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Chemical reactions in the xenon—acetylene systems irradiated with fast electrons at 16 K: formation of xenon-containing molecules and radicals

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The formation of HXeCCH molecules and $HXeCC^{\bullet}$ radicals resulting from chemical reactions in solid xenon—acetylene systems irradiated with fast electrons was studied by low-temperature IR and EPR spectroscopies. The data obtained confirm the assignment of an absorption band with maximum at 1478 cm^{-1} to the H—Xe stretching vibrations in the $HXeCC^{\bullet}$ radical. Relativistic density functional calculations with inclusion of anharmonic corrections permit a quantitative description of the vibrational spectra of xenon-containing molecules and radicals. Preliminary experimental and computational data on the magnetic resonance parameters of the $HXeCC^{\bullet}$ radical were obtained. This radical is characterized by large hyperfine coupling constants with magnetic nuclei of the xenon isotopes.

Key words: xenon hydrides, matrix isolation, IR spectroscopy, EPR spectroscopy, electron irradiation, quantum-chemical calculations.

Rare gas hydrides (compounds of the HRgX type, where Rg is the rare gas atom and X is an atom or atomic group with sufficient electronegativity) were first identified in 1995.[1,2] The existence of such molecules was unexpected and attracted considerable attention of experimentalists and theoreticians. The nature of chemical bonding in the new compounds, criteria for their stability, and their properties are of great interest for chemistry. Our EPR and IR spectoscopy studies showed that the formation of HRgX molecules is due to reactions of mobile H atoms in rare gas matrices.[3,4] This mechanism was also independently confirmed by other researchers.[5] Since then more than ten HRgX compounds were obtained, including the first neutral chemical compound of argon HArF.[6,7] A general procedure for preparing the HRgX (Rg = Xe, Kr) compounds involves dissociation of the precursor molecules HX in the solid rare gas matrix at low temperature (<20 K) followed by formation of the HRgX molecules as a result of thermal reactions proceeding on annealing of samples to the diffusion temperature of H atoms (40—45 K in xenon or 30—32 K in crypton). Dissociation of the HX molecules can be attained by exposing to UV light[1,2] or by irradiation with fast electrons.[3,4] All HRgX molecules correspond to metastable states (local minima) with energies lying 3—5 eV higher than the energies of the global minima corresponding to the HX molecules.[6] However, the new molecules are stable enough to have almost infinite lifetimes under the low-temperature matrix isolation conditions. Identification of the HRgX molecules is facilitated by the fact that the IR absorption bands corresponding to the H—Rg stretching vibrations are characterized by extremely high intensities (in some cases, they are an order of magnitude more intense than the corresponding HX bands) due to very large dipole moments of transitions.

The formation of organic molecules representing products of insertion of rare gas atoms into the C—H and O—H bonds is of particular interest. Recently,[8] the possibility for a number of metastable compounds of the HXeR and HXeOR (R is an organic radical) types to exist was predicted theoretically. More recently, we[9] and other researchers[10] simultaneously and independently obtained the first representative of this type of compounds, namely, HXeCCH (product of xenon insertion into acetylene mol-

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ecule) and then identification of HKrCCH molecule was reported.[11] According to calculations, the dissociation energy of HXeCCH molecule into fragments can be as high as 1.5 eV,[8] which means that, in principle, this compound can be stable at rather high temperatures.

The xenon—acetylene system appeared to be very fruitful from the standpoint of "new" chemistry of rare gases. Photochemical studies[10] of this system at high acetylene conversions showed that the IR spectrum exhibits bands, which were assigned to the $HXeCC^{\bullet}$ radicals and HXeCCXeH molecules. When this work was prepared for publication, a new study was reported,[12] presenting additional spectoscopic and kinetic arguments in favor of this identification and substantiated the mechanism of formation of HXeCCXeH. However, it should be noted that the use of IR spectoscopy only provides incomplete information on the structure of the new species and on the mechanisms of processes. Meanwhile, combined EPR and IR spectoscopic studies[4,9] permit quantitative characterization of the reaction mechanisms. The use of EPR spectroscopy is of crucial importance for establishment of the structure of paramagnetic species, in particular, $HXeCC^{\bullet}$ radical. Besides, establishment of correspondence between experimental data and results of calculations, especially for $HXeCC^{\bullet}$ radical, remains topical.

In this work we report the results of detailed EPR and IR spectoscopy investigations of the formation of new xenon compounds in irradiated xenon—acetylene systems and the results of quantum-chemical calculations using relativistic version of density functional theory, which makes it possible to attain much better agreement between theory and experiment.

Experimental and Calculation Procedure

High-purity xenon (99.99%) was used for the preparation of gas mixtures. Acetylene and deuterated acetylene were prepared by the reactions of calcium carbide with H_2O and D_2O, respectively. In order to minimize isotope exchange on the setup walls in the course of preparation of the gas mixtures and the deposition on the matrix, prior to carrying out the experiments with deuterated acetylene the setups were washed with D_2O vapor for at least 1 h. Since exchange cannot be ruled out completely, the deuterated acetylene represented a mixture of C_2D_2 with C_2HD, but the non-deuterated acetylene concentration in this mixture was negligible (see below).

A set of helium flow cryostats for radiation chemistry studies of the matrix samples, designed and manufactured at the L. Ya. Karpov Institute of Physical Chemistry,[13] was employed in this study. Gas mixtures were deposited on a cooled KBr plate at 30—32 K (in the case of IR spectroscopic experiments) or on the tip of a cylindrical sapphire rod placed immediately in the cavity of an EPR spectrometer (in the case of experiments involving a cryostat equipped with a vacuum cavity). The typical deposition time was 1—2 h. Samples thus obtained were irradiated with a fast electron beam (1 MeV) using a EG-2.5 Van-de-Graaf electron accelerator (electrostatic generator) at 16 K. The irradiation doses varied from 10 to 80 kGy. IR spectra in the range 4000—450 cm^{-1} at 16—19 K were recorded with a Perkin—Elmer 1710 FTIR spectrometer (100 scans, cooled MCT detector, with 1 cm^{-1} resolution). EPR spectra were recorded with an X-band (9.4 GHz) spectrometer with high-frequency modulation (100 kHz), manufactured by SPIN ZAO (Saint-Petersburg, Russia) at 15—17 K. To preclude saturation of EPR signals at low temperatures, the instrument operated at a low microwave power (at most 5 μW).

In order to study post-radiation thermal reactions, the irradiated samples were annealed at different temperatures (30—80 K) for 5 min and and then again cooled down to the temperature at which the spectra were measured. The samples were photolyzed at 15—17 K by unfiltered light of a 100 W filament lamp equipped with a water jacket to prevent heating.

Salient features of the experimental procedures were described in detail earlier.[14—16]

Quantum-chemical calculations were carried out using the PRIRODA program kindly submitted by the author, D. N. Laikov. Calculations were performed using the density functional approcah in the PBE approximation[17] using the scalar-relativistic one-electron Hamiltonian with a finite nucleus model[18] and an extended basis set of Gaussian-type functions and TZ2P-quality, which was supplied with the program.[19] The contact integrals hyperfine and dipole-dipole electron-nuclear interactions were calculated from the electric field gradients by integrating over the nuclear charge density. Anharmonic frequencies were determined by solving the vibrational problem for the potentials obtained by scanning the potential energy surface over each normal mode. Calculations were carried out on a supercomputer cluster at the Research Computational Center, M. V. Lomonosov Moscow State University.

Results and Discussion

The IR spectrum of a xenon—acetylene mixture, recorded at 16 K immediately after deposition is shown in Fig. 1 (spectrum *1*). The most intense spectral band has a maximum at 728 cm^{-1}, being accompanied by weak bands with maxima at 736.5, 744.5, and 752 cm^{-1}. The region of C—H stretching vibrations is characterized by bands with maxima at 3266 and 3280 cm^{-1} and by weak bands at 3229 and 3252 cm^{-1}. Based on the results of studies of the influence of acetylene concentration on the spectrum and comparison with the published data,[20] the bands with maxima at 728, 3266, and 3280 cm^{-1} were assigned to acetylene monomers while the bands at 736.5, 744.5, 752, 3229, and 3252 cm^{-1} were assigned to acetylene associates. Yet another characteristc absorption band of acetylene monomer has a maximum at 1317 cm^{-1}. At high dilutions (1 : 2000) mainly isomeric monomeric acetylene molecules are present in the xenon matrix.

The IR spectrum of a deposited sample of the xenon—deuterated acetylene system exhibits bands corresponding to C_2D_2 (bands with maxima at 536, 1031.3 and 2429 cm^{-1}) and C_2HD (bands with maxima at 675, 1237,

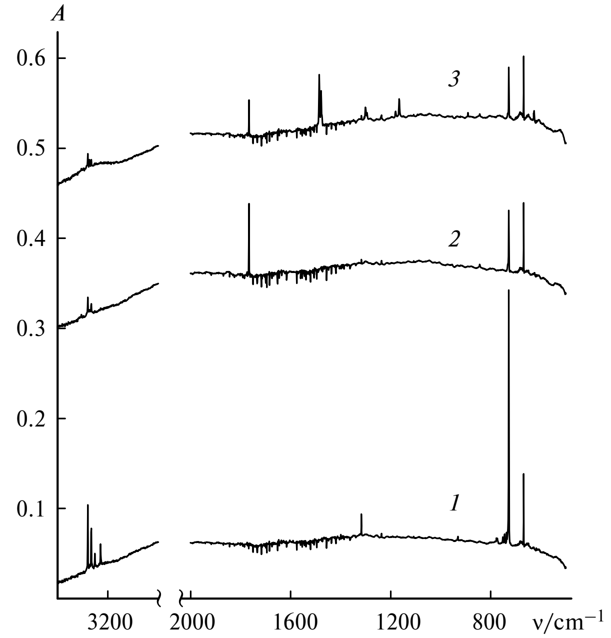

Fig. 1. IR spectra of a deposited xenon—acetylene (2000 : 1) mixture recorded immediately after deposition (*1*), after irradiation with fast electrons to a dose of 80 kGy at 16 K (*2*), and after annealing of the irradiated sample at 45 K for 5 min (*3*). Here and in Figs 2—7 all spectra were recorded at 16 K.

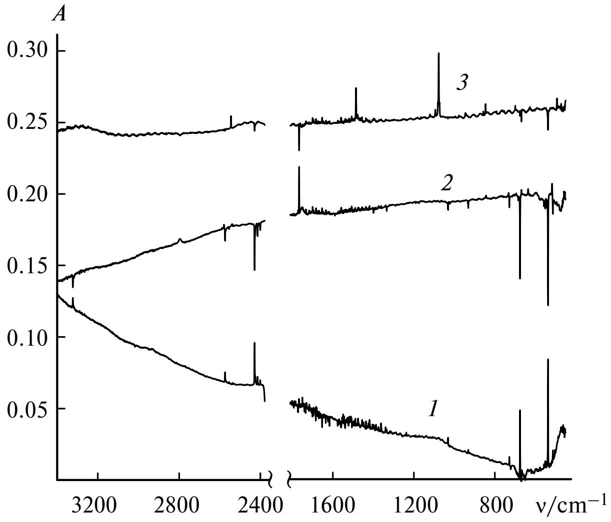

Fig. 2. IR spectrum of a deposited xenon—deuterated acetylene (2000 : 1) mixture (*1*); difference spectrum obtained by subtracting the spectrum of the deposited sample from the spectrum of the sample irradiated fast electrons at 16 K to a dose of 40 kGy (*2*); difference spectrum obtained by subtracting the spectrum recorded after subsequent annealing of the sample (45 K, 5 min) from the spectrum of the irradiated sample (*3*).

2574 and 3323 cm^{-1})[21] molecules (Fig. 2, spectrum *1*), the former group of bands being nearly twice as intense. Much weaker bands with maxima at 2401, 2414, 2536, 2554, and 3315 cm^{-1} correspond to molecular associates of perdeuterated and partially deuterated acetylene. No bands corresponding to C_2H_2 were detected.

Irradiation of samples causes a marked decrease in the acetylene band intensities, associates of C_2H_2 molecules being consumed somewhat faster than monomeric molecules. For instance, irradiation of the C_2H_2—Xe system (1 : 2000 dilution) to a dose of 40 kGy is followed by consumption of ~68% of the initial acetylene and ~87% of associates. Nevertheless, as mentioned above, the initial concentration of associates in dilute systems is negligible and the major products observed are formed from monomeric molecules. In the case of deuterated acetylene different isotopomers are consumed in different fashion, which indicates an isotope effect in the dissociation of acetylene molecules (irradiation to a dose of 40 kGy leads to consumption of 51% of C_2D_2 and ~65% of C_2HD despite the fact that the initial C_2D_2 concentration is higher).

As should be expected, the consumption of acetylene molecules increases as the irradiation dose increases, but at high doses the consumption rate is lowered (at 1 : 2000 dilution, a total of 37, 68, and 78% of monomeric molecules are consumed at doses of 10, 40, and 80 kGy, respectively). Such a "saturation" indicates the occurrence of secondary reactions at high doses, which was confirmed by EPR data (see below).

Irradiation of C_2H_2 in xenon matrix is followed by the appearance of new, relatively weak bands with maxima at 731.5, 843, 1767, and 1852—1855 cm^{-1} (see Fig. 1, spectrum *2*). The bands at 731.5 and 843 cm^{-1} were attributed to the Xe_2H^+ cation[22] (small amount of this cation is always generated on irradiation of various hydrogen-containing compounds in xenon matrices). A narrow band at 1767 cm^{-1} is most pronounced only after irradiation with high doses (40—80 kGy). The band corresponds[23] to the carbon—carbon stretching vibrations of the Xe—C_2 complex (assignment is based on the data of experiments with isotope substitution). A broad weak band with maximum near 1852—1855 cm^{-1} corresponds to the C≡C vibrations in the ethynyl radical $^{\bullet}C_2H$.[9,10,24] It should be noted that the bands of the Xe_2H^+ cation are characterized by very high extinction coefficients,[22] whereas the band of the ethynyl radical, on the contrary, is of medium intensity (expected extinction coefficient is nearly an order of magnitude lower), being substantially broadened. Therefore, the major radiolysis product observed in the IR spectrum at low irradiation doses is $^{\bullet}C_2H$ radical; an increase in the irradiation dose causes an increase in the concentration of the Xe—C_2 complex.

The IR spectrum (see Fig. 2) of the irradiated partially deuterated acetylene in xenon matrix exhibits new, rather weak bands of Xe_2H^+ (maxima at 731.5 and 843 cm^{-1}), Xe_2D^+ (517 cm^{-1}),[22] and Xe—C_2 (1767 cm^{-1}). Bands of the $^{\bullet}C_2D$ and $^{\bullet}C_2H$ radicals are probably of too low intensity to be reliably detected under these conditions.

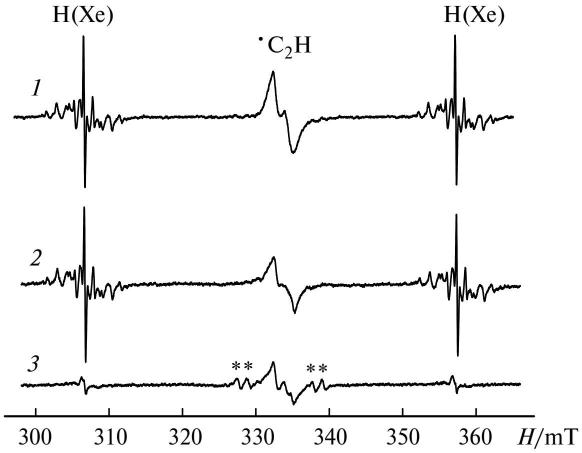

Fig. 3. EPR spectra of deposited xenon—acetylene (2000 : 1) mixtures irradiated with fast electrons at 16 K to doses of 10 (*1*) and 80 kGy (*2*); EPR spectrum of the sample irradiated to a dose of 80 kGy after annealing at 45 K for 5 min (*3*). The spectra were recorded at different gains; the lines corresponding to vinyl radical are asterisked.

In accordance with the available data[9] the EPR spectra of irradiated xenon—acetylene system (Fig. 3, spectra *1* and *2*) exhibit signals of hydrogen atoms (doublet with $a(1H) \approx 50.6$ mT and characteristic super-HFS due to the interaction with nuclei of the magnetic isotopes of the matrix, ^{129}Xe and ^{131}Xe) and ethynyl radicals (strongly broadened poorly resolved doublet with a splitting ~1.6 mT at the central part of the spectrum). The relative amounts of H atoms and $^{\bullet}C_2H$ radicals depend on the irradiation dose. Namely, at a dose of 10 kGy the integrated intensities of the corresponding signals are nearly equal (they differ by less than 10%); at a dose of 40 kGy the concentration of stabilized H atoms exceeds that of ethynyl radicals by ~27%, being ~1.8 times higher at a dose of 80 kGy. These results point that the secondary process of dissociation of $^{\bullet}C_2H$ radicals into C_2 and hydrogen atoms becomes more significant as the dose increases. Thus, the EPR and IR spectoscopy data show that the main processes occurring under conditions of low-temperature irradiation of the xenon—acetylene system with fast electrons can be quantitatively described by a simple scheme. Since at the component ratios used (1000 : 1 and higher) direct effect of radiation on acetylene is negligible, the energy of ionizing radiation is initially absorbed by the matrix. Energy transfer causes the formation of excited acetylene molecules, which undergo dissociation into ethynyl radicals and hydrogen atoms

$$C_2H_2^* \longrightarrow {}^{\bullet}C_2H + H^{\bullet}. \quad (1)$$

This reaction is responsible for the formation of almost equal amounts of hydrogen atoms and radicals in the initial steps (at low conversions). As the irradiation dose increases, the initial acetylene concentration decreases while the concentration of ethynyl radicals increases and they become efficient scavengers of excitation in xenon, thus competing with acetylene molecules. This results in decomposition of the radicals and formation of additional amount of hydrogen atoms

$$^{\bullet}C_2H^*(Xe) \longrightarrow Xe{-}C_2 + H^{\bullet}. \quad (2)$$

Analysis in the framework of this scheme permits determination of the relative concentrations of the $^{\bullet}C_2H$ radicals and Xe—C_2 complexes at different doses from the integrated intensity ratios of the EPR signals of $H^{\bullet}$ and $^{\bullet}C_2H$ and from the following equation

$$[^{\bullet}C_2H] : [Xe{-}C_2] = 2/(\alpha - 1),$$

where $\alpha = [H^{\bullet}]/[^{\bullet}C_2H]$. In particular, at the maximum dose used in this work (80 kGy) one has $\alpha \approx 1.8$ (see above) and $[^{\bullet}C_2H] : [Xe{-}C_2] \approx 2.5$ (correspondingly, $[H^{\bullet}] : [Xe{-}C_2] \approx 4.5$).

In the case of isotopically substituted acetylene the EPR spectrum of the irradiated mixture (Fig. 4, spectrum *1*) exhibits signals of the stabilized H atoms, D atoms, $^{\bullet}C_2D$ radicals, and, probably, $^{\bullet}C_2H$ radicals. The signal of deuterium atoms is a triplet with $a(D) \approx 7.8$ mT in accord with the ratio of the magnetic dipole moments of the nuclei, $\mu(H) : \mu(D)$. A super-HFS from the xenon magnetic nuclei (similarly to the case for H atoms in xenon matrix) is also observed in this case. The outermost components of the triplet of D atoms corresponding to the nuclear spin moment $M_I = \pm 1$ are clearly seen in the spectrum, whereas the central signal ($M_I = 0$) is strongly overlapped with the signal of $^{\bullet}C_2D$ radicals. The last-mentioned signal is a singlet because the expected splitting corresponding to $a(D) \approx 0.25$ mT cannot be resolved under the experimental conditions. This singlet can be

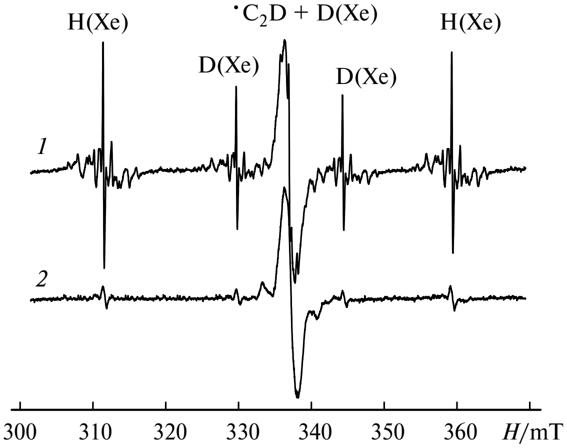

Fig. 4. EPR spectra of deposited xenon—deuterated acetylene (2000 : 1) mixtures irradiated with fast electrons at 16 K recorded immediately after irradiation to a dose of 40 kGy (*1*) and after annealing of the irradiated sample at 45 K for 5 min (*2*).

overlapped with a weaker signal of $^{\bullet}C_2H$ radical (see above), but the latter cannot be picked out. Similarly to IR spectoscopic results, the EPR spectoscopy data indicate a large isotope effect in the dissociation of acetylene. Indeed, the yields of hydrogen and deuterium atoms are similar, although in the case of random decomposition one would expect a large predominance of D atoms (see above).

No new bands appear in the IR spectrum after annealing of the irradiated samples at 30 K. But after annealing at 40—45 K, when diffusion of hydrogen atoms in the matrix is unfrozen,[3—6] the IR spectrum exhibits new bands with maxima at 626, 891, 1166, 1180.5, 1300, 1478, 1486 and 3273 cm^{-1} (see Fig. 1, spectrum *3*). Since diffusion of heavier species in xenon is impossible under these conditions,[4,25] all the bands mentioned above should be assigned to products of the reactions of hydrogen atoms with molecules and radicals. A relatively weak band with maximum at 891 cm^{-1} was attributed to vinyl radical[26] (product of reactions of H atoms with acetylene), a characteristic doublet with maxima at 1166 (more intense band) and 1180.5 cm^{-1} was assigned to xenon dihydride XeH_2,[2—6] and the most intense spectral band with maximum at 1486 cm^{-1} corresponds to the H—Xe vibrations in HXeCCH molecule (arguments in favor of this assignment were reported earlier[9,10]). The behavior of the relatively weak bands with maxima at 626 and 3273 cm^{-1} (dependence on the irradiation dose and temperature) correlates well with the behavior of the band with maximum at 1486 cm^{-1}. This allows the bands in question to be assigned to the bending vibrations of the H—C≡C— fragment (626 cm^{-1}) and the C—H stretching vibrations (3273 cm^{-1}) of HXeCCH molecule (this conclusion was drawn earlier[10]). The band with maximum at 1478 cm^{-1} is clearly seen at doses of at least 40 kGy while the band with maximum near 1300 cm^{-1} can be detected only at the maximum irradiation dose used in our study (80 kGy). These bands, which were observed in the photochemical studies, were assigned to $HXeCC^{\bullet}$ radicals and HXeCCXeH molecules, respectively.[10] Note that the band with maximum at 1300 cm^{-1} was not detected in our earlier study[9] owing to the use of lower irradiation doses. Annealing of samples at 45 K leads to a decrease in the intensities of the $^{\bullet}C_2H$ and Xe—C_2, and initial acetylene bands, which indicates that these species are involved in the reactions with hydrogen atoms.

In the experiments with isotopically substituted acetylene, annealing at 45 K is followed by similar changes in the IR spectrum (see Fig. 2, spectrum *3*). Since in this case the yield of H atoms is much lower, only the most intense bands of the H-containing species considered above, namely, the band with maximum at 1486 cm^{-1} and the rather weak band with maximum at 1166 cm^{-1} can be detected. The first band corresponds to the H—Xe vibrations in HXeCCD/HXeCCH. Here, it is hard to distinguish between the species mentioned above, because calculations predict that deuteration at the opposite end of the molecule has almost no effect on the H—Xe vibrational frequency, but the formation of HXeCCD is much more probable in the matrix with this isotopic composition. The second band is attributed to XeH_2. In addition to these bands, the absorptions of the products of reactions involving D atoms are observed. Among them, the most intense band with maximum at 1077.5 cm^{-1} corresponds to the D—Xe vibrations in DXeCCD (and, probably, DXeCCH)[9] molecules. Note that the large isotope effect (ν_H/ν_D ratio) is quite characteristic in this case, because it exceeds the corresponding value for the C—H stretching vibrations. This indicates that hydrogen is bonded to an atom that is heavier than the carbon atom. Two shoulders at 1081 and 1073 cm^{-1} are also clearly seen; the nature of the shoulders will be considered below. Weak bands with maxima at 2545 and 492 cm^{-1} correspond to the C—D stretching vibrations and bending vibrations of the D—C≡C— fragment in the DXeCCD molecule.[10] At the same time no bands that could be attributed to the C—H stretching vibrations and bending vibrations of the H—C≡C— fragment in DXeCCH molecule (see above) were detected, which indicates the formation of small amount of this isotopomer. This is due to low concentration of $^{\bullet}C_2H$ radicals (compared to $^{\bullet}C_2D$), which is quite explainable if we take into account the initial predominance of the C_2D_2 molecules and the preferred C—H bond cleavage in the C_2HD molecules. Besides, the IR spectrum exhibits relatively weak bands of XeD_2 (doublet with maxima at 846 and 856 cm^{-1}) and XeHD (maximum at 1093.5 cm^{-1})[2].

Changes in the EPR spectra observed on annealing of an irradiated sample (see Fig. 3, spectrum *3*) are in agreement with the results of IR spectroscopy studies. The concentration of H atoms decreases by an order of magnitude and the total concentrations of paramagnetic species and ethynyl radicals also somewhat decrease. This indicates the occurrence of reactions involving hydrogen atoms resulting in diamagnetic species (XeH_2 and HXeCCH). Simultaneously, characteristic signals of vinyl radicals[9] appear as a result of reactions of H atoms with acetylene molecules. At high doses after annealing the EPR spectrum exhibits additional lines of low intensity; their origin will be discussed below. A similar picture is also observed for the isotopically substituted acetylene (see Fig. 4, spectrum *2*), namely, almost all hydrogen and deuterium atoms disappear on annealing and the concentration of ethynyl radicals somewhat decreases. This is accompanied by various isotopomers of vinyl radicals (detailed analysis goes beyond the scope of this study).

Substantiation of identification and the analysis of spectroscopic characteristics of the $HXeCC^{\bullet}$ radical, which can be produced in the reactions of hydrogen atoms with Xe—C_2, is of particular interest. As mentioned above, the H—Xe stretching vibrations of this radical were assigned a band with maximum at 1478 cm^{-1}.[10] Here, a problem poses because this band is close to the HXeCCH band at 1486 cm^{-1}. Indeed, the "matrix" splittings (5—15 cm^{-1}) due to the different local environment are characteristic of "mild" polar molecules of the HXeY type[2,3,6] (typical example is provided by a doublet at 1166/1180.5 cm^{-1} observed in the case of XeH_2). The assignment[10] of the band with maximum at 1478 cm^{-1} to HXeCC$^{\bullet}$ is based on physicochemical data (peculiar features of accumulation in the photolysis, correlation with the formation of Xe—C_2). Recently,[12] spectoscopic arguments in favor of this assignment based on the experiments with isotopic substitution have been reported. Nevertheless, CCSD(T) calculations strongly overestimate the H—Xe vibrational frequency for HXeCC$^{\bullet}$ compared to the experimental value and predict a marked high-frequency shift of the corresponding band in the spectrum of the HXeCC$^{\bullet}$ radical relative to the ν(H—Xe) band in the IR spectrum of HXeCCH molecule (*cf.* a very small low-frequency shift observed in the experiment.)[10]

To clarify the situation, we thoroughly analyzed the behavior of the band with maximum at 1478 cm^{-1} and compared the results obtained with the changes in the EPR spectra and carried out additional quantum-chemical calculatios using the relativistic version of the DFT-PBE approach.

First of all we established that the dependence of the intensity of a given band on the irradiation dose is characterized by an induction period, which is in excellent agreement with the proposed scheme and the data obtained earlier.[10] Different dependences of the intensities of the bands with maxima at 1486 and 1478 cm^{-1} on the annealing temperature were also revealed. However, the most remarkable feature of the behavior of the band assigned to the HXeCC$^{\bullet}$ radical consists in selective sensitivity to visible light. Figure 5 shows that photolysis of the annealed sample the intensity of the band with maximum at 1478 cm^{-1} appreciably decreases. Simultaneously, the intensity of the Xe—C_2 band increases and the EPR spectra indicate production of a small amount of additional hydrogen atoms, as should be expected upon photochemical dissociation of HXeCC$^{\bullet}$ radical. Re-annealing causes partial re-appearance of the band with maximum at 1478 cm^{-1} and simultaneous decrease in the Xe—C_2 band intensity. It should be noted that the band intensities of HXeCCH (and all other products of radiolysis and subsequent annealings) remain unchanged on exposure to visible light. Thus, the behavior of the band in question is in excellent agreement with its assignment to HXeCC$^{\bullet}$ radical.

In the case of deuterated acetylene (Fig. 6) the shoulder at 1081 cm^{-1} (against the background of the DXeCCD band at 1077.5 cm^{-1}) is photosensitive, which permits its assignment to the D—Xe stretching vibrations in the DXeCC$^{\bullet}$ radical. At the same time the intensities of the low-frequency shoulder at 1073 cm^{-1} and the main band of DXeCCD remain unchanged on exposure to visible light. Probably, in the latter case we deal with position "splitting" for the D—Xe stretching vibrations in the DXeCCD molecule (in the case of HXeCCH molecule this "splitting" cannot be detected owing to a greater linewidth and superposition of the bands of the HXeCC$^{\bullet}$ radical).

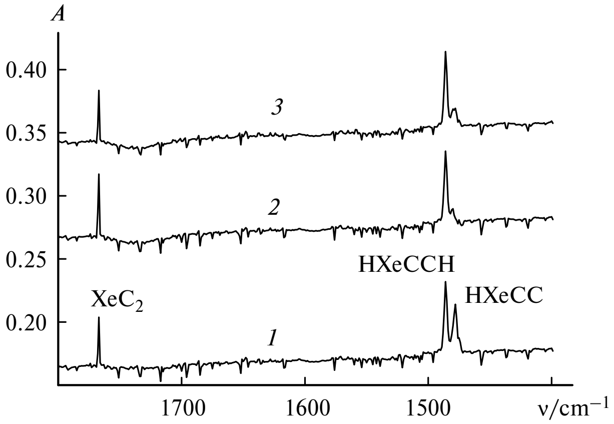

Fig. 5. Fragments of the IR spectra of a deposited xenon—acetylene (2000 : 1) mixture irradiated with fast electrons to a dose of 80 kGy at 16 K and subsequently annealed at 45 K for 5 min: after first annealing (*1*), after subsequent photolysis by visible light (30 min) (*2*), and after re-annealing at 45 K for 5 min (*3*).

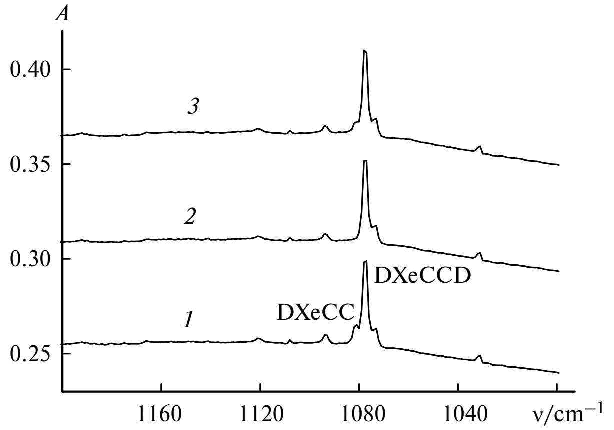

Fig. 6. Fragments of the IR spectra of a deposited xenon—deuterated acetylene (2000 : 1) mixture irradiated with fast electrons to a dose of 40 kGy at 16 K and subsequently annealed at 45 K for 5 min: after first annealing (*1*), after subsequent photolysis by visible light (30 min) (*2*), and after re-annealing at 45 K for 5 min (*3*).

Problems of theoretical description of the spectra of xenon-containing species are associated with correctness of the computational methods employed, necessity of allowance for strong vibrational anharmonicity, and large contribution of relativistic effects for many-electron atoms (this is of particular importance when calculating

Table 1. Calculated and experimental vibrational frequencies (in cm^{-1}) of the most intense absorption bands in the IR spectra of HXeCCH molecule and HXeCC$^{\bullet}$ radical

Vibration	Computational method				Experiment[9,10]
	MP2[8] [a]	CCSD(T)[8,10] [a]	R-DFT-PBE[a,b]	R-DFT-PBE[b,c]	
			HXeCCH[d]		
ν(H—Xe)	1736	1621	1588	1528	1486 (vs)
ν(C—H)	3462	3419	3382	3277	3273 (m)
δ(HCC)	648	658	638	643	626 (m)
			HXeCC$^{\bullet}$[e]		
ν(H—Xe)	—	1754	1570	1508	1478 (vs)
ν(CC)	—	1600	1777	1751	1748 (m)

[a] Calculated in the harmonic approximation.

[b] This work.

[c] Calculated with inclusion of vibrational anharmonicity.

[d] According to R-DFT-PBE calculations, the HXeCCH molecule has a linear structure with r(H—Xe) = 1.795 Å, r(C—Xe) = 2.359 Å, r(C—C) = 1.223 Å, and r(C—H) = 1.072 Å.

[e] According to R-DFT-PBE calculations, the HXeCC$^{\bullet}$ radical has a nonlinear structure with r(H—Xe) = 1.779 Å, r(C—Xe) = 2.415 Å, r(C—C) = 1.267 Å, and the C—C—Xe angle = 123.4°.

the magnetic resonance parameters of corresponding radicals). In particular, the MP2 method in the harmonic approximation provides quite a rough correspondence between the vibrational frequencies and qualitatively correct intensity distribution for xenon-containing molecules (closed-shell systems),[6,8] being absolutely inappropriate for calculations of radicals (open-shell systems).[10] The coupled cluster method (CCSD(T) version), which requires considerable computational resources, allows much better agreement with experimental data on the vibrational frequencies of molecules to be attained using the same basis set,[6,8] but can (at its best) provide only qualitative agreement for radicals.[8,27] In this work we performed calculations using a method based on scalar-relativistic density functional theory (DFT) including solution of the vibrational problem in the harmonic approximation and with allowance for anharmonicity. First of all, this method was evaluated taking HXeCCH molecule as an example. Comparison of the main vibrational frequencies calculated by different methods with the experimental results is given in Table 1. As can be seen, the results of R-DFT-PBE/TZ2P calculations in the harmonic approximation are similar to the results of CCSD(T) calculations, being in much better agreement with the experiment compared to the results of MP2 calculations.* The inclusion of anharmonicity in the R-DFT-PBE/TZ2P calculations gives nearly quantitative coincidence of the calculated frequencies with experimental ones and it is possible to quite correctly reproduce the H—Xe stretching frequencies characterized by the strongest anharmonicity. Then, this method was employed for calculating the equilibrium geometry and vibrational spectrum of the HXeCC$^{\bullet}$ radical. It was found (see Table 1) that the frequencies calculated by the R-DFT-PBE/TZ2P method in the harmonic approximation are in much better agreement with the experimental frequencies of the bands ascribed to this radical than the frequencies obtained from CCSD(T) calculations. In this case the inclusion of anharmonicity also leads to nearly quantitative agreement. It should be noted that the calculations performed in this work do predict a small low-frequency shift of the H—Xe stretching frequency of HXeCC$^{\bullet}$ radical compared to the HXeCCH molecule, which is in excellent agreement with the experiment. It should be emphasized that the carbon—carbon bond in this radical (in contrast to linear molecule HXeCCH) must not be treated as a triple bond. According to our calculations, this radical has a nonlinear structure, the carbon—carbon bond length is intermediate between the characteristic double and triple bond lengths, and the vibrational frequency is more similar to the stretching frequency of the carbon—carbon double bond.

We also calculated the magnetic resonance parameters of HXeCC$^{\bullet}$ radical by the R-DFT-PBE/TZ2P method. According to calculations, this radical is characterized by a rather high spin density on the nuclei of the terminal carbon atom (0.2264) and xenon atom (0.1967) and by very low spin density on the nuclei of the second C atom and H atom (−0.0010 and 0.0023, respectively). This is an indication of conjugation in the radical. The calculated isotropic HFC constants for magnetic nuclei are 8.7 (^{129}Xe), 2.5 (^{131}Xe), and 0.37 mT (H). According to calculations, in this case the dipolar (anisotropic) contribution to the HFC with xenon is relatively small (less than 20% of the isotropic HFC). Thus, the "visiting card" of HXeCC$^{\bullet}$ radical in the EPR spectrum should be a large characteristic splitting due to HFC between the un-

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* MP2 and CCSD(T) calculations were carried out with the LJ18(Xe),6-311++G(2d,2p) basis set.[8,12]

paired electron and the nuclei of magnetic isotopes of xenon (splitting on proton is small and most probably will not be resolved under the experimental conditions). Natural xenon has two isotopes with magnetic nuclei, namely, ^{129}Xe (I = 1/2, 26.44%) and ^{131}Xe (I = 3/2, 21.18%). Therefore, from the standpoint of expected EPR spectra the isotropic approximation distinguishes between three types of $HXeCC^{\bullet}$ radicals, *viz.*, $H^{129}XeCC^{\bullet}$ (26.44%, doublet with a splitting of ~8.7 mT), $H^{131}XeCC^{\bullet}$ (21.18%, quartet with a splitting of ~2.5 mT), and $HXeCC^{\bullet}$ radicals with diamagnetic nuclei of xenon isotopes with the mass numbers 124, 126, 128, 130, 132, 134, and 136 (a total of 52.38%, singlet with no HFS). Most probably, the g-factor of $HXeCC^{\bullet}$ radical will not be appreciably different from the corresponding values for $^{\bullet}C_2H$ radical and other carbon-centered radicals. Under such conditions a signal of the radicals containing no magnetic xenon nuclei (singlet in the central part of the EPR spectrum) will be hard to pick out among signals of other paramagnetic species present in the system in large amounts (see below). In accordance with the natural abundance of xenon isotopes and nuclear spin multiplicity the individual lines of the doublet of $H^{129}XeCC^{\bullet}$ radical should be nearly 2.5 times more intense than the lines of the quartet of the $H^{131}XeCC^{\bullet}$ radical. Thus, if the concentration of $HXeCC^{\bullet}$ radical present in the system is relatively low compared to other paramagnetic species, the easiest way is to detect the EPR signal of the $H^{129}XeCC^{\bullet}$ isotopomer, which is characterized by the largest splitting in the spectrum. In this case the most important qualitative criterion for assignment is selective photosensitivity of the $HXeCC^{\bullet}$ radical.

As can be seen in Fig. 7, two additional broad lines (asterisked) with a ~13 mT separation appear (in addition to the lines of vinyl radicals) in the central part of the EPR spectrum of the sample irradiated to the maximum dose on heating. These lines almost disappear on exposure to visible light (see Fig. 7, spectrum *2*) and re-appear on re-heating (see Fig. 7, spectrum *3*); *i.e.*, their behavior is consistent with the behavior of the IR band with maximum at 1478 cm^{-1}, assigned to $HXeCC^{\bullet}$. This permits a tentative assignment of the doublet observed in the EPR spectrum to the $H^{129}XeCC^{\bullet}$ isotopomer of this radical. Picking out lines of other isotopomers is problematic because of the overlap of broad intense signals of the ethynyl and vinyl radicals. The experimental hyperfine splitting is somewhat larger than the calculated value; however, exact calculations of the magnetic resonance parameters of multi-electron radicals of the $HXeCC^{\bullet}$ type is a stubborn problem, which is much more complicated than prediction of vibrational frequencies, and the level of theory employed in this work is most probably suitable for semiquantitative estimation only. Besides, one should take into account the HFC anisotropy, which cannot be correctly analyzed in the case of strong spectral overlap.

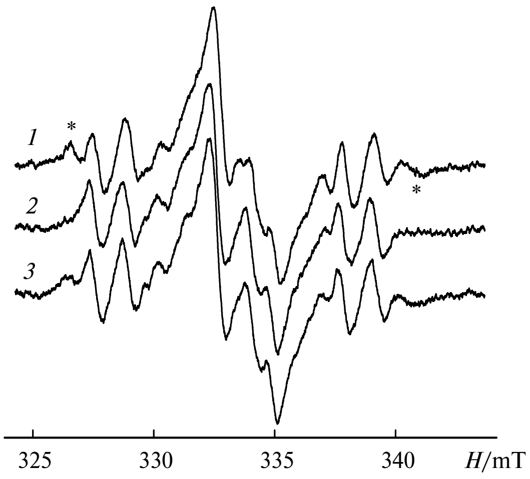

Fig. 7. Fragments of the EPR spectra of a deposited xenon—acetylene (2000 : 1) mixture irradiated with fast electrons to a dose of 80 kGy at 16 K and subsequently annealed at 45 K for 5 min: after first annealing (*1*), after subsequent photolysis by visible light (30 min) (*2*), and after re-annealing at 45 K for 5 min (*3*). The lines tentatively assigned to $HXeCC^{\bullet}$ radical are asterisked.

Proof of the formation of $HXeCC^{\bullet}$ radical and establishment of its structure are of fundamental importance for physical chemistry of rare gas hydrides. The case in point is the first polyatomic xenon-containing radical, which can be considered as an important "building block" in the design of new, more complex compounds (it is sufficient to mention the HXeCCXeH molecule[10,12] and a hypothetical molecule HXeCCKrH). Note that detailed determination of the characteristics of the EPR spectra of $HXeCC^{\bullet}$ radical requires carrying out additional experiments using, in particular, isotopically substituted xenon. These experiments are now in progress.

In conclusion we will consider a general scheme of thermal reactions in irradiated xenon—acetylene system, which can be quantitatively analyzed using IR and EPR spectoscopy data. As mentioned above, heating to 40—45 K causes reactions of mobile hydrogen atoms with radicals and molecules present in the system to occur.

$$H^{\bullet} + Xe + {}^{\bullet}C_2H \longrightarrow HXeCCH \qquad (3)$$

$$H^{\bullet} + Xe + H^{\bullet} \longrightarrow XeH_2 \qquad (4)$$

$$H^{\bullet} + C_2H_2 \longrightarrow C_2H_3^{\bullet} \qquad (5)$$

$$H^{\bullet} + Xe{-}C_2 \longrightarrow HXeCC^{\bullet} \qquad (6)$$

$$H^{\bullet} + Xe + HXeCC^{\bullet} \longrightarrow HXeCCXeH \qquad (7)$$

The products of all these reactions can be detected in the IR spectra while the EPR spectoscopy data permits monitoring of the decrease in the concentrations of the stabilized hydrogen atoms and ethynyl radicals and the formation of vinyl radicals and $HXeCC^{\bullet}$ radicals. Of course, the ratio of the contributions of different channels of the reactions involving hydrogen atoms depends on the relative concentrations of the partners (molecules and radicals) and, correspondingly, on the irradiation dose. Reaction (5) plays the most important role at low doses and becomes less significant as the acetylene is consumed with increasing the dose. An increase in the irradiation dose is initially accompanied by an increase in the contributions of reactions (3) and (4) and then, with accumulation of the $Xe—C_2$ species in the matrix, by an increase in the contribution of reaction (6). According to our estimates, the proportion of the hydrogen atoms entering the reaction (3) resulting in HXeCCH can be as high as 30% at an irradiation dose of 40 kGy. Reaction (6) makes the largest contribution at an irradiation dose of 80 kGy; here, $[^{\bullet}C_2H] : [Xe—C_2] \approx 2.5 : 1$, the concentration ratio of the stabilized H atoms and $Xe—C_2$ being nearly 4.5 : 1 (see above). Since the reactions of H atoms in xenon are diffusion controlled,[26] one can expect that the ratio of the yields of HXeCCH and $HXeCC^{\bullet}$ formed on annealing will be 2.5 : 1. Annealing of the sample causes the $Xe—C_2$ band intensity to decrease by about 40% due to reaction (6); it is easily seen that only ~9% of hydrogen atoms will be consumed in this reaction. In our experiments, the maximum concentration of $HXeCC^{\bullet}$ radicals is ~6% of the initial total concentration of paramagnetic species or ~17% of their total concentration after annealing. Because of this, signals of the $HXeCC^{\bullet}$ radicals can be detected only if they are not superimposed with lines of other radicals (see above). For the same reason reaction (7) in our experiments plays an insignificant role even at maximum irradiation dose and the band assigned to HXeCCXeH molecules[10,12] is of very low intensity. Much higher relative concentrations of $HXeCC^{\bullet}$ radicals can probably be obtained using post-radiation UV photolysis in the absorption band of ethynyl radical followed by annealing.

In conclusion, the results obtained point to considerable prospects for low-temperature radiation-chemical synthesis of new organic molecules and radicals containing rare gas atoms and demonstrate the possibility of comprehensive studies of the mechanisms of their formation in combined IR and EPR spectoscopic investigations.

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