

## COMMUNICATIONS

# Crossed beam reaction of the cyanogen radical, $\text{CN}(X^2\Sigma^+)$ , with acetylene, $\text{C}_2\text{H}_2(X^1\Sigma_g^+)$ : Observation of cyanoacetylene, $\text{HCCCN}(X^1\Sigma^+)$

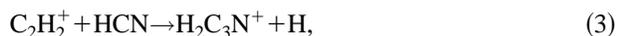
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The chemical dynamics to cyanoacetylene,  $\text{HCCCN}(X^1\Sigma^+)$ , formation via the neutral-neutral reaction of cyanogen,  $\text{CN}(X^2\Sigma^+)$ , with acetylene,  $\text{C}_2\text{H}_2(X^1\Sigma_g^+)$ , is investigated in a crossed molecular beams experiment at a collision energy of  $21.1 \text{ kJ mol}^{-1}$ . The laboratory angular distribution and time-of-flight spectra of the  $\text{HCCCN}$  product are recorded at  $m/e=51$  and  $50$ . Forward-convolution fitting of our data reveals that the reaction dynamics are governed by an initial attack of the  $\text{CN}$  radical to the  $\pi$  electron density of the acetylene molecule to form a  $\text{HCCHCN}$  collision complex on the  $^2A'$  surface. The four heavy atoms are rotating in plane almost perpendicular to the total angular momentum vector  $\mathbf{J}$  around the  $C$  axis of the complex which undergoes  $C-H$  bond rupture through a tight transition state to  $\text{HCCCN}$  and  $\text{H}$ . The  $\text{H}$  atom is emitted almost perpendicular to the  $\text{HCCCN}$  axis to yield a nearly "sideways" peaking of  $T(\theta)$ . The explicit identification of the cyanoacetylene reaction product represents a solid background for the title reaction to be included with more confidence in reaction networks modeling the chemistry in dark, molecular clouds, outflow of dying carbon stars, hot molecular cores, as well as the atmosphere of hydrocarbon rich planets and satellites such as the Saturnian moon Titan. © 1999 American Institute of Physics. [S0021-9606(99)02015-2]

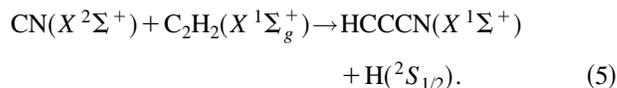
## I. INTRODUCTION

Ever since the very first detection of cyanoacetylene,  $\text{HCCCN}(X^1\Sigma^+)$ , in interstellar environments, the synthesis of highly unsaturated cyanopolyynes  $\text{H}-(\text{C}\equiv\text{C})_n-\text{CN}$  ( $n=1-5$ ) has been a challenge for astronomers and chemists.<sup>1</sup> Early models of interstellar cloud chemistry suggest ion-molecule reactions together with a dissociative recombination (1)–(4) as a possible source to form the simplest member of this class, cyanoacetylene:<sup>2</sup>



However, this reaction sequence yields a  $\text{HCCCN}$  number density two orders of magnitude less than observed astronomically.<sup>2</sup> It was therefore suggested that the bimolecular neutral-neutral reaction of the cyanogen radical,  $\text{CN}(X^2\Sigma^+)$ , with acetylene,  $\text{C}_2\text{H}_2(X^1\Sigma_g^+)$ , might produce cyanoacetylene in the out-flow of the circumstellar envelope

surrounding the carbon star  $\text{IRC}+10216$ ,<sup>3</sup> hot molecular cores,<sup>4</sup> and dark molecular clouds such as  $\text{TMC-1}$ :<sup>5</sup>



Recent laboratory measurements at ultralow temperatures as low as  $20 \text{ K}$  show that the reaction rate constant of reaction (5) increases as the temperature decreases, reaching a maximum of  $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at  $30 \text{ K}$ , i.e., in the order of gas phase collisions. However, these studies can monitor only the decay kinetics of the  $\text{CN}$  radical, and hence reaction products could not be determined explicitly.<sup>6</sup> This shortcoming clearly reveals that systematic experiments are necessary to probe the detailed chemical dynamics and reaction product(s) of the title reaction under single collision conditions as presented in this communication.

## II. EXPERIMENT AND DATA PROCESSING

The experiments are performed with the  $35''$  crossed molecular beams machine. The basic experimental details are described in Ref. 7 in detail. A pulsed supersonic cyanogen  $\text{CN}(X^2\Sigma^+)$  radical beam is generated in the primary source *in situ* via laser ablation of graphite at  $266 \text{ nm}$  and seeding the ablated carbon atoms in neat nitrogen carrier gas released by a Proch-Trickl pulsed valve operating at  $60 \text{ Hz}$ ,  $80 \mu\text{s}$  pulses, and  $4 \text{ atm}$  backing pressure.<sup>8</sup> The Spectra

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Physics GCR 270-30 Nd:yttrium–aluminum–garnet (YAG) laser operates at 30 Hz; typically 30 mJ per pulse are focused onto a rotating graphite rod with a 1500 mm focal length ultraviolet (UV)-grade fused silica lens to a spot of 0.3–0.5 mm diameter. A chopper wheel mounted 40 mm after the ablation zone selects a 9  $\mu\text{s}$  segment of the CN beam. This pulsed CN beam has a velocity  $v_0 = 1560 \pm 30 \text{ ms}^{-1}$  and speed ratio  $S = 6.8 \pm 0.5$ . It crosses a second, pulsed acetylene beam ( $v_0 = 900 \pm 15 \text{ ms}^{-1}$ ,  $S = 12.0 \pm 0.5$ , 510 Torr backing pressure) perpendicular in the interaction region at a collision energy of  $21.1 \pm 0.7 \text{ kJ mol}^{-1}$ . Scattered species were monitored using a triply differentially pumped detector consisting of a Brink-type electron-impact ionizer, quadrupole mass filter, and a Daly ion detector<sup>9</sup> in  $2.5^\circ$  steps between  $7.5^\circ$  and  $72.0^\circ$  with respect to the CN beam. Information on the reaction dynamics is extracted from the time-of-flight (TOF) spectra and the laboratory angular distribution (LAB) by using a forward-convolution technique.<sup>10</sup> This iterative approach initially guesses the angular flux-distribution  $T(\theta)$  and the translational energy flux distribution  $P(E_T)$  in the center-of-mass (CM) coordinate system assuming mutual independence.

The composition of the primary beam is characterized on axis recording TOF data to probe carbon and carbon–nitrogen containing species. These measurements show that besides  $\text{CN}(X^2\Sigma^+)$ , the beam contains  $\text{C}(^3P_j)$ ,  $\text{C}_2(X^1\Sigma_g^+)$ ,  $\text{C}_3(X^1\Sigma_g^+)$ , and  $\text{CN}_2$  isomers.<sup>11</sup> The contribution of  $\text{CN}_2$  is very weak. If we compare the integrals of the TOF at  $m/e = 26$  ( $\text{CN}^+$ ) and  $m/e = 40$  ( $\text{CN}_2^+$ ) and account for different ionization cross sections, relative intensities of  $[\text{CN}]/[\text{CN}_2] = 1000\text{--}2000$  are derived. Further, we calculate number densities of about  $2\text{--}3 \times 10^{11} \text{ cm}^{-3}$  CN in the interaction region. This is about a factor of 50 weaker compared to supersonic  $\text{C}(^3P_j)$  beams produced in our lab.

### III. RESULTS

Reactive scattering signal is observed at  $m/e = 51$  ( $\text{C}_3\text{NH}^+$ ) and  $50$  ( $\text{C}_3\text{N}^+$ ), c.f. Fig. 1. TOF spectra for several scattering angles are shown in Fig. 2. TOF spectra recorded at both mass to charge ratios reveal identical patterns, and hence  $m/e = 51$  fragments to  $m/e = 50$  in the electron impact ionizer of the detector. No higher masses were observed pointing out the reaction of  $\text{CN}_2$  isomers with  $\text{C}_2\text{H}_2$  does either not take place, its cross section is too low, or the signal is too weak. Although  $\text{C}(^3P_j)$  reacts with acetylene as well, the  $\text{C}_3\text{H}$  reaction product gives  $m/e = 37$  and  $36$ . Therefore, this reaction cannot contribute to  $m/e = 51$  and  $50 \text{ mol}^{-1}$ .<sup>12</sup>

Our LAB distribution of the HCCCN product peaks at  $27.0^\circ$ , slightly forward scattered with respect to the center-of-mass angle of  $\theta_{\text{CM}} = 30.0 \pm 1.0^\circ$ . The distribution is very broad and extends about  $45^\circ$  in the scattering plane. This finding implies a large fraction of the total available energy is released into translational degrees of freedom of the products. Further, the  $P(E_T)$  expects to reveal a peaking well away from zero. The best fit of the LAB distribution and TOF spectra were obtained with  $P(E_T)$ s extending to  $100\text{--}$

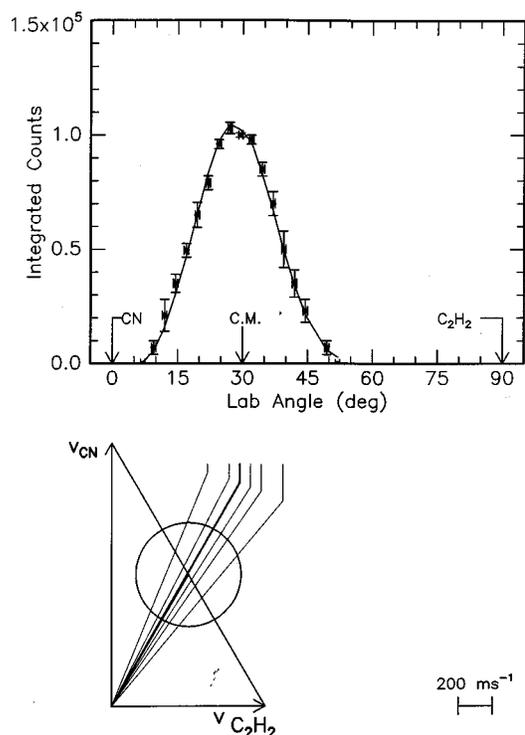


FIG. 1. Lower: Newton diagram for the reaction  $\text{CN}(X^2\Sigma^+) + \text{C}_2\text{H}_2(X^1\Sigma_g^+)$  at a collision energy of  $21.1 \text{ kJ mol}^{-1}$ . The circle stands for the maximum center-of-mass recoil velocity of the HCCCN product. Upper: Laboratory angular distribution of the HCCCN product at  $m/e = 50$ . Circles and error bars indicate experimental data, the solid line the calculated distribution.

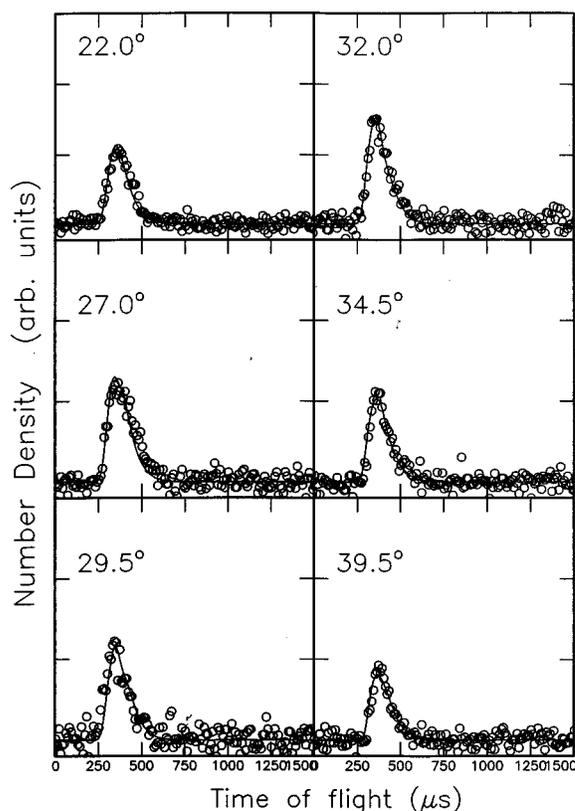


FIG. 2. Time-of-flight data of distinct laboratory angles as indicated in Fig. 1. The dots indicate the experimental data, the solid lines the calculated fit.

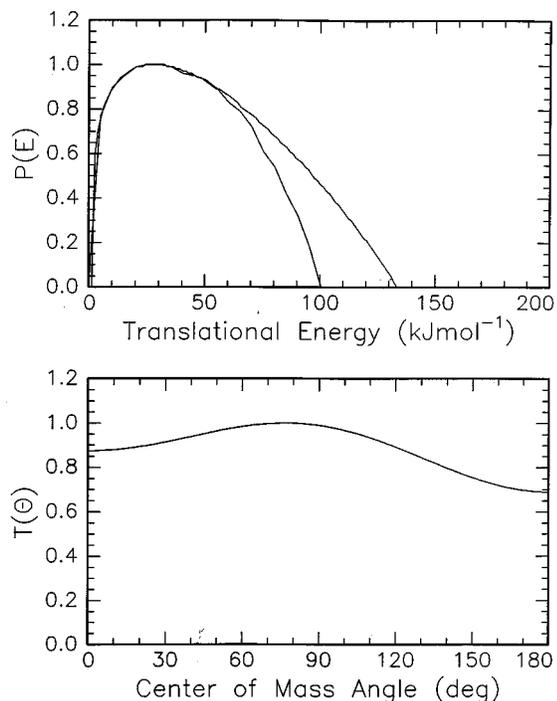


FIG. 3. Lower: Center-of-mass angular flux distribution for the reaction  $\text{CN}(X^2\Sigma^+) + \text{C}_2\text{H}_2(X^1\Sigma_g^+)$  at a collision energy of  $21.1 \text{ kJ mol}^{-1}$ . Upper: Center-of-mass translational energy flux distributions for the reaction  $\text{CN}(X^2\Sigma^+) + \text{C}_2\text{H}_2(X^1\Sigma_g^+)$  at a collision energy of  $21.1 \text{ kJ mol}^{-1}$ ; both curves represent best fits within upper and lower error limits.

$130 \text{ kJ mol}^{-1}$ . Correcting for the relative collision energy of  $21.1 \text{ kJ mol}^{-1}$ , the reaction of  $\text{CN} + \text{HCCH}$  to form  $\text{H}$  and  $\text{HCCCN}$  is exothermic by about  $80\text{--}110 \text{ kJ mol}^{-1}$ . Finally, the  $P(E_T)$  has a maximum at about  $20\text{--}35 \text{ kJ mol}^{-1}$  (Fig. 3). This implies that the exit transition state to the  $\text{H}$  and  $\text{HCCCN}$  products is tight (repulsive carbon–hydrogen bond rupture involving a significant electron rearrangement). Further, a large amount of energy on average is released into translational motion of the reactants, here  $48\text{--}55 \text{ kJ mol}^{-1}$ . The center-of-mass angular flux distribution  $T(\theta)$  is slightly forward scattered with respect to the  $\text{CN}$  beam and peaks on a

broad plateau between  $60^\circ$  and  $95^\circ$ . Both conclusions suggest the reaction involves indirect scattering dynamics via a  $\text{HCCHCN}$  complex whose lifetime is shorter than its rotational period. In addition, the light  $\text{H}$  atom is expected to be emitted almost perpendicular to the rotating  $\text{HCCCN}\cdots\text{H}$  complex to yield a nearly “sideways” peaking of  $T(\theta)$ .<sup>13</sup> The weak  $T(\theta)$  polarization results suggest a poor coupling between the initial  $\mathbf{L}$  and final orbital angular momentum  $\mathbf{L}'$  indicating that most of the total angular momentum channels into rotational excitation of the  $\text{HCCCN}$  product.

#### IV. DISCUSSION

The high-energy cutoff of the translational energy distribution is consistent with the formation of the cyanoacetylene molecule,  $\text{HCCCN}$ , in its  $X^1\Sigma^+$  electronic ground state. The experimentally determined reaction enthalpy of  $80\text{--}110 \text{ kJ mol}^{-1}$  lies within limits of recent *ab initio* calculations, i.e.,  $66\text{--}88 \text{ kJ mol}^{-1}$ .<sup>14</sup> Based on our data the following chemical reaction dynamics are likely. The  $\text{CN}(X^2\Sigma^+)$  radical attacks the  $\pi$  orbital of the  $\text{C}_2\text{H}_2$  molecule to form a carbon–carbon  $\sigma$  bond and a *cis* or *trans*  $\text{C}_2\text{H}_2\text{CN}$  complex {1} on the  ${}^2A'$  surface, c.f. Fig. 4. Electronic structure calculations document that this reaction pathway has no entrance barrier; {1} belongs to the  $C_s$  point group ( ${}^2A'$  electronic wave function) and is bound by  $210\text{--}240 \text{ kJ mol}^{-1}$  with respect to both reactants. Upon complex formation, the four heavy atoms are rotating in plane almost perpendicular to the total angular momentum vector  $\mathbf{J}$  around the  $C$  axis of {1}. {1} undergoes  $\text{C}\text{--}\text{H}$  bond rupture through a tight transition state to  $\text{HCCCN}$  and  $\text{H}$  located  $40\text{--}50 \text{ kJ mol}^{-1}$  below the reactants. The anisotropic exit potential excites the  $\text{HCCCN}$  molecule to  $B$  like rotations. Since our center-of-mass angular distribution depicts a forward-backward asymmetry as well as a broad peak between  $60^\circ$  and  $95^\circ$ , the  $\text{H}$  atom is emitted almost perpendicular to the  $\text{HCCCN}$  axis to yield a nearly sideways peaking of  $T(\theta)$ . Recent electronic structure calculations on the exit transition state support these experimental findings. Here, the exit transition state is found to be tight and located between  $30$  and  $50 \text{ kJ mol}^{-1}$  above the

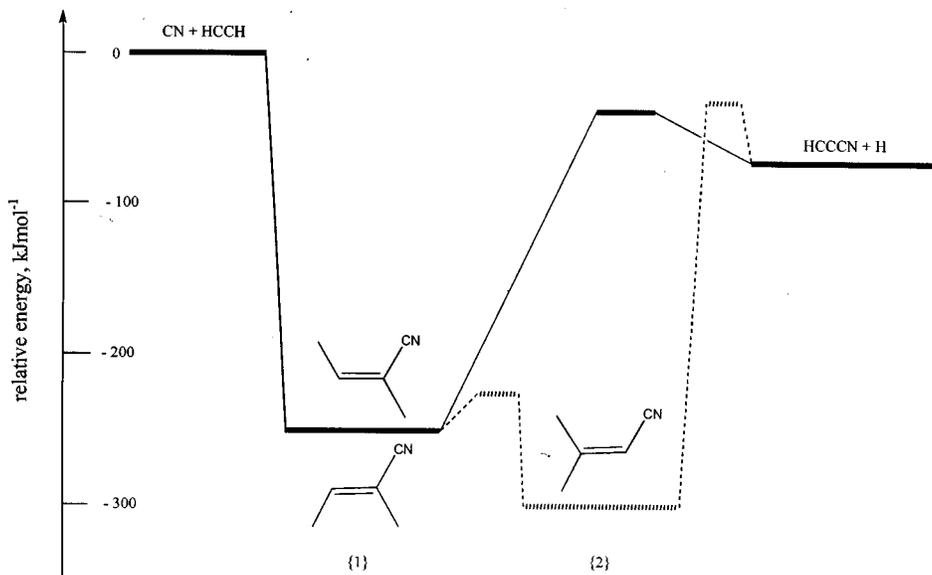


FIG. 4. Schematic energy level diagram for the reaction  $\text{CN}(X^2\Sigma^+) + \text{C}_2\text{H}_2(X^1\Sigma_g^+)$  adapted from Ref. 14. Dashed lines; no energetics available.

products. In addition, the bond distance between the departing H atom and the C atom is about 182.5 pm, the HCC---H angle about 109.8°, and the H---CCN angle circa 92.8°. Since however the  $T(\theta)$  shows a forward-backward asymmetry, the lifetime of the decomposing complex is less than its rotational period. Based on our experimental data alone, we cannot prove or disprove the possibility of a H atom migration from {1} to form {2} ( $C_s, ^2A'$ ) prior to H atom emission. Neither the barrier nor any energetics of {2} are known. Likewise, the role of a meta stable cyanovinylidene isomer CCHCN or isocyanovinylidene remains to be resolved.

Despite these open questions, the present crossed beams study demonstrates for the first time the formation of cyanoacetylene,  $HCCCN(X^1\Sigma^+)$ , via the neutral-neutral reaction of cyanogen radicals,  $CN(X^2\Sigma^+)$ , with acetylene,  $C_2H_2(X^1\Sigma_g^+)$ . The explicit identification of the reaction product represents a solid background for the title reaction to be included with more confidence in reaction networks modeling the chemistry in dark, molecular clouds as well as outflow of dying carbon stars. In addition, these results unravel Takano *et al.* observation of  $^{13}C$  isotopomers.<sup>15</sup> The authors discovered that the  $^{13}C$  isotope is concentrated in the carbon atom of the  $HCC^{13}CN$  molecule adjacent to the N atom. If  $^{13}C$  is already enriched in  $^{13}CN$  radicals, a reaction with  $C_2H_2$  could propagate this isotope enrichment to the newly formed  $HCC^{13}CN$  molecules.

Besides interstellar environments, reactions of CN radicals with unsaturated hydrocarbons are of fundamental relevance to the atmospheric chemistry in Saturn's moon Titan. Its atmosphere consists mainly of  $N_2$  and  $CH_4$  together with minor constituents  $C_2H_6$ ,  $C_3H_8$ ,  $C_2H_2$ ,  $HCN$ ,  $HC_3N$ , and  $C_2N_2$ .<sup>16</sup> Photochemically driven models of Titan's atmosphere suggest that a great variety of hitherto unobserved nitriles should be present as well, among them acrylonitrile,  $C_2H_3CN$ , cyanopropyne,  $CH_3CCCN$ , cyanoallene,  $H_2CCCHCN$ .<sup>17</sup> The following reactions could synthesize these CN containing molecules:



Until this time, reaction products of reactions (6) and (7) except HCCCN have not been detected in Titan's atmosphere. But these investigations will be part of the in the

frame of the NASA-ESA Cassini-Huygens mission to, including an orbiter (Cassini) around Saturn and a probe (Huygens) probing Titan's atmosphere.<sup>18</sup> Preliminary crossed beam experiments of reaction (6) identify a H versus CN displacement. The CN-H exchange channel was discovered in reaction (7) as well, but the assignment of the isomer is still in progress.

## ACKNOWLEDGMENTS

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