

Photogeneration of ions via delocalized charge transfer states. I. Xe_2H^+ and Xe_2D^+ in solid Xe

H. Kunttu, J. Seetula, and M. Räsänen

Department of Physical Chemistry, University of Helsinki, SF-00170 Helsinki, Finland

V. A. Apkarian

Institute for Surface and Interface Science, Department of Chemistry, University of California, Irvine, California 92717 USA

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Delocalized charge-transfer excitations in solid xenon multiply doped with atomic halogens (I, Br, Cl) and hydrogen are demonstrated to lead to charge separation by trapping of the positive charge. As evidence of such a concept we present the first vibrational spectra of Xe_2H^+ and Xe_2D^+ , which are believed to be vibrationally bound ions.

I. INTRODUCTION

In a series of detailed investigations Fajardo and Apkarian demonstrated that optically accessed charge-transfer states of solid xenon doped with atomic halogens (I, Br, Cl) are extensively delocalized: an electron of infinite effective mass localized on the halogen atom, and a delocalized hole in the valence band of the extended solid bound to the negative center.¹⁻³ The binding is essentially understood in terms of Coulombic interaction between the hole and the ion core screened by the host dielectric. The excitation resonances were successfully treated as a Rydberg series of a valence hole with an effective mass reflecting the full valence bandwidth.⁴ More recently, Kunz *et al.* showed that the same treatment is valid for excitations in Cl doped solid krypton in the spectral range of 5 to 7 eV.⁵ In F/Kr solids the excitation progression is completely collapsed, and delocalization is limited over the immediate nearest neighbors only.⁶ The recent growing interest in spectroscopy and photodynamics of hydrogen centers in rare gas solids has clearly established, that hole exciton progressions are not peculiar to halogen doped solids alone.^{5,7-10} It is now clear that delocalized excitations play a rather crucial role in photodynamics and photochemistry of a larger class of systems.

A rather fundamental consequence of delocalization of the positive charge is the issue of trapping of the mobile hole in the solid. It is well established that self-trapped states (STS) of valence band holes in rare gas solids are stable with respect to free hole states.¹¹⁻¹³ However, for xenon the STS are predicted to lie near the stability boundary. Regardless of the nature of STS, self-trapping is associated with large lattice displacements. Most of the experimental input concerning self-trapping of the hole in halogen doped rare gas solids originates from thermoluminescence experiments by Fajardo and Apkarian, who demonstrated long term electron-hole separation with storage densities as high as 10^{17} cm^{-3} in I, Br, and Cl doped solid xenon.³ They described the STS in the framework of small polaron theory,¹⁴ in which the charge is self-trapped by lattice relaxation. The experimental observables, phosphorescence and thermoluminescence, were ascribed to polaron tunneling and detrapping of the STS to a mobile state, respectively. Both of these distinct

channels eventually terminate in ion-hole recombination in a purely molecular charge-transfer state, $\text{Xe}_2^+ \text{X}^-$, which relaxes radiatively. Nevertheless, those experiments did not provide rigorous structural information concerning the STS created by the initial optical excitation.

The starting point for the present experimental studies is rather identical to Refs. 1-3, namely photodissociation of HX (X = I, Br, Cl) molecule in solid xenon followed by an optical excitation either within the delocalized Rydberg states of $\text{Rg}^+ \text{X}^-/\text{Rg}$, or beyond the ionization limit of the free hole. However, instead of relying on information extractable from thermoluminescence, we probe the trapped states (TS) directly by infrared spectroscopy. In the analysis to be presented the TS are treated as molecular ions. It will be shown that extensive trapping of holes is, indeed, achieved in these solids providing a new approach to ion spectroscopy in rare gas solids. These studies should also serve as a testing ground for theoretical developments regarding many-body dynamics in atomic solids doped with small charged species. As an example of the feasibility of this technique we present the first vibrational spectra of Xe_2H^+ and Xe_2D^+ . Although we limit the present paper to these ions, we note that several other ionic species have been observed in these solids and are presently the subject of systematic studies. Forthcoming publications will extend the concept to a larger class of ions.

II. EXPERIMENT

HI with nominal purity of 98% (Merck) was subject to further purification by low temperature distillation. DI was synthesized from D_2O , iodine, and red phosphorus.¹⁵ An analogous synthetic procedure was applied for HBr and DBr. HCl (Matheson) of technical purity was used without further purification, and DCl was synthesized from NaCl and deuterated sulfuric acid. Xenon of 99.997% purity (Messer Griesheim) was used with its original purity.

The gas mixtures were prepared in a glass manifold using standard manometric procedures. The premixed gas was sprayed through a 1/16 in. stainless steel capillary onto a CsI substrate. Substrate temperatures about 50 K were found to be optimal for growing well annealed films of high optical

and structural qualities essential for self-trapping. After deposition the solids were slowly cooled to 12 K, which caused significant cracking of the solid with a sharp reproducible onset at 46 K. Nevertheless, most of the solids maintained their excellent optical quality despite the cracking. For cooling, a closed cycle helium refrigerator (Displex, DE-202A) was used. The temperature measurements (accuracy 0.1 K) are based on the readout of a silicon diode attached on the frame of the cold substrate.

Xenon and mercury arc lamps equipped with appropriate water filters, or a multigas excimer laser, were used as irradiation sources. The excimer laser (Estonian Academy of Sciences, ELI-94) was operated on ArF (193 nm) or KrF (248 nm) transitions. The infrared spectra were recorded with a Nicolet 60SX Fourier transform spectrometer capable to a resolution of 0.25 cm^{-1} .

III. RESULTS

Irradiation of HX (X = I, Br, Cl) doped solid xenon causes appearance of a set of new absorptions in the 500 to 1300 cm^{-1} spectral region. In the case of HI and HBr doped solids, qualitatively identical observations were made with both photolyzing sources, arc lamps, and the excimer laser. However, only the 193 photolysis caused significant spectral changes in HCl/Xe solids.

Figure 1 represents a typical spectrum obtained after broad band Xe arc photolysis of a HBr/Xe solid. The spectrum displays a well defined sequence of narrow absorptions at $730.9, 842.8, 953.1, 1061.9$ and 1168.8 cm^{-1} . This series of absorptions is reproducible within $\pm 0.3 \text{ cm}^{-1}$ in all HX/Xe matrices, and is hereafter called "progression I." Characteristic to progression I absorptions are slightly asymmetric lineshapes associated with full width at half maximum (FWHM) from 3 cm^{-1} (first peak) to 11 cm^{-1} (1061.9

cm^{-1} peak). A red shift by a factor of 1.416 was observed for the origin of progression I upon deuteration of the precursor. Furthermore, a definite decrease in the relative intensities of the higher members of progression I is caused by deuteration: $516.7, 634.7,$ and 750 cm^{-1} are the only resolved absorptions in the deuterated progression. The observed bands of H and D doped solids are collected in Table I.

Figure 2 shows the growth of progression I as a function of irradiation time at 193 nm. The example is taken from a HBr:Xe 1:1500 sample. Progression I reaches its maximum value within the first 5000 laser shots, and further irradiation causes gradual decrease of the absorptions. Upon prolonged irradiation, a steady state situation is eventually established. Within the peak integration errors, an identical behavior was observed for the deuterated progression I in ternary HX:DX/Xe solids. The appearance of progression I correlates strongly with photodissociation of the parent HBr molecule as shown in Fig. 2. However, only a fraction of the initial precursor is converted to progression I: $\sim 60\%$ dissociation corresponds to the saturation limit of progression I. Moreover, this number is dependent on the concentration of the HX precursor: in dilute samples nearly complete dissociation was essential to reach the maximum value of progression I, while in the more concentrated ones (HX/Xe ~ 300) 10%–20% dissociation was sufficient.

A quite interesting observation was made concerning the thermal stability of progression I. Extensively irradiated solids, when left overnight in the dark at 15 K, show thermal decomposition with a clearcut halogen dependence: during 15 hours 50% thermal bleaching was observed in HBr and HI based solids, while when photogenerated from HCl/Xe, progression I was thermally stable at 15 K, and slowly decomposed at elevated temperatures. Note that growth of any new absorption in the spectral range of 400 to 4000 cm^{-1} could not be associated with decomposition of progression I.

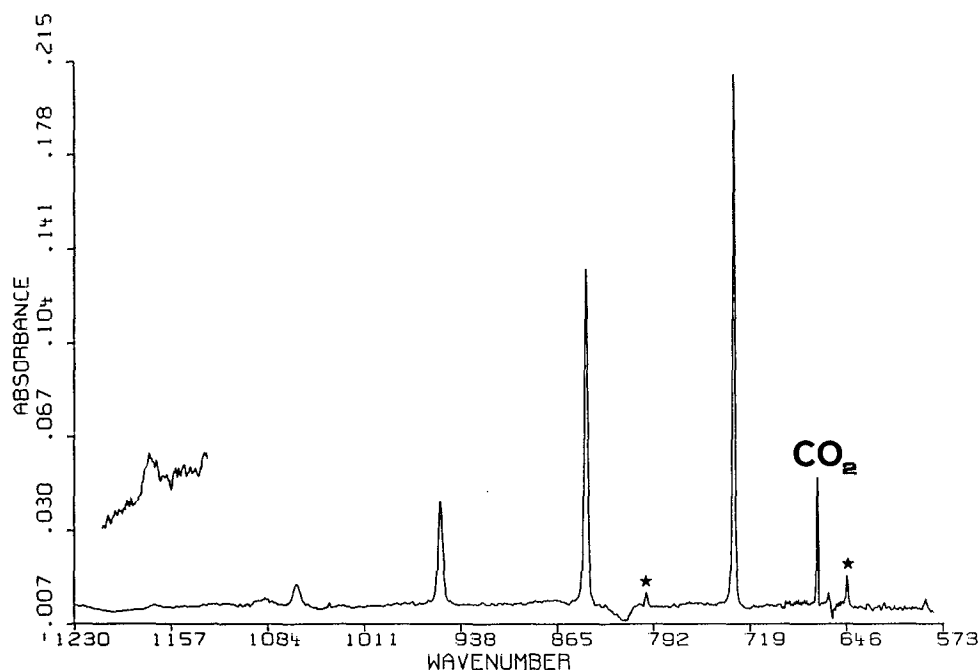


FIG. 1. Vibrational spectrum of Xe_2H^+ in solid xenon. The spectrum was recorded after two hours of Xe arc photolysis of a HBr:Xe = 1:1000 solid at 15 K. For band assignments, see Table I. The absorptions labeled with an asterisk are due to HBr_2^- ion.

TABLE I. The vibrational frequencies (cm^{-1}) and spectroscopic parameters for Xe_2H^+ and Xe_2D^+ .

	Xe_2H^+	Xe_2D^+
ν_3	730.9	516.7
$\nu_3 + \nu_1$	842.8	634.7
$\nu_3 + 2\nu_1$	953.1	749.8
$\nu_3 + 3\nu_1$	1061.9	
$\nu_3 + 4\nu_1$	1168.8	
$\omega_e(\nu_1)$	113.7	120.8
$\omega_e x_e(\nu_1)$	0.845	1.43
$D_e(\nu_1)$ (cm^{-1})	3824.8	2552.8

Most interestingly, no measurable thermal decomposition of the deuterated counterpart of progression I was observed up to temperatures above 60 K. Figure 3 illustrates this effect. The spectra are from a sample doubly doped with H and D. The spectrum in Fig. 3(a) is immediately after irradiation, while that in Fig. 3(b) is obtained after 16 hours at 15 K. Note the bleaching of the H lines while the D lines remain effectively constant.

IV. DISCUSSION

A. Spectroscopy

The present experimental evidence suggest that progression I originates from the parent HX molecules being permanently dissociated in the photolysis. Photobleaching of the ν (H-X) absorption as well as the visual observation of strong $\text{Xe}_2^+ \text{X}^-$ exciplexic emissions (see Ref. 2 for spectroscopic details of $\text{Xe}_2^+ \text{X}^-$) are direct indications of photodissociation. Furthermore, the role of the halogen may be considered as very minor, since the spectral features of progression I are virtually insensitive to the precursor. In the HX:DX/Xe ternary solids, two distinct progressions of absorptions are observed, hence suggesting that a single H (D) atom is involved in progression I. The above considerations lead to the

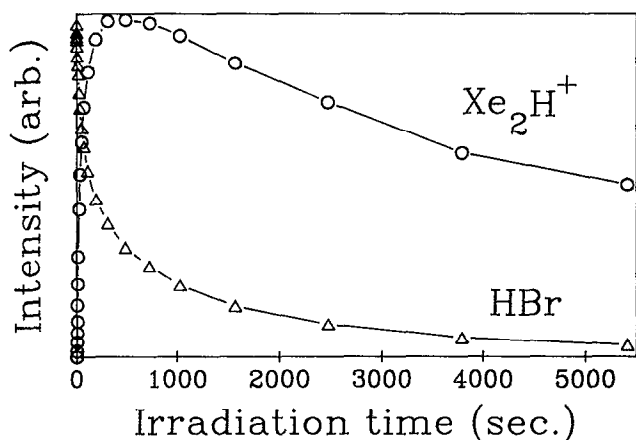


FIG. 2. The appearance of Xe_2H^+ absorptions vs photodissociation of HBr in solid xenon. The original sample composition is HBr:Xe = 1:1500. Photolysis is carried out with an excimer laser at 193 nm (4 mJ cm^{-2} , 10 Hz repetition rate). The concentration of HBr is monitored by integrating the R_0 band at 2531 cm^{-1} .

assignment of progression I to either a neutral or charged $\text{Xe}_n \text{H}$ species.

The solid state spectroscopy of rare gas hydrides originates from the pioneering paper by Bondybey and Pimentel who attributed the 905 and 852 cm^{-1} absorptions to O_h trapped neutral hydrogen atoms in solid argon and krypton, respectively.¹⁶ These absorptions were induced by microwave discharge of H_2/Ar and H_2/Kr mixtures prior to deposition. The absorbing species were subsequently reassigned to $\text{Ar}_n \text{H}^+$ and $\text{Kr}_n \text{H}^+$ by Andrews and Milligan.¹⁷ Importantly, the previous investigators report only a single absorption band, with $\nu(\text{H})/\nu(\text{D}) = 1.40$, for these ions. Also, attempts to observe the corresponding xenon species failed.

There exists an extensive literature on matrix isolated hydrogen dihalide anions of the type $(\text{X-H-X})^-$, which has been recently reviewed by Ault.¹⁸ These species are isoelectronic with $(\text{Rg-H-Rg})^+$ cations. As such, the spectrum of $(\text{Xe-H-Xe})^+$ is expected to mimic that of $(\text{I-H-I})^-$. Indeed, the spectra observed in the present work parallel those of $(\text{X-H-X})^-$ in general and $(\text{I-H-I})^-$ in particular. The vibrational spectrum of $(\text{I-H-I})^-$ isolated in argon shows a prominent progression of absorptions at 627, 803, and 929 cm^{-1} , which are assigned to ν_3 , $\nu_3 + \nu_1$, and $\nu_3 + 2\nu_1$.¹⁸ The progression shown in the spectrum of Fig. 1 can be assigned to $\nu_3 + n\nu_1$ in analogy. The assignments are collected in Table I. Both ν_3 and ν_1 frequencies occur in the expected range of 700 cm^{-1} and 120 cm^{-1} observed in the $(\text{X-H-X})^-$ species. Moreover, the observed isotopic shifts follow the same pattern as those observed in $(\text{X-H-X})^-$. In the case of the ν_3 mode, $\nu(\text{H})/\nu(\text{D}) = 1.415$ is observed, which would imply a purely H motion in a harmonic potential, while in the case of ν_1 , $\nu(\text{H})/\nu(\text{D}) = 0.94$ is observed. This inverse isotopic behavior is seen for ν_1 in all $(\text{X-H-X})^-$, in which $\nu(\text{D})$ is typically $\sim 3\%$ larger than $\nu(\text{H})$.¹⁹ Note that in the case of the ν_3 mode, a symmetric structure would yield $\omega_e(\text{H})/\omega_e(\text{D}) = 1.411$. Thus, observation of a shift exceeding the harmonic value is taken to imply the absence of cubic terms in the potential along ν_3 , and therefore a centrosymmetric ion. In summary, we conclude that by analogy with the isoelectronic $(\text{X-H-X})^-$ ions, the present spectra are consistent with the assignment of the observed vibrations to $(\text{Xe-H-Xe})^+$ and $(\text{Xe-D-Xe})^+$ ions with $D_{\infty h}$ symmetry.

It is worth noting that the assignment of progression I cannot be confused with that of $(\text{X-H-X})^-$. The latter is observed in concentrated solids along with progression I. The $(\text{Br-H-Br})^-$ absorptions are clearly visible and marked in the spectrum of Fig. 1.

Finally, we note that the parallel between $(\text{X-H-X})^-$ and $(\text{Rg-H-Rg})^+$ can be extended to the photogeneration mechanism as well. In the case of the dihalide ions, the most convenient method for their photogeneration is the codeposition of alkali atoms with the hydrogen halide of interest. Subsequent irradiation of such solids produces the ionic spectra, presumably by photoinduced electron transfer from the alkali atom to the XHX moiety. In the present, a hole is transferred from the halogen atom to the RgHRg moiety by irradiation.

It is important to note that although in the above analy-

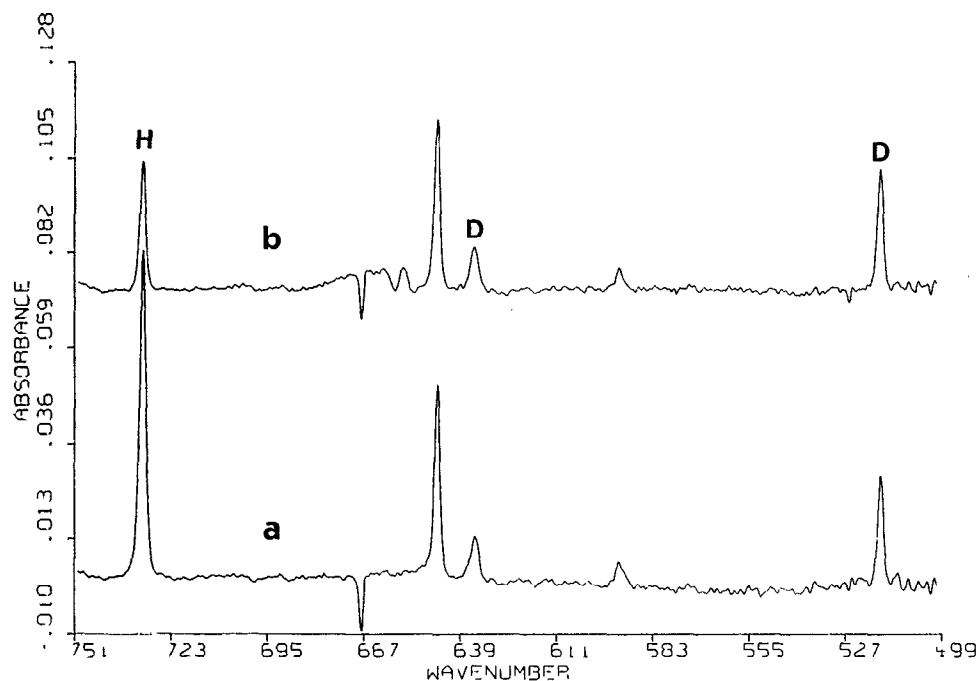


FIG. 3. Sections of infrared spectra of solid xenon doubly doped with H and D. The original sample composition is $\text{HBr}(\text{DBr}):\text{Xe} = 1:300$ with $\sim 20\%$ deuteration. Spectrum (a) was recorded immediately after extensive irradiation of the solid with an excimer laser at 193 nm, while spectrum (b) was obtained after the sample was left in the dark for 16 hours at 15 K. The absorption at 731 cm^{-1} (H) is assigned to ν_3 mode of Xe_2H^+ whereas the spectral features labeled with (D) correspond to ν_3 and $\nu_3 + \nu_1$ vibrations of Xe_2D^+ , respectively. The other absorptions seen are the ν_3 of HBr_2^- (646 cm^{-1}) and $\nu_3 + \nu_1$ of DBr_2^- (592 cm^{-1}).

sis, and in the case of $(\text{X}-\text{H}-\text{X})^-$ ions in matrices, normal mode language is used for the interpretation of spectra, this framework may not be appropriate. The more appropriate framework for discussing these systems may be that of vibrationally bound, heavy-light-heavy (HLH) systems, such as I-H-I, for which an extensive theoretical development has been advanced.²⁰ For the case of vibrationally bound HLH systems, both the inverse isotope dependence for ν_1 and the normal isotope effect on ν_3 arise naturally. Moreover, the decrease in the dissociation limit of ν_1 in going from H to D is predicted.²⁰ Thus the vibrationally bound HLH analysis requires that the ion be linear and centrosymmetric, moreover it would imply that the static $(\text{Xe}-\text{H}-\text{Xe})^+$ potential does not possess a minimum other than eccentric van der Waals minima (shallow minima in the entrance and exit channels of the linear triatomic potential). This is consistent with the theoretical assessment of binding of holes in self-trapped states. Umehara finds self-trapped holes in solid xenon, be it at S_2 (Xe_2^+ -like) or S_1 (Xe_3^+ -like) centers, to be only marginally stable with respect to free hole states.^{12,13} It is not expected that the addition of an H atom to Xe_2^+ center would create a deeper bound potential surface in the $(\text{Xe}-\text{H}-\text{Xe})^+$ ion. In fact, the vibrationally bound ion may form without any significant lattice relaxation.

In this paper we limit ourselves to the discussion of progression I, which as argued above is consistent with vibrationally bound $(\text{Xe}-\text{H}-\text{Xe})^+$ ion. We note, however, that based on theoretical grounds, this is not the expected stable structure for xenon hydride. In a recent semiempirical treatment, Last and George predict a linear $\text{Xe}(\text{XeH}^+)$ structure for this ion in large xenon clusters: a XeH^+ unit loosely bound to a neutral cluster.²¹ The hydrogen motion in such a structure would be expected to closely resemble that of the deeply bound diatomic ion with $\omega_e = 2270\text{ cm}^{-1}$.²² Quite surprisingly, there is no evidence of formation of such an ion under the present experimental conditions. In this context it

is worth noting that flowing afterglow experiments by Adams *et al.* show that in the case of lighter rare gases He, Ne, and Ar, the product ratio $\text{RgH}^+/\text{Rg}_2\text{H}^+$ is dependent on the hydrogen flow rate in the $\text{Rg}_2^+ + \text{H}_2$ reaction.²³

B. Mechanistic aspects

Two different approaches for treating charge-transfer excitations in rare gas solids have been proposed. The formalism of diatomics in ionic systems (DIIS) treats delocalization among the nearest neighbors only,²⁴⁻²⁷ while the rest of the solid is considered as a dielectric continuum. From the experimentally studied systems, F/Kr fits best in the framework of DIIS.⁶ The alternate approach considers more extensive delocalization by treating the charge transfer states as ion-hole pairs: a hole orbiting the negative ion resulting in a Rydberg progression of excitations.^{4,5} The convergence limit of the Rydberg series is taken as the top of the valence band, which corresponds to the ionization limit of the hole, i.e., creation of a free hole. The model is analogous, with reversed signs of the charges, to the conventional electronic Rydberg series which converge to the bottom of the conduction band. The Rydberg picture reproduces the observed excitation spectra of I, Br, and Cl doped solid xenon,⁴ and was more recently extended to Cl/Kr, H/Xe, and H/Kr solids.⁵

Since the excitation energies in the present experiments are well below the ionization energy of the matrix—the threshold for photoelectron emission in solid xenon is 9.7 eV—⁵ it is rather straightforward that delocalized charge-transfer followed by efficient permanent trapping of holes is responsible for ion formation in these solids. For the charge-transfer step, two distinct energy regimes can be considered, namely excitation within the metastable $\text{X}^-\cdots\text{Xe}^+$ Rydberg manifold vs access of the continuum of the free hole states. According to the excitation spectra of solid xenon doped with atomic halogens,² and the formalism of Refs. 4

and 5, it is safe to assume that 193 nm excitation of Cl, Br, and I doped xenon accesses states beyond the ionization limit of the hole. On the other hand, in I/Xe, having the highest hole ionization energy (5.17 eV),⁵ the state prepared by the optical excitation at 248 nm can be considered as a bound Rydberg state. *A priori*, one would expect the nature of the initial optical excitation to be of importance for charge separation and trapping processes. However, no evidence of such an expectation could be observed in the present studies. This is also in accord with the thermoluminescence studies, in which self-trapping efficiencies were found to be independent of excitation energy.³ Thus, it would seem that access of large radius Rydberg states is not necessary for charge separation. As long as the condition for stability of a Rydberg state is fulfilled, i.e., as long as the Rydberg orbit is greater than the shell radius, trapping of the hole occurs. The implication is that trapping is due to a dynamic hole-phonon coupling, moreover we may conclude that the charges can trap with relatively small interionic separation (~ 1 lattice site).

A rather mundane aspect concerning dynamics of ions in condensed phases is the issue of maximum storage density of the charged species. Although the present experiments do not provide direct rigorous information concerning this matter, an estimate can be given. The thickness and optical quality of the photolyzed solids were kept as constant as possible by depositing equal amounts of gas under identical conditions in each experiment. Independent of the precursor, and the precursor concentration, the final absorbance due to Xe_2H^+ was always surprisingly similar. Also, the extent of dissociation of HX needed to reach the maximum amplitude of Xe_2H^+ absorption was observed to be strongly dependent on the initial concentration. Both of these issues support the fact that a saturation limit of the ion density is reached in the photolysis. For example, in a 1:1500 HBr/Xe solid, $\sim 60\%$ dissociation yielded saturation in the Xe_2H^+ absorption. This would give an upper limit of the order of 10^{18} cm^{-3} for the ion density. However, the expected trapping of Xe_n^+ centers followed by charge transfer has obviously a contribution to the highest obtainable ion density in the solid. Consistently, the analysis of thermoluminescence data yielded charged pair storage densities of the order of 10^{17} cm^{-3} .³ Systematic studies of solids having different growth and annealing histories would, in principle, resolve the issue of whether the asymptotic behavior of the ion density is due to number of defects in the solids, or truly related to charge repulsion or whether a photochemical steady state dictates the final charge densities.

The formation kinetics of Xe_2H^+ is characterized by a fast rise followed by a slow fall to a steady state density (see Fig. 2). The origin of the fall is not straightforward. A rather likely mechanism responsible for the decay is, however, electron detachment from the anion, and subsequent electron-hole recombination at the cation site. There is evidence for such a mechanism in fluorescence and thermoluminescence data in I/Xe solids.²⁸ The proposed mechanism would obviously have serious bearings with respect to charge storage in these solids.

One of the most striking findings in the present studies is the dark decay of Xe_2H^+ absorptions, specific for the pro-

tonated species only. Moreover, the stability of the cation is unambiguously related to the type of the initial precursor with increasing stability from HI to HCl. This could, in principle, mean a correlation between the stability of the cation and the electronic polarizability of the counter anion X^- , which increases from 3.66 to $7.10 \times 10^{-24} \text{ cm}^3$ in going from Cl^- to I^- .²⁹ Note, however, that the vibrational spectrum of Xe_2H^+ is not affected by the anion. Based on the observation that the cation is formed even when low-lying Rydberg hole states are accessed, it was suggested that the separation between charges must be small. It would therefore be expected that the electron-hole pair may undergo tunneling recombination. This would explain the observed dependence of decay rates on the nature of the halide ion: the more extended the excess electron wave function, the larger the tunneling rate. However, this does not provide a direct interpretation for the dramatic difference between stabilities of D vs H ions, unless the tunneling involves internal coordinate of the ion. This is quite likely to be the case, since it is believed that the cation is vibrationally bound. We note that tunneling of H or D atoms cannot explain the dependence on the halide ion. Finally, proton tunneling would, in principle, be consistent with the observed dependences, however, given the ionization potentials of H and Xe we expect the charge to reside on Xe at all times. Direct observation of Xe_n^+ ion could greatly help in clarifying these mechanisms. The development of spectroscopical tools for detection of Xe_n^+ is underway in our laboratory.

V. CONCLUSIONS

The present studies represent a rather novel approach to generation of ions containing rare gas atoms in the solid state. The concept may be generalizable to a larger class of ionic systems. We have shown that UV photolysis of solid xenon doped with HX ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) leads to efficient generation of Xe_2H^+ ions. The vibrational spectrum of the hydride cation is independent of the halogen. The formation of Xe_2H^+ at energies well below the ionization energy of the solid is ascribed to long range, delocalized $\text{Xe}^+ \cdots \text{X}^-$ charge-transfer excitation followed by trapping of the positive charge in the form of a molecular ion. Although the role of the counter anion is not completely understood, it has a severe implication on the stability of the cation. Contrary to Xe_2H^+ , the corresponding deuterated species is thermally stable. In order to resolve the interesting dynamics involved in the delocalized charge transfer and self-trapping in these systems, further theoretical approaches are essential and strongly encouraged.

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