the expression $\sigma(E) = (7.5 \pm 1.5) \times 10^{-16} \times E^{-(1.29 \pm 0.03)} \text{ cm}^2$ over the collision energy range 1–100 meV. The thermal rate coefficient was deduced from the cross-section to be $\alpha(T) = (1.10 \pm 0.15) \times 10^{-6} \times (T/300)^{-(0.79 \pm 0.03)} \text{ cm}^3/\text{s}$. The reported branching fractions for $C_4D_2^+$ agree with previous experiments on the DR of $C_4H_2^+$ performed at the ASTRID storage ring in Aarhus, Denmark, and furthermore, indicate that the DR of $C_4D_2^+$ possesses only two channels leading to the following products: $C_4D + D$ (75%) and $C_2D + C_2D$ (25%).

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1. Introduction

In dissociative recombination (DR) a molecular cation recombines with a free electron and subsequently releases the excess energy gained in the recombination by dissociating into neutral fragments. The absence of an activation energy makes DR a fast process in colder plasmas such as those present in the interstellar medium, planetary ionospheres and in the comas of comets where it is an efficient pathway for the neutralization of cations. Although neutral diacetylene (HC_4H) is regarded as an important intermediate in the formation of larger carbon-containing molecules in the interstellar medium, its detection in the interstellar medium has been hampered by the fact that, as a non-polar-molecule, it lacks a pure rotational spectrum and therefore cannot be detected by radioastronomical observations. This together with the limitations of infrared (IR) observations through the earth's atmosphere has made identification of diacetylene in extraterrestrial environments dependent on space deployed spectrometers. Although diacetylene was detected in the atmosphere of Saturn's moon Titan in 1981 [1] through IR measurements during the flyby of the spacecraft Voyager 1, detection outside the solar system was not reported until

2001 [2], when it was identified with the Infrared Space Observatory (ISO) in the proto-planetary nebulae CRL 618 and towards CRL 2688. In our solar system diacetylene has been reported to be present in several planetary atmospheres, e.g., Jupiter [3], Uranus [4] and Saturn [5]. Recently (2007), evaluation of data obtained by the Composite Infra-Red Spectrometer (CIRS) and the Ultra Violet Imaging Spectrograph (UVIS) on board the Cassini–Huygens spacecraft yielded considerable abundance of C_4H_2 in the upper layers of Titan's atmosphere [6,7].

Furthermore, the detection of the polar isomer of diacetylene, butatrienylidene ($CCCCH_2$), using ground-based rotational spectroscopic observations in the dark cloud TMC-1 [8] could indirectly serve as a marker for diacetylene in this environment as butatrienylidene, alongside with diacetylene, is thought to be produced from the DR of $C_4H_3^+$ [9]. However, the major production pathway of diacetylene in extraterrestrial environments is probably the reaction between acetylene (C_2H_2) and the ethynyl radical (C_2H), as proposed in an early chemical model of Titan in 1984 [10]. It has been reported in a work using crossed beam-experiments and calculations [11] that this reaction lacks an entrance barrier, possible also without an exit barrier, and thus represents an efficient mechanism to produce diacetylene.

Once formed, diacetylene can be ionized by stellar UV as well as cosmic radiation [12] to yield the radical cation $C_4H_2^+$, a process which is included in models of Titan's ionosphere [13] and dark

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interstellar clouds [14]. Generally, ion-neutral reactions are efficient at low temperatures due to there being small or non-existing reaction barriers, which makes them important processes in the chemistry of cold molecular clouds. It is worth noting that the $C_4H_2^+$ ion is claimed to be involved in the formation of benzene in dense clouds [15], and in proto-planetary nebulae. $C_4H_2^+$ is thought to act as a route to incorporate sulfur into larger carbon species by reacting with atomic sulfur in an atom exchange process to form HC_4S^+ , which can further undergo DR to form the sulfur-containing interstellar molecules C_3S and C_4S [16]. For the purpose of modeling the ion chemistry of Titan, McEwan and Anicich [17] recently compiled a database in which a range of reactions involving $C_4H_2^+$ were included. The DR reactions of all these ions can efficiently compete with ion-neutral reactions therefore, DR rates and product branching fractions have to be established to estimate the efficiency of the ion-neutral processes in the synthesis of interstellar and atmospheric molecules. In the case of $C_4H_2^+$, DR may lead to the reactive C_4H radical, which has been experimentally shown to efficiently react with small hydrocarbons observed in the atmosphere of Titan [18].

In this paper we present the cross-section and branching fractions for the DR of deuterated diacetylene cation, $C_4D_2^+$ where, for experimental reasons (to obtain a better mass resolution at the detector), $C_4D_2^+$ was chosen instead of $C_4H_2^+$.

2. Experimental methods

The experiment was carried out at the ion storage ring CRYRING in Stockholm, Sweden. The experimental procedure is described elsewhere [19] and is only summarized here. The $C_4D_2^+$ ions were produced in a hollow cathode discharge ion source using deuterated butadiene $CD_2(CD)_2CD_2$ as the precursor molecule. The ions were subsequently extracted with a 40 kV potential and mass selected (52 a.m.u.) using a dipole magnet before being injected into the storage ring. Further acceleration to an energy of 1.73 MeV was carried out in the ring using an RF cavity. The stored ion beam was merged collinearly over a distance of 0.85 m with a cold electron beam, whose velocity could be varied in the electron cooler. After the acceleration, but prior to the measurement, the ion beam was stored for 3 s while the average velocities of the ions and electrons were kept the same. Although the heat exchange between the ions and the electrons is slow for such a heavy ion, this period allowed time for radiative de-excitation of vibrational modes to occur. Neutral products from the DR reaction in the electron cooler left the ring tangentially and were detected by an energy sensitive surface barrier detector (SBD). A measure of the beam intensity was provided by a signal from a micro-channel plate located after a straight section of the ring and provided a method for normalization of the measurements.

The electron velocity was changed by controlling the voltage on the electron gun cathode in the electron cooler. The detuning velocity is given by $v_d = |v_{e||} - v_{i||}|$, where $v_{e||}$ and $v_{i||}$ are the average longitudinal velocities of the electrons and ions in the lab frame, respectively, and the so-called detuning energy (E_d), can be found from the expression:

$$E_d = \frac{1}{2} m_e v_d^2 = (\sqrt{E_e} - \sqrt{E_{cool}})^2 \quad (1)$$

Here E_e and E_{cool} are the lab-frame kinetic energy of the electrons at E_d and the kinetic energy of the electrons when their longitudinal velocity is matched to that of the ions, i.e., at $v_d = 0$, respectively. At collision energies that are much larger than the thermal spread of the electrons, E_d equals the center of mass energy. During the cross-section measurement the electron velocity was varied relative to that of the ion velocity in such a way that corresponded to

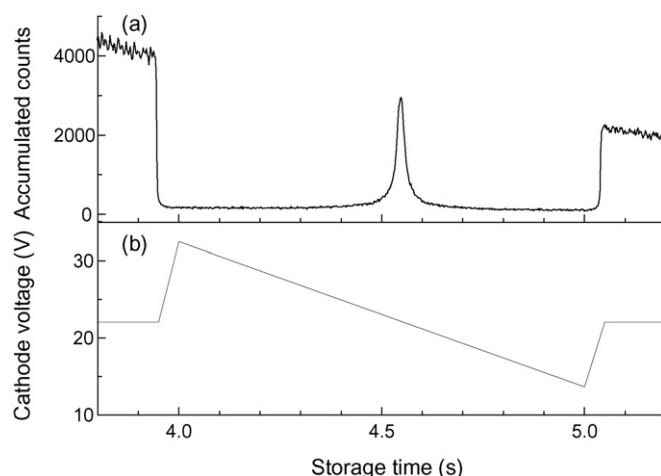


Fig. 1. Measurement of the DR cross-section of the diacetylene cation $C_4D_2^+$. (a) A spectra from the SBD accumulated over 1020 cycles (before background subtraction). The peak in the signal at 4.55 s occurs at the minimum collision kinetic energy of the reactants. (b) The electron gun cathode voltage as a function of time during the cross-section measurement.

the detuning energy changing from $E_d = 1$ eV through $E_d = 0$ eV to $E_d = 1$ eV. The signal recorded by the SBD, together with the voltage ramp applied to the electron-gun cathode, is shown in Fig. 1(a) and (b).

For the branching fraction measurement the SBD was connected to a multi-channel analyzer (MCA). A grid with a transmission probability $t = 0.297 \pm 0.015$ [19] was placed in front of the SBD. The probability for a particle to pass through the grid or to be stopped by the grid is t and $(1 - t)$, respectively. In the absence of any resonance at higher collision energy, the DR cross-section is negligible at $E_d = 2$ eV so signals measured at this energy are dominated by background processes. These data can then be used to determine the background contribution to the data taken at 0 eV.

2.1. Data reduction

All possible combinations of reaction products were considered, with the maximum possible kinetic energy release into each channel calculated in the same manner as described by Angelova et al. [20], assuming all the formed products at ~ 0 eV collision energy to end up in their electronic ground state. Due to the scarce supply of data for deuterium-containing species, the assumption was made that the standard heat of formation, $\Delta_f H^\circ$, of a compound is the same for deuterated as for undeuterated isotopologues. The values of the standard heat of formation at 298 K were taken from Refs. [21,22]. From all of these combinations, only eight channels were found to be exothermic and these are listed in Table 1.

Analysis of the data plotted in Fig. 2(a) showed that the detector resolution was not sufficient to distinguish between fragments which differed only by the number of deuterium atoms and the electrical noise in the detector made the identification of deuterium fragments (D and D_2) impossible. Therefore, only the probability of fragmentation of the different C–C bonds could be investigated. Deuterium fragments from a DR breakup in the channels (a) and (b), listed in Table 1, could have gained sufficient kinetic energy from the reaction to evade the detector. Peaks in the background corrected spectrum corresponding to fragments containing one and three C-atoms are not observed and are excluded from the analysis.

Table 1
Exothermic pathways for DR of $C_4D_2^+$

| | |
|---|-----|
| $C_4D_2^+ + e^- \rightarrow C_4D + D + 5.7\text{--}6.0\text{ eV}$ | (a) |
| $C_4D_2^+ + e^- \rightarrow C_4 + D_2 + 3.8\text{--}4.9\text{ eV}$ | (b) |
| $C_4D_2^+ + e^- \rightarrow C_2D_2 + C_2 + 3.7\text{--}5.5\text{ eV}$ | (c) |
| $C_4D_2^+ + e^- \rightarrow C_2D + C_2D + 3.0\text{--}3.5\text{ eV}$ | (d) |
| $C_4D_2^+ + e^- \rightarrow C_3D_2 + C + 0.3\text{--}2.6\text{ eV}$ | (e) |
| $C_4D_2^+ + e^- \rightarrow C_3 + CD_2 + 1.6\text{--}2.5\text{ eV}$ | (f) |
| $C_4D_2^+ + e^- \rightarrow C_3D + CD + 0.6\text{--}1.7\text{ eV}$ | (g) |
| $C_4D_2^+ + e^- \rightarrow c\text{-}C_4 + D + D + 0\text{--}0.4\text{ eV}$ | (h) |

The given range reflects both the uncertainties in the tabled values of the standard heat of formation and the possibility of formation of different isomers. Only the cyclic form of C_4 in channel (h) is exothermic.

An equation system to find the branching fractions of C–C cleavage is set up:

$$\begin{bmatrix} I_{4C} \\ I_{2C} \end{bmatrix} = \begin{bmatrix} t & t^2 \\ 0 & 2t(1-t) \end{bmatrix} \begin{bmatrix} \alpha' \\ \beta' \end{bmatrix}, \quad (2)$$

where I_{2C} and I_{4C} are the integrated intensities of each peak in Fig. 2(a), t is the transmission probability of the grid and α' , β' are the unknown number of DR events breaking up into C_4 , and $C_2 + C_2$ fragments, respectively.

For the absolute cross-section measurement, the experimentally measured DR rate coefficient, α_m , was calculated as

$$\alpha_m = \frac{\pi r_e^2 v_e(t) v_i e^2}{L I_i(t) I_e} \frac{dN}{dt} \quad (3)$$

Here, r_e is the radius of the electron beam, v_e and v_i are the velocities of the electrons and ions in the laboratory frame, respectively, L is the length of the parallel overlap between the beams in the electron cooler, I_i and I_e are the ion and electron currents, respectively, e is the fundamental charge and dN/dt is the count rate of DR events. The final DR rate coefficient, α , was obtained after corrections were made for the space charge effect [23], collisions with electrons having higher interaction energies in the toroidal regions of the electron cooler [24] and the estimated 2 meV transversal energy spread of the electrons [24,25]. The considerably lower longitudinal energy spread was not taken into account [24]. The cross-section,

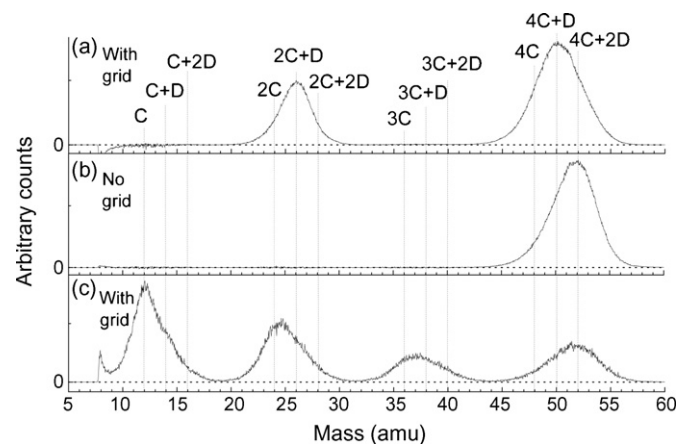


Fig. 2. Mass calibrated pulse height spectra from the branching fraction experiment of the diacetylene cation $C_4D_2^+$: (a) background corrected spectrum at ~ 0 eV collision energy with the grid in place; (b) background corrected spectrum at ~ 0 eV collision energy without the grid; (c) background obtained at $E_d = 2$ eV with a grid. Signals at less than 8 a.m.u. have been removed by the discriminator. The vertical dotted lines indicate the position of the possible fragment masses. Features below 9 a.m.u. are due to preamplifier noise.

$\sigma(v_d)$, was calculated from $\sigma = \alpha(E_d)/v_d$, where v_d is the detuning velocity used in Eq. (1). The thermal rate coefficient, $\alpha(T_e)$, was derived as a function of the electron temperature, T_e , in the interval 10–1000 K by integrating the energy-dependent cross-section over an isotropic Maxwellian electron velocity distribution:

$$\alpha(T_e) = \left(\frac{m_e}{2\pi k_B T_e} \right)^{(3/2)} \int_0^\infty v \sigma(v) \exp\left(\frac{-m_e v^2}{2k_B T_e} \right) 4\pi v^2 dv, \quad (4)$$

where k_B is the Boltzmann constant and m_e is the mass of the electron.

3. Results and discussion

3.1. Branching fractions

The results for the C–C cleavage in the DR of $C_4D_2^+$ are shown in Table 2, together with the results for the $C_4H_2^+$ isotopologue obtained at ASTRID by Angelova et al. [20].

The results from the two experiments are in reasonable agreement. Comparison between Fig. 6 in the ASTRID paper by Angelova et al. [20] and Fig. 2(a) in this paper indicates that the statistics is somewhat better in our CRYRING experiment. The differences between the results in the two experiments might be due to this, although an isotope effect cannot be ruled out. By making use of a few observations, the number of plausible contributing channels listed in Table 1 can be reduced from the original eight. The contribution from channels that would result in the appearance of $1C + xD$ and $3C + xD$ peaks ($x = 0, 1$ or 2) can be disregarded as these peaks are absent, thus channels (e), (f) and (g) are not populated. Furthermore, there are only two channels (c): $C_2D_2 + C_2$ and (d): $C_2D + C_2D$, that can contribute to the $2C + xD$ peak. A contribution from channel (c) would result in two peaks in Fig. 2(a) of equal intensity centered at the masses 24 and 28 a.m.u. from the fragments C_2 and C_2D_2 , respectively, whereas channel (d) produces two identical fragments with mass 26. The overall signal from the $2C + xD$ peak in the MCA spectrum must therefore be centered at the mass 26 a.m.u. Attempts were made to estimate the maximum possible contribution from channel (c) to the intensity of the $2C + xD$ peak. This was done by assuming the $2C + xD$ peak was made up by three peaks centered at the masses 24, 26 and 28 a.m.u. A Gaussian peak was centered on each one of the three masses and constrained such as both peaks centered at 24 and 28 a.m.u. should have the same intensity. It was further assumed that the FWHM of each Gaussian had a linear dependency of the mass. Constraints for this linearity were found by comparison with other peaks in the MCA spectra. By varying these constraints within their estimated uncertainties it was found that the contribution from channel (c) to the intensity of the $2C + xD$ peak was unlikely to exceed $\sim 10\%$.

The diacetylene cation in its ground state has experimentally been found to be close to linear with an overall length remaining almost unchanged to that of the neutral (5.90 Å) [26–29]. It thus seems unlikely that an electron capture would induce a sufficiently large bending motion in the molecule for the instantaneous

Table 2
Results of the dissociative recombination branching fraction measurement of $C_4D_2^+$ (CRYRING) and $C_4H_2^+$ (ASTRID) [20]

| | This work ($C_4D_2^+$) | ASTRID ($C_4H_2^+$) |
|-------|--------------------------|-----------------------|
| C_4 | 0.748 (16) | 0.784 (13) |
| C_3 | 0 | 0.040 (16) |
| C_2 | 0.252 (16) | 0.177 (15) |

The DR channels were grouped into those leading to retention of the C–C bonds (C_4) and those leading to cleavage of the terminal (C_3) and central (C_2) C–C bond. Estimated errors are given in the parentheses, see Section 3.1 for details.

formation of molecular deuterium as in channel (b): $C_4 + D_2$. Equally, the direct formation of a cyclic fragment, as in channel (h): $c-C_4 + D + D$, seems improbable. Channel (c): $C_2D_2 + C_2$, which involves substantial hydrogen migration is also not expected to contribute substantially to the DR reaction. Thus, the (b), (c) and (h) channels could be anticipated to give only a small, if any, contribution to the branching fractions.

If the above-mentioned assumptions are valid then only two channels remain to give a non-vanishing contribution to the DR breakup of diacetylene:



The $4C + xD$ peak in Fig. 2(a) is clearly centered at 50 a.m.u., consistent of being build up of mostly C_4D mass fragments with a slight asymmetric shape due to $C_4D + D$ and $2C_2D$ mass fragments contributing to a small unresolved peak at 52 a.m.u. With only the (a) and (d) channels taking part, α' and β' corresponds to DR events into the channels (a) and (d) with the breakup probability of $74.8 \pm 1.6\%$ and $25.2 \pm 1.6\%$, respectively, as given in Table 2. To find the errors originating from the transmission uncertainty, the grid transmission was varied within the uncertainty range, $\Delta t = 0.015(3\sigma)$ [19], while solving the equations. In addition, the background subtraction introduces an error that is not straightforward to include, although it could be expected to be minor as Fig. 2(b), after background subtraction shows no other features at lower masses. The uncertainty introduced from the background subtraction was estimated by varying the relative intensity of the $2C + xD$ peak versus the $4C + xD$ peak by 5% in both directions, a value thought to be an upper limit of the uncertainty. To best robustness, the two separate uncertainties were added to give an upper limit of the uncertainty of the given results.

If channel (c) contributes a maximum of 10% to the intensity of the $2C + xD$ peak, the branching fractions for the (a), (c) and (d) channels are approximately 75%, 2% and 23%, respectively. Thus the contribution from channel (c), if it exists, is negligible.

In the UMIST database for astrochemistry [15] from 2007, the DR of $C_4H_2^+$ is considered to occur only through channel (a), i.e., into $C_4H + H$ fragments. The Ohio State University database [30], on the other hand, includes two product channels from the titular reaction, leading to $C_4H + H$ (50%) and also $C_4 + H_2$ (50%). Both of these model input data are in disagreement with our interpretation of the experimental results, though it remains to be seen if these results have an impact on the predictions made by these models.

Unlike the acetylene cation, $HCCH^+$, where DR breaks the triple bond in 18% of the reactions [31], none of the two triple bonds in diacetylene appear to break during DR. This is in agreement with the observation that the triple bonds in diacetylene are not as weakened upon ionization as that in acetylene. The C–C bond length in acetylene increases upon ionization from 1.208 to 1.257 Å while the lengths of the terminal C–C bonds in diacetylene only change from 1.205 to 1.234 Å [27–29].

3.2. Cross-section

The cross-section, plotted in Fig. 3, was best fitted by the expression $\sigma(E) = (7.5 \pm 1.5) \times 10^{-16} \times E^{-(1.29 \pm 0.03)} \text{ cm}^2$ over the energy range $E_d = 1\text{--}100 \text{ meV}$. Higher energies were not included since there the background signal dominated the count rate, though it is noted that these energies are less relevant for colder plasmas such as those encountered in the interstellar medium and combustion processes. The thermal rate coefficient in the interval 10–1000 K was deduced from the cross-section

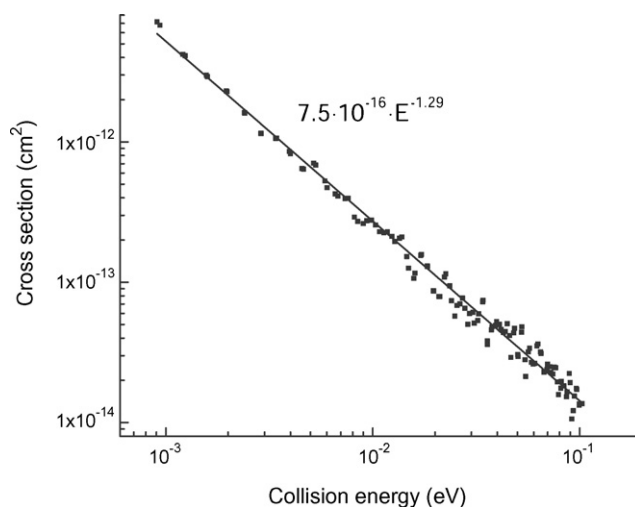


Fig. 3. The energy-dependent cross-section of the DR of the diacetylene cation $C_4D_2^+$. The straight line gives the fit of the cross-section between 1 and 100 meV detuning energy.

as $\alpha(T) = (1.10 \pm 0.15) \times 10^{-6} \times (T/300)^{-(0.79 \pm 0.03)} \text{ cm}^3/\text{s}$. The quoted errors include both statistical and systematical errors and were estimated by varying the experimental parameters within their uncertainty intervals during the analysis and represent a 1σ interval.

The DR thermal rate coefficient for the diacetylene cation is comparatively high. However, molecules of a similar size and mass have shown a tendency to have relatively large thermal rate coefficients, as seen for DC_3N^+ , CD_3CDO^+ , $C_3H_7^+$, $C_4H_5^+$ and $C_5H_9^+$ [32–35]. All these ions have a mass in the neighborhood of diacetylene and are reported to have thermal rate coefficients in the interval from 8×10^{-7} to $1.5 \times 10^{-6} \text{ cm}^3/\text{s}$ at room temperature. Compared with the acetylene cation ($C_2H_2^+$) [31], the diacetylene cation has a thermal rate coefficient nearly four times higher but shows a similar thermal power dependency (0.79 versus 0.76). The temperature dependency for the diacetylene cation is close to that found for most of the hydrocarbons studied, i.e., between 0.6 and 0.8 [36].

In some hydrogen-containing molecules the thermal DR rate coefficients of the light hydrogen isotopologues differ significantly from the deuterated isotopologue, e.g., for NH_4^+/ND_4^+ [37], H_3O^+/D_3O^+ [19] and H_2O^+/HDO^+ [38]. Conversely, in the DR of some heavier hydrogenated molecules, e.g., CH_2OH^+/CD_2OD^+ [39] and $CH_3OH_2^+/CD_3OD_2^+$ [40] such an effect was not observed to be significant. Therefore the thermal rate coefficients of $C_4D_2^+$ are expected to be equivalent to that of its isotopologue $C_4H_2^+$.

Both the UMIST [15] and the Ohio State University databases [30] employ the same DR thermal rate coefficient for $C_4H_2^+$, $\alpha(T) = 3 \times 10^{-7} \times (T/300)^{-0.5}$, which is something of a standard value in use for unknown DR thermal rates. The use of this expression gives a thermal rate at room temperature that is almost 3.5 times lower than the value reported here.

At 10 K, a temperature similar to that of a cold dense molecular cloud, this deviation from the measured value increases to a factor of 10.

Szczepanski et al. [41] reported on the laboratory identification of the vibrational frequencies for the C–H and the terminal C–C stretching modes in the diacetylene cation, $C_4H_2^+$. This principally enables the search for the diacetylene cation in the interstellar medium through IR observations although the expected low abundance of the ion, which can partly be ascribed to the large cross-section for DR at low temperatures, will complicate any attempt of detection.

No clear distinction is made between the neutral diacetylene and its isomer butatrienylidene in the previously mentioned databases [15,30]. Therefore, it is not straightforward to estimate the influence of the results presented in this paper on the carbon chemistry in a model of a molecular cloud, which uses the reactions listed in e.g., the UMIST database [15].

3.3. Possible contamination

In our experiment there was a possibility of contamination from the deuterated propane cation ($C_3D_8^+$), which has the same mass as deuterated diacetylene. We believe this contamination was negligible based on the following observation: The result from the branching fraction experiment of $C_3H_8^+$, made by Angelova et al. [42], is expected to be close to that of $C_3D_8^+$, consistent with the observations that differences of branching fractions between isotopologues are rare. Thus, in our experiment, the DR of $C_3D_8^+$ would have given rise to three peaks, $C+yD$, $2C+yD$ and $3C+yD$ ($y=0-8$), in the MCA spectrum shown in Fig. 2(a), with an intensity ratio of approximately 2:2:7, which is inconsistent with our observations.

Although the diacetylene cation can reasonably be expected to be the dominant species in the experiment, other isomers of this ion might also have been present in the ion beam, since our setup does not allow the selection of specific isomers. For the parent molecule (C_4D_2), a variety of cyclic isomers have been proposed to exist [43–45], although the only other isomer detected, to the best of our knowledge, is butatrienylidene, H_2CCCC [46]. Mabry and Johnson [47] presented a computational study of diacetylene isomers in which the lowest one, butatrienylidene, was calculated to be 2 eV higher in energy than diacetylene. According to the authors there was no facile connection from other isomers (including diacetylene) to this species. An efficient production of the butatrienylidene cation by ionization of neutral butatrienylidene produced in the discharge (e.g., by DR of $C_4D_3^+$) seems unlikely given the timescale of the ion production in the hollow cathode. Nevertheless, butatrienylidene has been produced in discharges through both acetylene and diacetylene [46,48]. In a charge-reversal experiment, Goldberg et al. [49] indirectly showed a minimal lifetime of 4 μ s for the butatrienylidene cation and thus its presence in both the present study as well as the former investigation of the DR of $C_4H_2^+$ at ASTRID by Angelova et al. [20] cannot be excluded.

If there existed a considerable amount of butatrienylidene in the two ion beams at ASTRID [20] and CRYRING, two explanations of the similar branching ratios exists. Either the isomeric fractions must have been similar in size in both experiments or both isomers show quite similar DR branching fractions. The first explanation is unlikely due to the use of different precursor molecules at ASTRID (*n*-butane) [20] and CRYRING (butadiene), respectively, and the second one because of the largely different geometry of the ions, which should lead to a considerable change of product branching fractions. It is more plausible to assume that the contaminations of the ion beam with other isomers than the diacetylene cation were minute.

3.4. Conclusions

We interpret the result from our DR experiment that $C_4D_2^+$ predominantly breaks up into either C_4D+D or C_2D+C_2D with a probability of 3:1 at a relative collision energy close to 0 eV. The deduced DR thermal rate coefficient, $\alpha(T_e)=1.10 \times 10^{-6} \times (T/300)^{-0.79}$, is close to 10 times higher than the value listed for 10 K in the UMIST [15] as well as in the Ohio State University database [30].

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