

## Laboratory observation of the valence anion of cyanoacetylene, a possible precursor for negative ions in space

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(Received 22 September 2009; accepted 9 October 2009; published online 23 October 2009)

Valence anions of cyanoacetylene,  $\text{HCCCN}^-$ , are synthesized by the  $1,2\text{-H}_2^+$  abstraction reaction of  $\text{O}^-$  with acrylonitrile,  $\text{H}_2\text{C}=\text{CHCN}$ , while the competing  $1,1\text{-H}_2^+$  channel of the same reaction yields the cyanovinylidene anions,  $\text{CCHCN}^-$ . The key to the formation of the elusive, adiabatically weakly bound  $\text{HCCCN}^-$  is the bent  $-\dot{\text{C}}=\dot{\text{C}}-\text{C}\equiv$  skeleton of the reactant. The photoelectron spectrum of  $\text{HCCCN}^-$ , measured by means of photoelectron imaging at 532 nm, consists of a broad structureless band with a vertical detachment energy of  $1.04 \pm 0.05$  eV. The observed anions are stable counterparts of the low-lying anionic resonances of cyanoacetylene, which may contribute (by way of dissociative attachment) to the formation of carbon-rich and CN-containing negative ions in extraterrestrial environments. © 2009 American Institute of Physics.  
[doi:10.1063/1.3257174]

We report the synthesis and characterization of the valence, adiabatically weakly bound anions of cyanoacetylene. Neutral cyanoacetylene ( $\text{HCCCN}$ ) is one of the most abundant organic molecules in extraterrestrial environments. It is found in the interstellar medium, the atmosphere of Titan, comet tails, etc.<sup>1,2</sup> The anionic states of cyanoacetylene are potentially of further astrochemical significance, as dissociative attachment of electrons to  $\text{HCCCN}$  has been proposed as a possible source of negative ions in space.<sup>3</sup> For example,  $\text{CCCN}^-$  has been detected both in interstellar molecular clouds and in the laboratory,<sup>4</sup> where it is synthesized as a product of dissociative attachment of low-energy electrons to cyanoacetylene.

The above-mentioned attachment processes involve the low-lying anionic  $\pi^*$  resonances of cyanoacetylene, previously predicted by theory.<sup>5</sup> These temporary states lead to several dissociative attachment products ( $\text{CCN}^-$ ,  $\text{CN}^-$ ,  $\text{HCC}^-$ , and  $\text{CC}^-$ ) but no stable  $\text{HCCCN}^-$ .<sup>3</sup> Nonetheless, scattering resonances often correlate to stable anionic states, whose very existence may have a profound effect on chemistry and interactions with low-energy electrons. In the case of  $\text{HCCCN}$ , the large molecular dipole moment and the unsaturated  $\pi$  system are responsible for the predicted existence of dipole-bound and valence anions.<sup>5</sup> These anions have, until now, eluded definitive experimental detection—not only in space, but also in the laboratory.

The principal challenge of generating the valence form of  $\text{HCCCN}^-$  stems from the unstable nature of the anion at the linear equilibrium geometry of neutral  $\text{HCCCN}$ . The antibonding character of the low-lying vacant orbitals of cyanoacetylene results in significant geometric distortions in the anion, rendering  $\text{HCCCN}$  a poor choice of the starting reactant for generating  $\text{HCCCN}^-$ . Sommerfeld and Knecht,<sup>5</sup> using high-level *ab initio* calculations, predicted a planar

roughly w-shaped equilibrium geometry of valence  $\text{HCCCN}^-$ . The predicted structure is stable with respect to adiabatic detachment by only 50 meV (most of which comes from the difference in the zero-point vibrational energies of the neutral and the anion). On the other hand, the anion is predicted to have a respectable 1.25 eV vertical detachment energy (VDE). Thus, the calculated adiabatic and especially the vertical energetics suggest that  $\text{HCCCN}^-$  should exist.

We generate the valence cyanoacetylene anion by the  $1,2\text{-H}_2^+$  abstraction reaction of  $\text{O}^-$  with acrylonitrile ( $\text{H}_2\text{C}=\text{CHCN}$ ). The bent  $-\dot{\text{C}}=\dot{\text{C}}-\text{C}\equiv$  skeleton of the reactant is the key to the formation of  $\text{HCCCN}^-$ . In fact, this anion was once proposed in electron attachment to acrylonitrile, but the assignment had not been confirmed.<sup>6</sup>

The chemical structure of acrylonitrile is shown in Fig. 1. The shading in Figs. 1(a) and 1(b) marks the hydrogen centers to be eliminated via the *trans*- $1,2\text{-H}_2^+$  and *cis*- $1,2\text{-H}_2^+$  abstraction processes, yielding  $\text{HCCCN}^-$  in the nascent *trans* and *cis* configurations, respectively. The competing  $1,1\text{-H}_2^+$  abstraction channel of the  $\text{O}^- + \text{H}_2\text{C}=\text{CHCN}$  reaction, illustrated in Fig. 1(c), yields the cyanovinylidene anion,  $\text{CCHCN}^-$ . This process has been indicated in a previous study of the reaction of  $\text{O}^-$  with 2-deuteroacrylonitrile ( $\text{H}_2\text{C}=\text{CDCN}$ ),<sup>7</sup> but no evidence for the simultaneous formation of the cyanoacetylene anion has been reported.

The synthesis is carried out in a supersonic expansion of room-temperature acrylonitrile vapor entrained in neat  $\text{N}_2\text{O}$  carrier gas with a backing pressure of 2.5 atm. The expanded mixture is bombarded by 1 keV electrons from an electron gun inside the high-vacuum source chamber of the negative-ion spectrometer described in detail elsewhere.<sup>8</sup> Dissociative attachment of slow secondary electrons to  $\text{N}_2\text{O}$  generates highly reactive  $\text{O}^-$  radicals, which in turn abstract  $\text{H}_2^+$  from acrylonitrile to form the cyanoacetylene and cyanovinylidene anions. The mass-selected anions are irradiated with linearly polarized 532 nm frequency-doubled output of a Nd:yttrium

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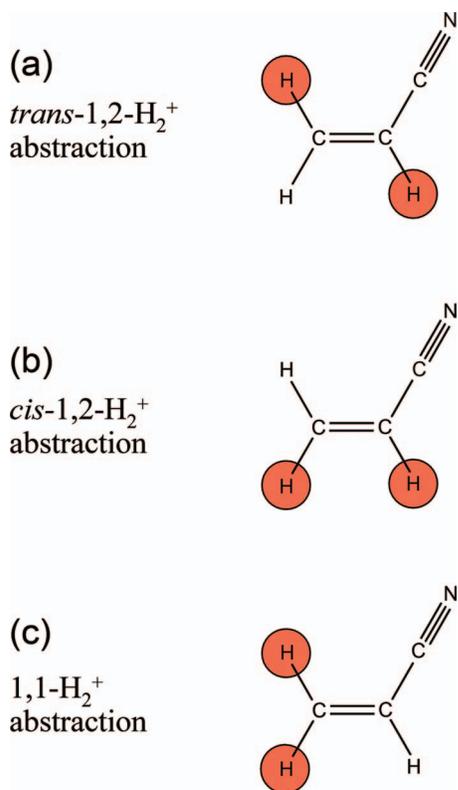


FIG. 1. The chemical structure of acrylonitrile  $\text{H}_2\text{C}=\text{CHCN}$ , with the shaded circles marking the hydrogen centers abstracted via the three possible channels of the  $\text{O}^- + \text{H}_2\text{C}=\text{CHCN} \rightarrow \text{C}_3\text{HN}^- + \text{H}_2\text{O}$  reaction, as follows: (a) the *trans*-1,2-H<sub>2</sub><sup>+</sup> abstraction reaction, yielding nascent *trans*-HCCCN<sup>-</sup> products; (b) the *cis*-1,2-H<sub>2</sub><sup>+</sup> abstraction pathway, yielding nascent *cis*-HCCCN<sup>-</sup> products; and (c) the 1,1-H<sub>2</sub><sup>+</sup> abstraction channel, yielding the cyanovinylidene anion CCHCN<sup>-</sup>.

aluminum garnet laser (30 mJ, 8 ns pulses). The photodetached electrons are analyzed using a velocity-map<sup>9</sup> imaging<sup>10</sup> assembly, following published procedures.<sup>11,12</sup>

The 532 nm photoelectron image and the corresponding spectrum for the  $m/z=51$  anions (HCCCN<sup>-</sup> and CCHCN<sup>-</sup>) is presented in Fig. 2. The image shows two distinct features: A diffuse outer band, A, peaking in the direction parallel to the laser polarization axis, and an inner ring progression, B, peaking in the perpendicular direction. Feature A corresponds to a broad structureless band in the photoelectron spectrum, with an onset at an electron binding energy (eBE) of about 0.5 eV and a maximum at  $1.04 \pm 0.05$  eV, while band B exhibits a well-resolved vibrational structure.

The origin of band B at  $\text{eBE}=1.85 \pm 0.01$  eV is in remarkable agreement with the 1.85 eV electron affinity predicted at the G3(MP2) level of theory for the cyanovinylidene anion.<sup>5</sup> The assignment of this band to CCHCN<sup>-</sup> is further supported by the Franck–Condon analysis, to be reported elsewhere.<sup>13</sup> In short, the similar ground-state geometries of the cyanovinylidene anion and neutral result in a sharp onset of band B and the appearance of a simple vibrational progression. This assignment reaffirms the previous observation of CCHCN<sup>-</sup> in the reaction of O<sup>-</sup> with acrylonitrile,<sup>7</sup> although the photoelectron spectrum is reported here for the first time.

Band A in Fig. 2 appears at lower binding energies relative to band B and, therefore, corresponds to a different spe-

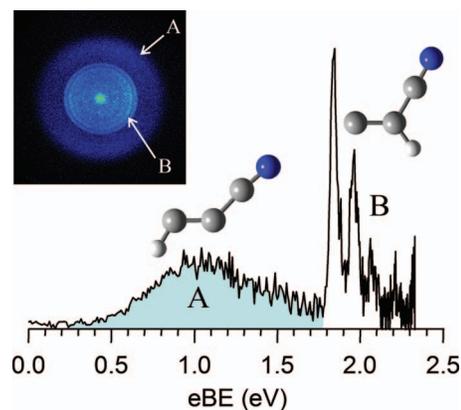


FIG. 2. The photoelectron image and the corresponding spectrum of HCCCN<sup>-</sup> and CCHCN<sup>-</sup> obtained at 532. The laser polarization axis is vertical in the plane of the image. Band A (shaded) is assigned to HCCCN<sup>-</sup>, while band B corresponds to CCHCN<sup>-</sup>. The corresponding equilibrium anion geometries are shown schematically above the corresponding bands in the photoelectron spectrum. The geometric parameters of the planar HCCCN<sup>-</sup> structure, as determined by Sommerfeld and Knecht (Ref. 5) at the CCSD(t)/aug-cc-pVDZ level of theory, are as follows:  $R(\text{H}-\text{C}1) = 1.1103$  Å,  $R(\text{C}1-\text{C}2) = 1.3306$  Å,  $R(\text{C}2-\text{C}3) = 1.4157$  Å,  $R(\text{C}3-\text{N}) = 1.1958$  Å,  $\angle\text{HC}1\text{C}2 = 123.08^\circ$ ,  $\angle\text{C}1\text{C}2\text{C}3 = 133.07^\circ$ ,  $\angle\text{C}2\text{C}3\text{N} = 172.60^\circ$ . The geometry of CCHCN<sup>-</sup> is described elsewhere (Ref. 13).

cies. We assign it to the previously unobserved cyanoacetylene form of the anion HCCCN<sup>-</sup>. The optimized geometry of valence HCCCN<sup>-</sup>, predicted by Sommerfeld and Knecht,<sup>5</sup> is shown above the spectrum of the corresponding photodetachment band in Fig. 2, with the specific geometric parameters given in the figure caption. The HCCCN<sup>-</sup> equilibrium is separated from the CCHCN<sup>-</sup> structure by a large potential barrier,<sup>13</sup> and therefore the two anionic isomers are not expected to interconvert easily into one another.

The experimental  $\text{VDE}=1.04 \pm 0.05$  eV, determined as the eBE of band A's maximum, is compared to the 1.25 eV value predicted for HCCCN<sup>-</sup> based on the CCSD(T)/aug-cc-pVDZ calculations.<sup>5</sup> The agreement is quite satisfactory, considering that electron affinities and detachment energies of weakly bound anions are notoriously difficult to calculate. The broad, structureless profile of band A is consistent with the large geometry difference between HCCCN<sup>-</sup> and the linear ground-state structure of HCCCN. Due to the geometry difference, several vibrational modes should be excited in the photodetachment, giving a broad and congested photoelectron spectrum with no identifiable origin. The difficulty in identifying the transition origin makes it impossible to deduce the adiabatic electron affinity of cyanoacetylene from the data. However, the observed spectrum is consistent with the theoretical prediction (50 meV) of Sommerfeld and Knecht.<sup>5</sup>

The successful formation of HCCCN<sup>-</sup> in the present work is due to the matching geometry of the starting reactant. To illustrate the importance of the geometric factor, consider the admittedly crude sudden limit of H<sub>2</sub><sup>+</sup> abstraction from acrylonitrile. The removal of 1,2-H<sub>2</sub><sup>+</sup> from the equilibrium structure of  $\text{H}_2\text{C}=\text{CHCN}$ , without changing any other bond distances or angles, yields either *trans*-nascent or *cis*-nascent structures of HCCCN<sup>-</sup>, as illustrated in Figs. 1(a) and 1(b), respectively. Despite being unstable with respect to

geometry relaxation, both of the resulting anionic forms are stable (by  $\geq 2$  eV) (Ref. 13) with respect to vertical electron detachment.

One could speculate that *trans*-1,2-H<sub>2</sub><sup>+</sup> abstraction, illustrated in Fig. 1(a), is most likely to proceed via a sequential mechanism, while *cis*-1,2-H<sub>2</sub><sup>+</sup> abstraction [Fig. 1(b)] may be either sequential or simultaneous. In a sequential process, for which the sudden approximation is even less appropriate, O<sup>-</sup> first abstracts one of the protons from H<sub>2</sub>C=CHCN to form an intermediate OH radical, which then scavenges a hydrogen to form H<sub>2</sub>O and HCCCN<sup>-</sup>. Under the simultaneous mechanism, both H and H<sup>+</sup> are abstracted in a single step. The simultaneous abstraction would favor the *cis* pathway, where the affected H centers are in proximity of each other. However, theoretical calculations do not indicate an HCCCN<sup>-</sup> potential minimum corresponding to a *cis* geometry.<sup>13</sup> That is, while *cis*-HCCCN<sup>-</sup> is vertically stable with respect to electron detachment, it is unstable with respect to the rearrangement to the *trans* form of the anion. Therefore, regardless of the mechanistic details, 1,2-H<sub>2</sub><sup>+</sup> abstraction from acrylonitrile yields vertically stable HCCCN<sup>-</sup>, which can then be relaxed toward the stable *trans*-HCCCN<sup>-</sup> geometry.

The convenient starting geometry of acrylonitrile plays a crucial role in this synthesis by allowing access to the part of the HCCCN<sup>-</sup> potential energy surface where the desired anion is more stable than the corresponding neutral. This realization is not new in itself. Examples of negative ions, whose equilibrium geometries differ vastly from the corresponding neutral structures, are abundant. Among them is CO<sub>2</sub><sup>-</sup>, which is stable with respect to vertical electron detachment at its bent equilibrium geometry, but extremely difficult to form by electron attachment to neutral (linear) CO<sub>2</sub> molecules or clusters of CO<sub>2</sub>.<sup>14-17</sup> Another example, energetically very similar to cyanoacetylene, is OCS<sup>-</sup>. The adiabatic electron affinity of carbonyl sulfide is approximately zero, yet the bent anionic structure is vertically stable by  $\sim 1.4$  eV.<sup>18-20</sup> Due to the geometric differences in the neutral and anion structures (linear and bent, respectively), OCS<sup>-</sup> anions are not formed effectively by electron attachment to neutral OCS molecules or clusters.<sup>19</sup> They are, however, formed in abundance in the photodissociation of the (OCS)<sub>2</sub><sup>-</sup> covalent dimer anion, whose equilibrium structure combines two *bent* OCS moieties.<sup>21</sup>

In summary, we have reported the synthesis and observation of the valence negative ions of cyanoacetylene, which had until now eluded definitive experimental detection. The anions are generated by the 1,2-H<sub>2</sub><sup>+</sup> abstraction reaction of O<sup>-</sup> with acrylonitrile H<sub>2</sub>C=CHCN, whose bent CCC skel-

eton is the key to the formation of HCCCN<sup>-</sup>. The VDE of HCCCN<sup>-</sup> is determined to be  $1.04 \pm 0.05$  eV. These anions are stable (albeit adiabatically weakly bound) counterparts of the low-lying anionic resonances of cyanoacetylene. The corresponding electronic state may contribute (by way of dissociative attachment) to the formation of negative ions in extraterrestrial environments. The competing 1,1-H<sub>2</sub><sup>+</sup> abstraction channel of the O<sup>-</sup> reaction with acrylonitrile yields the cyanovinylidene anion, CCHCN<sup>-</sup>. The simultaneous formation of CCHCN<sup>-</sup> and HCCCN<sup>-</sup> allows access to both the reactant and the product sides of the neutral potential energy surface for the cyanovinylidene  $\rightarrow$  cyanoacetylene rearrangement.<sup>13</sup>

## ACKNOWLEDGMENTS

We have benefited greatly from discussions of reaction mechanisms with Professor Indraneel Ghosh (The University of Arizona). This research is supported by the National Science Foundation (Grant No. CHE-0713880).

<sup>1</sup>M. Morris, B. E. Turner, P. Palmer, and B. Zuckerman, *Astrophys. J.* **205**, 82 (1976).

<sup>2</sup>S. Petrie and E. Herbst, *Astrophys. J.* **491**, 210 (1997).

<sup>3</sup>K. Graupner, T. L. Merrigan, T. A. Field, T. G. A. Youngs, and P. C. Marr, *New J. Phys.* **8**, 117 (2006).

<sup>4</sup>P. Thaddeus, C. A. Gottlieb, H. Gupta, S. Brunken, M. C. McCarthy, M. Agundez, M. Guelin, and J. Cernicharo, *Astrophys. J.* **677**, 1132 (2008).

<sup>5</sup>T. Sommerfeld and S. Knecht, *Eur. Phys. J. D* **35**, 207 (2005).

<sup>6</sup>M. Heni and E. Illenberger, *Int. J. Mass Spectrom. Ion Process.* **73**, 127 (1986).

<sup>7</sup>J. H. J. Dawson and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Phys.* **33**, 3 (1980).

<sup>8</sup>L. Velarde, T. Habteyes, and A. Sanov, *J. Chem. Phys.* **125**, 114303 (2006).

<sup>9</sup>A. Eppink and D. H. Parker, *Rev. Sci. Instrum.* **68**, 3477 (1997).

<sup>10</sup>D. W. Chandler and P. L. Houston, *J. Chem. Phys.* **87**, 1445 (1987).

<sup>11</sup>V. Dribinski, A. Ossadtchi, V. A. Mandelshtam, and H. Reisler, *Rev. Sci. Instrum.* **73**, 2634 (2002).

<sup>12</sup>A. Sanov and R. Mabbs, *Int. Rev. Phys. Chem.* **27**, 53 (2008).

<sup>13</sup>D. J. Goebbert, D. Khuseynov, and A. Sanov, "Photoelectron imaging of cyanovinylidene and cyanoacetylene anions," *J. Phys. Chem. A* (unpublished).

<sup>14</sup>C. E. Klots and R. N. Compton, *J. Chem. Phys.* **67**, 1779 (1977).

<sup>15</sup>C. E. Klots, *J. Chem. Phys.* **71**, 4172 (1979).

<sup>16</sup>M. L. Alexander, M. A. Johnson, N. E. Levinger, and W. C. Lineberger, *Phys. Rev. Lett.* **57**, 976 (1986).

<sup>17</sup>M. J. DeLuca, B. Niu, and M. A. Johnson, *J. Chem. Phys.* **88**, 5857 (1988).

<sup>18</sup>G. L. Gutsev, R. J. Bartlett, and R. N. Compton, *J. Chem. Phys.* **108**, 6756 (1998).

<sup>19</sup>E. Surber, S. P. Ananthavel, and A. Sanov, *J. Chem. Phys.* **116**, 1920 (2002).

<sup>20</sup>E. Surber and A. Sanov, *J. Chem. Phys.* **116**, 5921 (2002).

<sup>21</sup>A. Sanov, S. Nandi, K. D. Jordan, and W. C. Lineberger, *J. Chem. Phys.* **109**, 1264 (1998).