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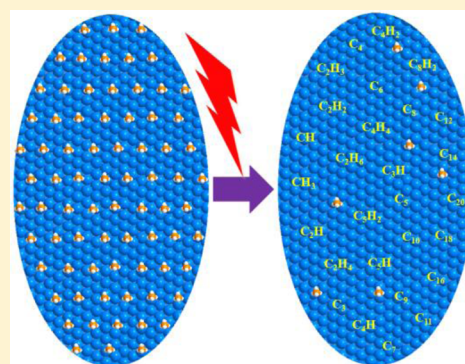
Vacuum-Ultraviolet Photolysis of Methane at 3 K: Synthesis of Carbon Clusters up to C_{20}

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ABSTRACT: Samples of pure methane and of methane dispersed in solid neon at 3 K subjected to irradiation at wavelengths less than 165 nm with light from a synchrotron yielded varied products that were identified through their infrared absorption spectra, including CH_3 , C_2H_2 , C_2H_3 , C_2H_4 , C_2H_6 , C_4H_2 , C_4H_4 , C_5H_2 , C_8H_2 , C_nH with $n = 1-5$, and carbon chains C_n with $n = 3-20$. The efficiency of photolysis of methane and the nature of the photoproducts depended on the concentration of methane and the wavelength selected for irradiation; an addition of H_2 into solid neon enhanced the formation of long carbon chains.



1. INTRODUCTION

After Dewar achieved the liquefaction of H_2 in London in 1898, he and H. O. Jones in Cambridge applied their production of low temperatures to stabilize what was claimed to be product CS from an electric discharge of CS_2 , but no direct evidence of the nature of the product was practicable.¹ The combination of samples at temperatures less than 80 K with spectrometric observations began in 1954 with atoms and radicals trapped in glassy hydrocarbon solvents by Norman and Porter;² two conditions that they stated to be effective for the trapping of reactive species are that reaction with the solvent must not occur and that diffusion must be prevented. The former condition for a solid phase is best accomplished with neon, which forms no stable compound in a form of neutral molecule, but diffusion is less readily controlled. The standard melting point of neon is 24.5 K, but a crystalline or glassy deposit is too volatile for use in our open system above 9 K.

Most applications of dispersions in solid noble-gas elements for photochemical experiments have involved either the photolytic decomposition of a selected precursor or the photochemical production of an atom or small radical that reacts with another species in the solid sample to generate a larger product. A pertinent instance of the former application was the photolysis of methane dispersed in solid argon to produce methyl radicals, whereas the presumed reaction of methylene with nitrogen dispersant is an instance of the latter application, both as reported by Milligan and Jacox.³ In our experiments involving photolysis, with light of wavelength less than 165 nm, of methane, but dispersed in solid neon at 3 K and with a synchrotron as a source of radiation, we have produced large clusters of carbon atomic centers, up to C_{20} ,

which is contrary to the conventional destructive process. A highly novel aspect of our experiments is not only such a production but also that the yield of such agglomerates increased both with a decreasing initial concentration of methane dispersed in solid neon and with added hydrogen. The photochemistry of methane in condensed phases hence differs from that of gaseous methane,⁴⁻⁶ and our generation of long carbon chains from methane on photolysis is a highly novel result.

2. EXPERIMENTS

The apparatus for photolysis of solid samples was similar to that described previously.⁷⁻⁹ A well-mixed, gaseous sample containing methane was deposited on a CsI window before its irradiation at a selected wavelength; a known quantity (number of moles) of absorbing molecules was deposited in each experiment, but the fraction of that quantity interrogated with the infrared beam is unknown. A closed-cycle refrigerator (Janis RDK-415) cooled the CsI substrate to 3 K. A turbomolecular pump backed with a scroll pump evacuated the chamber to a pressure less than 4 μ Pa. The source of radiation for photolysis was an undulator with periodically spaced permanent magnets (90 mm, U90) attached to the storage ring of an electron accelerator (energy, 1.5 GeV) at beamline BL21A2 of National Synchrotron Radiation Research Center, Taiwan. Harmonics from the undulator were suppressed through absorption by Ar at 1.33 kPa and a filter window: LiF for 120 and 121.6 nm,

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CaF₂ for 130 and 140 nm, and silica (Suprasil) for 165 nm. The ultraviolet radiation incident on our samples in a nearly rectangular beam of cross section $\sim 3.5 \times 5$ mm² emanated from that undulator that provided trains of 160 pulses at a 2 ns interval during each 400 ns; although the mean flux of photons was 2.4×10^{15} photons s⁻¹ (bandwidth 2%), each pulse of Gaussian profile and width 25 ps comprised 6×10^6 photons. The storage ring of our synchrotron is operated to maintain a constant beam current of electrons in the storage ring by means of injection of a few electrons into it every minute; the electron current maintains 99.5% stability.

At each stage of an experiment, absorption spectra were recorded with an interferometric infrared spectrometer (Bomem DA8, KBr beamsplitter, HgCdTe detector cooled to 77 K) covering the mid-infrared spectral range, 500–5000 cm⁻¹, involving 400–600 scans at resolution 0.2–0.5 cm⁻¹. The uncertainty of wavenumber measurement is ± 0.1 cm⁻¹.

Difference spectra of the absorbance curve after irradiation of a sample with ultraviolet light for some cumulative period minus the absorbance curve before irradiation emphasized the variation of the chemical composition caused by primary photolysis and possible secondary photolysis or reaction of the primary products. The direct absorbance curves were ratios of the spectra of the sample and of the background. The image of the infrared beam at the sample was nearly circular, of diameter ~ 5 mm. The overlap of the beam from the photolysis source with the detection beam in this work was imperfect; for this reason and because of an unknown fraction of the gaseous sample frozen within the region interrogated with the infrared beam, our experiments yield comparative, rather than absolute, photometric information, in common with laboratories elsewhere.

We measured the absorption spectrum of pure solid methane in the vacuum-ultraviolet (VUV) region to the limit of transmission of optical components, about 106 nm, with a separate double-beam absorption apparatus at spectral resolution 0.2 nm that was adequate for the unstructured spectrum.^{10–12} CH₄ was deposited onto a LiF window maintained at 10 K with a refrigerator system (APD HC-DE204S). The light from beamline BL03 dispersed with a monochromator (cylindrical grating, 6 m) and transmitted through this LiF window and the sample impinged on a glass window coated with sodium salicylate; the fluorescence was detected with a photomultiplier tube (Hamamatsu R943) in a photon-counting mode.

CH₄ (99.999%, Matheson Gases), CD₄ (isotopic purity 99%, Cambridge Isotopic Laboratories), ¹³CH₄ (isotopic purity 99.9%, Cambridge Isotopic Laboratories), C₂H₂ (99.0%, Matheson Gases), C₂H₄ (99.99%, Matheson Gases), C₂H₆ (99.995%, Matheson Gases), H₂ (99.9999%, Matheson Gases), and Ne (99.999%, Scott Specialty Gases) were used without further purification. For photolysis experiments, either pure methane or mixtures of methane with Ne at ratios 1:100, 1:1000, 1:2000, or 1:10 000 or mixtures of methane and H₂ with Ne at ratio 1:6:1000 were deposited over periods from 2 min to 170 h depending on the nature of the sample. To verify the identification of products from the photolysis of pure methane, we prepared and deposited mixtures of C₂H₂, C₂H₄, or C₂H₆ with CH₄ at ratio 1:250 to record their infrared absorption spectra.

3. RESULTS

3.1. VUV Absorption Spectra of Methane. Vacuum-ultraviolet absorption spectra of solid methane as a thin film at 10 K and absolute cross section for gaseous methane at 300 K in range 100–160 nm were reported in our previous works.^{9,13} Both spectra exhibit continuous profiles in this measured range.

When the wavelength is decreased from an apparent threshold near 151 nm (8.21 eV), the absorption of solid methane exhibits a local maximum near 124.2 nm (9.983 eV), a local minimum near 116.4 nm (10.652 eV), and a continuous increase to the limit of measurement about 106 nm. The absorption of gaseous methane in the same region from an apparent onset at about 145 nm (8.55 eV) contains two broad maxima near 127.5 (9.724 eV) and 118 nm (10.51 eV) and a substantial increase to the same limit of measurement at 106 nm; a weak feature is indicated near 119.3 nm (10.393 eV) on top of the broad feature, and more pronounced structure, perhaps of the nature of Fano resonances, is discernible less than 110 nm. The threshold of absorption of solid methane appears to be shifted about 6 nm to greater wavelength relative to the onset for gaseous CH₄,¹³ but the first maximum of solid CH₄ is shifted about 3.3 nm to smaller wavelength. According to the reported absorption spectrum,⁹ the relative absorbance of solid methane is 0.027 at 140 nm, 0.889 at 130 nm, and 1.30 at 120 nm.

3.2. Infrared Absorption Spectra of Methane in Solid Samples. In the mid-infrared region, the principal vibration–rotational bands of gaseous CH₄ in fundamental vibrational modes have centers near 1306.4 cm⁻¹, assigned to deformation mode ν_4 , and near 3018.9 cm⁻¹, associated with stretching mode ν_3 . Figure 1 presents spectra of CH₄ in solid samples, all

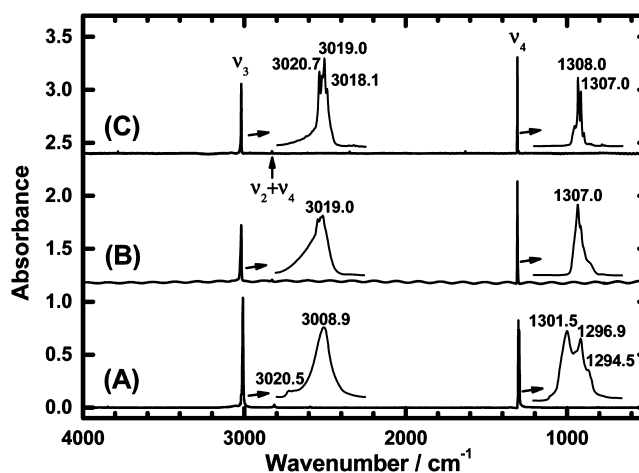


Figure 1. Absorption spectra of (A) pure CH₄, (B) CH₄:Ne = 1:100 (ordinate scale offset +1.2), (C) CH₄:Ne = 1:1000 (ordinate scale offset +2.4), all at 3 K; resolution, 0.2 cm⁻¹ from 600 coadded interferograms; the widths of inset plots are 30 cm⁻¹.

at 3 K. For pure methane as a thin film, deposited at 7.6×10^{-7} μmol s⁻¹ for 120 s, the feature corresponding to ν_3 comprises a single prominent line with maximum at 3008.9 cm⁻¹, a shoulder at about 3020.5 cm⁻¹, and width 5.9 cm⁻¹ at half-maximum intensity; for ν_4 a partially resolved doublet, width 8.2 cm⁻¹, appears at 1301.5 and 1296.9 cm⁻¹, with a shoulder at 1294.5 cm⁻¹, as shown in Figure 1A.

For methane dispersed in solid neon, the characteristic features appear as multiplets; the spectra of samples of CH₄

Table 1. Spectral Lines (Wavenumber per Centimeter) of Products of Photolysis of Pure Methane, Methane at Varied Molar Ratios Dispersed in Neon, and Methane and Hydrogen Dispersed in Neon at 3 K upon Photolysis at 121.6 nm

species	pure CH ₄	CH ₄ :Ne = 1:100	CH ₄ :Ne = 1:1000	CH ₄ :Ne = 1:2000	CH ₄ :Ne = 1:10 000	CH ₄ :H ₂ :Ne = 1:6:1000
CO	—	2141.1	2141.1	2141.1	2141.1	2141.2
H ₂ CO	—	—	—	—	—	1748.5 (ν_2), 2782.2 (ν_1)
CH	—	2732.9/2743.0	2732.9/2743.5?	2732.9/2743.5?	2732.9/2743.5?	2733.1/2743.5?
CH ₃	608.8 (ν_2)	602.9/604.7 (ν_2)	602.6/604.5/608.9/620.2 (ν_2), 1388.0/1389.9/1392.0 (ν_4) 3161.9 (ν_3)	602.5/604.5/608.9/619.9 (ν_2), 1388.0/1389.9/1392.0 (ν_4), 3161.8 (ν_3)	602.5/604.5/608.7/620.0 (ν_2), 1387.8/1390.0/1392.0 (ν_4), 3161.7 (ν_3)	602.4/604.4/608.7/619.8 (ν_2), 1387.8/1390.0/1392.0 (ν_4), 3161.7 (ν_3)
C ₂ H	—	—	1835.9 (ν_3)	1835.4 (ν_3)	1835.7 (ν_3)	1835.4 (ν_3)
C ₂ H ₂	736.5 (ν_5)	732.2 (ν_5), 1329.9 ($\nu_4+\nu_5$), 3281.6 (ν_3), 3295.1 ($\nu_3+\nu_4+\nu_5$)	732.2 (ν_5), 1330.0 ($\nu_4+\nu_5$), (ν_3), 3296.0 ($\nu_3+\nu_4+\nu_5$)	731.9 (ν_5), 1330.1 ($\nu_4+\nu_5$), (ν_3), 3296.1 ($\nu_3+\nu_4+\nu_5$)	731.9 (ν_5), 1329.8 ($\nu_4+\nu_5$), (ν_3), 3295.6 ($\nu_3+\nu_4+\nu_5$)	732.1 (ν_5), 1329.8 ($\nu_4+\nu_5$), (ν_3), 3295.6 ($\nu_3+\nu_4+\nu_5$)
C ₂ H ₃	—	895.8 (ν_6)	895.3 (ν_6), 1357.5 (ν_5)	895.4 (ν_6), 1357.5 (ν_5)	895.3 (ν_6), 1357.5 (ν_5)	895.5 (ν_6), 1357.5 (ν_5)
C ₂ H ₄	950.8 (ν_7), 1436.2 (ν_{12}), 2979.4 (ν_{10})	950.5 (ν_7), 1441.6 (ν_{12}), 2986.5 (ν_{10})	950.3 (ν_7), 1441.6 (ν_{12}), 2986.4 (ν_{10})	950.0 (ν_7), 1441.7 (ν_{12})	950.3 (ν_7), 1441.7 (ν_{12})	950.0 (ν_7), 1441.6 (ν_{12}), 2987.2 (ν_{10})
C ₂ H ₆	821.6 (ν_{12}), 1372.5 (ν_6), 1463.4 (ν_{11}), 2882.7 (ν_3), 2975.1 (ν_{10})	822.6 (ν_{12}), 1378.2 (ν_6), 1469.7 (ν_{11}), 2893.5 (ν_3), 2982.6 (ν_{10})	1470.0 (ν_{11}), 2894.1 (ν_5), 2982.5 (ν_{10})	1470.0 (ν_{11}), 2982.4 (ν_{10})	1470.3 (ν_{11})	1469.9 (ν_{11}), 2982.4 (ν_{10})
C ₃	—	—	2036.9/2038.7/2041.1/2043.5 (ν_3)	2036.5/2038.6/2041.1/2043.7 (ν_3)	2036.5/2038.6/2041.1/2043.7 (ν_3)	2036.8/2038.6/2041.1/2043.6 (ν_3)
C ₃ H	—	1827.3 (ν_2)	1827.5 (ν_2)	1827.5 (ν_2)	1827.5 (ν_2)	1827.6 (ν_2)
C ₄	—	—	1547.0 (ν_3)	1547.1 (ν_3)	1547.1 (ν_3)	1547.2 (ν_3)
C ₄ H	—	2063 (ν_3)	2063.5 (ν_3)	2063.3 (ν_3)	2063.5 (ν_3)	2063.3 (ν_3)
C ₄ H ₂	—	3330.6 (ν_4)	3330.5 (ν_4)	2017.0 (ν_5), 3331.0 (ν_4)	628.9 (ν_6), 2016.4 (ν_5)	629.4 (ν_6), 2016.4 (ν_5), 3331.7 (ν_4)
C ₄ H ₃	—	—	—	1879.3	1879.5	1879.6
C ₅	—	—	2165.4 (ν_3)	1443.2 (ν_4), 2165.5 (ν_3)	1443.4 (ν_4), 2165.5 (ν_3)	1443.4 (ν_4), 2165.5 (ν_3)
C ₅ H	—	—	1955.6 (ν_3)	1955.7 (ν_3)	1955.6 (ν_3)	1955.5 (ν_3)
C ₅ O	—	—	—	2253.4	2253.2	—
C ₅ H ₂	—	—	—	—	1813.7	—
C ₆	—	1958.8 (ν_4)	1958.7 (ν_4)	1958.6 (ν_4)	1199.3 (ν_5), 1958.6 (ν_4)	1958.6 (ν_4)
C ₇	—	—	1897.2 (ν_5), 2135.2 (ν_4)	1897.2 (ν_5), 2135.1 (ν_4)	1897.1 (ν_5), 2134.8 (ν_4)	1897.2 (ν_5), 2135.0 (ν_4)
C ₈	—	—	—	—	—	—
C ₈ H ₂	—	—	—	2067.8 (ν_5)	1707.5 (ν_6), 2067.8 (ν_5)	—
C ₉	—	—	—	624.8 (ν_{14})	624.7 (ν_{14})	624.6 (ν_{14})
C ₁₀	—	—	—	2010.2 (ν_6)	1602.6 (ν_7), 2010.0 (ν_6)	2010.3 (ν_6), 2078.6 (ν_5)
C ₁₁	—	—	—	—	1915.7, 2074.5	—
C ₁₂	—	—	—	—	1854.0 (ν_8), 1938.6 (ν_7)	1938.8 (ν_7)
C ₁₄	—	—	—	—	1821 (ν_9), 2003.5 (ν_8)	1822.0 (ν_9), 2003.3 (ν_8)
C ₁₆	—	—	—	—	1399.9, 2220.8	854.8, 1399.8, 2221.0
C ₁₈	—	—	—	—	645.4	644.4, 738.1, 1370.2, 2098.0
C ₂₀	—	—	—	—	646.5	645.8, 1378.2, 2087.6, 2215.4
U ^a	912.6	912.1	613.4	—	609.5?	609.6, 2016.9, 2128.7
				613.4, 1736.1	613.5, 617.5, 1204.9, 1208.7, 1735.4, 1813.7, 2080.6	613.6, 1736.0, 2962.2, 3169.9, 3193.8, 3254.1

^aUnidentified lines.

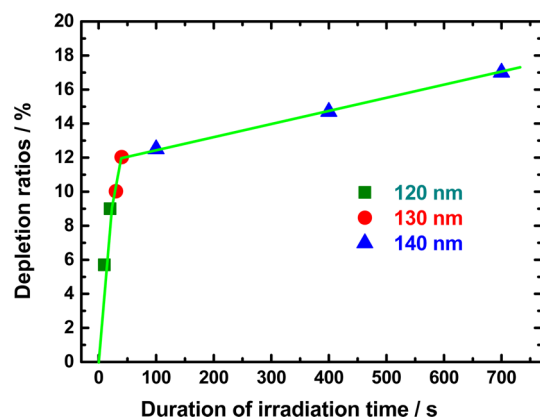


Figure 3. Temporal profiles of depletion ratios for $\text{CH}_4:\text{Ne} = 1:1000$ at 3 K irradiated at indicated wavelengths.

rate of depletion varied with wavelength at 120, 130, and 140 nm in a sequence consistent with the relative absorption coefficients of solid methane at those wavelengths. For a separate sample irradiated at 165 nm, no depletion of CH_4 was observed, consistent with the negligible absorption of CH_4 at a wavelength greater than 151 nm. On irradiation of CH_4 in solid neon with light of wavelength less than 151 nm, the infrared absorption features of methane exhibited a decrease initially roughly linearly proportional to the duration of photolysis and subsequently at a decreasing rate. This depletion was due to either the direct dissociation of methane or its reaction with the products of dissociation of methane.

3.3.4. Identification of Photolysis Products from Methane Dispersed in Solid Neon at 1:1000. Figure 4 shows difference spectra in selected regions between 500 and 3500 cm^{-1} produced after irradiation at 120 nm for 45 min of samples of CH_4 , $^{13}\text{CH}_4$, or CD_4 in Ne (1:1000); the relative depletion of methane was about 35%. A feature pointing upward indicates the absorbance of a given photoproduct; a feature pointing downward indicates a depletion of the parent molecule. After photolysis, many new features appear in Figure 4; the wavenumbers of these lines and their assignments appear in Table 2. Because the initial amount of methane deposited in dispersions with neon at a large ratio was constrained by conditions of the apparatus, with most products of photolysis the proportion of a product was much smaller than the depletion of methane, and the spectral lines of these products were correspondingly weak; the wavenumbers and relative intensities of lines were entirely reproducible in experiments at the same ratio and the same wavelength of radiation, and these wavenumbers are sufficiently characteristic of particular carbon species or carbon hydrides for diagnostic purposes.

These experiments with methane containing ^{12}C , ^{13}C , H, and D enabled a definitive identification of the photolysis products through the wavenumbers of their characteristic infrared absorptions. The wavenumbers of products that contained no hydrogen remained unaltered in the experiments with CD_4 , whereas the absorption lines of species containing H atoms exhibited isotopic shifts on the substitution of D for H. For instance, the vibrational modes of CH, ^{13}CH , and CD radicals were observed at 2732.9 , 2725.3 , and 2030.6 cm^{-1} in agreement with gaseous data 2732.5 ,¹⁵ 2724.1 ,¹⁶ and 2030.8 cm^{-1} ,¹⁵ respectively. New spectral lines discernible near 602.6 , 604.5 , 620.2 , and 1392.0 cm^{-1} are attributed to CH_3 radicals in modes ν_2 (three split lines) and ν_4 ,³ for $^{13}\text{CH}_3$, the corresponding lines

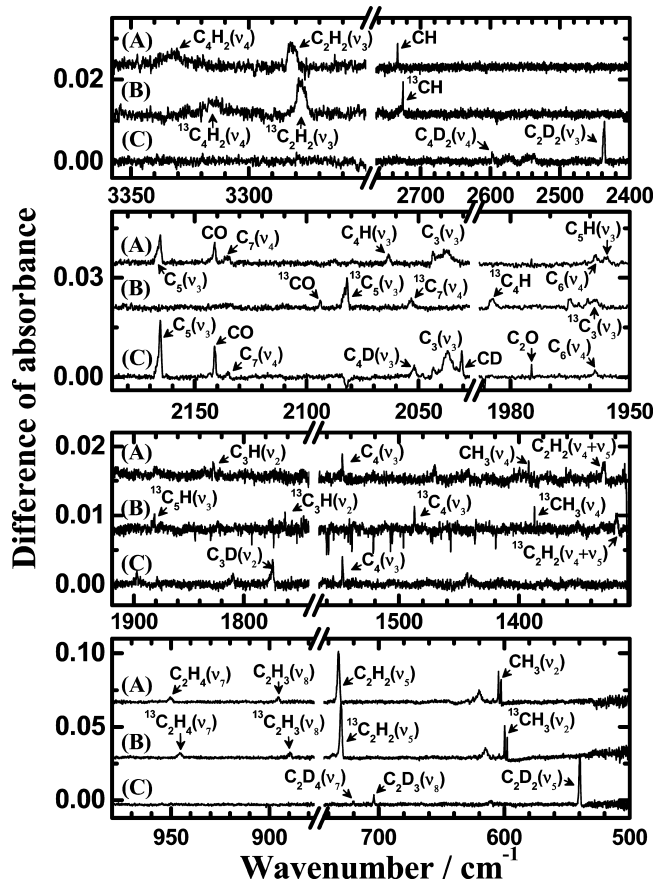


Figure 4. Difference infrared spectra of methane in solid Ne (1:1000) at 3 K after irradiation at 120 nm for 50 min: (A) CH_4 , (B) $^{13}\text{CH}_4$, and (C) CD_4 . Some assignments are indicated.

occur at 597.7 , 599.6 , 614.9 , and 1387.1 cm^{-1} , respectively. For CD_3 , ν_2 shifts to about 460 cm^{-1} , which is beyond our range of detection, but we identified its modes ν_4 at 1027.8 and ν_3 at 2378.9 cm^{-1} .

Apart from these two free radicals that might be produced directly from CH_4 on photochemical dissociation, we detected several molecular products containing multiple carbon atomic centers with hydrogen. For instance, on the basis of the photolysis of C_2H_2 and of C_2H_4 ,^{7,8,17} we identified unambiguously ethyne, ethene, and butadiyne as stable products in these experiments. For these species, spectral lines near 732.2 , 1329.6 , 3282.2 , and 3296.3 cm^{-1} are attributed to C_2H_2 molecules in modes ν_5 , $\nu_4+\nu_5$, ν_3 and $\nu_3+\nu_4+\nu_5$,¹⁷ respectively; near 950.4 cm^{-1} to C_2H_4 molecules in mode ν_7 ,⁷ and near 3330.5 cm^{-1} to C_4H_2 in mode ν_4 .⁸

For the corresponding products $^{13}\text{C}_2\text{H}_2$, we measured lines at 730.1 (ν_5), 1319.1 ($\nu_4+\nu_5$), and 3278.7 cm^{-1} (ν_3); for $^{13}\text{C}_2\text{H}_4$ line at 945.5 cm^{-1} (ν_7);⁷ and for $^{13}\text{C}_4\text{H}_2$ at 3313.7 cm^{-1} (ν_4);⁸ for C_2D_2 at 539.7 (ν_5) and 2436.3 cm^{-1} (ν_3);¹⁷ for C_2D_4 at 720.1 cm^{-1} (ν_7);⁷ and for C_4D_2 at 2597.4 cm^{-1} (ν_4).⁸ For some related free radicals, ν_3 vibrational modes of ethynyl radicals C_2H were detected at 1835.9 , $^{13}\text{C}_2\text{H}$ at 1776.0 , and for C_2D at 1737.6 cm^{-1} , for comparison with absorptions reported at 1835.7 ,¹⁷ 1776.1 ,⁸ and 1737.6 cm^{-1} ,¹⁷ respectively. For the vinyl radical, we recorded its most intense ν_8 mode of C_2H_3 at 895.3 cm^{-1} , $^{13}\text{C}_2\text{H}_3$ at 889.5 cm^{-1} , and C_2D_3 at 703.9 cm^{-1} , which agree with 895.3 , 889.3 , and 704.8 cm^{-1} ,⁷ respectively. Singly hydrogenated carbon chains C_nH were detected as

infrared spectra of methane dispersed in solid neon at ratios 1:2000 and 1:10 000 upon irradiation at 121.6 nm at 3 K for 50 min; the infrared absorption lines of identified products are listed in Table 1. In contrast with more concentrated dispersions, the dilute samples generated additional species with carbon atoms in longer chains. Besides lines of all species observed in the sample with $\text{CH}_4:\text{Ne} = 1:1000$, we recorded other lines at 2067.8 and 2010.2 cm^{-1} from the sample $\text{CH}_4:\text{Ne} = 1:2000$; on the basis of published data, those further lines are attributed to C_8 and C_9 ,^{26,27} respectively. Photolysis at 121.6 nm of the most dilute sample, $\text{CH}_4:\text{Ne} = 1:10\,000$, yielded even further infrared lines of products, which are readily assigned to C_{10} (1915.7 and 2074.5 cm^{-1}), C_{11} (1854.6 and 1938.6 cm^{-1}), C_{12} (1821.0 and 2003.5 cm^{-1}), and C_{14} (1399.9 and 2220.8 cm^{-1}) according to reported data.^{27,28} Other lines, assigned and unassigned, are listed also in Table 1.

On the basis of vibrational wavenumbers of size-selected clusters of C_{16} , C_{18} , and C_{20} isolated in solid N_2 recorded in surface-plasmon polariton-enhanced Raman spectra,²⁹ three weak lines at 645.4, 646.5, and 609.5 cm^{-1} are near lines at 646, 650, and 605 cm^{-1} attributed to C_{16} , C_{18} , and C_{20} , respectively, which we tentatively assign accordingly. According to these assignments, carbon clusters up to C_{20} in $\text{CH}_4:\text{Ne} = 1:10\,000$ formed on photolysis at 121.6 nm, whereas the largest carbon clusters were C_7 formed from the sample at $\text{CH}_4:\text{Ne} = 1:1000$ and C_9 from $\text{CH}_4:\text{Ne} = 1:2000$.

3.3.6. Photolysis Products versus Wavelength. As the rate of depletion of methane upon photolysis is related to the wavelength of radiation incident upon a sample, the wavelength of excitation might affect the nature or proportions of the products of photolysis. To test this possibility, we subjected samples of CH_4 in Ne (1:10 000) to photolysis at wavelengths 121.6, 130, 140, and 165 nm. No product was observed after irradiation at the latter wavelength for 76 min, consistent with 165 nm being beyond the threshold of absorption, about 151 nm. At 121.6 nm, many lines are readily assigned, as displayed in Figure 5B and discussed above; the wavenumbers, relative maximum absorbances, and assignments of various products after photolysis at 121.6, 130, and 140 nm are compared in Table 3.

Fewer lines and species were detected after irradiation at 130 and 140 nm than at 121.6 nm; carbon clusters beyond C_{16} were lacking at 130 nm and beyond C_{12} at 140 nm. Other species, including CH , C_2H , C_2H_3 , C_2H_4 , C_2H_6 , C_3H , C_4H , C_4H_2 , and C_5H were not detected at 140 nm. In our experiments, the wavelength of greatest efficiency of photolysis was 121.6 nm, but products of irradiation at 140 nm of methane in Ne were still measurable.

3.3.7. Temporal Behavior of Photolysis of Methane in Solid Neon at 1:10 000. Among the methane samples in neon, as we detected the most products, about 29 distinct chemical species, from the $\text{CH}_4:\text{Ne} = 1:10\,000$ sample irradiated at 121.6 nm, we analyzed in detail the temporal behavior of precursor methane and various photolytic products under that condition. Figure 6A displays the temporal profile of the depletion ratio of methane dispersed in neon 1:10 000 irradiated at 121.6 nm. As the integrated photon flux from our synchrotron is constant over time, the photon dose is linearly proportional to the duration of exposure to the light from the undulator. As shown in Figure 6A, the depletion of methane amounted to about half after 76 min; although it is almost linear in the initial period of photolysis, it becomes nonlinear after about 5 min. To monitor the temporal variation of photolysis products, we integrated the

Table 3. Relative Intensities of Absorption Lines of Products Observed after Photolysis of $\text{CH}_4:\text{Ne} = 1:10\,000$ at the Indicated Wavelengths^a

species	wavenumber (cm^{-1})	$\text{CH}_4:\text{Ne} = 1:10\,000^a$		
		140 nm	130 nm	121.6 nm
CO	2141.1	m	s	m
CH	2732.9	—	m	m
CH_3	604.5 (ν_2), 1389.9 (ν_4)	w	m	s
C_2H	1835.7 (ν_2)	—	w	w
C_2H_2	731.9 (ν_3), 1330.1 ($\nu_4+\nu_5$)	w	m	m
C_2H_3	895.3 (ν_8), 1357.5 (ν_5)	—	w	w
C_2H_4	950.3 (ν_7), 1441.7 (ν_{12})	—	w	w
C_2H_6	1470.3 (ν_{11})	—	w	w
C_3	2036.5 (ν_3)	w	s	m
C_3H	1827.5 (ν_2)	—	w	w
C_4	1547.1 (ν_3)	w	s	m
C_4H	2063.5 (ν_3)	—	w	w
C_4H_2	628.9 (ν_8), 2016.4 (ν_5)	—	w	w
C_4H_4	1879.5	w	w	w
C_5	1443.3 (ν_4), 2165.4 (ν_3)	m	s	m
C_5H	1955.6 (ν_3)	—	w	w
C_5O	2253.2	w	w	w
C_5H_2	1813.7	w	w	w
C_6	1199.3 (ν_5), 1958.6 (ν_4)	w	m	w
C_7	1897.1 (ν_5), 2134.8 (ν_4)	w	m	w
C_8	1707.5 (ν_6), 2067.8 (ν_5)	w	w	w
C_9	1602.6 (ν_7), 2010.0 (ν_6)	w	m	w
C_{10}	1915.7, 2074.5	w	w	w
C_{11}	1854.0 (ν_8), 1938.6 (ν_7)	w	m	w
C_{12}	1820.6 (ν_{10}), 2003.5 (ν_8)	w	w	w
C_{14}	1399.7, 2220.8	—	w	w
C_{16}	645.4, 1370.2	—	w	w
C_{18}	646.5	—	—	w
C_{20}	609.5	—	—	w

^aw = weak; m = medium; s = strong.

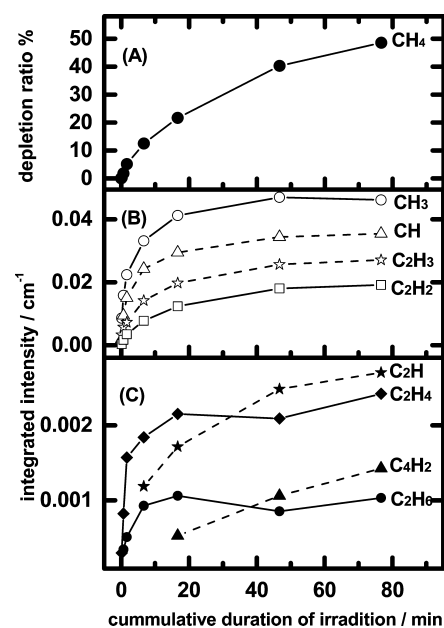


Figure 6. For $\text{CH}_4:\text{Ne} = 1:10\,000$ at 3 K irradiated at 121.6 nm, (A) temporal profile of depletion ratio for CH_4 ; (B) temporal profiles of formation of CH , CH_3 , C_2H_2 , and C_2H_3 ; and (C) temporal profiles of formation of C_2H , C_2H_4 , C_2H_6 , and C_4H_2 .

representative spectral lines of products after each period of irradiation and analyzed their profiles. Figure 6B shows the temporal profiles of formation of CH, CH₃, C₂H₂, and C₂H₃; Figure 6C of C₂H, C₂H₄, C₂H₆, and C₄H₂; Figure 7A of carbon clusters C₃–C₇; Figure 7B of C₈–C₁₂; and Figure 7C of clusters C₁₄, C₁₆, C₁₈, and C₂₀.

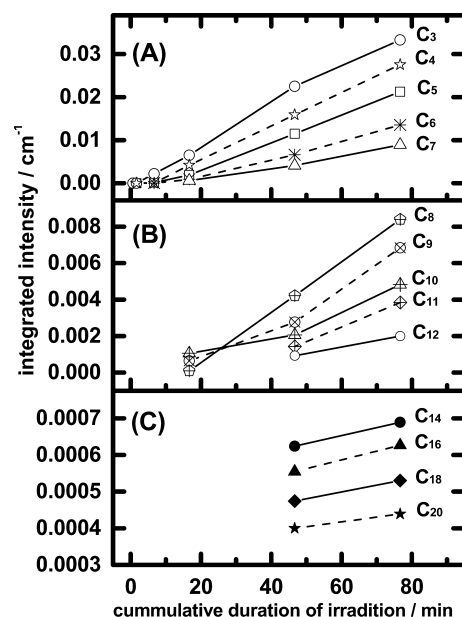


Figure 7. For CH₄:Ne = 1:10 000 at 3 K after irradiation at 121.6 nm, (A) temporal profiles of formation of C₃–C₇; (B) temporal profiles of formation of C₈–C₁₂; and (C) temporal profiles of formation of C₁₄, C₁₆, C₁₈, and C₂₀.

3.3.8. Photoysis of Methane Dispersed in Neon with Added Dihydrogen. The formation of each carbon chain or cluster from C₇ to C₂₀ leaves 28–80 H atoms unaccounted from the precursor CH₄ molecules. To test the effect of extra hydrogen on the photolysis of solid methane dispersed in neon at 3 K, we included H₂ in the original sample, preparing mixtures with CH₄:H₂:Ne = 1:6:1000, and performed irradiation at 121.6 nm; the identified products, numbering about 30, are listed also in Table 1. Relative to a sample with only methane and neon at the same ratio, 1:1000, the addition of hydrogen into the solid neon enhanced the formation of long carbon chains through photolysis. Figure 8 displays partial spectra that emphasize these long chains.

Among further lines of clusters C₁₄, C₁₆, and C₁₈ detected after photolysis of CH₄:H₂:Ne = 1:6:1000, absorptions at 854.8, 1399.7, and 2221 cm⁻¹, near values reported at 851, 1394, and 2218 cm⁻¹ in solid N₂,²⁸ are attributed to C₁₄; lines observed at 644.4, 738.1, 1370.2, and 2098.0 cm⁻¹, near values reported at 646, 735, 1372, and 2096 cm⁻¹ in solid N₂,²⁹ are attributed to C₁₆; and lines recorded at 645.8, 1378.2, 2087.6, and 2215.4 cm⁻¹, near values at 650, 1380, 2088, and 2212 cm⁻¹ in solid N₂,²⁹ are attributed to C₁₈. These results confirm the formation and identification of carbon chains C₁₄, C₁₆, and C₁₈ in our experiments. Three additional weak lines at 609.3, 2016.9, and 2128.7 cm⁻¹, near lines at 605, 2014, and 2128 cm⁻¹ attributed to linear C₂₀ in solid N₂,²⁹ are reasonably associated with a C₂₀ chain. The tentative assignments of lines attributed to species C₁₄, C₁₆, C₁₈, and C₂₀ recorded in the sample with CH₄:Ne = 1:10 000 irradiated at 121.6 nm are thus confirmed.

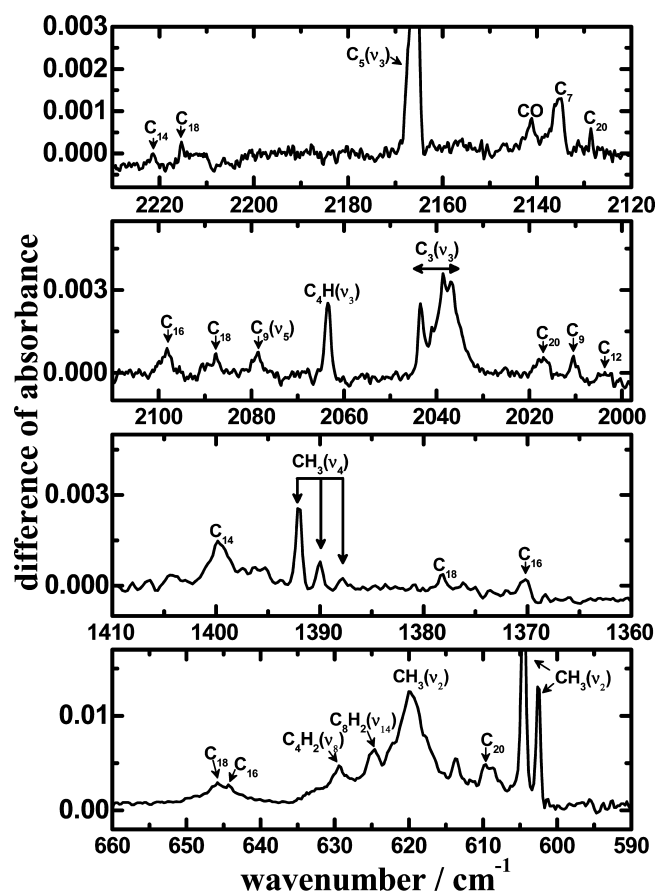


Figure 8. Difference infrared spectra of CH₄:H₂:Ne = 1:6:1000 at 3 K after irradiation at 121.6 nm for 76 min at 3 K. Some assignments are indicated.

4. DISCUSSION

Before Norman and Porter (1954) delineated conditions to maintain free radicals for leisurely examination with absorption spectra,² several chemists and physicists had reported related experiments: deposits were collected at temperatures <100 K after the liquefaction of dihydrogen in 1898, even with irradiation of samples, such as by Dewar and Jones (1910),¹ and emission spectra were recorded from deposits of discharged gases by McLennan and Shrum (1924) and by Vegard (1924).^{30,31} For successful trapping of free radicals for protracted spectral observation, Norman and Porter specified that the solid solvent must be chemically inert to those radicals and that diffusion of a radical to the vicinity of another radical must be prevented. The latter criteria were satisfied for the detection of the methyl radical trapped in solid argon at 14 K after photolysis of methane at 121.6 nm during deposition by Milligan and Jacox.³ Although methyl was the only radical identified in infrared spectra recorded during those experiments, both it and the methyldene radical, CH, in a trace proportion, were detected in visible and near-ultraviolet spectra. Methyl radicals have since been produced in various ways and stabilized in various dispersants, such as in solid dihydrogen,³² but the photochemical decomposition of methane in solid phases has been little explored. Experiments involving photolysis of gaseous methane,⁶ at 121.6 nm, indicated that the methylene radical, CH₂, had the major quantum yield of the primary photochemical products. For this reason we re-examined the photolysis of methane, utilizing solid neon at 3

K as a dispersant to try to suppress secondary reactions; the greatly increased sensitivity of our interferometric spectrometer might enable the detection of chemical species not previously encountered in this system by Milligan and Jacox,³ and the tunable wavelength of radiation from our synchrotron source provided a further experimental variable to probe the photochemical processes. Our experiments reveal that, although neon remained inert, the effect of dilution was to increase the number of the products and that, instead of facilitating the formation of hydride products, added dihydrogen had the effect of enhancing the production of species with long carbon chains.

The most remarkable aspects of the results of our experiments are the number and the diversity of the products from a simple precursor, methane, upon irradiation of samples in solid phases at 3 K with light from a synchrotron. Although pure methane yielded only methyl radicals and three readily identified stable products, with only one further spectral line unassigned, more than 28 products comprising carbon or hydrocarbon molecules or fragments, apart from species containing oxygen from adventitious sources, were identified in experiments with initial mixtures of methane and dihydrogen highly diluted in neon, as Table 1 shows. Because of this diversity of products that arose from an initial quantity of methane constrained by physical limitations imposed by the apparatus, the net absorbances of their infrared spectral lines were small, but the reproducibility of the wavenumbers and the relative absorbance in many separate experiments, with varied ratio of dispersion and wavelength of irradiation, enables confidence in these assignments. Moreover, the diversity increased with the extent of dilution by neon, as Table 1 again attests. Such results have no precedent.

Both gaseous methane and pure solid methane absorb ultraviolet light at the wavelengths from 120 to 140 nm utilized in our experiments, which is a requisite for a photochemically initiated reaction; the ultraviolet spectrum of absorption by CH₄ molecules dispersed in solid neon is likely to resemble the absorption profiles of the gaseous substance and of the pure solid. For gaseous methane, such absorption is followed by dissociation.⁶ The standard enthalpies of reaction for the dissociation of methane and its fragment radicals CH₃, CH₂, and CH and the corresponding wavelengths as a threshold for those dissociations appear in Table 4; further thresholds of greater energies exist for dissociation into electronically excited species, such as CH₂. As the selected photon wavelengths from 120 to 140 nm, including 121.6 nm, are less than the absorption threshold, likely near 151 nm, and much less than the wavelength corresponding to the minimum energy causing dissociation of methane, the photochemical decomposition of methane in solid neon is feasible at this wavelength. The depletion of methane upon irradiation and the appearance of infrared absorption lines of many products prove that methane was consumed under the conditions of our experiments. The information in Table 4 indicates that, for all but three processes corresponding to complete atomization, the energy available in a single photon of wavelength less than 152 nm is sufficient to break multiple C–H bonds. The standard enthalpies of reaction for the dissociation of CH₄ and its fragment radicals CH₃, CH₂, and CH and the corresponding wavelengths as a threshold for those dissociations in Table 4 indicate that the threshold wavelengths to break a single C–H bond are from CH, 351.2 nm; from CH₂, 284.4 nm; from CH₃, 260 nm; and from CH₄, 270.5 nm. In our experiments with methane in neon, we detected infrared absorption lines of CH and CH₃ radicals

Table 4. Standard Enthalpies of Reaction at 300 K and the Corresponding Thresholds of Wavelength for the Dissociation of Gaseous Hydride Species into Other Atomic and Molecular Species in Their Ground States

	$\Delta_r H^\circ$ (kJ mol ⁻¹)	$\lambda_{\text{threshold}}$ (nm)
CH + $h\nu \rightarrow$ C + H	340.5	351.2
CH ₂ + $h\nu \rightarrow$ CH + H	420.5	284.4
→ C + H ₂	325.1	367.9
→ C + 2H	761.1	157.1
CH ₃ + $h\nu \rightarrow$ CH ₂ + H	460.2	260
→ CH + H ₂	444.7	268.9
→ CH + 2H	881	135.7
→ C + 3H	1221	97.9
CH ₄ + $h\nu \rightarrow$ CH ₃ + H	442	270.5
→ CH ₂ + H ₂	466.5	256.4
→ CH ₂ + 2H	902.5	132.5
→ CH + H + H ₂	887	134.8
→ CH + 3H	1323	90.4
→ C + 2H ₂	791.5	151.1
→ C + 4H	1664	71.9

directly upon irradiation at 121.6 nm and even a line of CH₃ directly on irradiation of pure methane; the temporal profiles of the formation of CH and CH₃ in neon are initially similar, as shown in Figure 6B. These results might indicate that radicals CH and CH₃ are primary products of decomposition of methane upon photolysis at 121.6 nm. Although experiments on gaseous methane with photolysis at 121.6 nm indicate that the primary products have quantum yields 0.42 for CH₃, 0.51 for CH₂, and 0.07 for CH,⁶ in our experiments we found no direct spectral evidence for the production of CH₂, despite accurate knowledge of the vibrational modes of free CH₂. The reason might be either an efficient secondary photolysis of CH₂ into fragments, any such reaction being possible according to Table 4, or the small absorption coefficients of methylene in vibrational modes of any isotopic variant, such that detection is impeded; the known absorption coefficients for free methylene make the latter possibility unlikely. We examined carefully the spectra in wavenumber regions in which methylene radicals are expected to absorb; lines unassigned in Table 1 are unlikely to belong to CH₂. Methylene radicals are known to absorb light strongly in diffuse bands in this ultraviolet region;³³ their dissociation into fragments with much energy is likely one source of the carbon atoms that comprise the observed long chains.

The photochemical behavior of species isolated in a solid dispersion differs from that in the gaseous phase: at a small density, gaseous fragments readily move apart after photolytic dissociation, whereas fragments produced in a solid phase might have insufficient energy to escape from the immediate environment. Impeded by the surrounding atoms, fragments might be constrained typically to remain at or near their original site and either to recombine to the original molecule or to form an isomeric structure. The latter constraint is likely inapplicable to photochemical processes with light in the vacuum-ultraviolet region for the following reason. For methane dispersed in solid neon, no product was observed after irradiation at wavelength 165 nm (photon energy 7.514 eV), but products were observed after irradiation at wavelength 140 nm (8.856 eV), which is 4.27 eV greater than the threshold energy for dissociation of gaseous CH₄ at 4.584 eV (corresponding to 270.5 nm). Upon photolytic dissociation

of methane in solid neon, if diffusion plays a key role in generating isolated photolysis products, the excess energy that might become kinetic energy of the fragments would hence exceed 4.27 eV, which is enormous relative to the atomic lattice energy of solid neon. That excess energy must facilitate migration or diffusion of atomic or molecular fragments through the solid deposit despite the temperature, 3 K, that is well below the melting point of solid neon at 24.5 K and despite the distance between possible reactants: at ratio $\text{CH}_4:\text{Ne} = 1:1000$ and under an assumption of a substitutional site in the host neon lattice, on average about 9 Ne atoms lie between two nearest methane molecules, whereas at dispersant ratio 10 000 on average about 21 Ne atoms lie between two nearest methane guests.

Figures 6 and 7 display temporal profiles of the formation of other hydrocarbon and carbon species. The profiles of temporal formation of C_2H_2 and C_2H_3 show that their formation occurs slightly later than that of CH and CH_3 , indicating that these C_2 species result from secondary reactions that are photochemically initiated. The fact that, according to Figure 6, the absorption intensities of both CH and CH_3 approach plateau values even though most CH_4 remains intact implies that both CH and CH_3 are subject to photochemical decomposition, or to reaction, under the conditions of our experiments; the formation of all other products, up to C_{20} , indicates that C, CH, or other fragments originating from methane are able to migrate through the solid neon to react with methane or other fragments to form eventually all identified products. Although the neon dispersant remained unreactive, the diffusion of atoms such as C or H and even of molecules such as CH, C_2 , or CH_2 in solid neon at 3 K clearly cannot be prevented. After dissociation of a C–H bond with radiation of wavelength 121.6 nm, or even 140 nm, the excess energy of the photons, according to Table 4, can be converted to kinetic energy of the fragments not only enabling the translational motion but also forcing open a path between neon atoms in the solid deposit for that translation to occur; that excess energy would be available also to overcome any energy of activation required to enable a combination of fragments. This interpretation regarding the excess energy is consistent with our observation that the extent of products increased with wavelength of incident light decreasing from 140 to 121.6 nm or the increasing energy of the respective photons. The temporal profiles of species containing multiple carbon centers indicate that, their formation occurs after the formation of C_2H_2 or whatever species combine to form C_2H_2 .

The photolysis of methane dispersed in solid neon at 3 K generated many products that we have identified according to their characteristic infrared absorption lines. Whereas the experiments on photolysis of methane dispersed in solid argon at 14 K yielded definitely only five distinct products generated from only two,³ at most, methane molecules as precursors, our experiments with more dilute samples yielded many products, implying up to 20 methane molecules as precursors. Instead of inhibiting the formation of multiple-carbon species, dihydrogen added to our samples increased both their yields and the number of carbon atomic centers per molecule. The latter effect is clearly not chemical but physical: the presence of H_2 effectively distorts the lattice, facilitating the migration of atoms or small molecular entities. Like the experiments of Milligan and Jacox, we find ethyne to be a product much more abundant than ethane and ethene, except for photolysis of pure

methane; those authors proffered no specific mechanism for the favored formation of ethyne, nor can we.

After photolysis at 193 nm of ethyne in para-dihydrogen in an unknown proportion and at 5 K,³⁴ Hoshina et al. detected C_3 , C_5 , and C_7 chains with carbon atoms of odd number despite the precursor C_2H_2 containing carbon atoms of even number; these authors found no explanation for this phenomenon, but attributed the origin of these products to clusters of C_2H_2 . In our experiments, there is no spectral evidence of clusters of methane in our samples in neon; regarding the question whether a statistical distribution of methane molecules within solid neon pertains to our experiments, there is no indication of clusters of methane molecules before photolysis according to our investigation of the spectra of methane dispersed in solid neon.¹⁴ Moreover, in one photochemical experiment, deposition at 3 K and at a much smaller rate endured 170 h for a quantity of methane and neon typically deposited over 15 h in other experiments; the distribution of carbon and hydrocarbon products differed insignificantly from those of experiments with more rapid deposition. We conclude that the clusters or chains of carbon atoms in the products did not reflect a presence of clusters of methane molecules before photolysis. Moreover, under our experimental conditions, the ability of solid neon at 3 K to trap radicals is beyond doubt because the presence of CH, CH_3 , and other small free radicals is here established according to their characteristic infrared absorption lines. In our experiments, not only did the long chains of carbon atoms persist at dilution 1:10 000 but also chains of even number were favored under those conditions. The crystal structure at 5–8 K of para-dihydrogen that is less densely packed than solid neon would be expected to allow diffusion of atoms or small molecular species more readily than solid neon at 3 K; the melting point of H_2 at 14 K is much less than that of neon at 24.7 K.

The distribution of our products from the photolysis of methane dispersed in neon at 3 K differs radically from that of the original experiments involving mixtures of methane and argon at ratios 1:200 to 1:600 at 14 K.³ In the latter experiments with concurrent deposition and irradiation with light from a lamp emitting at mostly 121.6 nm, only products ethyne, carbon oxide, and methyl radical were identified according to their infrared absorption spectra; products methylidene, dicarbon, and methyl radicals, and possibly C_3 , were identified according to their visible and ultraviolet absorption spectra. Concurrent deposition and photolysis, for durations 5–7 h, were necessary “to maximize the yield of photolysis products”.³ In our experiments, concurrent deposition and photolysis were impracticable, but there was no difficulty obtaining signals of products after irradiation of samples fully condensed at 3 K containing neon rather than argon and depleting more than half the original methane; we recorded the appearance of products after only 10 s of irradiation. Part of the disparity of the nature and the yield of products between the compared experiments is undoubtedly due to the nature of the intensity of the effective radiation. A lamp excited with a microwave or electric discharge of gaseous H_2 and He might provide continuously 10^{14} – 10^{15} photons s^{-1} into a condensed sample, or 4000–40 000 photons within an interval of 25 ps, equivalent to 1/1000–1/100 times the intensity of our pulsed beam from the synchrotron, but we make no suggestion of multiphoton processes in our experiments. Another factor pertinent to the disparity is that our experiments were performed with methane and neon at ratios

over a large range, from 1:100 to 1:10 000, apart from pure methane; moreover, we discovered the greatest range of products at the largest ratio. Relevant also is that our samples comprised mostly solid neon, which scatters light in the infrared or ultraviolet regions much less strongly than solid argon; for this reason the penetration of potent photolytic radiation into a solid sample of neon is much more effective than into solid argon, facilitating dissociation within the bulk of that neon sample.

Our application of infrared spectra as a means of identifying the products of photolysis either in the primary photochemical step or as the result of subsequent reactions between species dispersed in neon precludes detection of H, H₂, C, or C₂ in any isotopic variant. We examined our infrared spectra for electronic transition ${}^3\Pi_u \nu' \leftarrow X {}^1\Sigma_g^+ \nu = 0$ of C₂, of which lines for $\nu' = 0, 1, 2$ lie within our range of observation, without finding a trace, but that electronic transition is intrinsically weak. For H₂, there is perceptible absorption in neither the infrared region for detection nor the ultraviolet region >119 nm that we applied for irradiation; the identified products have in common a lack of hydrogen atoms relative to precursor methane; for instance, the production of C₂₀ implies 80 H atoms or 40 H₂ molecules. As for the fate of that hydrogen liberated from methane on photolysis, whether this element existed as H or H₂, or other, is unknowable from our present experiments, but clearly much hydrogen in some form or forms remains unaccounted.

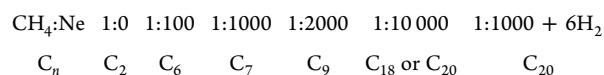
In relation to photochemistry in the region 120–165 nm applicable in our experiments, one should consider the possible presence of ions. As the ionization energy of gaseous CH₄ is 12.61 eV, corresponding to wavelength 98.3 nm, direct ionization of CH₄ is infeasible. For gaseous CH₃ as a primary photochemical product, the ionization energy is 9.84 eV, corresponding to wavelength 126 nm; this process is practicable during irradiation at 120 or 121.6 nm, unlike for the gaseous methylene radical for which ionization energy 10.4 eV corresponds to wavelength 119.4 nm, just below the range of our experiments. The spectra of our samples after irradiation provide no evidence of the production of methyl cations or other ions.

We identified C₂H₆, C₂H₂, and C₂H₄ from the dissociation of pure solid methane at 121.6 nm; these compounds were also major products from a sample with CH₄:Ne = 1:100. When the concentration of methane in solid neon was decreased, the relative yields of these species also decreased and C₂H₂ became much more abundant than C₂H₄ or C₂H₆. In contrast, not only were significantly larger molecular products generated from more dilute dispersions of methane in solid neon on irradiation, but also especially long carbon chains (clusters) were formed. Milligan and Jacox who observed C₂H₂ but neither C₂H₄ nor C₂H₆ made no comment about this formation of C₂H₂ without the intermediacy of C₂H₄ or C₂H₆, which is difficult to understand; the same factor of lack of penetration of radiation at 121.6 nm into their Ar sample, which protected the CH₄, would also protect any C₂H₄ or C₂H₆ that might have been formed. A particular mechanism of the formation of a specific product would be purely speculative, from which we accordingly refrain.

5. CONCLUSION

With light from a synchrotron of wavelength less than 165 nm, we irradiated samples of pure solid methane and of methane dispersed in solid Ne at ratios CH₄:Ne from 1:100 to 1:10 000,

all at 3 K. We identified, via infrared absorption spectra, products comprising CH₃, C₂H₂, C₂H₃, C₂H₄, C₂H₆, C₄H₂, C₄H₄, C₅H₂, C₈H₂, C_nH ($n = 1-5$), and carbon clusters C_n ($n = 3-20$). Unlike the original experiments on the photolysis of methane in solid argon at 14 K by Milligan and Jacox,³ in our experiments with methane dispersed in solid neon at 3 K over a much greater range of concentrations, with nearly monochromatic radiation of varied wavelength and much greater pulsed intensity, and with added H₂, we have identified numerous chemical products, with carbon chains even up to C₂₀. Regarding the two conditions stated by Norman and Porter (1954) to achieve effective trapping of free radicals in inert solid dispersions,² although the neon host material remained unreactive, the migration in solid neon of energetic atoms, such as C or H and even of molecules such as CH or C₂ or CH₂, was clearly not prevented, even at 3 K. The disparities between the results of our experiments and those of Milligan and Jacox reflect the dissimilar hosts, concentrations, and light sources (a continuous electric discharge versus pulses of radiation from a synchrotron), but the evidently complicated mechanism of formation of each separate product is undecipherable from our present information. The same factor that required Milligan and Jacox to conduct concurrently the deposition and photolysis of their samples in argon, namely that their samples in solid argon strongly scattered light in the vacuum-ultraviolet region, effectively protected their primary products from secondary photolysis; in contrast, the ease of photolysis of methane in our solid neon samples, which the same ultraviolet light clearly penetrated effectively, promoted the secondary photolysis of our primary products, likely CH₃, CH₂, and CH, as in the gaseous phase; the migration through the solid neon of atomic fragments C and H, or possibly also CH, C₂, and CH₂, failed to be inhibited, such that large carbon clusters were produced. As demonstrated in Table 3, the extent of the carbon chains increased with the energy of the photons, indicating that the energy in excess of the dissociation energy enhanced the extent of migration through the solid sample. A highly novel aspect of our experiments is not only such a production but also that the yield of such agglomerates increased both with a decreasing initial concentration of methane dispersed in solid neon and with the addition of H₂ in small proportion; in this synopsis of results, n in C_n denotes the maximum number of carbon atomic centers in products identified in the pertinent experiments.



At CH₄:Ne = 1:10 000 and $\lambda = 121.6$ nm, the yield of C₂₀, detected with only one weak absorption line, was much smaller than when H₂ was present in a mixture of proportions CH₄:H₂:Ne = 1:6:1000; three characteristic lines were then clearly present and measured.

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Notes

The authors declare no competing financial interest.

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