

Fluorine-Free Organoxenon Chemistry: HXeCCH, HXeCC, and HXeCCXeH

Leonid Khriachtchev,* Hanna Tanskanen, Jan Lundell, Mika Pettersson, Harri Kiljunen, and Markku Räsänen

Department of Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland

Received February 4, 2003; E-mail: Leonid.Khriachtchev@Helsinki.Fi

The first Xe-containing compound was the salt $\text{Xe}^+[\text{PtF}_6]^-$.¹ A large number of Xe derivatives including species with a Xe–C bond have been prepared, and xenon difluoride (XeF_2) has been extensively used for synthesis.^{2,3} It appears that the vast majority of Xe derivatives contain fluorine. The field of rare-gas (Rg) chemistry was expanded by the family of HRgY molecules (where Y is an electronegative fragment like Cl, OH, CN, etc.) prepared in low-temperature rare-gas matrixes using UV photolysis of a HY precursor and subsequent thermal mobilization of H atoms.⁴ By this procedure, we identified the first argon compound (HArF),^{5,6} a neutral Xe-containing radical (HXeO),⁷ and a molecule with a Xe–C bond (HXeCN).⁸ It has been recently suggested that Xe can be inserted into H–C bonds of hydrocarbons, providing a novel way to activate the H–C group.⁹ Here we report the identification of HXeCCH , HXeCC , and HXeCCXeH , prepared by photolysis and annealing of $\text{C}_2\text{H}_2/\text{Xe}$ solids. The assignments are supported by experiments with deuterated species and by ab initio calculations.

The $\text{H}_2\text{C}_2/\text{Xe}$ ($\sim 1/1000$) matrixes were photolyzed at 8 K by 193 and 250 nm light pulses; the experimental details appear elsewhere.^{4–8} Upon photolysis, the IR absorption spectra show decomposition of acetylene¹⁰ and appearance of C_2H radicals (a broad band at $\sim 1852\text{ cm}^{-1}$)¹¹ and C_2 molecules complexed with Xe (1767 cm^{-1}).¹² The result of 193 nm photolysis is presented by spectrum a in Figure 1. The C_2H radicals are the primary photolysis products of H_2C_2 , and photodissociation of C_2H radicals produces C_2 molecules.¹² Accordingly, the $\text{C}_2/\text{C}_2\text{H}$ ratio was observed to increase during photolysis. It was also found that the $\text{C}_2/\text{C}_2\text{H}$ ratio is larger upon irradiation at 250 nm when compared with irradiation at 193 nm, and this can be explained by the different photodissociation efficiencies of C_2H and H_2C_2 at these two wavelengths. Some formation of XeHXe^+ ,¹³ C_4H ,¹⁴ and C_4 ¹⁵ was also seen especially in samples containing acetylene dimers.

Annealing of a photolyzed sample at $\sim 40\text{ K}$ activates motion of H atoms, promoting their reactions with neutral Xe–Y centers and leading to HXeY species with very strong H–Xe stretching absorption.⁴ Accordingly, we observed the annealing-induced formation of several IR absorption bands (see Figure 1). In addition to known HXeH (1166 and 1180 cm^{-1}), three previously unreported absorbers with bands at (1) 1486 cm^{-1} , (2) 1478 cm^{-1} , and (3) 1301 cm^{-1} systematically appear in the spectra. Importantly, no corresponding bands with normal matrix shifts are found in analogous experiments in an Ar matrix, which suggests that these absorbers are due to novel Xe-containing species, and we measure their H–Xe stretching absorption. With certainty, these bands belong to three different species because their proportion varies strongly in various experimental situations (see Figure 1). Moreover, these species have very characteristic photostabilities: the 1478 cm^{-1} band is the least photostable, the 1301 cm^{-1} band is more photostable, and the 1486 cm^{-1} band is the most photostable. Additional bands are found to belong to species (1) and (2): the bands at 3273 and 626 cm^{-1} correlate with the 1486 cm^{-1} band

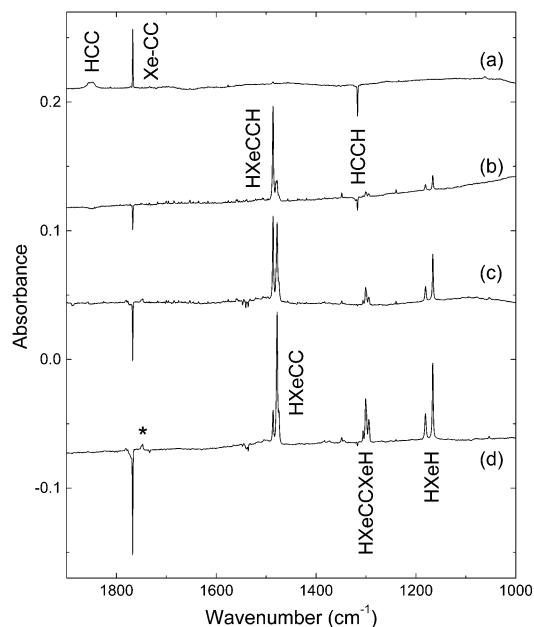


Figure 1. Difference IR absorption spectra demonstrating results of photolysis of acetylene in solid Xe (a) and annealing of photolyzed samples at 45 K (b–d). Spectrum a corresponds to precursor photolysis with 60 pulses of 193 nm radiation ($\sim 20\text{ mJ/cm}^2$). Spectra b–d were obtained by annealing after 60 pulses of 193 nm radiation, 6×10^3 pulses of 193 nm radiation, and 1.5×10^4 pulses of 250 nm radiation ($\sim 2\text{ mJ/cm}^2$), which decomposed $\sim 15\%$, 80% , and 65% of acetylene, respectively. The known self-limitation process due to photolysis-induced UV absorbers limits the photodissociation rate upon long irradiation.¹⁷ The 1748 cm^{-1} band marked with an asterisk is assigned to the $\text{C}\equiv\text{C}$ stretching mode of HXeCC . The spectra were measured at 8 K with a resolution of 1 cm^{-1} .

[absorber (1)], and the band at $\sim 1748\text{ cm}^{-1}$ (marked with an asterisk in Figure 1) correlates with the 1478 cm^{-1} band [absorber (2)]. An additional species forming upon annealing is C_2H_3 (891 cm^{-1}),¹⁶ showing reactions of H atoms with a residual H_2C_2 precursor.

Next, we discuss the assignment of these three absorbers. The amount of absorber (1) with the H–Xe stretching band at 1486 cm^{-1} correlates with the HC_2 concentration after photolysis, and its bands at 3273 and 626 cm^{-1} fit well the H– $\text{C}\equiv\text{C}$ stretching and H–CC bending modes. It is safe to assign absorber (1) to HXeCCH predicted recently.⁹ The measured H–Xe stretching frequency of 1486 cm^{-1} is smaller than the theoretical value at the MP2 and CCSD(T) levels (1736 and 1621 cm^{-1} , respectively); however, a similar overestimation is common for the HRgY molecules,⁴ indicating either a lack of the theoretical accuracy or an effect of the matrix surrounding.⁶ In accord with the experiment, the H–C stretching and H–CC bending modes of HXeCCH are computationally strong, and the $\text{C}\equiv\text{C}$ stretching mode is weak.⁹ The deuteration experiments support our assignment, showing the D–Xe stretching, D–C stretching, and D–CC bending vibration bands

at 1077.5, 2545, and 491.5 cm^{-1} , that is, giving H/D ratios of 1.379, 1.286, and 1.275, respectively. We performed computations of HXeCCH and DXeCCD species at the MP2/LJ18,6-311++G-(2d,2p) level of theory^{4,9} and obtained similar H/D ratios of 1.409, 1.306, and 1.273, respectively.

Absorber (2), with the H–Xe stretching band at 1478 cm^{-1} , can be enhanced using longer 193 nm or 250 nm initial photolysis, producing a larger amount of C_2 molecules. The C_2 fragment is strongly electronegative,¹² and an H atom can react with the Xe– C_2 center. The 1748 cm^{-1} band of absorber (2) fits the $\text{C}\equiv\text{C}$ stretching mode. Selective photodissociation of absorber (2) leads to an increase of the C_2 concentration. Thus, we assign absorber (2) to HXeC₂, which is, to the best of our knowledge, the first neutral four-atom rare-gas radical. The corresponding D–Xe stretching absorption is at 1081.5 cm^{-1} (H/D ratio of 1.367), and the $\text{C}\equiv\text{C}$ stretching frequency (1748 cm^{-1}) is practically unchanged upon deuteration. On the basis of our experience with HXeO,⁷ open-shell rare-gas species are difficult to compute, and the MP2 level of theory is unsatisfactory to describe the vibrational frequencies. We performed calculations on HXeCC at the CCSD(T)/LJ18,6-311++G(2d,2p) level of theory, and they reveal its intrinsic stability. The H–Xe and Xe–C distances are 1.725 and 2.419 Å, respectively, which are similar to the corresponding values of HXeCCH (1.767 and 2.351 Å).⁹ The natural bond orbital analysis indicates a strong ionic character for HXeCC, with a positive charge on the Xe atom (+0.89) and a negative charge on the inner C atom (–0.86). The calculated H–Xe stretching frequency is at 1754 cm^{-1} , and the deviation from the measured value is similar to the case of HXeO.⁷ In agreement with the experiment, deuteration does not change the $\text{C}\equiv\text{C}$ stretching frequency at the CCSD(T) level (1600 cm^{-1}). As estimated at the MP2 level, the $\text{C}\equiv\text{C}$ stretching mode of HXeCC is IR active (71 km/mol), which supports its experimental detection.

We assign absorber (3), with the H–Xe stretching mode at 1301 cm^{-1} , to HXeCCXeH, and it is the first neutral rare-gas hydride molecule containing two Xe atoms. The ab initio calculations show the stability of this species and predict a decrease (by $\sim 140 \text{ cm}^{-1}$) of its H–Xe stretching frequency as compared with that of HXeCCH,⁹ which agrees with the measured value of 177 cm^{-1} . The experiments with partially deuterated acetylene provide a conclusive method to identify this species. For HXeCCXeD, one can expect two intense bands corresponding to the H–Xe and D–Xe stretching modes, and these bands are probably shifted from the corresponding bands of HXeCCXeH and DXeCCXeD. Indeed, our MP2 calculations predicted blue shifts of 40 and 24 cm^{-1} for the H–Xe and D–Xe stretching frequencies of HXeCCXeD, respectively, from the corresponding values of HXeCCXeH and DXeCCXeD. This is exactly what we observed experimentally (see Figure 2): Upon partial deuteration, the spectra show three additional annealing-induced bands. The 945 cm^{-1} band is assigned to the D–Xe stretching absorption of DXeCCXeD with a characteristic H/D frequency ratio of 1.377. The bands at 1342 and 972 cm^{-1} are assigned to H–Xe and D–Xe stretching modes of HXeCCXeD, and the experimental blue shifts by 41 and 27 cm^{-1} are in numerical agreement with our theoretical prediction. The observed difference of the corresponding vibrations of the HXeCCXeH isotopologues presumably originates from a strong coupling between the normal modes even though the terminal H–Xe bonds are “separated” by the –XeCCXe– group.

In summary, we have identified three Xe-containing organic compounds, HXeCCH, HXeCC, and HXeCCXeH. They are

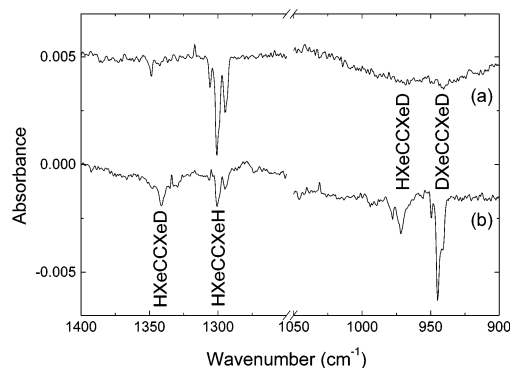


Figure 2. Difference IR absorption spectra demonstrating results of photodissociation of HXeCCXeH isotopologues (a) without deuteration and (b) with deuteration (degree of deuteration $\sim 70\%$). The species were obtained by 250 nm photolysis (1.5×10^4 pulses, $\sim 2 \text{ mJ/cm}^2$) of acetylene in solid Xe and annealing at 45 K.

prepared in a low-temperature Xe matrix using UV photolysis of acetylene and subsequent annealing at 40–45 K. This work demonstrates a new way to activate the H–C \equiv C– group and can promote organoxenon chemistry. It is believed that the replacement of H–C \equiv with H–Xe–C \equiv should significantly increase the reactivity of this functional group, which can find novel synthetic applications.

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Note Added after ASAP: In the version published on the Web 3/28/03, the structure H=C in the right-hand column on the first page is incorrect. In the final Web version published 3/28/03 and print version it is correct as H–C \equiv .

References

- (1) Bartlett, N. *Proc. Chem. Soc.* **1962**, 218.
- (2) Brel, V. K.; Pirkuliev, N. Sh.; Zefirov, N. S. *Russ. Chem. Rev.* **2001**, *70*, 231–264.
- (3) Frohn, H.-J.; Bardin, V. V. *Organometallics* **2001**, *20*, 4750–4762.
- (4) Lundell, J.; Khriachtchev, L.; Pettersson, M.; Räsänen, M. *Low Temp. Phys.* **2000**, *26*, 680–690.
- (5) Khriachtchev, L.; Pettersson, M.; Runeberg, N.; Lundell, J.; Räsänen, M. *Nature (London)* **2000**, *406*, 874–876.
- (6) Khriachtchev, L.; Pettersson, M.; Lignell, A.; Räsänen, M. *J. Am. Chem. Soc.* **2001**, *123*, 8610–8611.
- (7) Khriachtchev, L.; Pettersson, M.; Lundell, J.; Tanskanen, H.; Kiviniemi, T.; Runeberg, N.; Räsänen, M. *J. Am. Chem. Soc.* **2003**, *125*, 1454–1455.
- (8) Pettersson, M.; Lundell, J.; Khriachtchev, L.; Räsänen, M. *J. Chem. Phys.* **1998**, *109*, 618–625.
- (9) Lundell, J.; Cohen, A.; Gerber, R. B. *J. Phys. Chem. A* **2002**, *106*, 11950–11955.
- (10) McDonald, S. A.; Johnson, G. L.; Keelan, B. W.; Andrews, L. *J. Am. Chem. Soc.* **1980**, *102*, 2892–2896.
- (11) Forney, D.; Jacox, M. E.; Thompson, W. E. *J. Mol. Spectrosc.* **1995**, *170*, 178–214.
- (12) Maier, G.; Lautz, C. *Eur. J. Org. Chem.* **1998**, 769–776.
- (13) Kunttu, H.; Seetula, J.; Räsänen, M.; Apkarian, V. A. *J. Chem. Phys.* **1992**, *96*, 5630–5635.
- (14) Dismuke, K. I.; Graham, W. R. M.; Weltner, W., Jr. *J. Mol. Spectrosc.* **1975**, *57*, 127–137.
- (15) Szczepanski, J.; Ekern, S.; Chapo, C.; Vala, M. *Chem. Phys.* **1996**, *211*, 359–366.
- (16) Shepherd, R. A.; Doyle, T. J.; Graham, W. R. M. *J. Chem. Phys.* **1988**, *89*, 2738–2742.
- (17) Khriachtchev, L.; Pettersson, M.; Räsänen, M. *Chem. Phys. Lett.* **1998**, *288*, 727–733.

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