Laser Irradiation of Monomeric Acetylene and the T-Shaped Acetylene Dimer in Xenon and Argon Matrices

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Irradiation of acetylene (**4**) in an argon matrix with an ArF laser (λ = 193 nm) yields the ethynyl radical $C_2H^\bullet$ (**5**) and C_2 (**6**). If the same wavelength is used to irradiate **4** in a xenon matrix, only the infrared signal of the compound Xe–C_2 (**7**) can be detected. The same band is found on irradiation at λ = 248 nm (KrF laser) in a xenon matrix, despite the fact that acetylene (**4**) does not absorb light of this wavelength. Irradiation of the T-shaped acetylene dimer **9** in an argon or xenon matrix at λ = 193 nm yields butadiyne (**11**) and vinylacetylene (**12**). However, irradiation with a KrF laser (λ = 248 nm) in a xenon matrix additionally yields cyclobutadiene (**13**). The dependence of the mechanisms of the fragmentation and dimerization of acetylene (**4**) on the matrix material is discussed.

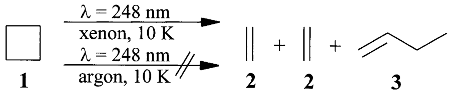
The fundamental requirement for the use of photoexcitation in generating reactive species in inert rare-gas matrices is the absorption of light by the organic precursor. An alternative to this direct photolysis is the use of an indirect method, in which the energy is absorbed by the matrix material. In this case, the stored energy has to be transferred to the precursor in a second step in order to initiate a chemical reaction.

When pure rare gases are used, very short wavelength radiation must be employed to excite the matrix. With argon as the matrix material, light of wavelength λ = 103 nm (12.1 eV) is necessary; a xenon matrix requires at least λ = 148 nm (8.4 eV) to reach the exciton state[1].

The application of light sources producing these short wavelengths is difficult. Alternatively, the energy necessary for exciton formation can be attained using a UV laser through two-photon absorption. Böttcher and Schmidt[2] detected the generation of charge carriers during the irradiation of solid xenon with an excimer laser (KrF: λ = 248 nm; ArF: λ = 193 nm), whereas Schwentner et al.[3] detected the solid-phase emission from Xe_2^* excimers (λ = 172 nm) formed upon laser irradiation. This emission is identical to that observed in a one-photon process when solid xenon is irradiated at λ = 148 nm[1].

Lawrence and Apkarian[4] used this indirect method of excitation for the photochemically-induced fragmentation of N_2O in a xenon matrix with the light of a KrF excimer laser (λ = 248 nm; 5.0 eV). The two-photon-induced generation of excitonic states in the solid xenon and the subsequent exciton-molecule encounters led to an efficient dissociation of N_2O.

As we have recently shown[5], the same kind of fragmentation can also be achieved in organic molecules. Irradiation of cyclobutane (**1**)[5] in a xenon matrix with a KrF laser yields ethene (**2**) and 1-butene (**3**), although the molecule does not absorb light of the wavelength λ = 248 nm. If argon is used as the matrix material, no fragmentation is detected because exciton formation with light of this wavelength is impossible in an argon matrix[1].



1 **2** **2** **3**

The goal of this investigation was to find out whether indirect excitation using the absorption of the matrix material rather than the absorption of the precursor itself can also be used to induce dimerization instead of fragmentation reactions. We chose acetylene (**4**) as the “test compound”, because it shows no absorption above λ = 237 nm[6] in the gas phase and may perhaps lead to candidates of the C_4H_4 hypersurface. For comparison purposes, we also studied the products arising from the direct excitation at different wavelengths.

In addition, we studied the influence of the matrix material on the fragmentation products of monomeric acetylene (**4**) and found astonishing differences in product formation upon laser irradiations of **4** in xenon and argon matrices.

Irradiations of Monomeric Acetylene

Irradiation at λ = 193 nm (ArF Laser)

It is reported[7][8] that the ethynyl radical $C_2H^\bullet$ (**5**) is the primary product of gas-phase photolysis of diluted acetylene (**4**)/rare gas mixtures at λ = 193 nm. In a two-photon sequential dissociation, the remaining hydrogen atom can be split off and C_2 (**6**) is also formed.

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$$C_2H_2\ (\mathbf{4}) \xrightarrow{\lambda = 193\ \mathrm{nm}} C_2H\cdot\ (\mathbf{5}) + H\cdot$$

$$C_2H\cdot\ (\mathbf{5}) \xrightarrow{\lambda = 193\ \mathrm{nm}} C_2\ (\mathbf{6}) + H\cdot$$

The irradiation of acetylene (**4**) in an argon matrix [ratio acetylene (**4**)/Ar = 1:1000] with an ArF laser (λ = 193 nm) yields small amounts of $C_2H^{\bullet}$ (**5**) after several hours, in accordance with the results obtained in the gas phase. The bands of **5** are found at $\tilde{\nu}$ = 1846.6, 2104.5, 4022.4, and 4132.8 cm^{-1}, in agreement with the data published by Jacox et al.[9]. Moreover, the UV/Vis spectrum exhibits an absorption band at λ = 237 nm, which can be assigned to C_2 (**6**)[10]. Thus, the results of the experiment in an argon matrix are in accordance with those of the gas-phase study.

More surprising is the fact that the irradiation of acetylene (**4**) in a xenon matrix with light from the same radiation source leads to completely different spectra. The infrared spectrum shows one single band at $\tilde{\nu}$ = 1767.0 cm^{-1} and none of the aforementioned signals assigned to the radical $C_2H^{\bullet}$ (**5**) (Figure 1). The UV/Vis spectrum does not show a band at λ = 237 nm, but several new bands centered around λ = 198 nm and λ = 423 nm instead (Figure 2).

With light of wavelength λ = 193 nm, there are two possibilities for the excitation of acetylene (**4**) in a xenon matrix: The direct absorption of the acetylene (**4**) molecule, which absorbs strongly below λ = 200 nm[6], or the absorption of the matrix material as described above (the mechanism of energy transfer including exciton states will be discussed later).

Irradiation at λ = 248 nm (KrF Laser)

If the emission from a KrF laser (λ = 248 nm) is used, only the absorption of the matrix material is possible, because acetylene (**4**) shows no absorption above λ = 237 nm (gas phase[6]). The transparency of acetylene (**4**) at λ = 248 nm could be verified. In an argon matrix, no conversion could be detected even after several hours of irradiation.

To prove the hypothesis that the species formed upon irradiation of **4** at λ = 193 nm in xenon may also be obtained by an indirect excitation of the matrix, the experiment was repeated using a KrF laser (λ = 248 nm). Indeed, the infrared (Figure 1) and the UV/Vis spectra (Figure 2) corresponded to those obtained following irradiation at λ = 193 nm. Again, the infrared spectrum showed only one signal at $\tilde{\nu}$ = 1767.0 cm^{-1}.

The intensity of the signal at $\tilde{\nu}$ = 1767.0 cm^{-1} remains unchanged on annealing of the matrix (stepwise annealing at 38 K, 46 K, and 50 K; 30 minutes at each temperature), but decreases on irradiation with light of $\lambda \geq$ 254 nm (the wavelengths λ = 436 nm, $\lambda \geq$ 385 nm, $\lambda \geq$ 295 nm, and λ = 254 nm all lead to a decrease of the signal; λ = 254 nm has the largest effect). No new signal appears in the infrared spectrum during these secondary irradiations. The groups of UV/Vis bands centered at λ = 198 nm and λ = 423 nm decrease accordingly as the IR band diminishes.

A shift of almost $\Delta\tilde{\nu} = -80\ cm^{-1}$ (1767.0 vs. 1846.6 cm^{-1}) for the proposed ethynyl radical $C_2H^{\bullet}$ (**5**) in xenon seems to be too high merely for a change of the matrix material. In order to unequivocally rule out that the signal at $\tilde{\nu}$ = 1767.0 cm^{-1} belongs to a molecule with at least one hydrogen atom, the deuterated compounds [D_1]acetylene ([D_1]-**4**) and [D_2]acetylene ([D_2]-**4**) were also irradiated. The synthesis of the deuterated precursor molecules (see Experimental Section) yielded a mixture of **4**, [D_1]-**4** and [D_2]-**4**, and this mixture was used with xenon in a ratio of 1:1000 for the matrix experiments.

Figure 1. IR difference spectrum after the irradiation (ArF laser, λ = 193 nm, or KrF laser, λ = 248 nm) of acetylene (**4**) in a xenon matrix; the bands with negative values diminish, while those with positive values are enhanced upon irradiation

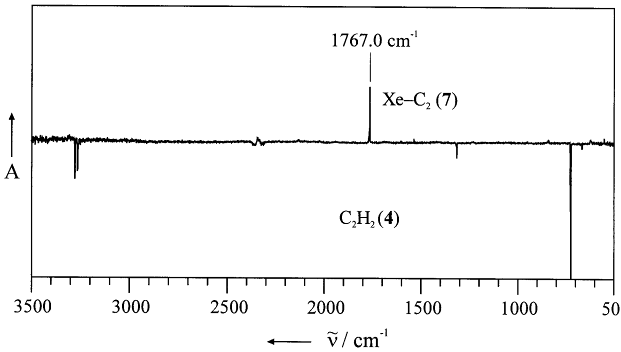


Figure 2. UV/Vis spectrum after the irradiation (ArF laser, λ = 193 nm, or KrF laser, λ = 248 nm) of acetylene (**4**) in a xenon matrix; the broken line indicates the base line before irradiation

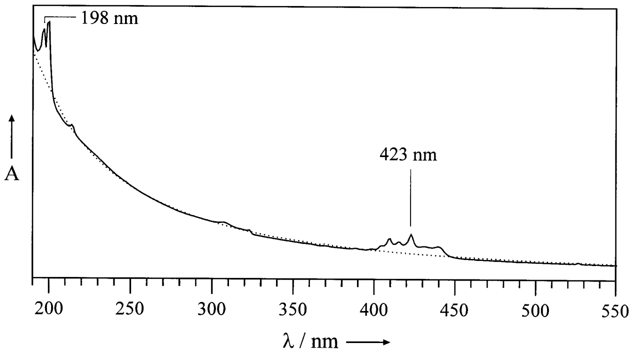
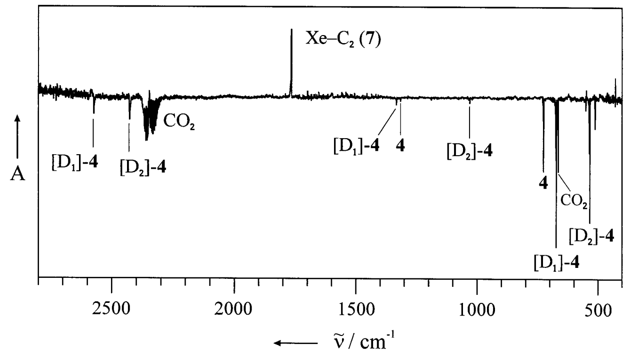
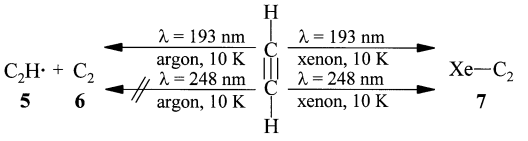


Figure 3. IR difference spectrum after the irradiation (KrF laser, λ = 248 nm) of a mixture of acetylene (**4**), [D_1]acetylene ([D_1]-**4**) and [D_2]acetylene ([D_2]-**4**) in a xenon matrix; the bands with negative values diminish, while those with positive values are enhanced upon irradiation

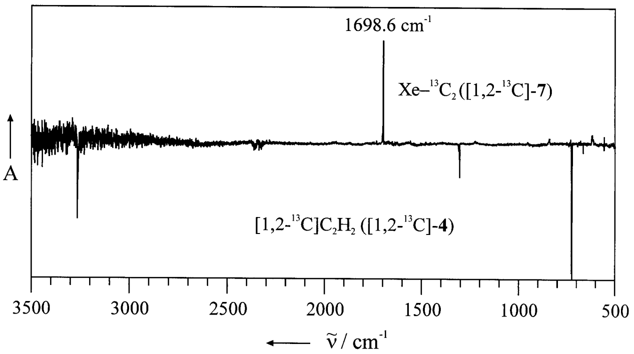


The result of the irradiation at λ = 248 nm was unambiguous: Only the signal at $\tilde{\nu}$ = 1767.0 cm^{-1} appeared in the infrared spectrum, while all the signals for the acetylenes **4**, [D$_1$]-**4**, and [D$_2$]-**4** decreased upon irradiation (Figure 3). The UV/Vis spectrum showed no difference to that obtained from the photolysis of **4** alone (Figure 2). Thus, the signal in the IR spectrum, and probably the UV/Vis absorptions as well, can be attributed to a species that contains no hydrogen atoms. Secondary irradiation of the mixture of isotopomers at λ = 254 nm yielded the familiar result, i.e. decrease of the signals in both the IR and UV/Vis spectra.



Which molecule is responsible for the signal at $\tilde{\nu}$ = 1767.0 cm^{-1}? Because of the simplicity of the precursor acetylene (**4**) and the fact that the produced molecule contains no hydrogen atom, the photoinduced generation of C_2 (**6**) is the only plausible explanation. Since C_2 (**6**) should show no infrared band, we postulate that a new compound Xe$-C_2$ (**7**), formed by reaction of **6** with the matrix material xenon, gives rise to the observed signal in the IR spectrum. To verify this hypothesis, [1,2-^{13}C]acetylene ([1,2-^{13}C]-**4**) was irradiated in a xenon matrix (ratio 1:1000) with light from a KrF laser.

Figure 4. IR difference spectrum after the irradiation (KrF laser, λ = 248 nm) of [1,2-^{13}C]acetylene ([1,2-^{13}C]-**4**) in a xenon matrix; the bands with negative values diminish, while those with positive values are enhanced upon irradiation

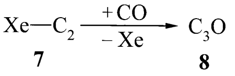


The irradiation again produced only one signal in the infrared spectrum, but at $\tilde{\nu}$ = 1698.6 cm^{-1} rather than at $\tilde{\nu}$ = 1767.0 cm^{-1} (Figure 4). The shift of $\Delta\tilde{\nu} = -68.4$ cm^{-1} corresponds very well with the theoretical value of $\Delta\tilde{\nu} = -69.3$ cm^{-1} calculated from $(m^{12}\mathrm{C}/m^{13}\mathrm{C})^{1/2} = 0.9608$ for a diatomic molecule containing two ^{13}C atoms. Once again, subsequent irradiation at λ = 254 nm led to a decrease of the signals in the IR and UV/Vis spectra.

The UV/Vis spectrum exhibits the same features as in the case of the ^{12}C isotopomer of **4**, with the absorptions shifted to longer wavelengths by only 1 nm. The progressions of the UV/Vis bands formed upon irradiation of acetylene (**4**) and [1,2-^{13}C]acetylene ([1,2-^{13}C]-**4**) are between 300 and 750 cm^{-1} and cannot be assigned to any vibration of a compound containing a C_2 molecule (**6**), because the progression for the C=C stretching fundamental is completely absent. Therefore, the bands in the UV/Vis spectra cannot be assigned unambiguously to the compound Xe$-C_2$ (**7**).

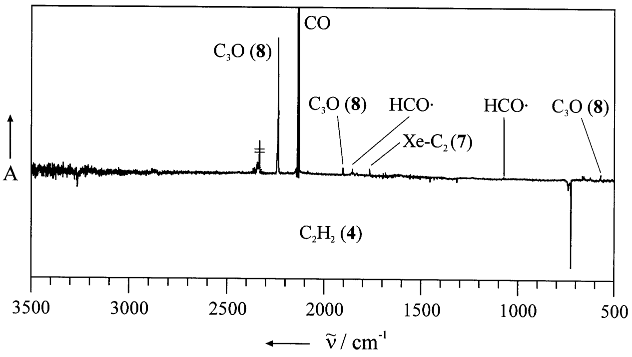
Trapping Experiments with Xe$-C_2$ (7)

In order to obtain a final proof for the structure of the adduct **7** between Xe and C_2 (**6**), we irradiated matrices containing CO together with acetylene (**4**) or [1,2-^{13}C]acetylene ([1,2-^{13}C]-**4**), in the hope of producing the cumulenes C_3O (**8**) or [2,3-^{13}C]C_3O ([2,3-^{13}C]-**8**) as reaction products from the photolytically generated Xe$-C_2$ (**7**). The matrices for these experiments were made by co-condensation of a CO/xenon gas mixture (ratio 100:1000) with a xenon gas mixture containing **4** or [1,2-^{13}C]-**4** in a ratio of 3:1000.



$$\underset{\mathbf{7}}{\mathrm{Xe{-}C_2}} \xrightarrow[-\mathrm{Xe}]{+\mathrm{CO}} \underset{\mathbf{8}}{\mathrm{C_3O}}$$

Figure 5. IR difference spectrum after the irradiation (KrF laser, λ = 248 nm) of a matrix produced by co-condensation of acetylene (**4**)/xenon (3:1000) and CO/xenon (100:1000) gas mixtures; the bands with negative values diminish, while those with positive values are enhanced upon irradiation; the assignment of the product bands was made with the aid of ref.[11] for C_3O (**8**) and ref.[12] for the radical HCO•



Besides the signals at $\tilde{\nu}$ = 1767.0 cm^{-1} in the case of acetylene (**4**) and $\tilde{\nu}$ = 1698.6 cm^{-1} in the case of [1,2-^{13}C]acetylene ([1,2-^{13}C]-**4**), the two spectra clearly exhibit the bands for the three most intense infrared transitions of C_3O (**8**) or [2,3-^{13}C]C_3O ([2,3-^{13}C]-**8**)[11], respectively (Figure 5). Clearly, the adduct **7** of C_2 (**6**) and Xe reacts with carbon monoxide to give the more stable cumulene **8**.

Moreover, the two most intense bands of the radical HCO• can be detected in both spectra at $\tilde{\nu}$ = 1856.3 cm^{-1} and $\tilde{\nu}$ = 1076.6 cm^{-1}[12]. This species is formed by the reaction of CO with hydrogen atoms originating from the fragmentation of **4** or [1,2-^{13}C]-**4**. The spectra for the two cumulenes were calculated at the BLYP/6-311+G* level of theory in order to allow a comparison of the experimentally derived isotopic shifts with the theoretical values. The agreement is satisfactory (Table 1).

Table 1. Experimental (xenon, 10 K) and calculated (BLYP/6-311+G*) IR spectra of C_3O (**8**) and [2,3-^{13}C]C_3O ([2,3-^{13}C]-**8**) (observed shifts on isotopic substitution are given in parentheses)

	Experiment		BLYP/6-311+G*	
	$\tilde{\nu}$/cm^{-1}	Int.	$\tilde{\nu}$/cm^{-1}	Int.
ν_1 [C_3O (**8**)]	2237.2	100.0	2259.9	100.0
ν_2 [C_3O (**8**)]	1904.4	1.3	1888.5	1.6
ν_3 [C_3O (**8**)]	571.9	1.7	590.7	3.1
ν_1 ([2,3-^{13}C]-**8**)	2219.0 (−18.2)	100.0	2236.1 (−23.8)	100.0
ν_2 ([2,3-^{13}C]-**8**)	1847.4 (−57.0)	1.3	1834.8 (−53.7)	4.0
ν_3 ([2,3-^{13}C]-**8**)	568.4 (−3.5)	2.8	586.1 (−4.6)	3.3

The Infrared Spectrum

The experiment with [1,2-^{13}C]acetylene ([1,2-^{13}C]-**4**) clearly proves that the signal in the infrared spectrum belongs to a compound containing a C_2 (**6**) molecule. The presence of only one signal in the infrared spectrum reflects a preference for a compound with a fixed number of xenon atoms directly adjacent to **6**.

The C=C stretching fundamental of the molecule C_2 (**6**) is found at $\tilde{\nu}$ = 1854.6 cm^{-1} in the gas phase[13], whereas the experimental value for the infrared signal of the new compound **7** is $\tilde{\nu}$ = 1767.0 cm^{-1} in a xenon matrix. This shift of $\Delta\tilde{\nu}$ = −87.6 cm^{-1} is too high to be caused merely by complexation of C_2 (**6**) with the matrix material xenon. Jacox[14] studied the shifts in the ground-state vibrational fundamental frequencies of diatomic molecules upon trapping in argon matrices and found that the matrix shift relative to the gas-phase position is less than 2%.

Furthermore, it is known[15] from the comparison of measured vibrational frequencies in rare-gas matrices with the corresponding gas-phase values that in rare gas/hydrogen halide complexes (Rg−HX) the correlation between the vibrational shifts of the rare gas/hydrogen halide complex and the polarizability of the rare-gas atoms is fairly linear. In all cases, the stretching vibrations are red-shifted compared to the free, gas-phase hydrogen halide fundamental. The red-shift increases on going from neon to xenon as the polarizability of the matrix material increases, but the shifts are smaller than $\Delta\tilde{\nu}$ = −87.6 cm^{-1}, even in the case of a xenon matrix.

The electron affinity of C_2 (**6**) (EA = 3.27 eV)[16] is almost as high as the electron affinity of the bromine atom (EA = 3.36 eV)[17] and enables the molecule **6** to accept electron density. The LUMO, which is the acceptor orbital for negative charge, is placed at −3.19 eV in the molecular orbital scheme [calculated at the MP2 (fc)/6-311+G* level of theory] and possesses the largest orbital coefficients outside the carbon atoms on the axis connecting the nuclei [see ref.[18] regarding the molecular orbital scheme of C_2 (**6**)]. This indicates a preference for a linear compound with one xenon atom adjacent to each of the two carbon atoms of C_2 (**6**).

To examine the influence of various rare-gas atoms on linear compounds with **6**, we calculated the properties of the complexes Rg−C_2 (Rg = Ne, Ar, Kr, Xe) with respect to the vibrational frequency shift, the infrared intensity of the C=C stretching fundamental, the stability of the complex, and the charge transfer between the rare gas atom and the C_2 molecule (**6**). In order to permit description of such a complex even with a xenon atom, the MP2 method was used together with the LANL2DZ basis set (Table 2).

These calculations confirm the hypothesis of a linear compound Xe−C_2 (**7**) with only one xenon atom. The increase in charge transfer, complex stabilization, and especially the increase of the infrared intensity of the C=C stretching fundamental on going from neon to xenon is convincing. However, the calculated vibrational frequency shift of $\Delta\tilde{\nu}$ = −16.8 cm^{-1} (1798.7 vs. 1815.5 cm^{-1}) is still far from the observed shift of $\Delta\tilde{\nu}$ = −87.6 cm^{-1} (1767.0 vs. 1854.6 cm^{-1}) between the gas-phase and the matrix value. This indicates that Xe−C_2 (**7**) cannot simply be described as a complex of C_2 (**6**) with Xe, but as a compound with a relatively strong bond between Xe and C_2 (**6**), which is not predicted by the MP2 (fc)/LANL2DZ calculations. If the polarizability of Xe, the electron affinity of C_2 (**6**), and the results of the calculations are taken into account, the compound Xe−C_2 (**7**) is best described by two resonance structures.

$$\left[\mathrm{Xe{-}C_2} \longleftrightarrow \mathrm{Xe^+\ C_2^-}\right]$$

7

This assumption is supported by comparison with the C=C stretching fundamental of C_2^- in the gas phase at $\tilde{\nu}$ = 1781.2 cm^{-1}[19], which is close to the experimental value of $\tilde{\nu}$ = 1767.0 cm^{-1} for Xe−C_2 (**7**) in the xenon matrix.

Despite the use of the basis set LANL2DZ, our postulate of a linear compound **7** is in good agreement with a calculation at the high ab initio level CCSD-T/aug-cc-pVTZ for the van der Waals complex Ar−C_2[20]. The global minimum of energy is predicted to occur for a linear Ar−C_2 geometry, while a saddle point is predicted for a T-shaped geometry. This T-shaped geometry represents the global minimum for all other rare-gas complexes with heavier symmetric diatomic molecules of second-row atoms, e.g. Ar−N_2.

Naumkin and McCourt[20] also performed calculations on complexes with more than one Ar atom and found minima for the complexes Ar$_n$−C_2 with n = 2−4. The experimental spectra in our case, however, indicate that there is a preference for one single compound, since only one signal is observed in the infrared spectrum. On the basis of the electronic structure of the molecule C_2 (**6**), a linear compound Xe−C_2 (**7**) seems to be preferred with respect to all other species.

Irradiations of Dimeric Acetylene

IR Spectrum of the T-Shaped Acetylene Dimer 9

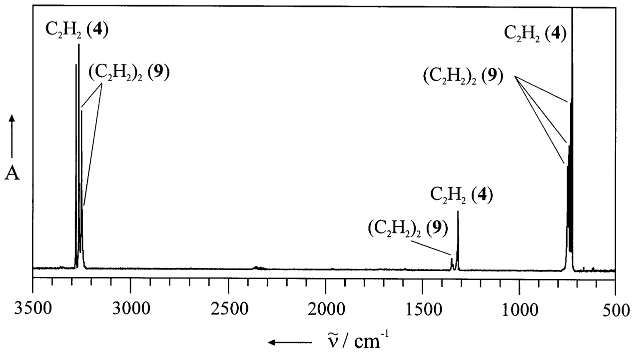
To answer the question whether indirect photolysis can also be used to induce dimerization of acetylene (**4**), rare-gas matrices containing a higher concentration of **4** were produced. The ratio acetylene (**4**)/rare gas was 30:1000.

Table 2. Comparison of the calculated (MP2 (fc)/LANL2DZ) properties of complexes Rg$-$C$_2$ (distances d in Å; q denotes the charge at the atoms, calculated from an NPA; C=C stretching fundamental is given in cm^{-1}, the intensity of this vibration in km·mol^{-1}; E_{stab} is the stabilization of the complex in kcal·mol^{-1} compared to its fragments, which were calculated at the same level of theory)

Complex	d(Rg$-$C$_1$)	d(C$_1$=C$_2$)	q(Rg)	q(C$_1$)	q(C$_2$)	$\tilde{\nu}_{C=C}$	Int.	E_{stab}
C$_1$=C$_2$	–	1.295	–	0.0	0.0	1815.5	0.0	–
Ne$-$C$_1$=C$_2$	3.157	1.295	+0.004	−0.005	+0.001	1815.4	0.5	0.26
Ar$-$C$_1$=C$_2$	3.505	1.295	+0.007	−0.011	+0.004	1814.6	1.4	0.21
Kr$-$C$_1$=C$_2$	3.378	1.296	+0.018	−0.029	+0.011	1811.5	10.9	0.31
Xe$-$C$_1$=C$_2$	3.317	1.297	+0.047	−0.069	+0.023	1798.7	91.8	0.46

The infrared spectra of these matrices show the intense signals of monomeric acetylene (**4**) along with new signals that can only be attributed to acetylene oligomers (Figure 6).

Figure 6. IR spectrum before irradiation of a matrix produced from an acetylene (**4**)/xenon gas mixture with a ratio of 30:1000



The acetylene dimer **9** has a T-shaped geometry with C_{2v} symmetry. According to ab initio calculations, this weakly bound van der Waals complex **9** is the global minimum on the $(C_2H_2)_2$ potential energy surface[21]. The T-shaped structure could be confirmed through high-resolution vibration-rotation spectra in a pulsed supersonic free jet[22] and through microwave spectra obtained for the ground vibrational state using a pulsed-nozzle Fourier transform microwave spectrometer[23]. The most intense infrared signals of the dimer **9** were obtained by Collins[24] upon irradiation of 2-butyne in a xenon matrix, and by Bothur[25] upon photolysis of cyclobutadiene (**13**).

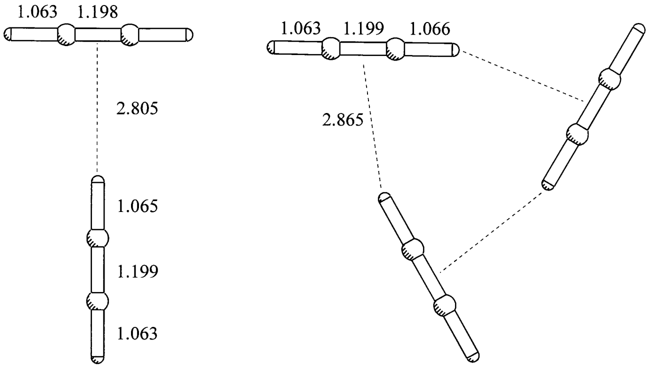
The acetylene trimer **10** was calculated to have C_{3h} symmetry[21]. From the experimentally derived rotation-vibration spectrum one could not discriminate between C_{3h}- and D_{3h}-symmetric structures[26].

For a comparison of the experimental spectrum with the theoretical ones, we recalculated acetylene (**4**), the acetylene dimer **9**, and the trimer **10** at the B3LYP/6-311G** level of theory. Figure 7 shows the optimized structures for the acetylene dimer **9** and trimer **10** with C_{2v} and C_{3h} symmetry, respectively. The calculated binding energies of these van der Waals complexes are E = 0.69 kcal·mol^{-1} and E = 2.16 kcal·mol^{-1} (zero-point energy corrected values).

The calculated infrared frequencies of both complexes are listed in Table 3, together with the band positions from the matrix experiment.

On the basis of the ratio acetylene (**4**)/xenon available, the concentration of the dimer **9** should be higher than that of the trimer **10** in the experimental spectrum (Figure 6). This assumption can be confirmed by comparing the calculated infrared spectra for **9** and **10** with the experimental one. A preference for the acetylene dimer **9** in comparison with the acetylene trimer **10** is indicated simply by the number of signals in the experimental infrared spectrum. The intensities of the signals, however, show no good agreement between experiment and theory. The reason for this weak-

Figure 7. Calculated (B3LYP/6-311G**) structures for the acetylene dimer **9** (C_{2v}) and the acetylene trimer **10** (C_{3h}); distances are given in Å



9 **10**

Table 3. Comparison of the calculated (B3LYP/6-311G**) IR spectra for the acetylene dimer **9** and trimer **10** with the experimental (xenon, 10 K) IR spectrum from an acetylene (**4**)/xenon gas mixture with a ratio of 30:1000

Acetylene dimer **9** (C_{2v})		Acetylene trimer **10** (C_{3h})		Experiment	
$\tilde{\nu}$/cm^{-1}	Int.	$\tilde{\nu}$/cm^{-1}	Int.	$\tilde{\nu}$/cm^{-1}	Int.
646.2	1.9			606.5	<0.1
654.2	2.2	654.1	2.2	616.2	1.6
664.2	1.2	673.3	2.6	622.1	1.2
772.3	19.0			729.0	–[a]
781.7	68.2			736.2	99.3
788.1	87.9	799.7	50.4	744.0	100.0
797.6	43.1	801.9	62.1	751.3	86.3
2063.7	2.1	2062.0	0.9	1963.4	0.4
2066.8	<0.1			1967.8	0.4
3401.5	100.0	3397.3	100.0	3248.6	24.2
3418.0	57.8			3251.5	90.2
3511.5	0.7	3508.0	0.3	3345.5	<0.1
3521.0	<0.1			3358.1	<0.1

[a] The most intense signal strongly overlaps with the most intense signal of the monomeric acetylene (**4**) and thus cannot be integrated.

ness is the problem of integration in the experimental spectrum, because most of the bands strongly overlap, especially the intense ones.

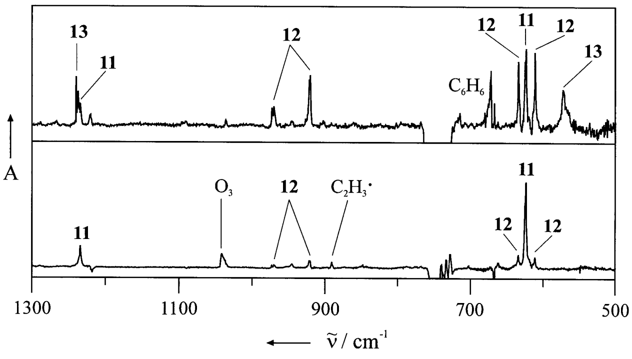
The most obvious reason for the preference of the dimer **9** is the observed photochemistry, which will be described below. Nevertheless, traces of benzene can also be detected among the products of the irradiations, and thus it is clear that small amounts of the acetylene trimer **10** are also present, despite the still low concentration of acetylene (**4**)/ xenon = 30:1000. Hence, it cannot be excluded that signals of the dimer **9** are overlapped by the intense signals of the trimer **10**.

Irradiation at λ = 193 nm (ArF Laser)

Butadiyne (**11**) is the main product of photolysis of gaseous acetylene (**4**) at λ = 193 nm; ethene (**2**), 1,3-butadiene, and vinylacetylene (**12**) are formed as by-products[27]. The mechanisms of product formation in this gas-phase reaction have been studied in detail by Seki and Okabe[28].

For a comparison of the products from the direct photolysis with those from the indirect photolysis, irradiations of the matrices containing the acetylene dimer **9** were first carried out with light from an ArF laser (λ = 193 nm), since acetylene (**4**) absorbs strongly below λ = 200 nm[6]. In this case, the products of the photolyses were found to be independent of the matrix material, i.e. the results were the same for an argon and a xenon matrix. The main products were butadiyne (**11**) and vinylacetylene (**12**). Figure 8 (lower spectrum) shows the difference spectrum from the irradiation in a xenon matrix. Two additional signals can be detected in this infrared spectrum: The signal at $\tilde{\nu}$ = 1767.0 cm^{-1}, assigned to Xe−C_2 (**7**) (this band is missing if an argon matrix is used), and a signal at $\tilde{\nu}$ = 890.9 cm^{-1}. The latter could be assigned to the vinyl radical $C_2H_3^{\bullet}$[29], but no further investigations were made to prove this assignment.

Figure 8. IR difference spectra obtained after laser irradiation of acetylene dimer **9** in xenon matrices; lower spectrum: photolysis of **9** with an ArF laser (λ = 193 nm); upper spectrum: photolysis of **9** with a KrF laser (λ = 248 nm); all bands shown are enhanced upon irradiation



The products from the irradiation of the acetylene dimer **9** at λ = 193 nm in a rare-gas matrix clearly correspond to those formed in the photochemical excitation of gaseous acetylene (**4**). The photochemistry in the two "media" is therefore very similar. The same results can be obtained with a low-pressure mercury lamp at a wavelength of λ = 185 nm.

Irradiation at λ = 248 nm (KrF Laser)

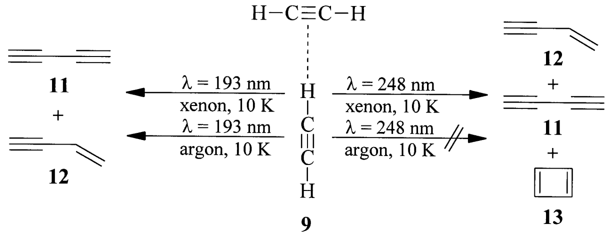
The transparency of acetylene (**4**) at λ = 248 nm was again confirmed upon irradiation of the acetylene dimer **9**; no conversion was detected in an argon matrix. However, a change of the matrix material from argon to xenon made the indirect photolysis possible, and reactions of the dimer **9** could be initiated.

Besides traces of benzene, vinylacetylene (**12**), cyclobutadiene (**13**), and butadiyne (**11**) were detected as the main products of the indirect photolysis (Figure 8, upper spectrum).

Since the overall conversion of the acetylene dimer **9** is low even after irradiation for 10 h, only the two most intense signals of the seven expected fundamentals of cyclobutadiene (**13**) could be detected. As an additional proof for the formation of **13**, the matrix was irradiated with light of the wavelengths λ = 250−420 nm. This light is most effective in inducing the fragmentation of **13** into two acetylene (**4**) molecules[30], and, in fact, only the intensities of the two signals at $\tilde{\nu}$ = 573.3 cm^{-1} and $\tilde{\nu}$ = 1237.7 cm^{-1} were seen to decrease.

All products appear simultaneously in the IR spectrum, so each molecule has to be considered as a product of the primary photochemically induced chemistry, despite the fact that vinylacetylene (**12**) is a known product of the irradiation of cyclobutadiene (**13**) at λ = 248 nm[31]. Butadiyne (**11**), however, is only produced photolytically from vinylacetylene (**12**) at wavelengths below λ = 200 nm[32].

Comparison with the irradiation at λ = 193 nm shows a new product formed only at λ = 248 nm, namely cyclobutadiene (**13**) (Figure 8), and a lower concentration of butadiyne (**11**), whereas the concentration of vinylacetylene (**12**) compared to that of **11** increases. Hence, the products must originate from different mechanisms.



Discussion

The irradiation of monomeric acetylene (**4**) with light of the wavelength λ = 193 nm proceeds differently in xenon and argon matrices. In argon, $C_2H^{\bullet}$ (**5**) and C_2 (**6**) are the products, whereas in the xenon matrix, no $C_2H^{\bullet}$ (**5**) can be detected and a new compound, Xe−C_2 (**7**), is formed as the sole product. This different behaviour can clearly only be attributed to the matrix material. The formation of the stable compound **7** is only possible in xenon, and for this reason the elimination of the second hydrogen atom from $C_2H^{\bullet}$ (**5**) is favoured and no signal for **5** can be detected in this matrix material. The exceptional feature of this irradiation is that the polarizability of the matrix material xenon allows the formation and infrared detection of the species Xe$-$$C_2$ (**7**).

The preferred elimination of both hydrogen atoms from acetylene (**4**) in xenon could be confirmed by irradiation of **4** in the presence of CO. In this case, C_3O (**8**) was formed as a trapping product and again no signal for $C_2H^\bullet$ (**5**) could be detected in the infrared spectrum.

Compound Xe$-$$C_2$ (**7**) is not only formed by irradiation at $\lambda = 193$ nm in a xenon matrix, but also upon irradiation with the light of a KrF laser ($\lambda = 248$ nm), even though acetylene (**4**) shows no absorption at this wavelength. This can clearly be explained in terms of the different mechanisms of excitation, namely by the absorption of the matrix material in the case of xenon with light of the wavelength $\lambda = 248$ nm, and the direct absorption of the organic precursor in an argon or xenon matrix at $\lambda = 193$ nm. Two-photon-induced generation of excitonic states in solid xenon followed by exciton-molecule encounters can therefore also be used to generate the compound Xe$-$$C_2$ (**7**).

As far as the photochemistry of the acetylene dimer **9** upon irradiation at $\lambda = 193$ nm is concerned, a comparison between the gas-phase chemistry of **4**[27][28] and the matrix experiments can be drawn. The formation of butadiyne (**11**) upon irradiation of gaseous acetylene (**4**) at $\lambda = 193$ nm is explained by a two step process.

$$C_2H_2\,(\mathbf{4}) \xrightarrow{\lambda = 193\text{ nm}} C_2H\cdot\,(\mathbf{5}) + H\cdot$$

$$C_2H\cdot\,(\mathbf{5}) + C_2H_2\,(\mathbf{4}) \longrightarrow [C_4H_3\cdot] \longrightarrow C_4H_2\,(\mathbf{11}) + H\cdot$$

The same mechanism can also be applied to the matrix experiments. However, since the fragments are not mobile in the matrix as they are in the gas phase, the formation of the products can alternatively be explained in terms of disproportionation of the acetylene dimer **9** to form an ethynyl radical $C_2H^\bullet$ (**5**) and a vinyl radical $C_2H_3^\bullet$, which can subsequently form vinylacetylene (**12**) by recombination.

$$(C_2H_2)_2\,(\mathbf{9}) \longrightarrow [C_2H\cdot\,(\mathbf{5}) + C_2H_3\cdot]_{\text{matrix cage}}$$

$$[C_2H\cdot\,(\mathbf{5}) + C_2H_3\cdot]_{\text{matrix cage}} \longrightarrow C_4H_4\,(\mathbf{12})$$

Vinylacetylene (**12**) is not stable under the experimental photolytic conditions and forms butadiyne (**11**)[32]. This explains the low concentration of **12** obtained in the matrix experiments (Figure 8, lower spectrum).

None of these intermediates can, however, explain the product formation and distribution observed in the experiments at $\lambda = 248$ nm. Acetylene (**4**) does not absorb light of this wavelength and thus the energy has to be transferred to the organic precursor through exciton-molecule encounters[4].

The irradiation of a xenon matrix with the light of a KrF laser ($\lambda = 248$ nm) generates delocalized excitons Xe_n* by two-photon absorption. These excitons can be localized by self-trapping, forming an excimer center Xe_2*, which decays with emission of radiation ($\lambda = 172$ nm)[1].

$$n\,Xe + 2\,h\nu \longrightarrow Xe_n^*$$

$$Xe_n^* \longrightarrow Xe_2^* + (n-2)\,Xe$$

$$Xe_2^* \longrightarrow 2\,Xe + h\nu'$$

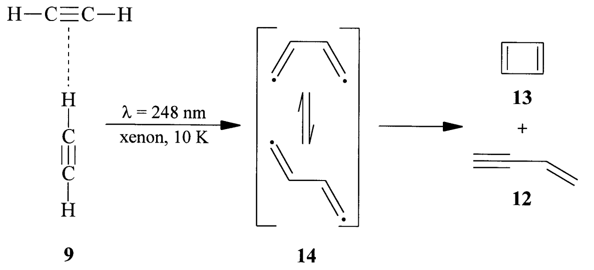
If the matrix is further doped with molecules such as the acetylene dimer **9**, exciton-molecule encounters are highly probable because of the large mobility of the free excitons (25$-$260 Å)[1]. The energy stored in the exciton can be released through this process and transferred to the embedded molecule. The possible mechanisms for this energy transfer are discussed in a review article by Schwentner et al.[33].

We assume that the transfer of energy through exciton-molecule encounters in the host lattice is sufficient to bring the dimer **9** to a highly excited state $(C_2H_2)_2$* (electronically or vibrationally).

$$Xe_n^* + (C_2H_2)_2\,(\mathbf{9}) \longrightarrow n\,Xe + (C_2H_2)_2^*$$

$$(C_2H_2)_2^* \longrightarrow \text{diradical } \mathbf{14} \longrightarrow \text{reaction products}$$

Our proposed mechanism for this photochemically induced reaction involves a 1,4-diradical **14** as an intermediate. Cyclobutadiene (**13**) can be formed by ring closure, while vinylacetylene (**12**), which is the source of the third product butadiyne (**11**), can be formed by a 1,3-hydrogen shift. The addition of a third acetylene (**4**) molecule to the diradical **14** in the same matrix cage readily explains the formation of benzene from the acetylene trimer **10**.



Bally et al.[34] explain their ab initio results on the reaction of acetylene (**4**) with its radical cation using a very similar reaction scheme.

Considering the energy necessary for the process of exciton formation, light of the wavelength $\lambda = 193$ nm (6.4 eV) should be able to induce the exciton state of solid xenon (8.4 eV) in a two-photon process even more readily[1][2][3]. At this wavelength, however, the two processes of direct and indirect absorption compete with each other. An estimation, using a formula given by Lawrence and Apkarian[4], together with the absorption cross-section of acetylene (**4**)[28] and the two-photon excitation cross-section of solid xenon[2] at $\lambda = 193$ nm, clearly shows that the direct absorption of the precursor acetylene (**4**) predominates at this wavelength. Consequently, the experimental results of irradiations of the acetylene dimer **9** at $\lambda = 193$ nm in xenon and argon matrices are the same.

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Experimental Section

Cryostat for Matrix Isolation: Closed-cycle compressor unit RW2 with coldhead base unit 210 and extension module ROK from Leybold. − *Spectrometers:* IR: FT-IR spectrometer IFS 85 from Bruker, resolution 1 cm^{-1}; UV/Vis: Diode array spectrometer HP 8453 from Hewlett-Packard, resolution 0.5 nm. − *Light Sources:* Excimer laser LPX 105 from Lambda Physik, mercury high-pressure lamp HBO 200 from Osram, and mercury low-pressure spiral lamp from Gräntzel.

[D$_1$]Acetylene ([D$_1$]-**4**) *and [D$_2$]Acetylene* ([D$_2$]-**4**): At a temperature of −30°C, acetylene (**4**) was passed through 200 ml of a stirred solution of *n*BuLi in hexane (ca. 1.5 M) for 15 min. The reaction mixture was then heated to reflux for 2 h, cooled to −30°C once more, and then 15 ml of D_2O was added by means of a dropping funnel. The gaseous products were collected in a cold trap (77 K) by passing a gentle stream of helium through the apparatus. The synthesis yielded a mixture of **4**, [D$_1$]-**4** and [D$_2$]-**4** free of impurities, which was used without further purification.

[1,2-^{13}C]Acetylene ([1,2-^{13}C]-**4**) was purchased from Promochem.

Calculations: The calculations were performed with the GAUSSIAN-94 package of programs[35].

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