EXPERIMENTAL EVIDENCE FOR RADIATIVE ATTACHMENT IN ASTROCHEMISTRY FROM ELECTRON ATTACHMENT TO NCCCCN

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ABSTRACT

Electron attachment to NCCCCN, dicyanoacetylene (2-butynedinitrile), has been observed. Metastable parent anions, $NCCCCN^{-*}$, with microsecond or longer lifetimes are formed close to 0 eV electron energy with a cross section of ≥ 0.25 Å^2. The stability of $NCCCCN^{-*}$ suggests that radiative attachment to NCCCCN and similar linear carbon chain molecules may be an important mechanism for the formation of negatively charged molecular ions in astrophysical environments. $CCCN^-$ and CN^- fragment anions are formed at ~3 and ~6 eV.

Subject headings: astrochemistry — ISM: molecules — molecular processes

1. INTRODUCTION

This investigation of electron attachment to NCCCCN, dicyanoacetylene or 2-butynedinitrile, was inspired by the recent first astronomical observations of the negatively charged molecular ions C_4H^- (Sakai et al. 2008), C_6H^- (McCarthy et al. 2006), C_8H^- (Brunken et al. 2007), and $CCCN^-$ (Thaddeus et al. 2008). The formation of anions in astrophysical environments has been predicted in chemical models for some time (Herbst 1981; Millar et al. 2000, 2007) where negative ions are formed by radiative attachment

$$AB + e^- \rightarrow AB^{-*} \rightarrow AB^- + h\nu, \qquad (1)$$

where AB^{-*} is a metastable temporary negative ion (TNI). The metastable ion must be stable on millisecond timescales or longer for photon emission, which is usually in the infrared, to proceed; for example, *s*-wave low-energy electron attachment to SF_6 gives SF_6^{-*} states with millisecond and longer lifetimes (Odom et al. 1975; Foster & Beauchamp 1975; Rajput et al. 2008). Radiative attachment rates have been calculated for linear molecules such as C_3N, C_n, and HC_n (Herbst 1981; Petrie & Herbst 1997; Terzieva & Herbst 2000; Herbst & Osamura 2008) assuming efficient *s*-wave attachment of electrons close to 0 eV. There are few examples of small molecules, however, that form long-lived metastable parent anions by electron attachment; SF_6, SF_4, SOF_2, SO_2F_2 (Sauers et al. 1993) and larger molecules, such as 1,3-dinitrotoluene (Zappa et al. 2008), were known previously. Most metastable anions loose their excess energy by autodetachment

$$AB + e^- \rightarrow AB^{-*} \rightarrow AB \ (or \ AB^*) \ + e^- \qquad (2)$$
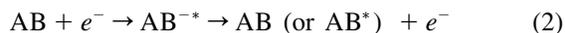
to give the neutral, AB, which may be excited, AB^*, or by molecular dissociation

$$AB + e^- \rightarrow AB^{-*} \rightarrow A + B^-. \qquad (3)$$

This final process is dissociative electron attachment, which is another possible mechanism for negative ion formation in astrophysical environments. For example, dissociative electron attachment to HCCCN gives $CCCN^-$ (Graupner et al. 2006), but the minimum electron energy required is 1.3 eV, which is rather high for molecular clouds. $CCCN^-$ could, however, be formed by dissociative electron attachment to HNCCC (Petrie & Herbst 1997) with close-to-zero-energy electrons. Similarly, HC_6^- and HC_8^- could be formed in dissociative electron attachment to the carbenes H_2C_6 (Sakai et al. 2007) and H_2C_8 (Herbst & Osamura 2008) close to zero energy. Formation of HC_4^- from H_2CCCC is, however, endothermic (Herbst & Osamura 2008).

NCCCCN was chosen for this experimental investigation because it is made up of acetylenic -CC- and cyanide -CN groups, like C_4H^-, C_6H^-, C_8H^-, and $CCCN^-$. Delocalized doubly degenerate π orbitals run along the length of all these linear molecules. It was also chosen because it is isoelectronic to the astronomically observed molecules HCCCCCCH (Cernicharo et al. 2001) and HCCCCCN (Johansson et al. 1984). NCCCCN has not been observed outside the solar system yet, probably because it does not have a microwave rotational spectrum, but it has been observed on Titan by *Voyager 1* (Coustenis et al. 1999) and on Neptune by *Voyager 2* (Maguire 1995) by infrared spectroscopy.

2. EXPERIMENT

The preparation of NCCCCN, described previously (Moureu & Bongrand 1909; Coll et al. 1999), is only outlined here. Briefly, 2-butynedioic acid dimethyl ester ($CH_3OOC_4OOCH_3$) reacted with aqueous ammonia to form 2-butynediamide ($NH_2OC_4ONH_2$), which was dried and then dehydrated by heating with P_2O_5 to give NCCCCN under vacuum; the volatile product was collected in a trap immersed in a carbon dioxide/acetone slush bath. Excess heat in the second step led to formation of HCN by-product. NCCCCN was stored under vacuum at 0 °C and below as it decomposes at room temperature.

The electron attachment apparatus has been described previously (Field et al. 2005). Briefly, low-energy electrons from a trochoidal electron monochromator attach to the gaseous sample in the source region of a time-of-flight spectrometer, which detects the negatively charged ions formed. The flight time of $NCCCCN^{-*}$ ions was 4.2 μs in the mass spectrometer. A magnetic field of ~80 G guides the electrons and enables the electron beam energy to be reduced to close to 0 eV in the source region. At electron energies above ~10 eV positive ions are formed, which can be observed by reversing the mass spec-
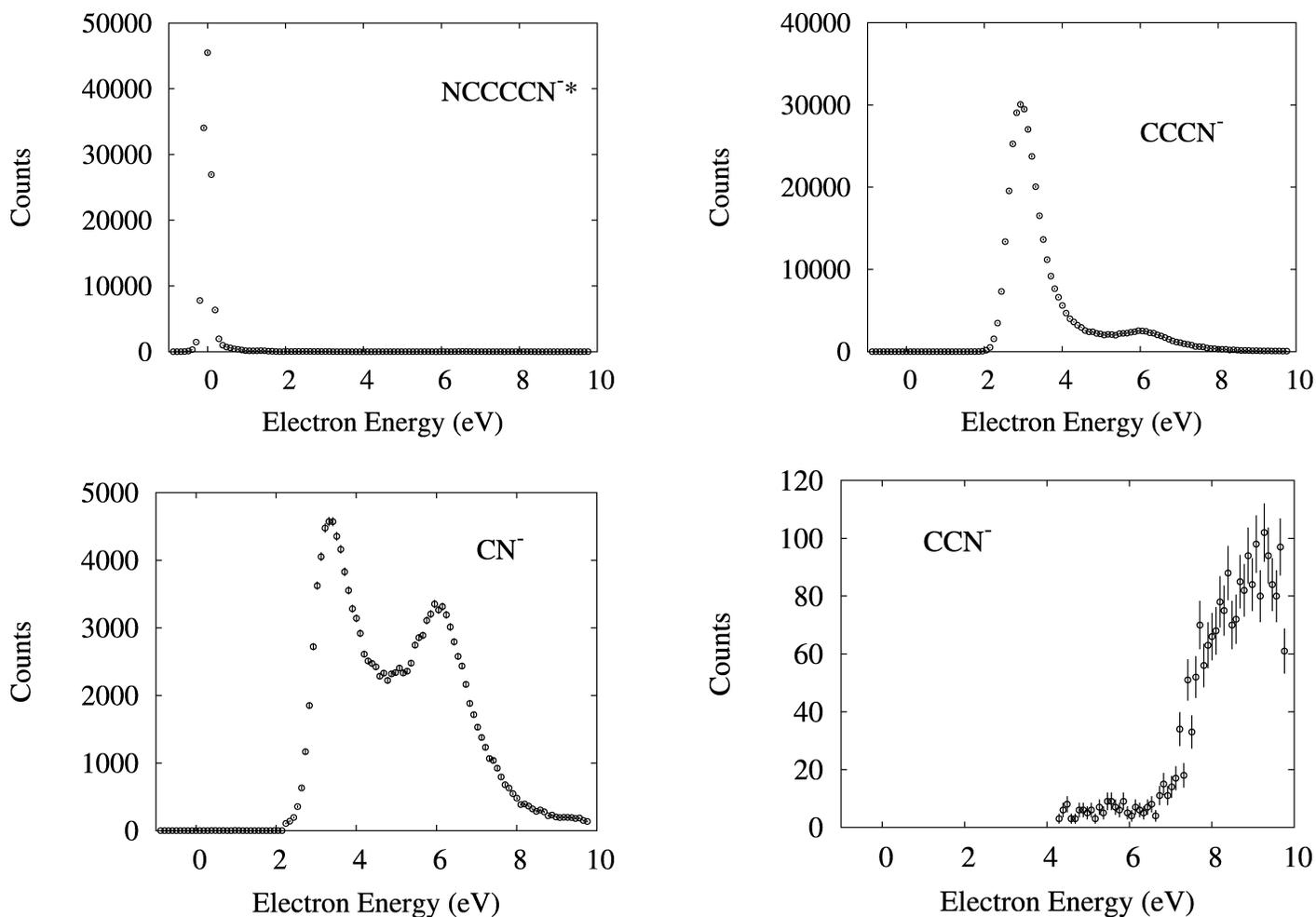
Fig. 1.—Intensities of NCCCCN^{-*}, CCCN$^-$, CN$^-$, and CCN$^-$ formed following electron attachment to NCCCCN. CCN$^-$ is only shown above 4 eV due to noise from more intense ions at lower energies.

trometer potentials. The electron energy resolution (FWHM) was determined to be 250–300 meV from the width of the SF$_6^{-*}$ peak from electron attachment to SF$_6$ at 0 eV. NCCCCN entered the source region effusively at room temperature, but the sample holder was kept below 0°C.

3. RESULTS AND DISCUSSION

The intensities of negative ions formed following electron attachment to NCCCCN are shown in Figure 1 as a function of electron energy. At 0 eV the parent anion, NCCCCN^{-*}, is observed, while above 2 eV CCCN$^-$, CCN$^-$, and CN$^-$ are formed. The energies of peak maxima are presented in Table 1. Several

measurements at different pressures and with different samples were made to ensure the parent anion signal at 0 eV was genuine. The NCCCCN^{-*} yield is shown in more detail in Figure 2 with the SF$_6^{-*}$ yield. The widths of both peaks, ~250–300 meV, were determined by the electron energy resolution.

The asymmetric shapes of the CN$^-$ and CCCN$^-$ peaks at 2.93 and 3.35 eV suggest these ions appear at their thermo-

TABLE 1
SUMMARY OF PROCESSES OBSERVED FOLLOWING ELECTRON ATTACHMENT PROCESSES TO NCCCCN WITH ESTIMATED ABSOLUTE CROSS SECTIONS; NCCCCN + e^- → A + B$^-$

Anion (B$^-$)	Neutral (A)	Peak Maximum (eV)	Cross Section (Å^2)
NCCCCN$^-$	...	0	≥0.25[a]
CCCN$^-$	CN	2.93 ± 0.15	0.17
CCCN$^-$	CN	5.95 ± 0.20	0.014
CCN$^-$	CCN	>8	0.0006
CN$^-$	CCCN	3.35 ± 0.15	0.025
CN$^-$	CCCN	5.95 ± 0.20	0.019

[a] This is a lower limit (see text).
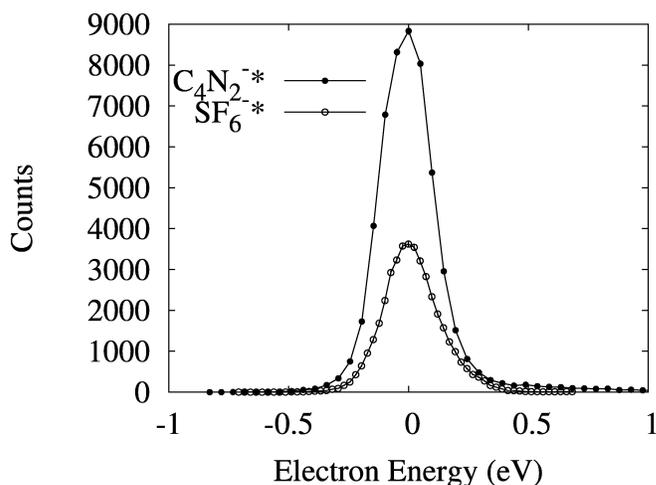
Fig. 2.—SF$_6^{-*}$ and NCCCCN^{-*} peaks at 0 eV; both peak widths are determined by the experimental electron energy resolution.

dynamic thresholds. Thresholds should, in theory, give vertical rises in the ion yields, but the finite electron energy resolution leads to steep slopes that can be analyzed to determine experimental electron energy resolutions and thermodynamic limits; energies for formation of CN^- + CCCN and $CCCN^-$ + CN from NCCCCN are determined to be 2.88 ± 0.15 eV and 2.56 ± 0.15 eV, respectively, here. FWHM electron energy resolutions calculated from the low-energy rises of the CN^- and $CCCN^-$ peaks, 250–300 meV, agree with other measurements of the electron energy resolution. Combination of the well-known electron affinity of CN, 3.862 eV (Linstrom & Mallard 2005), with the experimental threshold for CN^- + CCCN production gives an energy of 6.74 ± 0.15 eV for formation of NC + CCCN from NCCCCN. The difference between this bond energy and the threshold for $CCCN^-$ + CN formation gives a CCCN electron affinity of 4.18 ± 0.20 eV, which is consistent with the CCCN electron affinity, 4.59 ± 0.25 eV, determined from dissociative electron attachment to HCCCN (Graupner et al. 2006).

Absolute cross sections, shown in Table 1, were estimated from measurements of electron attachment to a mixture of NCCCCN and H_2S; the intensity of HS^- from H_2S at ∼2.20 eV, which has a cross section of 0.017–0.018 $Å^2$ (Fiquet-Fayard et al. 1972; Azria et al. 1972; Rao & Srivastava 1993), was compared with the intensities of anions from NCCCCN. The relative number densities of NCCCCN and H_2S were determined from electron-impact ionization measurements and absolute cross sections for positive ion formation, which had to be calculated here for NCCCCN with the BEB (Binary-Encounter-Bethe) method (Kim & Rudd 1994) with data from GAMESS Hartree Fock calculations (Schmidt et al. 1993; Gordon & Schmidt 2005[1]) also made here using the 6-31G* basis set. H_2S BEB cross sections calculated here with the same method agree to better than 98% with literature BEB cross sections (Kim et al. 2004) calculated with a larger basis set, 6-3111G (Kim et al. 1997). The calculated BEB cross sections for NCCCCN will be presented elsewhere (K. Graupner et al. 2008, in preparation). The absolute cross section for formation of $NCCCCN^{-*}$ is difficult to determine with the present experimental resolution because cross sections can double within a couple of meV close to 0 eV. A lower limit to the cross section for formation of $NCCCCN^{-*}$ is given, 0.25 $Å^2$. It is clear from the data, however, that the cross section for formation of $NCCCCN^{-*}$ is at least an order of magnitude lower than the cross section for formation of SF_6^{-*} from SF_6 close to zero energy.

The NCCCCN molecule has three empty doubly degenerate valence antibonding π^* orbitals, which electrons can attach to through shape resonances. In shape resonances electrons with nonzero angular momentum tunnel through a centrifugal potential barrier close to the molecule, which they become trapped behind. Electron attachment into the π^* orbitals gives $^2\Pi$ anion states and must be p-wave, viz., with 1 unit of angular momentum. The energies at which electrons attach into unoccupied orbitals can be predicted by semiempirical scaling of calculated orbital energies (Aflatooni et al. 2000) as applied successfully to the π^* orbitals of HCCCN (Graupner et al. 2006). An identical procedure was used here; briefly, ab initio Hartree Fock calculations were performed with GAMESS using the STO-3G basis set, and scaled energies of −0.97, 2.46, and 5.48 eV were obtained for electron attachment into the three valence π^* orbitals.

The predicted energies of shape resonances due to electron attachment into the higher two π^* orbitals, 2.46 and 5.48 eV, are in fairly good agreement with the positions of the maxima

observed for $CCCN^-$, 2.93 and 5.95 eV, and CN^-, 3.35 and 5.95 eV. In fact, the agreement is good considering the rather basic method used to predict the resonance positions. Thermodynamic thresholds for formation of $CCCN^-$ and CN^- close to 3 eV may make the experimental resonance energies of 2.93 and 3.35 eV higher than electron attachment resonance maxima (K. Graupner et al. 2008, in preparation). The agreement between experiment and prediction makes it most likely that electron attachment into the two higher π^* orbitals, probably by shape resonances, leads to the formation of $CCCN^-$ and CN^- close to 3 and 6 eV.

Attachment to the lowest π^* orbital is predicted to be at −0.97 eV, which of course is a bound state rather than a resonance, although this value may be too low as the other predicted π^* resonance energies are below experimental peak positions. The sign of the resonance energy may change from negative to positive in response to small changes in the molecular geometry. In such situations nuclear excited Feshbach resonances may occur (Gauyacq & Herzenberg 1981) where the nuclei move as the electron approaches the molecule; in effect, the electron transfers some of its energy to molecular vibrations so that it cannot autodetach immediately. Feshbach resonances can have long lifetimes and are the most likely cause for the present observation of $NCCCCN^{-*}$. Feshbach resonances can be s-wave, but as the electron attaches into a π^* orbital here it is more likely to be p-wave attachment. Theoretically, s-wave cross sections rise to infinity at zero energy, but p-wave cross sections fall to zero. However, p-wave electron attachment was observed close to 0 eV in formation of Cl^- by dissociative electron attachment to Cl_2, where s-wave attachment is symmetry forbidden (Barsotti et al. 2002). The cross section for Cl^- formation has a maximum of 2.5 $Å^2$ at 50 meV and falls toward 0 eV, but is still ∼1 $Å^2$ at 5 meV.

The present observations provide some experimental evidence for radiative attachment to NCCCCN and similar molecules with three or more valence π^* orbitals. By contrast, experiments have shown HCCCN (Graupner et al. 2006) and HCCCCH (May et al. 2008), which both have two π^* orbitals, do not form long-lived metastable parent anions in electron attachment. Calculations for HCCCN (Graupner et al. 2006) and HCCCCH (K. Graupner et al. 2008, in preparation) predict the lowest π^* resonances at ∼0.5 and ∼1 eV, respectively. Radicals, such as C_4H, have singly occupied molecular orbitals that could accommodate an extra electron in low-energy electron attachment; further calculation and experiments may shed light on radiative attachment to these species.

4. CONCLUSIONS

Electron attachment and dissociative electron attachment to NCCCCN have been observed at 0, ∼3, and ∼6 eV. Close to 0 eV $NCCCCN^{-*}$ is observed on the microsecond timescale of the present experiment. This long-lived anion is most likely formed by a Feshbach resonance with electron attachment into the lowest empty π^* orbital of NCCCCN. It is possible that states of $NCCCCN^{-*}$ will have long enough lifetimes for photon emission and, thus, overall radiative attachment. Similar linear molecules with three or more π^* orbitals may also radiatively attach through a similar mechanism. At ∼3 and ∼6 eV there is electron attachment into the other two valence π^* orbitals, probably through shape resonances, followed by dissociation to give $CCCN^-$ and CN^- fragment ions.

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[1] See also http://www.msg.chem.iastate.edu/gamess/.

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