

Selective and reversible control of a chemical reaction with narrow-band infrared radiation: HXeCC radical in solid xenon

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The light-induced $\text{H} + \text{XeC}_2 \leftrightarrow \text{HXeCC}$ reaction is studied in solid Xe, and the full optical control of this reaction is demonstrated. By narrow-band excitation in the IR spectral region, HXeCC radicals can be decomposed to a local metastable configuration and then selectively recovered by resonant excitation of the XeC_2 vibrations. The novel recovery process is explained by short-range mobility of the reagents promoted by vibrational energy redistribution near the absorbing XeC_2 molecule. This means that a chemical reaction can be selectively promoted in a desired place where the chosen absorber locates. The obtained results make a strong case of solid-state reactive vibrational excitation spectroscopy of weak radiationless transitions. © 2006 American Institute of Physics. [DOI: 10.1063/1.2201445]

Optical control of chemical reactions is a practical and fundamental challenge, especially for organic and biological chemistry and for nanoscale science.^{1,2} Laser excitation (photodissociation) is often applied to modern chemical synthesis; however, these approaches often use high-energy photons to promote the reactions, and this limits the selectivity. As an example of recent progress in photochemistry, a number of organo-noble-gas (Xe and Kr) insertion molecules prepared from acetylene and diacetylene has been identified in solid noble gases.^{3–7} One of these compounds is the HXeCC radical, and it is a promising precursor for predicted Xe containing polymers,⁸ which has been demonstrated by preparation and identification of the first HXeCCXeH hydride containing two Xe atoms.^{3,7} The developed synthesis procedure of these HNgY molecules (Ng = noble gas atom and Y = electronegative fragment) combines UV photolysis of the HY precursors in a low-temperature noble-gas matrix and thermal mobilization of the photogenerated hydrogen atoms. For HXeI molecule in solid Xe, it has been shown that its formation essentially involves the $\text{H} + \text{Xe} + \text{I}$ reaction of neutral fragments, and this conclusion is probably correct for other HNgY molecules as well.^{9,10} Here we report on full optical control of the $\text{H} + \text{XeC}_2 \leftrightarrow \text{HXeCC}$ reaction in solid Xe using infrared light. The novel recovery process is explained by short-range mobility of the reagents promoted by vibrational energy redistribution near the absorbing XeC_2 molecule. These results present a novel case of laser vibrational excitation spectroscopy of molecules embedded in solid host. In general, our results show that a chemical reaction can be selectively promoted by infrared light in a desired place of solid host where a chosen absorber locates.

The acetylene/Xe ($\sim 1/1500$) matrixes were photolyzed at 8 K by 250-nm light pulses from an optical parametric oscillator (OPO Sunlite, Continuum, with IR extension, 10 Hz). As a result of photolysis, acetylene decomposes

producing mainly C_2 molecules complexed with Xe (absorption at 1767 cm^{-1}) and minor amounts of C_2H (a broad band at $\sim 1852 \text{ cm}^{-1}$),¹¹ and hydrogen atoms are isolated in the interstitial matrix sites. Annealing of a photolyzed sample at $\sim 45 \text{ K}$ activates diffusion of hydrogen atoms promoting their reactions with neutral Xe-Y centers and leading to HXeY species with the very intense H-Xe stretching absorption.¹⁰ Accordingly, we observed annealing-induced formation ($\sim 45 \text{ K}$) of several IR absorption bands. In the fragment of an IR absorption spectrum shown in Fig. 1(a), the bands of HXeCCH (1486 cm^{-1}) and HXeCC (1478 cm^{-1}) and their deuterated isotopic analogs (1078 and 1081 cm^{-1} , respectively) are seen. The band at 1094 cm^{-1} belongs to HXeD.¹⁰

Very different photostabilities of these noble-gas species are observed.^{3,7} For instance, radiation at 488 nm from an Ar ion laser efficiently bleaches the HXeCC bands whereas other species are practically unchanged as demonstrated in Fig. 1(b). The HXeCC radical was found to decompose even upon irradiation with the spectrometer globar on a timescale of hours. By using optical filters, it was found that the photon energy needed for decomposition of HXeCC is above 4000 cm^{-1} , and in further experiments the IR absorption spectra were measured through a filter transmitting radiation only below 1500 cm^{-1} , which prevented the globar-induced decomposition.

Using tunable IR radiation of the OPO, we studied the decomposition rate of HXeCC as a function of the excitation photon energy. The result is shown in Fig. 2 for the HXeCC and DXeCC species. The decomposition starts approximately at 4500 cm^{-1} , saturates at $\sim 7000 \text{ cm}^{-1}$, and decreases above 10000 cm^{-1} . The profiles are similar for the HXeCC and DXeCC isotopic analogs. This similarity suggests decomposition of these species via photodissociation continuum or broad excited electronic states. This mechanism is different from the earlier studied photodecomposition of HXeI involving the second H-Xe stretching overtone and hence having a relatively narrow profile.⁹ The position of the

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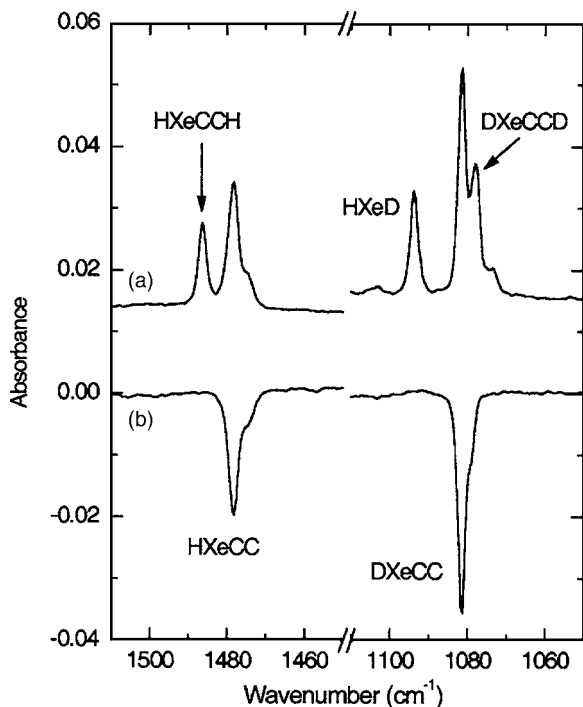


FIG. 1. FTIR spectra of noble-gas molecules prepared from acetylene in solid Xe. (a) Spectrum of the photolysed and thermally annealed (45 K) $\text{H}_2\text{C}_2/\text{D}_2\text{C}_2/\text{Xe}$ solid mixture. (b) Difference spectrum showing the result of irradiation of the photolysed and thermally annealed sample at 488 nm. The spectra were measured with a Nicolet 60 SX FTIR spectrometer (resolution of 1 cm^{-1}) at 8 K.

HXeCC photodissociation limit is presumably somewhat lower than the obtained threshold of $\sim 4500\text{ cm}^{-1}$ because some excess energy is needed to mobilize the hydrogen atom. A small H/D isotope effect on the decomposition rate is observed. The decomposition of the deuterated species starts at higher energies (by $\sim 500\text{ cm}^{-1}$) and reaches lower levels compared to HXeCC. The observed isotope effect at higher photon energies can be connected with different excitation probabilities and cage exit dynamics. The different

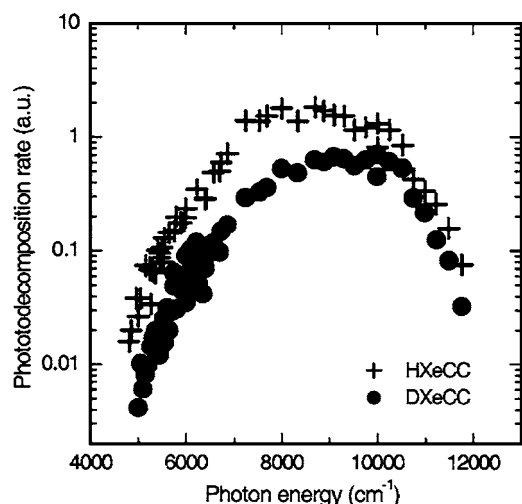


FIG. 2. Photodecomposition spectrum of HXeCC and DXeCC in solid Xe at 8 K. With a pulse energy density of $\sim 1\text{ mJ/cm}^2$, 200 pulses at 8000 cm^{-1} decomposes about a half of HXeCC radicals, which estimates photodecomposition cross-section of $\sim 10^{-18}\text{ cm}^2$.

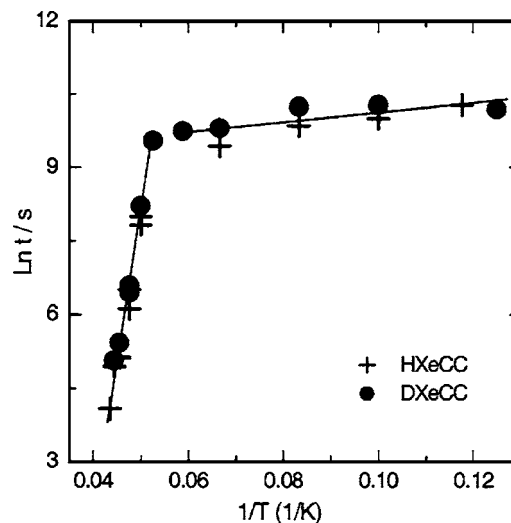


FIG. 3. Dark-recovery time of HXeCC and DXeCC as a function of $1/T$. In the beginning, the molecules were partially decomposed by IR light. The recovery time was found by fitting the kinetics data with a single exponent.

zero point energies of HXeCC and DXeCC can contribute to the photodissociation thresholds. The H/D isotope effects on photodissociation of small molecules in the ultraviolet spectral region are known.^{12,13}

It was found that HXeCC radicals decomposed by IR light slowly recover in dark even at the lowest temperature of our apparatus (8 K), and the recovery rate is temperature dependent. The characteristic recovery time is shown in Fig. 3 as a function of $1/T$. The temperature dependence is similar for HXeCC and DXeCC species, and it consists of a flat region below 18 K and a fast increase of the recovery rate for higher temperatures. Above 22 K, the recovery time is shorter than 1 min, which complicates the kinetic measurements. It should be emphasized that these temperatures ($\sim 20\text{ K}$) are much lower than the temperatures needed for thermal diffusion of hydrogen atoms in solid Xe (above 37 K).^{14,15} It follows that this recovery process involves short-range (local) atomic mobility, which needs lower activation energies.¹⁶ The absence of global mobility of hydrogen atoms here is further evidenced by the fact that no essential losses of the HXeCC concentration occurs after numerous decomposition-recovery cycles. The hydrogen atom dissociated from HXeCC by IR light is most probably stabilized in an interstitial matrix site sharing the same Xe atom with the “substitutional” CC molecule as it was discussed for the case of HXeI.¹⁷ In one possible configuration, the H-Xe-C angle is $\sim 135^\circ$, and the hydrogen atom is already influenced by the attractive HXeCC potential. In accord with this image, the thermal recovery of HXeCC observed here is considerably faster than for the more weakly bound HXeI species studied earlier.⁹ As another relevant example, the shortest reaction-free distance between H and F atoms in an Ar matrix was computationally studied, and a relatively high barrier of $\sim 2500\text{ cm}^{-1}$ with the thickness of $\sim 1.3\text{ \AA}$ was predicted for the formation of HArF.¹⁸ It has been recently found that the H atom can form HArF molecule from a local configuration presumably via a tunneling

mechanism indicated by a strong H/D isotope effect (factor of ~ 50).¹⁹

The rise of the HXeCC recovery rate above 18 K is characterized by an activation energy of ~ 400 cm⁻¹ with the pre-exponential factor of $\sim e^{21}$ 1/s. This process presumably corresponds to thermally activated overbarrier jumps of the hydrogen atom from a vicinal interstitial matrix site to a position where the H+XeC₂ reaction occurs. Only a small (~ 1.2) H/D isotope effect is seen here, in agreement with the similar zero point energies of H and D atoms for such loose short-range trapping.¹⁵ More complicated is the interpretation of the flat recombination region below 18 K. Such non-Arrhenius behavior can originate from proton transfer by a tunneling mechanism dominating at low temperatures.²⁰ The tunneling mechanism is usually accompanied with a strong H/D effect whereas in the present experiments the H/D effect in this region is only ~ 1.4 , which cannot be considered as a good tunneling fingerprint.²¹ It is still probable that the present results represent an unusual case of tunneling transfer without strong isotope effect when the contribution of medium reorganization essentially controls the reaction rate. Some other interpretations were also considered. First, we considered that the deuterium transfer could be accelerated by IR radiation through the used filter, activating some low-energy modes. However, the reaction rate is found to be practically the same when the global irradiation is fully blocked so that this mechanism is ruled out. Second, we cannot exclude the possibility of a local phase transition in the vicinity of the H atom. This scenario assumes that the matrix relaxes at a low temperature to the morphology providing an extremely shallow well for hydrogen atom stabilization, and the depth strongly increases above 18 K. Under this assumption, the flat region corresponds to the second Arrhenius processes with a very low barrier and small pre-exponential factor. The remaining barrier might originate from the differences in geometries of the XeC₂ molecule and the corresponding fragment in the HXeCC radical. Indeed, computationally the XeC₂ molecule is bent with an angle of 147°,²² whereas HXeCC is linear. In this situation, the activation of the XeC₂ bending motion (computationally 87 cm⁻¹) can contribute to the process.

In the IR absorption spectra of the photolyzed samples, a relatively weak band at 3510.5 cm⁻¹ was found and assigned to the first C-C stretching overtone of XeC₂ supported with the ¹²C/¹³C isotope substitution. Upon resonant excitation of this band, we observed a novel effect of light-induced recovery of HXeCC, after it was decomposed with IR light (see Fig. 4). The recovery process takes place with the same photon energy and with similar efficiency for HXeCC and DXeCC. The achieved light-induced formation is many orders of magnitude faster than the thermal reaction at 8 K. Cycles of light-induced decomposition and light-induced recovery can be repeated many times without essential losses of the HXeCC concentration. Moreover, resonant excitation of XeC₂ prior to annealing at 45 K does not produce HXeCC. Thus, we explain this phenomenon based on local activation of the lattice promoted by vibrational excitation of XeC₂ molecules. The position for the vicinal hydrogen atom was discussed above. The vibrational energy redistribution

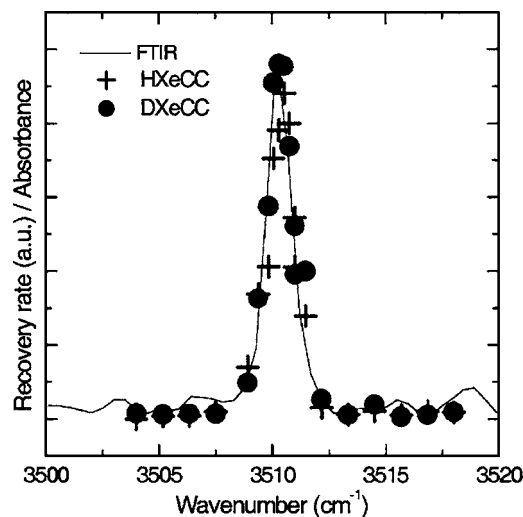


FIG. 4. Recovery profiles of HXeCC and DXeCC (symbols) and FTIR spectrum of the first C-C stretching overtone of XeC₂. The Burleigh WA-4500 wavemeter provided the OPO radiation frequency with absolute accuracy better than 1 cm⁻¹, and the fine shift of the frequency scale is provided by the correction obtained in Ref. 24.

process leads to a local energy flow to lattice atoms, which allows overbarrier crossing of the vicinal hydrogen atom. The barrier for a short-range jump of the hydrogen atom (~ 400 cm⁻¹) is much lower than the photon energy so that the effect can be efficient. We estimated the quantum yield of this recovery process. By comparing the number of photons absorbed at 3510.5 cm⁻¹ and the number of promoted recovery events, we conclude that the quantum yield is close to unity, indeed. The accuracy of such estimates is limited by a number of uncontrolled sources, in particular, by Rayleigh scattering.²³ Importantly, these experiments undoubtedly show that the HXeCC radical is formed in reaction of neutral XeC₂ molecule, and ionic channels are negligible, which is not a trivial fact as discussed previously.^{6,9,10} A similar light-induced reaction of shortly-separated two sulfur atoms was found upon sulfur electronic excitation at 456 nm in solid Ar.¹⁶ In that study, the participation of the laser-excited lattice phonons in the S₂ formation was indicated by the broad and intense phonon band. In the present work, the profile represents the zero-phonon line, and the interaction with the surrounding is probably enhanced due to participation of one lattice atom in the excited XeC₂ molecule.

In addition, we found an efficient promotion of the H+XeC₂→HXeCC local reaction by optical excitation at 5231.8 cm⁻¹. We connect the HXeCC formation triggered by this light with the XeC₂ absorption at the second C-C stretching overtone (this band is not observed with our apparatus in the IR absorption spectra). In order to describe the effect in this spectral region numerically, we have to consider two processes: (1) energy-independent decomposition of the radical with the rate σ_d , and (2) selective recovery of the radical with the rate $\sigma_r(\nu)$. In the approximation of small changes of the concentrations during the time Δt , the corresponding differential equation yields:

$$\sigma_r = \frac{\Delta[\text{HXeCC}]}{(1 - [\text{HXeCC}])\Delta t} + \frac{[\text{HXeCC}]}{(1 - [\text{HXeCC}])} \sigma_d, \quad (1)$$

where the concentrations are normalized by the initial HXeCC concentration measured after thermal annealing. By using this approach, we obtained the recovery cross-section as a function of the excitation photon energy, and the recovery profile in this spectral region is as narrow as 2 cm^{-1} , the process being equally seen for HXeCC and DXeCC. In addition, the efficiency of this process is nearly linear with respect to the excitation light intensity; hence, this is certainly a one-photon process. At the maximum, the formation rate of DXeCC is more than an order of magnitude higher than the decomposition rate in this region. By tuning the excitation from the maximum by $\geq 2 \text{ cm}^{-1}$, we reverse the light-induced reaction from the HXeCC construction to its destruction.

The observed phenomenon of selective light-induced formation of HXeCC provides a powerful approach of reactive vibrational excitation (RVE) spectroscopy allowing detection of very weak and broad transitions. In this method, the absorption of a species is detected via a low-noise signal, which is the strong H-Xe stretching absorption here. In the present work, the RVE spectrum provided the frequency of the second C-C stretching overtone of XeC_2 at 5231.8 cm^{-1} , in addition to the fundamental absorption at 1767.5 cm^{-1} and the first C-C stretching overtone at 3510.5 cm^{-1} . The two overtone absorptions yield practically the same $2\omega_e x_e$ anharmonicity of the C-C stretching mode (24 cm^{-1}). A relevant RVE approach has been demonstrated for molecules with rotational isomerism where the other rotational isomer was produced with narrow-band IR radiation.²⁴ Another example of vibrational promotion of a chemical reaction is provided by works of Frei and Pimentel.²⁵ They could activate the low-barrier $\text{F}_2 + \text{C}_2\text{H}_4$ reaction by exciting various transitions of ethylene, and obtained the quantum yield up to 30%. The present situation with the $\text{H} + \text{XeC}_2$ reaction is different because the barrier is essentially established by the host whereas the reaction itself presumably has a negligible barrier. The mechanism of this constructive reaction of a hydrogen atom involves the energy redistribution of a local matrix surrounding, which makes this case general. The promotion of chemical reaction by local and selective excitation is an attractive possibility of laser control of chemical reactions in solid phase. The local vibrational excitation of a reagent can lead to a reaction in a desired place or bond, of course, with certain temperature limitations.

In conclusion, we demonstrated the formation and decomposition of HXeCC radical in solid Xe produced by narrow-band excitation in the IR spectral region. The pro-

cesses are explained by local atomic mobility promoted by vibrational energy redistribution near the absorbing molecule. It is shown that a chemical reaction can be selectively promoted in a desired place where a chosen absorber locates. In addition, the obtained results make a strong case of reactive vibrational excitation spectroscopy of weak radiationless transition.

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