Dissociative electron attachment to HCCCN

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Abstract. Dissociative electron attachment to cyanoacetylene (propiononitrile) HCCCN has been observed in the electron energy range 0–12 eV. Negative ions are formed in two main bands with maxima at ∼1.6 eV (CCCN⁻) and ∼5.3 eV (CCCN⁻, CN⁻, HCC⁻ and CC⁻). There are also weaker resonances which lead to dissociative electron attachment to form CN⁻, HCC⁻ and CC⁻ with a maximum intensity at ∼8.1 eV and CCCN⁻, CN⁻ and CC⁻ at ∼11.2 eV. A trace of CCN⁻ is observed at ∼9.1 eV. The positions of the main dissociative attachment bands observed are close to positions of π* resonances recently calculated by Sommerfeld and Knecht. Calculations have also been performed in this work, which confirm the position of the π* orbitals. The electron affinity of the CCCN radical is determined as 4.59 ± 0.25 eV from the threshold for CCCN⁻ formation at 1.32 ± 0.15 eV. Dissociative electron attachment to this molecule will act as a source of negative ions in extraterrestrial environments where electrons are present with more than 1.3 eV energy.

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1. Introduction

The cyanoacetylene, or propiolonitrile, molecule HCCCN has been widely observed. It has been detected in the atmosphere of Titan [1], comets [2, 3], interstellar gas clouds [4, 5] and circumstellar envelopes [6]. Spectra of vibrationally excited cyanoacetylene molecules have been used to derive physical properties of a protoplanetary nebula [7]. There has also been tentative detection of HCCCN in external galaxies [8]. The presence of free electrons in these environments is a motivation for this study of low energy electron collisions with cyanoacetylene.

In the present work, dissociative electron attachment to cyanoacetylene has been observed. Dissociative electron attachment to a general molecule AB can be represented by

$$\text{AB} + e^- \rightarrow (\text{AB}^-)^* \rightarrow \text{A} + \text{B}^-,$$  \hspace{1cm} (1)

where a free electron $e^-$ attaches to form $(\text{AB}^-)^*$, a temporary negative ion, which can dissociate to give the neutral and negatively charged fragments A and B$^-$. The temporary negative ion can also loose an electron by autodetachment to leave the molecule intact.

The cyanoacetylene molecule has a conjugated $\pi$-system with two doubly degenerate unoccupied $\pi^*$ orbitals, which can accommodate an additional electron to form a temporary negative ion. Sommerfeld and Knecht [9] have calculated resonance energies for electron attachment into these empty orbitals. The dipole moment of this linear molecule, 3.72 Debye, is large enough to support dipole bound anionic states. In fact, Sommerfeld and Knecht have calculated the energies of dipole bound HCCCN$^-$, in the linear geometry of neutral HCCCN, and valence bound HCCCN$^-$, in its distorted nonlinear equilibrium geometry, to be almost identical. They predict the dipole bound state could act as an efficient ‘doorway’ to formation of the valence anion [9].

One proposed mechanism for the formation of cyanoacetylene in the interstellar medium proposed by Petrie and Herbst [10] is by associative detachment between atomic hydrogen and
the CCCN\(^{-}\) ion

\[
H + \text{CCCN}^{-} \rightarrow \text{HCCCN} + e^{-}.
\]  

(2)

It is interesting to note that this reaction is equivalent to dissociative electron attachment in reverse. Petrie and Herbst have calculated the rate of formation of CCCN\(^{-}\) by radiative attachment to the CCCN radical

\[
\text{CCCN} + e^{-} \rightarrow (\text{CCCN}^{-})^* \rightarrow \text{CCCN}^{-} + h\nu.
\]  

(3)

They predict a ratio of CCCN\(^{-}\) ions to neutral CCCN molecules of about 1\% from the rates of processes (2) and (3).

Other proposed routes of cyanoacetylene synthesis in interstellar space include neutral–neutral and positive ion–neutral reactions between hydrocarbons and nitriles [11, 12].

The possible role of cyanoacetylene in prebiotic synthesis of biological molecules has been discussed. Cytosine, one of the nucleobases of DNA and RNA, can be produced in a solution of HCCCN and OCN [13, 14]. The importance of this synthesis, however, under conditions of the early Earth has been questioned [15].

To our knowledge, the only previously reported experimental investigation of dissociative electron attachment to HCCCN is that of Dibeler et al [16] who reported appearance energies of 3.5 eV for CCCN\(^{-}\) and 6.0 eV for CN\(^{-}\).

2. Method

2.1. Synthesis of cyanoacetylene

The cyanoacetylene sample was synthesized with the procedure of Miller and Lemmon [17]. Methylpropionate, HCCCOOH\(_3\) reacted with ammonia

\[
\text{HCCCOOCH}_3 + \text{NH}_3 \rightarrow \text{HCCCONH}_2 + \text{CH}_3\text{OH}
\]  

(4)

to give propiolamide HCCCONH\(_2\). In the second step of the reaction, the amide was dehydrated with phosphorous pentoxide to give cyanoacetylene or propionitrile

\[
\text{HCCCONH}_2 \xrightarrow{\text{P}_2\text{O}_5(-\text{H}_2\text{O})} \text{HCCCN}.
\]  

(5)

Methylpropionate (≈6 g) was added slowly dropwise over a period of an hour to a large excess of liquid ammonia (≈40 ml), stirred in a round bottomed flask and at its boiling point (−33°C). The white precipitate of propiolamide, HCCCONH\(_2\), was separated from the ammonia and methanol by-product by pumping on the mixture after all the methylpropionate had been added. When all visible signs of ammonia and methanol had been removed, the amide was dried under vacuum for at least 1 h more. The melting point of the amide observed, 50 to 55°C, was a little lower than that observed by Miller and Lemmon, 60 to 61°C, but this intermediate product was used without further purification. The reaction yield of ≈90\% was also a little lower than the ≈100\% reported by Miller and Lemmon [17].

In the second step of the synthesis, 1.5 g of the amide was mixed with ≈5 g of P\(_3\)O\(_2\) and ≈7 g of acid washed sand. This mixture was heated under vacuum to ≈230°C. As the mixture was heated, it turned yellow then darkened first to orange, red and finally black. Generation of
the gaseous product was clearly observed from $\sim 210^\circ$C. The product was collected in a trap immersed in a slush bath of ethanol and dry ice at $\sim -78^\circ$C. A second trap immersed in liquid nitrogen was also employed in front of the pump. A small quantity, $<5\%$, of the product passed through the first trap and was collected in the second. The product was collected in the first trap as a colourless solid. It was observed that the cyanoacetylene rapidly turned a deep blue or even black at room temperature. It appeared that the presence of air accelerated this process, but this was not investigated in detail. Presumably the colour is due to polymerization of the cyanoacetylene to form a conducting polymer. The reaction yield was not determined due to difficulty of weighing the product; at low temperature ice forms on the sample tube and the product goes off as it warms up. Miller and Lemmon [17] reported a yield of 81\% for the second step. The first trap included taps to isolate the product under vacuum. This trap was stored in liquid nitrogen or otherwise cooled.

The appearance energies of positive ions from cyanoacetylene were measured by recording mass spectra at electron impact energies of 10 to 30 eV with the mass spectrometer described below. The purity of the product was confirmed by comparison of these appearance energies with values reported by Dibeler et al [16] and Harland [18]. HCCCN has an ionization potential of 11.6 eV, but fragments appear above $\sim 18$ eV, so the mass spectrum is quite distinctive with just the parent HCCCN$^+$ ion at electron energies below 18 eV. The expected positive ion fragments were observed above 18 eV.

2.2. Electron attachment measurements

The spectrometer used to investigate electron attachment to cyanoacetylene has been described previously [19] and is shown in figure 1. Briefly, the electron attachment spectrometer consists...
of a trochoidal electron monochromator and a time-of-flight spectrometer. The electrons emitted
from a filament pass through the monochromator guided by a magnetic field, which enables the
electron beam energy to be reduced to close to 0 eV in the interaction region. The strength of
the magnetic field was varied between 20 and 80 Gauss. The deflection plate in the Faraday cup
moves the electrons off-axis so that they cannot be guided back into the interaction region by
the magnetic field. The electron energy was set by floating the electron gun potentials relative to
the interaction region.

Fragment anions formed in dissociative electron attachment are observed with a time-of-
flight mass spectrometer. The ion repeller pushes ions from the source region into the acceleration
region where they are further accelerated before they pass through the drift region and strike the
multichannel plate detector. At higher electron energies, positive ions are formed by electron
impact ionization. The potentials of the mass spectrometer can be reversed to detect positive
ions. The electron energy resolution (FWHM) was determined using the attachment resonance
of SF₆ at 0 eV to be approximately 300 meV.

The overall experiment is pulsed. A plate near the filament is pulsed to send short, ∼1 µs,
pulses of electrons through the interaction region. After the electrons have left the interaction
region, the ion repeller is pulsed to push ions towards the ion detector. The repetition rate of this
pulse scheme is 12 kHz. The apparatus is operated under conditions where at most one ion is
detected per ten cycles to minimize any paralysis of the detector due to the arrival of two ions at
the same time.

The experiment was carried out at room temperature. The sample was held at −2 to −5°C
near the apparatus in an ice salt bath. The vapour pressure of cyanoacetylene at this temperature
is ∼0.1 bar. Cyanoacetylene entered the interaction region effusively.

2.3. Molecular orbital calculations

The energies at which electrons attach into unoccupied orbitals can be determined theoretically
with Koopmans’ theorem and molecular orbital calculations [20]–[22]. From Koopmans’ theorem
[23], the kinetic energy required for an electron to attach into a particular unoccupied molecular
orbital is equal to the orbital energy, but this is an approximation [20] because, for example, it is
assumed the electronic configuration of the molecule is not effected by the addition of an extra
electron into an unoccupied molecular orbital. More sophisticated methods include R-matrix
theory, see e.g. [24, 25], and ab initio calculations with complex absorbing potentials, see e.g.
[26]–[28], where calculations are made of the negatively charged molecular ion.

The larger the basis set used, the more accurate the calculated molecular orbital energies will
be. There is the problem, however, that the calculated unoccupied molecular orbitals will include
so called ‘Orthogonalized Discretized Continuum’ solutions [29, 30], which can be thought of
as solutions to the Schrödinger equation for an electron confined within the basis just like a
particle in a box. Discretized continuum solutions do not correspond to unoccupied orbitals
of the molecule; they are ‘artefacts’ of the calculation. The basis set restricts the electrons to
certain volume surrounding the molecule; hence the analogy with the well-known quantum
mechanical problem of a particle confined to a box. The energy of wavefunctions for a particle
in a box, of course, depend on the size of the box. In the same way, the size of the basis set has a
large influence on the energies of the discretized continuum solutions. Large basis sets will give
more discretized continuum solutions at low energies than smaller basis sets. Therefore, large
basis sets are desirable because the molecular orbital energies are more accurate, but they are
undesirable because they give more discretized continuum orbitals at low energy, which can be confused with unoccupied molecular orbitals.

In calculations with large basis sets, such as those of Sommerfeld and Knecht [9], it is necessary to identify which unfilled states are unoccupied molecular orbitals and which are discretized continuum solutions. The calculations of Sommerfeld and Knecht also include a complex absorbing potential. This absorbing potential can be thought of as ‘absorbing’ the electron at large distances from the molecule, which facilitates calculation of unbound resonant states of the negative ion.

A different and simpler approach is to use a small or minimal basis set. The discretized continuum solutions are relatively high in energy with small basis sets and so the lowest calculated empty states will usually be the lowest unoccupied molecular orbitals. The orbital energies calculated with smaller basis sets, of course, are less accurate and semiempirical scaling is employed to relate calculated energies to vertical electron attachment energies [20]. The same scaling parameters will frequently map calculated data to experimental results for a series of related molecules [21]. This is the approach taken here.

*Ab initio* Hartree–Fock calculations have been performed with the GAMESS program [31]–[33] to predict the energies of the unoccupied molecular orbitals of HCCCN. The geometry of the HCCCN molecule was optimized using RHF/6–31G* level of theory. Hartree Fock molecular orbital calculations were then performed with the STO–3G, 3–21G and 6–31G* basis sets at the equilibrium geometry. Similar calculations have also been performed on the molecules HCN, CH3CN and CH2CHCN to provide a dataset for scaling the calculated unoccupied molecular orbitals to experimentally observed energies.

### 3. Results and discussion

#### 3.1. Dissociative electron attachment

A two-dimensional representation of the experimental data is shown in figure 2. The vertical axis is electron energy and the horizontal axis is the time-of-flight of ions in the mass spectrum. The positions of the ions \( \text{CC}^- \), \( \text{HCC}^- \), \( \text{CN}^- \), \( \text{CCN}^- \) and \( \text{CCC}^- \) are indicated. The most striking
The feature of the spectrum is dissociative electron attachment at 5 to 6 eV where CC$^-$, HCC$^-$, CN$^-$ and CCCN$^-$ are formed. CCCN$^-$ is also observed at about 1.5 eV and there are weaker attachment processes above 7 eV.

Figure 3 shows the integrated signal of CCCN$^-$, CN$^-$, HCC$^-$ and CC$^-$, as a function of electron energy. Error bars of plus or minus one standard deviation are included on all data points, but are frequently inside the circular data points, particularly for CN$^-$ and CCCN$^-$.

The peak positions and widths of dissociative electron attachment processes observed are summarized in Table 1. All four fragment anions are most intense at 5 to 6 eV electron energy. The positions of the maxima appear to shift to higher energy from $5.08 \pm 0.15$ eV for CCCN$^-$ to $5.57 \pm 0.15$ eV for HCC$^-$. The position of the dissociative electron attachment peak for formation of CCCN$^-$ at lower energy is $1.56 \pm 0.15$ eV. Closer examination of this dissociative electron attachment band, see Figure 4, reveals an asymmetric shape. The shape of the rise of this dissociative electron attachment band is as steep as can be expected with the present electron beam energy resolution. The electron beam energy resolution calculated assuming that the actual onset is vertical is $\sim 200$ meV, better than the resolution measured at 0 eV with SF$_6$. Thus, it appears that the steep rise is at the position of the thermodynamic limit for formation of CCCN$^-$. The present experimental value for this limit is $1.32 \pm 0.15$ eV measured from the electron energy half way up the rise. The relationship between this experimental threshold and the two thermodynamic thresholds for formation of CCCN$^-$ shown in Table 1 is discussed below in subsection 3.4.

Therefore, the position of the dissociative electron peak energy at 1.56 eV is not related to the peak of the electron attachment.
Table 1. Energetics of dissociative electron attachment (DEA) to HCCCN. All values in eV. See text for references.

| Anion B⁻ | Neutral A | D(A – B) | EA(B) | Calculated AE(B⁻) | DEA peak position | DEA peak width (FWHM) |
|----------|-----------|----------|-------|--------------------|-------------------|-----------------------|
| CCCN⁻    | H         | 5.91 ± 0.20 | 2.39  | 3.52 ± 0.20        | 1.56 ± 0.15       | 0.78 ± 0.20           |
| CCCN⁻    | H         | 5.91 ± 0.20 | 4.538 | 1.37 ± 0.20        | 1.56 ± 0.15       | 0.78 ± 0.20           |
| CCCN⁻    | H         |           |       | 5.08 ± 0.15        |                   | 1.56 ± 0.20           |
| CN⁻      | HCC       | 6.37 ± 0.09ᵃ | 3.862 ± 0.005ᵇ | 2.51 ± 0.09       | 5.28 ± 0.15       | 1.66 ± 0.20           |
| CN⁻      | HCC       |           |       | ~8.2               |                   |                       |
| CN⁻      | HCC       |           |       | ~11.5              |                   |                       |
| HCC⁻     | CN        | 6.37 ± 0.09 | 2.969 ± 0.006ᵇ | 3.40 ± 0.09       | 5.57 ± 0.15       | 1.86 ± 0.20           |
| HCC⁻     | CN        |           |       | 8.11 ± 0.15        |                   |                       |
| CC⁻      | HCN       | 7.18 ± 0.22 | 3.273 ± 0.008ᵇ | 3.91 ± 0.22       | 5.47 ± 0.15       | 1.66 ± 0.20           |
| CC⁻      | HCN       |           |       | ~8.3               |                   |                       |
| CC⁻      | HCN       |           |       | ~11.6              |                   |                       |
| CCN⁻     | CH        | 8.3 ± 0.4  | >2.3  | <6.0               | 9.1 ± 0.3         | 1.7 ± 0.3             |
| H⁻       | CCCN      | 5.91 ± 0.20 | 0.754ᵇ | 5.16 ± 0.20ᶜ      | (not observed)     |                       |

ᵃ Calculated in [34].
ᵇ Taken from the NIST webbook, see [35].
ᶜ To illustrate the possibility of this dissociation process.

Figure 4. Expanded view of the lowest energy dissociative electron attachment band of CCCN⁻ from HCCCN.

resonance, but rather depends on the threshold energy for CCCN⁻ formation and the instrumental resolution. The electron attachment resonance responsible for this dissociation process is most likely to have a peak energy lower than 1.56 eV.

Above 7 eV, there is another dissociative electron attachment band at 8 to 9 eV which is most visible in the HCC⁻ intensity in figure 3. It is also visible in the CN⁻ signal and weakly in CC⁻, but there is no production of CCCN⁻. Higher in energy at 11.2 eV, another resonance leads to formation of CCCN⁻, CN⁻ and (weakly) CC⁻, but no HCC⁻.

A very weak dissociative attachment process yielding H⁻ anions was also detected with a maximum at 6.5 eV and an appearance energy of approximately 5 eV. This band has been
Figure 5. Spectra of ions with mass 35 and 38; $^{35}\text{Cl}^-$ and CCN$^-$. Cl$^-$ is formed from CCl$_4$ background with its characteristic peak at 0 eV. CCN$^-$ is formed from HCCCN. These ion spectra have an ‘artefact’ band of similar intensity between 4 and 6 eV (see text).

assigned to dissociative electron attachment to background water in the experimental apparatus as these values are in agreement with previously reported measurements for water vapour [36]. There was probably also a trace of water in the sample. A weaker O$^-$ signal consistent with water was also observed and a trace of O$^-$ may just be visible on the top left-hand-side corner of figure 2; the time-of-flight of O$^-$ ions is $\sim$2600 ns. The intensity profile of the weak O$^-$ signal is in agreement with previous water measurements [36]. The possibility that the H$^-$ signal from water masks a very weak H$^-$ signal from HCCCN cannot be fully precluded. Any H$^-$ signal from HCCCN would be at least one or two orders of magnitude smaller than the intensity of the CC$^-$ and HCC$^-$ ions observed.

Careful measurement was made of the variation of anion intensity with pressure of the sample in the apparatus. All signals were found to vary in a linear fashion apart from the H$^-$ due to background water. No evidence was found for any secondary reactions in the ion source.

A signal at mass 38, which must be due to CCN$^-$, is observed at 9.1 eV about two orders of magnitude weaker than CC$^-$ and HCC$^-$. Also just visible in figure 2 are very weak signals of $^{33}\text{Cl}^-$ and $^{37}\text{Cl}^-$ at 0 eV with flight times just above 3500 ns from CCl$_4$ desorption from the walls of the gas inlet system. Integration over masses 35 and 38 is shown in figure 5. The Cl$^-$ peak at zero energy is clearly visible. Both ion channels have an ‘artefact’ band between 4 and 6 eV, which is part of a band of weak signal visible in the two-dimensional plot in figure 2 between the CN$^-$ and CCCN$^-$ ions. The intensity of this weak signal is less than 1% of the CN$^-$ and CCCN$^-$ peak intensities. This weak signal may be due to cross-talk in the timing electronics from the intense CN$^-$ and CCCN$^-$ signals or detector double pulsing or a combination of the two. Dissociative electron attachment to form CCN$^-$ at 9 eV is clearly visible above the noise level, but the uncertainties in the peak position and width in table 1 reflect the quality of the data. The integrated $^{35}\text{Cl}^-$ signal is shown with the CCN$^-$ signal to illustrate that the ‘artefact’ band is the same for both ions and that no CCN$^-$ is observed between 4 and 6 eV. The peak of the integrated $^{35}\text{Cl}^-$ signal at zero energy also confirms the energy calibration of the experimental data, which was made independently with SF$_6$.

Finally, no HCCCN$^-$ parent anion signal was observed in this experiment. Sommerfeld and Knecht [9] calculated positive electron affinities for dipole bound HCCCN$^-$ in the equilibrium...
geometry of neutral HCCCN and valence bound HCCCN\(^{-}\) in its equilibrium geometry. One would, however, expect dipole bound HCCCN\(^{-}\) to be formed in collisions of cyanoacetylene molecules with Rydberg states where the Rydberg electron is bound by \(\sim 9\) meV, which is the electron affinity of the dipole bound state, rather than in collisions with low energy free electrons.

### 3.2. Assignment of the electron attachment resonances which lead to dissociation

Sommerfeld and Knecht [9] predicted resonances due to electron attachment into \(\pi^*\) orbitals at 0.7 and 6.2 eV. These energies are close to the energies of the dissociative electron peaks observed at 1.56 eV (CCCN\(^{-}\)) and 5.1 to 5.6 eV (CCCN\(^{-}\), CN\(^{-}\), HCC\(^{-}\) and CC\(^{-}\)).

The position of the dissociative electron attachment peak at 1.56 eV appears to be due to the thermodynamic threshold for CCCN\(^{-}\) formation and the electron attachment resonance peak is most likely lower in energy as discussed in subsection 3.1. Therefore, the electron attachment resonance that leads to formation of CCCN\(^{-}\) here could be the first \(\pi^*\) attachment channel predicted by Sommerfeld and Knecht near 0.7 eV. If this is the case then the observed dissociative electron attachment signal is due to the high energy tail of this resonance.

The position of the second \(\pi^*\) attachment channel predicted by Sommerfeld and Knecht [9] at 6.2 eV, is significantly higher than the experimentally observed dissociative electron attachment peak maxima between 5.1 and 5.6 eV. They expected their calculation to give a value a few tenths of an eV higher than the experimental value, but the separation here is \(\sim 1\) eV. Furthermore, in this experiment, of course, the resonance is not probed directly, but rather fragment ion formation from temporary negative ion resonances is observed. The rate of autodetachment, where the temporary negative ion loses an electron prior to dissociation, generally increases with increasing energy and so the probability of dissociation will be highest at lower energies. This is the root cause of the effect known as the ‘survival probability shift’, see e.g. [37], where ‘resonance peaks’ observed by dissociative electron attachment are lower in energy than the positions of resonances observed, for example, with electron transmission experiments [38]. Therefore, the survival probability shift and the uncertainty predicted in the calculated values could perhaps explain the difference in energy between the observed experimental ‘resonances’ at 5.1 to 5.6 eV and the calculated resonance energy of 6.2 eV.

In this work, molecular orbital calculations have been performed to compare with the experimental data and the calculations of Sommerfeld and Knecht. \textit{Ab initio} Hartree–Fock calculations of HCCCN have been performed with the GAMESS program [31]–[33] as described in subsection 2.3. The related molecules HCN, CH\(_3\)CN and CH\(_2\)CHCN have also been calculated to generate a dataset for scaling the calculated unoccupied molecular orbitals to experimentally observed electron resonance energies from electron transmission spectroscopy [30, 39], which are generally close to dissociative electron attachment peak energies for these molecules [40]–[42]. Calculations with the three basis sets used, STO–3G, 3–21G and 6–31G\(^*\), all showed good correlation between the calculated unoccupied molecular orbital energies and the experimentally observed resonance positions. The best correlation was obtained with STO–3G, the smallest basis set. Calculations employing STO–3G were also found to give the best correlation for chloroalkanes [21]. The correlation between energies calculated with the STO–3G basis set and experimental energies is shown in figure 6.

The scaled results of calculations with all three basis sets are presented in table 2. The position of the two \(\pi^*\) orbitals are reasonably consistent with all the basis sets and also close to the energies of Sommerfeld and Knecht. It is interesting to note that the energies of the second
Figure 6. Scaling of molecular orbital energies calculated with the STO–3G basis set (see text). The straight line is given by \( AE = 0.67 \text{ MOE} - 4.07 \), where \( AE \) is the attachment energy and MOE is the calculated molecular orbital energy. The solid squares indicate the positions of calculated molecular orbital energies of previously observed electron attachment resonances from the dataset of similar compounds. These points have been used to determine the best fit straight line for semiempirical scaling of calculated molecular orbital to electron attachment resonance energies. The open circular markers placed on the best fit line illustrate the scaling process for the \( \pi^* \) orbitals of HCCCN.

Table 2. Calculated energies of HCCCN unoccupied molecular orbitals after semiempirical scaling.

| Molecular orbital | STO–3G | 3–12G | 6–31G\* | Sommerfeld and Knecht energy (eV) |
|-------------------|--------|--------|---------|----------------------------------|
| \( \pi_1 \)       | 0.5    | 0.5    | 0.5     | 0.7                              |
| \( \sigma_1^* \)   | 3.4    | 3.1    |         |                                  |
| \( \pi_2 \)       | 5.1    | 5.2    | 5.5     | 6.2                              |
| \( \sigma_1^{*\text{STO-3G}} \) | 5.3   |         |         |                                  |
| \( \sigma_2^* \)   | 5.6    | 5.3    |         |                                  |
| \( \sigma_2^{*\text{STO-3G}} \) | 8.1   |         |         |                                  |

The \( \pi^* \) orbital obtained here, between 5.1 and 5.5 eV, are very close to the experimental dissociative electron attachment peak energies. The energies of the \( \sigma^* \) orbitals, however, depend sensitively on the basis set chosen. The shapes of these orbitals also vary widely with basis set, which may suggest that they are discretized continuum solutions or a mixture of discretized continuum and \( \sigma^* \) unoccupied molecular orbitals. Similar problems have been encountered previously in the calculation of C–C and C–H \( \sigma^* \) orbitals of chloroalkanes [21]. If the \( \sigma^* \) solutions of the calculation are continuum states, this would explain why they were not identified by Sommerfelt.
and Knecht. The $\sigma^*_1$ and $\sigma^*_2$ orbitals have similar energies, but quite different shapes. Therefore, it appears unlikely that electron attachment into a $\sigma^*$ orbital close to 5 eV contributes to the main dissociative electron attachment bands between 5.1 and 5.6 eV, but this possibility cannot be ruled out.

The electron attachment resonances responsible for the dissociative electron attachment bands observed above 7 eV cannot be identified from the present calculations or those of Sommerfelt and Knecht. It is possible that they are due to ‘core excited’ resonances, where one of the molecular electrons is excited at the same time as the electron attaches to the molecule. For example, one of the electrons from the $\pi$ HOMO could be excited to the LUMO and the extra free electron could attach into the LUMO to give a core excited resonance with $\Pi$ symmetry.

In summary, comparison of the experimental data with the calculations of Sommerfeld and Knecht and those made here suggest that dissociative electron attachment processes observed at 1.6 and 5.1–5.6 eV are due to electron attachment to the two unoccupied $\pi^*$ orbitals of HCCCN. The electron attachment resonances responsible for dissociative electron attachment processes above 7 eV have not been identified from these calculations.

3.3. Fragmentation dynamics

3.3.1. Dissociation at 1.6 eV. On the basis that the extra electron attaches into a $\pi^*$ orbital at 1.6 eV, the electronic state of the HCCCN$^-$ temporary negative ion will be $^2\Pi$ in the $C_{\infty v}$ point group. The combined electronic state of the ground state products observed at 1.6 eV CCCN$^-$ ($^1\Sigma^+$) + H ($^2S$) is $^2\Sigma^+$ in $C_{\infty v}$. Therefore, dissociation of HCCCN$^-$ to CCCN$^-$ + H at 1.6 eV is symmetry forbidden under $C_{\infty v}$ symmetry, namely with linear geometry. The symmetry of the molecule, however, drops to $C_s$ if it is bent, but retains one reflection plane of symmetry. Under $C_s$ symmetry, the $^2\Pi$ HCCCN$^-$ resonance is split into two components, $^2A'$ and $^2A''$, and the $^2\Sigma^+$ product state becomes $^2A'$. Therefore, dissociation can proceed at 1.6 eV on distortion of the parent anion to $C_s$ symmetry through the $^2A'$ component of the initially $^2\Pi$ resonance. From the point of view of the molecular orbitals, the doubly degenerate $\pi^*$ orbital is split by distortion into a ‘$\pi$’ type orbital above and below the plane of the molecule of symmetry $A''$ and a ‘$\sigma$’ type orbital of symmetry $A'$.

Two possible causes of molecular distortion are considered; firstly, distortion of the neutral molecule prior to electron attachment, and secondly, distortion of the molecular anion in the resonance state.

The neutral molecule could be distorted prior to electron attachment by one of the doubly degenerate vibrational bending modes, which have low frequencies due to the length of the molecule. The lowest bending frequencies are 220, 500 and 663 cm$^{-1}$ [43]. It is estimated that $\sim$40% of HCCCN molecules at laboratory temperature will be in the ground vibrational state, $\sim$25% will have one quantum of vibration in the lowest bending mode and the remainder will be in higher vibrational states. Therefore, over half of the neutral HCCCN target molecules will be distorted by vibration excitation.

The Renner–Teller effect complicates the vibrational structure of linear molecules in degenerate electronic states, such as the $^2\Pi$ HCCCN$^-$ resonance, and can cause them to have a bent equilibrium geometries [44]. It is similar to the Jahn–Teller effect, which causes nonlinear molecules in degenerate electronic states to have distorted equilibrium geometries where the distortion breaks the degeneracy of the electronic state [45, 46]. In contrast to the Jahn–Teller effect, however, the Renner–Teller effect for linear molecules may or may not cause
the equilibrium geometry to be distorted into a bent configuration where the degeneracy of the electronic state is broken [44, 47]. Thus in general, $^2A'$ and $^2A''$ states under $C_3$ may have a common linear equilibrium geometry at the point where they combine to form a $^2\Pi$ state under $C_{\infty v}$. Alternatively, one or both of the $^2A'$ and $^2A''$ states may have a bent equilibrium geometry.

In the case of the $^2\Pi$ resonance of HCCCN− observed here at 1.6 eV, the valence anion calculations of Sommerfeld and Knetch are helpful [9]. They calculated that the equilibrium geometry of the valence anion has $C_3$ symmetry with a trans-bent structure [9]. Furthermore, they predict the ground electronic state to be $^2A'$. This ground $^2A'$ state will correlate adiabatically to the $^2\Pi$ resonance of HCCCN− considered here. Therefore, it is likely that after electron attachment into the lowest $\pi^*$ orbital the molecule will immediately distort towards the equilibrium geometry of the valence anion in the $^2A'$ electronic ground state, which is the correct symmetry for dissociation. Very fast molecular distortion on the femtosecond timescale caused by the Renner–Teller effect has been observed for CO$_2$ [48] and N$_2$O [49] molecules in $\Pi$ electronic states generated by excitation of a 1s core electron into a $\pi^*$ orbital. The Jahn–Teller effect has been considered theoretically for transient resonant states [50], but the authors are not aware of a similar study for the Renner–Teller effect in short-lived species.

The details of the dissociation mechanism through the $^2A'$ resonant electronic state are not known, but may include avoided crossings with states arising from attachment of the electron into $\sigma^*$ orbitals. Potential energy surface calculations of the resonant states may shed light on the dissociation process. For example, calculation with the complex absorbing potential method has confirmed the predicted crossing between states arising from electron attachment into ‘$\pi^*$’ and ‘$\sigma^*$’ orbitals of chloroethene (vinyl chloride) [51]. Such calculations are beyond the scope of the present work.

In summary, fragmentation to form CCCN− + H is not allowed in linear geometry from the $^2\Pi$ resonant state at 1.6 eV, but is allowed if the molecule is bent. The neutral ground state may be bent due to population of low frequency bending modes prior to electron attachment and the anionic resonant state may be bent rapidly due to the Renner–Teller effect.

Finally, CCCN− is the only ion observed in this dissociative electron attachment band at 1.6 eV because it is the only energetically allowed fragment ion, see table 1 and subsection 3.4.

3.3.2. Dissociation at 5.1–5.6 eV. It appears that at 5.1–5.6 eV, the extra electron attaches into a $\pi^*$ orbital to give a $^2\Pi$ HCCCN− resonance state as at 1.6 eV. The symmetries of all the ground state products are $^2\Sigma^+$ under $C_{\infty v}$; H + CCCN− is described above; HCC ($^2\Sigma^*$) + CN− ($^1\Sigma^*$) is equivalent to $^2\Sigma^*$, CN ($^2\Sigma^*$) + HCCN− ($^1\Sigma^*$) is equivalent to $^2\Sigma^*$ and HCN ($^1\Sigma^*$) + CC− ($^2\Sigma^*$) is equivalent to $^2\Sigma^*$; These ground state products can be formed on distortion of the molecule as described above for dissociation at 1.6 eV. In the case of formation of HCN + CC−, of course, the molecule must distort for the hydrogen to migrate.

One difference here compared to the discussion above for the 1.6 eV dissociation is that the products may be formed in electronically excited states. In the CN + HCC− channel, for example, the CN could be formed in its excited $^A^2\Pi$ state which lies 1.1 eV above the ground state [52]; the expected appearance energy for these products with excited CN, 4.5 eV, is slightly higher than the experimental onset for HCC− in figure 3. The combined electronic state of CN ($^2\Pi$) + HCC− ($^1\Sigma^*$) is $^2\Pi$ under $C_{\infty v}$, and so dissociation in linear geometry would be allowed. For the HCC + CN− channel, the $^A^2\Pi$ state of HCC lies only 0.46 eV above the ground state [53]. Again HCC ($^2\Pi$) + CN− ($^1\Sigma^*$) is equivalent to $^2\Pi$, so dissociation with linear geometry is allowed and the expected appearance energy is 2.97 eV. In the case of dissociation to form
H + CCCN\textsuperscript{−} the first excited state of H is, of course, 10 eV above the ground state and too high to warrant consideration here. It was not possible to locate spectra of CCCN\textsuperscript{−}, but it is isoelectronic with HCCCN, which has its first singlet excited electronic state at 4.8 eV above the ground state \footnote{Guenther et al. 1997}. If CCCN\textsuperscript{−} has an excited state at 4 eV above the neutral the threshold for formation of H + excited CCCN\textsuperscript{−} would be 5.32 eV and might need to be taken into consideration.

It is concluded that distortion of the molecule is required for formation of ground state fragment channels including the ions CCCN\textsuperscript{−}, CN\textsuperscript{−}, HCC\textsuperscript{−} and CC\textsuperscript{−}, but excited state channels are available to allow dissociation without distortion in the case of CN\textsuperscript{−}, HCC\textsuperscript{−} and perhaps also for CCCN\textsuperscript{−}.

### 3.3.3. Fragmentation above 7 eV

It may be noted that at 8 eV, where CC\textsuperscript{−}, HCC\textsuperscript{−} and CN\textsuperscript{−} are formed, all fragmentation channels involve cleavage of the C–C bond at the centre of the delocalized π bond. This suggests that the electron may attach into an unoccupied orbital with significant antibonding character for this C–C bond and that dissociation is rapid. On the other hand, dissociation is not so fast that the hydrogen atom does not have time to move in the formation of CC\textsuperscript{−} + HCN. There may be a similar situation at 9 eV where only CCN\textsuperscript{−} is observed and only the terminal C–C bond is broken. By contrast at 11 eV, the same argument does not apply as both CCCN\textsuperscript{−} and CN\textsuperscript{−} are observed.

### 3.4. Energetics and main resonances of the dissociative processes

In general the appearance energy AE(B\textsuperscript{−}) of a fragment anion B\textsuperscript{−} in dissociative electron attachment to a molecule AB can be estimated using the equation

\[
AE(B^-) = D(A-B) - EA(B) + E^*,
\]

where \(D(A - B)\) is the dissociation energy of the chemical bond that is broken, \(EA(B)\) is the electron affinity of the radical B and \(E^*\) is the excess energy above the thermodynamic limit. This method has been used to predict the appearance energies in table 1 except in the case of CC\textsuperscript{−} formation where

\[
AE(CC^-) = D(H−CCCN) + D(HCC−CN) − D(H−CN) − EA(CC) + E^*
\]

is used \footnote{Guenther et al. 1997}. It is assumed that the neutral fragment is HCN and hence the bond energy \(D(H−CN) = 5.1 \pm 0.05\) eV \footnote{Guenther et al. 1997} must be included. The values shown in table 1 were calculated with the assumption in all cases that \(E^*\) is equal to zero.

Two lines are shown in table 1 for the formation of CCCN\textsuperscript{−} in the first resonance at 1.56 eV because of the range of electron affinities reported for CCCN. Two experimental measurements indicate electron affinities of 2.39 and 2.4 eV \footnote{Guenther et al. 1997}, but calculation and another experiment suggest higher values of 4.538 eV \footnote{Guenther et al. 1997} and 4.11 ± 0.32 eV \footnote{Guenther et al. 1997}. The present data clearly show the onset of CCCN\textsuperscript{−} at 1.32 ± 0.15 eV, which is in agreement with the threshold at 1.4 eV predicted from calculated electron affinities of ~4.5 eV. The H−CCCN bond energy shown in table 1 has been determined in this work from the heats of formation of H, CCCN and HCCCN; 218 \footnote{Proctor et al. 1977}, 706 \footnote{Proctor et al. 1977} and 354 kJ mol\textsuperscript{−1} \footnote{Proctor et al. 1977} respectively. The value obtained for the bond strength here, 5.91 ± 0.20 eV, is in agreement with previously reported values of 6.0 eV \footnote{Proctor et al. 1977} and 5.5 eV \footnote{Proctor et al. 1977}. The uncertainty in the bond strength has been estimated here because the heats of formation...
were quoted without uncertainties. If the bond strength is taken as 5.91 ± 0.20 eV, the electron affinity of CCCN determined from the present experimental data is 4.59 ± 0.25 eV. The present electron affinity supports previously reported values of 4–4.5 eV. The reason for the discrepancy with previous measurements near 2.4 eV is not clear. One of these values, 2.39 eV, was determined by Dibeler et al [16] from their appearance energy for CCCN− from C₄N₂. Dibeler et al also reported an appearance potential of 3.5 eV for CCCN− from HCCCN which is significantly higher than the value determined here, 1.32 ± 0.15 eV.

The production of CCCN− is the only energetically allowed dissociation channel below 2.5 eV which explains why it is the only fragment ion observed in the first resonance at 1.56 eV. The fragments CN−, HCC− an CC− appear around 4 eV, above or close to their calculated appearance energies.

Formation of CCN− was not expected as a nominally triple carbon–carbon bond is broken. The delocalization of the π system over the three carbon and nitrogen atoms, however, will strengthen the central bond and weaken the nominally triple bonds [61]. The bond dissociation energy for this process has been calculated from heats of formation of HC, CCN and HCCCN, 594.13 [35], 562 [35] and 354 kJ mol⁻¹ [18]. The electron affinity of CCN is >2.3 ± 0.2 eV [35]. The threshold for formation of CCN− calculated here, <6.0 eV, is in agreement with the experimental threshold of ≈8 eV.

As shown in table 1, the formation of H− is energetically possible above 5.2 eV, but as noted above any H− production is very weak.

4. Conclusions

Dissociative electron attachment to cyanoacetylene has been observed at ∼1.6 and ∼5.3 eV. The dissociation reactions observed are

\[
\begin{align*}
\text{HCCCN} + e^{-} &\rightarrow \text{H} + \text{CCCN}^{-}, \\
\text{HCCCN} + e^{-} &\rightarrow \text{HCC} + \text{CN}^{-}, \\
\text{HCCCN} + e^{-} &\rightarrow \text{CN} + \text{HCC}^{-}, \\
\text{HCCCN} + e^{-} &\rightarrow \text{HCN} + \text{CC}^{-}.
\end{align*}
\]

The loss of H is the only reaction observed at ∼1.6 eV and all four are observed at ∼5.3 eV. Comparison of the experimental data with previous [9] and the present calculations suggest that dissociation at these energies follows electron attachment into the two π∗ doubly degenerate vacant molecular orbitals. The peak of the electron attachment resonance to the lower π∗ orbital is expected to be lower than 1.6 eV because the dissociative electron attachment band is cut off at ∼1.3 eV, which is the threshold for formation of CCCN−.

Weaker dissociative electron attachment processes are also observed above 7 eV at ∼8.1 and ∼11.2 eV. At 9.1 eV, the process

\[
\text{HCCCN} + e^{-} \rightarrow \text{CH} + \text{CCN}^{-}
\]

is observed very weakly. It has not been possible to assign the electron attachment processes at these energies.
These measurements indicate that dissociative electron attachment to cyanoacetylene could act as a source of $\text{CCCN}^-$ and $\text{CN}^-$ in the interstellar medium, circumstellar shells and other extraterrestrial environments. No negative ions, however, have yet been detected in space due, perhaps, to lack of spectral data [62]. The population of these negative ions, however, will depend on the abundance of electrons at the energies required and the rate of negative ion destruction. No negative ions are formed by dissociative electron attachment at electron energies below 1.3 eV, the threshold for formation of $\text{CCCN}^-$. Finally, the electron affinity of $\text{CCCN}$ determined from the present experimental data, 4.59 ± 0.25 eV, is in agreement with previously reported values close to 4.5 eV [10, 58], but in contrast to measurements close to 2.4 eV [16, 57].

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