

# Synthesis of Long Carbon Chains upon VUV Photolysis of Methane in Solid Neon

Upon irradiation of methane in solid neon with vacuum ultraviolet light, we produced a series of long carbon chain molecules up to  $C_7$ . Among these photoproducts, IR spectrum of CH stretching and CC stretching modes of  $C_nH$  was obtained for the first time.

In the space, stars might form within the densest regions of the interstellar medium (ISM) or molecular clouds. These regions consist of an extremely dilute mixture of ions, atoms, molecules, larger dust grains, and filled with cosmic rays. The chemistry occurring in these regions has many unusual features, especially in synthesis of carbon, silicon, and metal related molecules. For example, the IRC +10216; the well-studied carbon-rich star, more than 50 chemical compounds have been identified, listed in Fig. 1, in the circumstellar envelope.

Molecules identified in IRC+ 10216

CO	$C_2H$	$HC_3N$	$C_2S$	SiO	NaCl
CS	$C_3H$	$HC_5N$	$C_3S$	SiS	AlCl
CN	$C_4H$	$HC_7N$	$C_3N$	SiC	KCl
HCN	$C_5H$	$HC_9N$	$C_5N$	SiN	AlF
HNC	$C_6H$	$C_4H_2$	$HC_4N$	SiC <sub>2</sub>	MgNC
CH <sub>4</sub>	$C_7H$	$C_6H_2$	$C_3H_2$	SiC <sub>3</sub>	MgCN
NH <sub>3</sub>	$C_8H$	$HC_2N$	CH <sub>3</sub> CN	SiCN	AlNC
H <sub>2</sub> S		$C_3$	CP	SiC <sub>4</sub>	KCN
$C_2H_2$		$C_5$	PN	SiH <sub>4</sub>	NaCN
$C_2H_4$					

Fig. 1: Identified species in IRC +10216

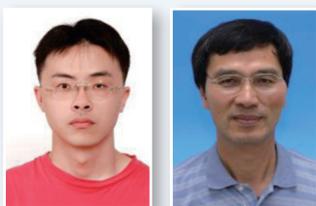
## Beamline

21A2 U9 White Light

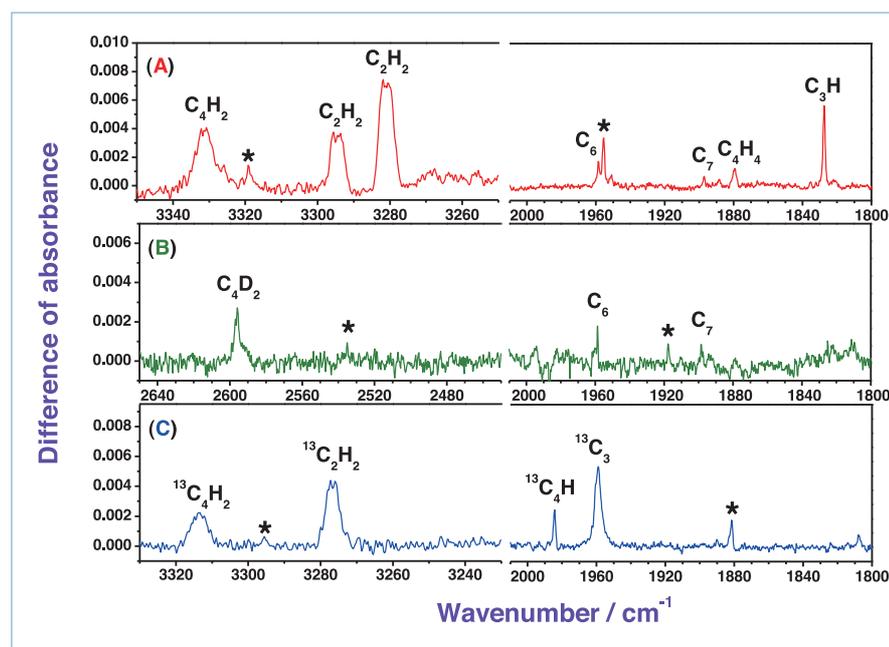
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The identified species in this object contain carbon and acetylenic chains. To date, it is unclear the reaction mechanism of formation of carbon chains. The complex chemical reaction in space has received much attention in several decades. Scientists use various methods, such as pyrolysis, ion bombardment, and photolysis, to activate chemical reactions to model the astro-environment in a laboratory. The complex chemistry might be better explained, if we understand how the starting single carbon molecules form new carbon-carbon bonds. Hence, we used VUV synchrotron light to photolysis the methane diluted in solid matrix and detected the photoproducts



**Fig. 2:** Partial IR spectra of solid methane/Ne (1/1000) samples with isotopic variants after irradiation at 130 nm for 2 h: (A) CH<sub>4</sub>/Ne, (B) CD<sub>4</sub>/Ne, and (C) <sup>13</sup>CH<sub>4</sub>/Ne.

by the IR absorption spectroscopy. The results of our work might provide insight into our understanding on formation mechanism for long carbon chains in the deep space.

We performed the photolysis experiment using a matrix-isolation/FTIR end-station coupled to the white branch of the U9 undulator. In our work, a Ne gas containing methane (1/500 or 1/1000) was deposited onto a 3 K target; which was maintained by a closed cycle refrigerator. The IR absorption spectra were recorded at various stages of experiments with a FTIR spectrometer (Bomem, DA8) equipped with a KBr beamsplitter and a MCT detector (cooled to 77 K) to cover the spectral range 500–5000 cm<sup>-1</sup>. Spectra with 400 scans and resolution 0.5 cm<sup>-1</sup> were typically recorded at each stage.

Absorption of gaseous methane begins at 145 nm with cross section about 0.003 Mb (1 Mb = 10<sup>-18</sup> cm<sup>2</sup>) and increases monotonically and continuously to smaller wavelengths; these cross sections are greater than 10 Mb for λ < 134 nm. To photolyze methane efficiently, we selected radiation at 130 nm at which the gaseous cross section is 18 Mb. Irradiation at 130 nm of CH<sub>4</sub> in a Ne matrix for 2 hours caused the intensities of lines of CH<sub>4</sub> to decrease by about 40% and produced various products – carbon clusters and hydrocarbons including CH, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>, C<sub>3</sub>H, C<sub>4</sub>, C<sub>4</sub>H, C<sub>4</sub>H<sub>2</sub>, C<sub>5</sub>, C<sub>6</sub>, and C<sub>7</sub>.

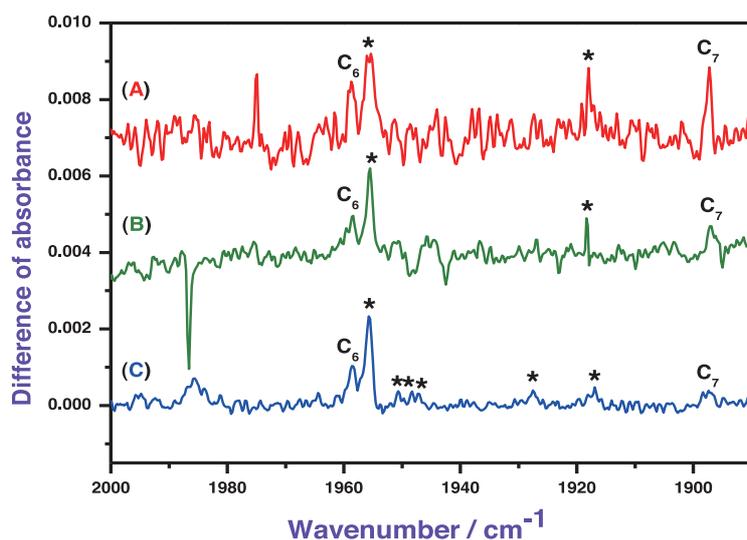
Figure 2(A) shows a partial difference IR absorption spectrum of a sample CH<sub>4</sub>/Ne (1/1000) after photolysis at 130 nm for 2 h; this difference spectrum was derived on subtracting the spectrum recorded after irradiation from

the preceding deposition spectrum. Photoproducts of known species in these spectral regions are marked in the figure. Two absorption lines appearing at 3319.3 and 1955.5 cm<sup>-1</sup> (denoted \*) are previously unreported.

To identify the carriers of unassigned lines based on isotopic shifts and line splitting, we undertook experiments with isotopic substitution (CD<sub>4</sub>, CH<sub>2</sub>D<sub>2</sub>, CH<sub>4</sub>/CD<sub>4</sub>, <sup>12</sup>CH<sub>4</sub>/<sup>13</sup>CH<sub>4</sub>, and <sup>13</sup>CH<sub>4</sub>) of methane dispersed in solid Ne under the same conditions of VUV photolysis; the difference IR absorption spectra for these isotopic samples are shown also in Fig. 2. Photolysis of a CD<sub>4</sub>/Ne sample at 130 nm produced pertinent unreported lines shifted to 2535.1 cm<sup>-1</sup> and 1917.9 cm<sup>-1</sup>, as shown in Fig. 2(B); the shifts yield isotopic ratios 0.7637 and 0.9808, respectively. For a <sup>13</sup>CH<sub>4</sub>/Ne sample, the corresponding lines appeared at 3295.6 and 1881.5 cm<sup>-1</sup>, as shown in Fig. 2(C), consistent with <sup>13</sup>C-isotopic ratios 0.9929 and 0.9622, respectively.

For a CH<sub>2</sub>D<sub>2</sub>/Ne or CH<sub>4</sub>/CD<sub>4</sub>/Ne sample under the same experiments, as shown in Fig. 3, the appearance of only two pertinent lines at 1955.5 and 1917.9 cm<sup>-1</sup> indicates that the carrier contains only one hydrogen atom.

To determine definitely the carbon number of this monohydride carbon species, we performed an experiment with mixed isotopic sample of <sup>12</sup>CH<sub>4</sub>/<sup>13</sup>CH<sub>4</sub>/Ne (0.9/0.1/500) under the same conditions of VUV photolysis; the difference IR absorption spectra for these isotopic samples are shown also in Fig. 3. The single line at 1955.5 cm<sup>-1</sup> observed in the <sup>12</sup>CH<sub>4</sub>/Ne experiment split into six peaks in the <sup>12</sup>CH<sub>4</sub>/<sup>13</sup>CH<sub>4</sub>/Ne experiment. Considering the composition ratio of <sup>12</sup>C/<sup>13</sup>C, we expect



**Fig. 3:** Partial difference IR absorption spectra of methane in Ne matrix samples with isotopic variants after irradiation at 130 nm for 2 h: (A)  $\text{CH}_2\text{D}_2/\text{Ne}$  (1/1000), (B)  $\text{CH}_4/\text{CD}_4/\text{Ne}$  (0.5/0.5/1000), (C)  $^{12}\text{CH}_4/^{13}\text{CH}_4/\text{Ne}$  (0.9/0.1/500).

the formed carbon monohydride might only contain one  $^{13}\text{C}$ . The observed splitting including one intense and five weak peaks implies that the carrier contains five carbon atoms. Therefore, the absorption features of the new lines at 3319.3 and 1955.6  $\text{cm}^{-1}$  might correspond to  $\text{C}_5\text{H}$ . Comparison of known D-isotopic ratios of C-H stretching modes of  $\text{C}_n\text{H}$  indicates that our observed D-isotopic ratio is reasonable for the  $\text{C}_5\text{H}$  species.

Our experimental findings have been corroborated by accurate calculations of fundamental vibrational wavenumbers of  $\text{C}_5\text{H}$ . According to the previous and our theoretical investigations, the most energetically stable isomer of this radical is *linear-C<sub>5</sub>H*. Also, the mean absolute deviation between the corresponding computed and measured fundamental wavenumbers of *l-C<sub>5</sub>H* (and its isotopic variants) is 28  $\text{cm}^{-1}$ . This agreement is deemed entirely satisfactory when one takes into account that the experiment is performed in a solid neon matrix whereas the calculations pertain to an isolated molecule as in the gaseous phase. We thus conclude that the present theoretical results constitute a strong confirmation of our experimental assignment of the observed spectral lines to *l-C<sub>5</sub>H*.

Acetylenic linear carbon-chain radicals  $\text{C}_n\text{H}$  play important roles in interstellar chemistry and combustion. Up to  $n=8$ , these radicals have been detected in interstellar molecular clouds and envelopes of evolving stars with large radio telescopes. In the laboratory, these singly hydrogenated, long-chain, carbon radicals have been identified mostly by Fourier transform microwave (FTM) spectra ( $n \leq 14$ ). Other spectral data of carbon chains up to  $\text{C}_{10}\text{H}$  were obtained from fluorescence, cavity ring-down

absorption and photoionization. Infrared absorption spectra that provide information about the bonding and structures of molecules are limited compared with other optical spectra for  $\text{C}_n\text{H}$  ( $n=2\sim 4, 6$ ) radicals. Vibrational characterization of longer carbon chains has not yet been achieved, and the IR spectrum of  $\text{C}_5\text{H}$  has been lacking. Therefore, our report on the generation of  $\text{C}_5\text{H}$  radicals by VUV photolysis of methane isolated in solid Ne at 3 K and identification of IR fundamental vibrational modes of  $\text{C}_5\text{H}$  will be useful for laboratory investigation and astronomical observation of this species.

In summary, we have demonstrated a method to produce long carbon-chain molecules in a neon matrix by photolysis of  $\text{CH}_4$  with vacuum ultraviolet light. Using this method, we generated and identified *linear-C<sub>5</sub>H* radicals. The absorption features at 3319.3 and 1955.5  $\text{cm}^{-1}$  are assigned to the C-H stretching and C=C stretching modes of  $\text{C}_5\text{H}$  based on observed D- and  $^{13}\text{C}$ - isotopic shifts, line splittings, and theoretical predictions of line positions, infrared intensities and isotopic ratios of  $\text{C}_5\text{H}$ .

### Experimental Station

Matrix-isolation / FT-IR end station

### Publication

Y.-J. Wu, H.-F. Chen, C. Camacho, H. A. Witek, S.-C. Hsu, M.-Y. Lin, S.-L. Chou, B.-M. Cheng, and J. F. Ogilvie, *Astrophys. J.* **701**, 8 (2009).

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