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High-resolution EPR spectroscopy of small radicals in a solid ^{136}Xe matrix

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The well-resolved EPR spectra of small radicals were obtained in a monoisotopic ^{136}Xe matrix, which opens new prospects for the studies of structure, motional and chemical dynamics of such species over a wide temperature range.

Matrix isolation EPR spectroscopy is a powerful method for characterization of the structure and dynamics of radicals and radical ions.[1,2] High-resolution EPR spectra of small species can be obtained in solid neon or argon matrices.[3,4] However, the temperature range available for such studies is limited (up to 10 K for neon and *ca.* 35 K for argon), which limits the investigations of dynamics and chemical reactions. Among the noble-gas matrices, xenon has the widest range of thermal stability (at least up to 75–80 K). Furthermore, a xenon matrix is suitable for the preparation of organic radicals by reactions of thermally mobilized H atoms occurring at *ca.* 40 K.[5–8] Such reactions in solid xenon were applied for synthesis of novel-type species, xenon hydrides HXeY (Y is an electronegative atom or fragment).[9–11] More recently, this approach was used for obtaining organic hydrides HXeR (R is an organic radical)[12,13] and open-shell species with the H–Xe bond,[12,14] which is of particular interest for EPR investigations.

Main limitation for EPR studies in solid xenon is concerned with severe line broadening usually attributed to the presence of isotopes with magnetic nuclei in natural xenon (^{129}Xe, $I = 1/2$, natural abundance 26.44% and ^{131}Xe, $I = 3/2$, 21.18%). The most direct way to overcome this limitation is to eliminate the isotopes with non-zero nuclear spin. Here we report the first results of EPR studies of small radicals trapped in an isotopically pure ^{136}Xe matrix ($I = 0$), which does not interact magnetically with the studied radicals. A monoisotopic ^{136}Xe (99.4%) gas was obtained from the Russian Scientific Centre Kurchatov Institute. The experimental technique and set-up for matrix EPR studies of radicals generated by fast electron irradiation were described previously.[15,16] Gaseous mixtures were deposited onto a cooled sapphire rod inserted into a vacuum resonator cavity at 30 K and then irradiated with fast electrons (1 MeV) at *ca.* 16 K. The EPR spectra were measured with an X-band spectrometer (SPIN, St. Petersburg, Russia) at a low microwave power ($\leq 5\ \mu$W). Acetylene was used as a model compound since the mechanism of its radiation-induced transformations in solid xenon was studied in detail.[13,17]

Irradiation of acetylene in a xenon matrix results in dissociation of parent molecules to the ethynyl radical ($\cdot C_2H$) and H atoms (other reaction channels become significant only at high doses[17]). The EPR spectra obtained after irradiation in natural xenon and in monoisotopic ^{136}Xe are shown in Figure 1. Dramatic difference between these spectra obviously results from the lack of magnetic matrix interactions in the latter case. The signal from H atoms in a ^{136}Xe matrix (a doublet with extremely large splitting of *ca.* 50 mT) shows no super-hyperfine structure characteristic of interaction with magnetic matrix nuclei in natural xenon. The signal from ethynyl radical, poorly resolved in natural xenon, becomes a rather sharp doublet with a splitting of 1.67 mT and a linewidth of 0.18 mT, when xenon isotopes with magnetic nuclei are eliminated. This pattern is qualitatively similar to the EPR spectrum of ethynyl radical in argon;[18] however, the signal in non-magnetic xenon is broader and almost symmetrical. Note that the line sharpness implies strong increase in the measurement sensitivity (more than by an order of magnitude), which makes it possible to record the spectra at much lower gain than in natural xenon.

Annealing the irradiated sample at 45 K leads to almost complete decay of H atoms partially reacting with acetylene to yield vinyl radicals ($\cdot C_2H_3$).[8,13,17] According to Tanskanen *et al.*,[8] the EPR spectrum of these radicals in natural xenon at 16 K represents a broad triplet of doublets with a(2H) ~ 5.2 mT and a(1H) ~ 1.35 mT (the outer doublets are seen quite clearly, while the inner doublet overlaps strongly with the lines from ethynyl radicals). Again, the signal recorded in a ^{136}Xe matrix exhibits much sharper lines ($\Delta H_{pp} = 0.12$–0.15 mT). Meanwhile, in this case, the EPR spectrum is essentially different from those in solid argon at 4 K.[18,19] First, the spectrum in argon shows a typical anisotropic powder pattern, which can be analyzed in terms of rigid hyperfine coupling (hfc) tensor.[19] In contrast, the lines in a ^{136}Xe matrix are sharper and the residual anisotropy is seen only from the lineshape of the high-field doublet. This implies rapid (although not completely free) rotation of the vinyl radical in solid xenon at 16 K on the EPR time scale. Second, an apparent equivalence of two β-protons in a xenon matrix implies rapid inversion between two tautomeric forms of $\cdot C_2H_3$. A similar-type dynamic spectrum was recorded in an oriented solid neon matrix.[20] On the other hand, the spectrum in argon reveals that all the three protons are magnetically inequivalent with the isotropic coupling constants of 6.59, 3.96 and 1.38 mT,[19] which is the case for static situation (no inversion).

A well-defined EPR spectrum of the vinyl radical can be recorded at temperatures up to 80 K. As shown in Figure 1, increasing the measurement temperature results in a further decrease in the linewidth (to 0.06 mT at 60 K). The high-field doublet becomes more symmetrical, which indicates increasing frequency of the radical rotation ($\nu > 10^9$ s^{-1}). On the other hand, the *cis–trans* inversion does not become much faster since the central doublet has much lower relative intensity than

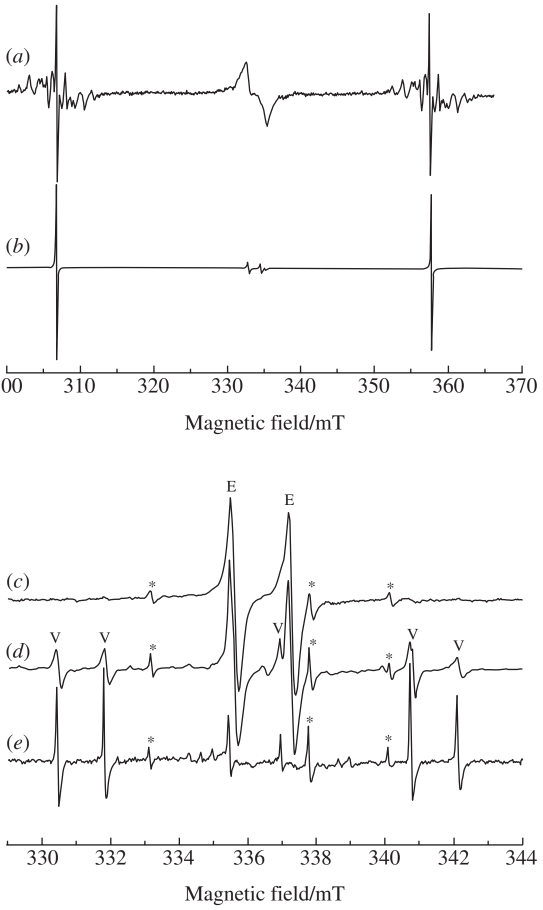

Figure 1 EPR spectra of deposited acetylene–xenon mixtures (1/2000) irradiated with fast electrons at 16 K and measured at 16 K [except for (*e*)]: (*a*) C_2H_2 in natural xenon, (*b*) C_2H_2 in ^{136}Xe; (*c*) central part of spectrum (*b*) at higher gain; (*d*) the same as (*c*) after annealing the sample at 45 K for 5 min; (*e*) central part of spectrum in ^{136}Xe recorded at 60 K. Letters E and V denote the lines belonging to ethynyl and vinyl radicals, respectively. Asterisks show the lines from methyl radicals originating from some impurity present in trace amounts.

that expected for complete averaging. Note that the virtual absence of a central doublet in the EPR spectrum of the vinyl radical recorded in liquid ethylene at 77 K was explained by a very strong linewidth alternation due to *cis–trans* inversion at an intermediate frequency ($\nu \sim 10^8$ s^{-1}).[21] The vinyl radical is often used to illustrate dynamic effects in the EPR spectra. Nevertheless, in fact, the dynamics of this fundamentally important species is not understood in detail, the role of tunneling is unclear and the quantitative model is lacking. We hope that detailed studies in a ^{136}Xe matrix using acetylene isotopomers may finally resolve this issue. Meanwhile, this communication is focused on general demonstration of the potential of EPR spectroscopy in a ^{136}Xe matrix.

One more implication is concerned with matrix effects on the electronic structure of radicals determined in the absence of matrix magnetic interactions. Indeed, xenon has much higher polarizability than those of neon and argon, so it should exhibit strong electrostatic interactions with polar and polarizable species. The linear ethynyl radical has a significant negative charge at the terminal carbon atom and a positive charge on the H atom. Comparison of proton isotropic hfc constant obtained in our work (1.67 mT) with the data reported[22] for argon (1.57 mT) reveals a marked difference (*ca.* 6%), which probably reflects the effect of xenon on charge and spin distribution in the radical. As to vinyl radical, the matrix effect seems negligible: the α-proton isotropic hfc constant in ^{136}Xe (1.37 mT at 60 K) is virtually the same as that reported[19] in argon (1.38 mT).

In summary, we have obtained well-resolved EPR spectra of ethynyl and vinyl radicals in a non-magnetic ^{136}Xe matrix. Residual linewidth is intrinsically informative as it is determined by polar interactions and dynamic effects. Possible applications of this unique matrix may include: (1) detailed studies of radical dynamics over a wide temperature range; (2) investigation of the matrix effect on the electronic structure of radical (using hyperfine coupling as a very sensitive characteristic); (3) characterization of kinetics and mechanism of reactions of mobile H atoms with molecules and radicals in solid xenon; (4) EPR studies of polyatomic xenon-containing radicals.

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