Neutral rare-gas containing charge-transfer molecules in solid matrices. II. HXeH, HXeD, and DXeD in Xe

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Photolysis of hydrogen halides (and some other hydrogen containing small molecules) in solid Xe yields in a two step process charged centers, one of them being $XeHXe^+$. Annealing of the irradiated doped solids produces, in addition to H–Xe–Y (Y=Cl, Br, or I) species characterized by us previously, a fairly strong doublet at 1181 and 1166 cm^{-1} and a weak absorption at 701 cm^{-1}. Deuterated precursors yield a doublet at 846 and 856 cm^{-1}. Also peaks belonging to mixed H/D form are found, indicating that the absorbing species contains two H/D atoms. The new species responsible for these absorptions are assigned as neutral linear centrosymmetric HXeH, HXeD, and DXeD. The nature of the bonding can be understood in terms of the resonance between the two ionic forms HXe^+H^- and H^-Xe^+H, analogously to the valence bond description of the well known XeF_2. The pseudopotential (LANL1DZ) *ab initio* calculations at the MP2 level are in good agreement with the observed spectra. © *1995 American Institute of Physics.*

I. INTRODUCTION

This is a second paper in a series that deals with new neutral rare-gas containing molecules isolated in rare-gas matrices. In our first paper[1] we reported the existence of HXeCl, HXeBr, HXeI, and HKrCl. These molecules are easily observed due to their extremely strong absorptions in the 1000–1700 cm^{-1} region. The HXY (X=Xe,Kr; Y=Cl,Br,I) molecules are the first examples of a hydrogen rare-gas bond in a neutral stable molecule, and quite interestingly Last and George[2] were able to predict the existence of the HXeCl in 1988 by the semiempirical diatomics-in-ionic-systems (DIIS) method. The bonding in the HXY molecules can be understood in terms of their constituent ionic fragments X^+H and X^+Y^-, which are both strongly bound.[3,4]

Fajardo and Apkarian[5–7] have demonstrated that ultraviolet-irradiation of hydrogen halides in rare-gas matrices leads to permanent charge separation. The first step in that process is the photodissociation of a precursor, which yields separated hydrogen and halogen atoms isolated in a rare-gas environment. The next step is a photoinduced charge-transfer X^+Y^- and subsequent delocalization of the positive charge.[7] The charge-transfer state may relax radiatively but also another channel is possible; localization of the positive and negative charges in different separated sites. The deepest trapping site in these systems for the negative charge is the halogen atom and for the positive charge X_2^+ or X_3^+ have been suggested.[7] It has been found experimentally in our laboratory[8] that linear centrosymmetric XHX^+ species is one trapping site for the positive charge and YHY^- centers represent one trapping site for the negative charge.[9] Both the XHX^+ and YHY^- species can be identified by their characteristic $\nu_3+n\nu_1$ ($n=1,2,...$) vibrational progressions.[8,9] Part of the total photogenerated trapped positive charge can be induced into a mobile state by annealing the matrix. This results in a recombination of charges and radiative neutralization can be seen as thermoluminescence with a very long halflife.[7] In our previous paper[1] we postulated that the HXY molecules are formed when a thermally mobilized hole ''collides'' with a halogen anion surrounded by rare-gas atoms and a hydrogen atom.

In addition to the absorptions assigned to the HXY molecules, annealing yields new absorptions belonging to previously unknown species. These absorptions have been detected only in xenon matrices and they possess only hydrogen dependence as reported by Kunttu and Seetula.[10] In other words all the hydrogen halides studied so far, i.e., HCl, HBr, and HI, produce after photolysis and annealing the same peaks in xenon appearing at 1181, 1166, and 701 cm^{-1} for the H form and at 856 and 846 cm^{-1} for the D form. It is also to be noted that there are no observable shifts in these frequencies due to different precursors, which indicates that the new species is expected to be well separated from the halogen atoms. Because the new peaks are formed simultaneously with peaks belonging to the HXY species it is tempting to try to see if the same kind of arguments that led to the discovery of HXY could be applied also in this case. In the following we will show that the assignment of the new species as xenon dihydride explains completely the observed spectra.

II. COMPUTATIONAL DETAILS

All calculations were performed with the GAUSSIAN 92 (Ref. 11) package of computer codes. The basis set used was the standard LANL1DZ set by Wadt and Hay.[12–14] In the LANL1DZ presentation Xe is described with 8 valence electrons while the core electrons are pictured with effective potentials. For hydrogen atom basis set used was the standard $3s1s$ basis within the LANL1DZ approach. Electron correlation was taken into account via Møller–Plesset perturbation theory to the second order (MP2). The calculations were carried out on Convex C3840 supercomputer at the Center for Scientific Computing (Espoo, Finland).

III. EXPERIMENT

The experimental details are given in Ref. 1. In short, HI of 98% purity (Merck) and DBr (99% D, Cambridge Isotope

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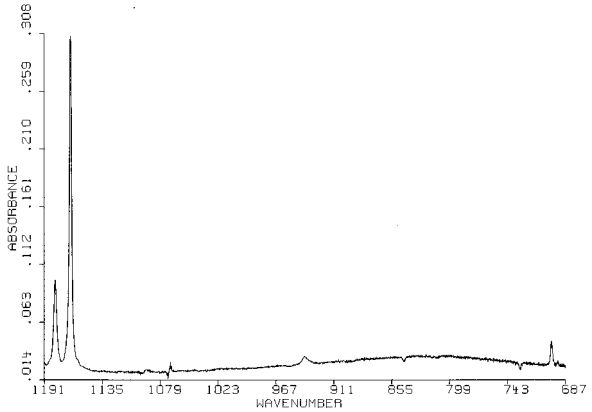


FIG. 1. Thermally induced absorptions at 1181, 1166, and 701 cm^{-1} of a HI:Xe=1:1000 sample. The mixture was deposited at 50 K and the sample was irradiated at 15 K with a Xe arc lamp for 2 h. After irradiation the sample was annealed to 50 K for 45 min and cooled back to 15 K. The cold sample was irradiated with a quartz-halogen lamp for a few minutes before recording the spectrum.

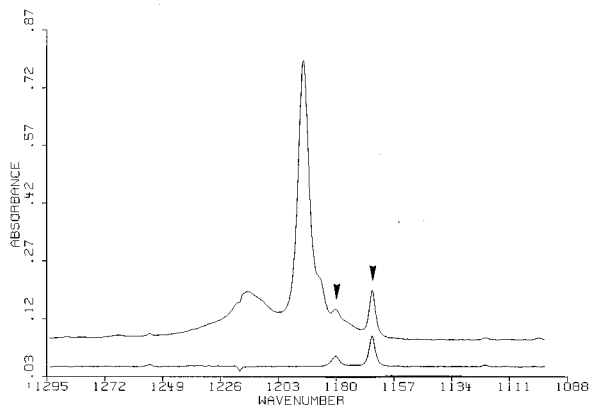


FIG. 2. Photobleaching of the HXeI absorptions. The upper trace shows the situation after annealing (50 K) the HI:Xe=1:1000 sample, deposited at 50 K and irradiated with the KrF laser at 15 K (248 nm, ~30 mJ/pulse, 1600 pulses). The broad unlabeled absorptions belong to HXeI. The lower trace shows the situation after irradiation of the sample with the quartz-halogen lamp for 17 min. Both spectra were recorded at 15 K. The absorptions at 1166 and 1181 cm^{-1} are marked with arrows.

Laboratory) were subjected to low temperature distillation. Xe of 99.997% purity (CF_4 free, AGA) was used without further purification. Premixed gas was sprayed through a 1/16 in. stainless steel capillary onto a CsI substrate. Typical substrate temperature was 50 K during deposition and after deposition the solids were slowly cooled to 15–20 K. Excimer laser, Xe arc and quartz-halogen lamps were used for irradiations. Infrared spectra were recorded with a Nicolet 60 SX FTIR spectrometer capable to a resolution of 0.25 cm^{-1}.

IV. RESULTS AND DISCUSSION

A. Spectral observations

Annealing of the UV irradiated hydrogen halide doped Xe matrices yields the appearance of new IR absorptions. The extremely strong absorptions due to the HXY species are at 1193, 1504, and 1649 cm^{-1} for HXeI, HXeBr, and HXeCl, respectively. The additional spectral features encountered during annealing of an irradiated (Xe arc) HI:Xe (1:1000) sample are displayed in Fig. 1. Quite interestingly the same peaks are obtained from different precursors containing hydrogen atom(s) and there are no detectable shifts in the peaks shown in Fig. 1 obtained from different precursors. The peaks are reproducible at least from HCl, HBr, HI, H_2O, CH_4, and HCN. No corresponding absorptions can be found in Ar or Kr matrices, suggesting the participation of Xe in the species responsible for these absorptions.

In some matrices the extremely strong absorptions of the HXY species overlap with the peaks under investigation making their observation rather difficult. However, we have found a convenient way to separate the peaks from each other. When the annealed matrices are irradiated with a broad band quartz-halogen lamp the HXY molecules are photobleached but the new absorptions survive. 193 nm laser irradiation destroys both the HXY and the new species. The process is illustrated in Fig. 2 where the major feature in the upper trace is the broad absorption belonging to HXeI. In the lower spectrum, recorded after quartz-halogen lamp irradiation for 17 min HXeI has been quantitatively destroyed and the two peaks at 1181 and 1166 cm^{-1} are well resolved. When deuterated precursors are used the 1181/1166 cm^{-1} doublet shifts to 856/846 cm^{-1} indicating the deuterium shift of 1.38. In some matrices the very weak absorption at 513 cm^{-1} has been observed and it is tentatively assigned to the deuterium counterpart of the 701 cm^{-1} absorption.

When DCl, DBr, or DI are used as precursors it is almost impossible to get only deuterated forms into the matrix because there is always some water adsorbed on the walls of the gas handling system and some hydrogen exchange takes place. Therefore also hydrogen forms are present in the deuterium experiments. If the species under investigation contained only one hydrogen atom, no additional peaks to those described above should appear in mixed H/D matrices. On the other hand if there were two or more hydrogen atoms then peaks belonging to mixed forms should be observed. Figure 3 represents a spectrum obtained from a (DBr/HBr):Xe ($M/A=1580$) sample. After photolysis and annealing the dominant features in the upper spectrum are the strong peaks belonging to HXeBr (1504 cm^{-1}) and DXeBr (1100 cm^{-1}). In the lower spectrum these strong peaks have been photobleached with quartz-halogen broad band visible irradiation. Figure 4 represents the lower spectrum of Fig. 3 in detail. In addition to the 1181/1166 cm^{-1} and 856/846 cm^{-1} peaks mentioned above there are two new features; a doublet at 1093 and 1121 cm^{-1} with some fine structure and a single peak at 753 cm^{-1}. Furthermore, a weak absorption at 621 cm^{-1} most probably belongs to the same species.

If the new absorptions belong to a mixed H/D form of the species under investigation the relative intensities of the peaks belonging to D, H, and D/H forms should depend on the H/D-ratio of the precursors. Figure 5 represents (DBr/HBr):Xe ($M/A=1570$) sample in which the precursor HBr/DBr-ratio is different from that in the experiment displayed in Fig. 3. The ratio of the peaks belonging to HXeBr and DXeBr can be taken as a measure of the effective degree of deuteration for the present case by assuming that the new

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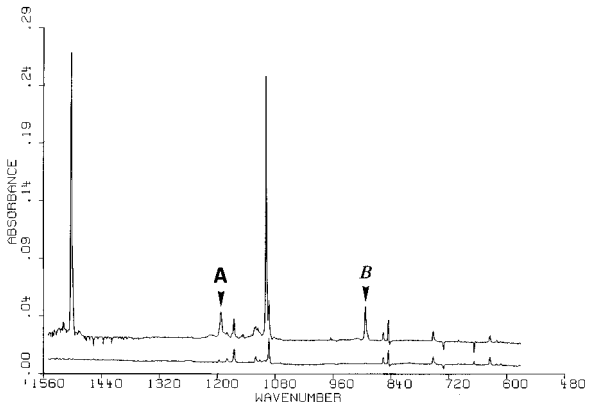


FIG. 3. Photolysis of HBr/DBr in Xe ($M/A=1580$). The sample was deposited at 50 K and irradiated with the ArF laser (193 nm, ~9 mJ/pulse, 11 300 pulses) at 15 K. The upper trace shows the situation after annealing the irradiated sample to 55 K and cooling back to 15 K after 30 min. The dominant features are the strong absorptions belonging to HXeBr (1504 cm^{-1}) and DXeBr (1100 cm^{-1}). The absorption (A) belongs to HXeI and (B) belongs to DXeI which are present in small amounts as impurities from previous experiment. The lower spectrum has been recorded after 5 min irradiation of the sample with a quartz-halogen lamp equipped with a water filter.

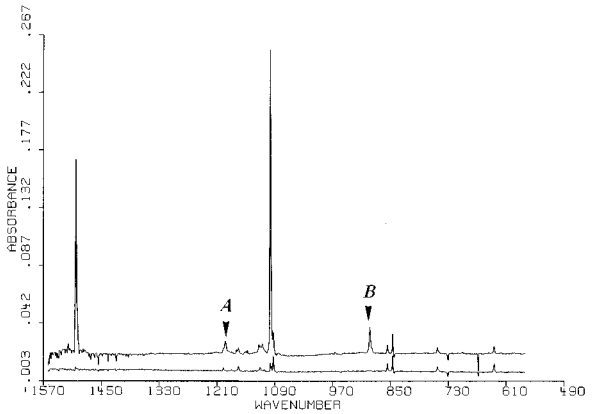


FIG. 5. A DBr/HBr:Xe ($M/A=1570$) sample with a different HXeBr/DXeBr-ratio than in the sample displayed in Fig. 3. The sample was deposited at 50 K and irradiated with an ArF laser (6800 pulses) at 15 K. The upper trace shows the situation after the temperature cycle 15 K→55 K (1 h 30 min)→15 K. The lower spectrum has been recorded after irradiating the former sample with the quartz-halogen lamp equipped with a water filter for 4 min. The peaks marked with A and B are HXeI and DXeI impurity absorptions.

species is formed by a similar mechanism as the HXeBr and DXeBr molecules. The lower spectrum of Fig. 5 is shown in Fig. 6 in detail. Inspection of the spectra shown in Figs. 3 and 5 show that the HXeBr/DXeBr-ratio between these two experiments differs by a factor of ~1.7. This results in a clear increase of the relative intensity of the 1093/1121 cm^{-1} and 846/856 cm^{-1} absorptions compared with the 1166/1181 cm^{-1} bands and in an increase of the relative intensity of the 846/856 cm^{-1} absorptions compared with the 1093/1121 cm^{-1} peaks seen by comparison of Figs. 4 and 6. Inspection of Figs. 4 and 6 show also that the degree of deuteration does not influence the 1093/753 cm^{-1} intensity ratio. Experiments with other H/D ratios are in agreement with these results.

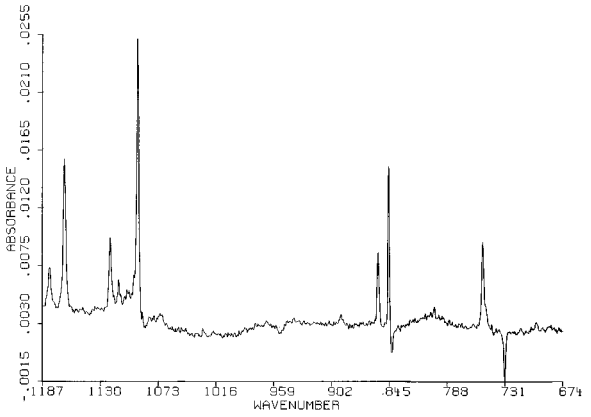


FIG. 4. The lower wave number part of the lower spectrum of Fig. 3 rescaled. The negative absorptions at 731 and 843 cm^{-1} belong to $XeHXe^+$ which is present in the background spectrum in larger amounts than in the sample spectrum. The shoulder on the low-frequency side of the 753 cm^{-1} absorption belongs to $XeDXe^+$, evidencing the different stabilities of the $XeHXe^+$ and $XeDXe^+$ cations. For more details about the cations see Refs. 8 and 10.

B. Interpretation

While attempting to identify the species responsible for the new absorptions we have taken the same approach as in our previous report.[1] In that paper the bonding in HXeCl, HXeBr, HXeI, and HKrCl could be interpreted in terms of ionic pair potentials. We suggested that interaction of a hydrogen atom with a charge transfer molecule X^+Y^- could result in a significant lowering of energy due to strong HX^+ bond formation. Similarly, substitution of the halogen atom by a hydrogen atom in the charge-transfer molecule yields HXeH. In this case, due to the symmetry of the molecule we have to consider it as a resonance structure between the two ionic forms HXe^+H^- and H^-Xe^+H. According to our knowledge there is no reliable data on the potential energy surface of the diatomic xenon hydride charge-transfer molecule. Anyway, it is expected to be strongly bound like the xenon halide charge-transfer molecules.[15] The total energy of

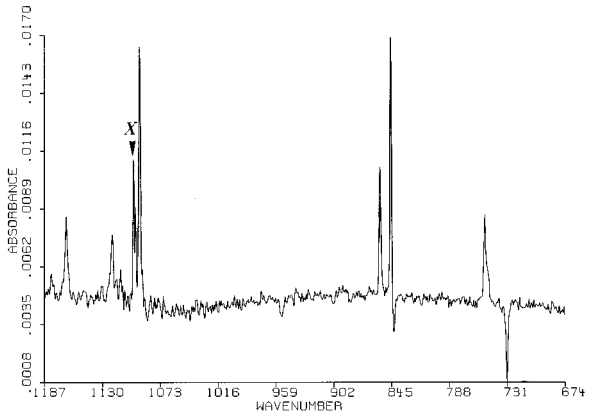


FIG. 6. The lower frequency part of the lower spectrum of Fig. 5 in detail. The negative absorptions and the shoulder of the 753 cm^{-1} peak are explained in the caption of Fig. 3. The peak marked with (X) belongs to DXeBr which has not been completely photobleached.

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TABLE I. Calculated properties of XeH_2 at the MP2/LANL1DZ level.

r (Xe–H)/Å	2.019
α (H–Xe–H)	180.0
q (Xe)[a]	+0.42
q (H)[a]	−0.21
E/hartree	−16.155 449 2

[a]Partial charges based on Mulliken population analysis at the MP2 level.

the xenon halide charge-transfer molecules is lowered significantly due to the large electron affinities of the halogen atoms (3.06–3.61 eV).[16] This effect is much smaller in the case of hydrogen because of its low electron affinity (0.75 eV).[16] However, based on these arguments, the existence of XeH_2 seems possible.

In order to test the idea above we have made some preliminary *ab initio* calculations on XeH_2 and the results are given in Table I. The MP2/LANL1DZ calculations support the idea and the linear centrosymmetric HXeH molecule is reproduced. The Mulliken population analysis yields partial charges that support the charge-transfer nature of the molecule. Also the calculated harmonic frequencies are in a good agreement with the experimental ones as shown in Table II. Although this good agreement can partly be a coincidence rather than a result of a sophisticated calculation it provides us with an opportunity to check the spectral assignment for DXeH and DXeD. Because the calculated spectrum of the XeH_2 corresponds well with the experimental spectrum, it is expected that the observed peaks for the H/D forms should be reproduced as well and in deed, this seems to be the case. The wave number for the ν_1 mode of HXeD is quite near the stretching modes of XeD_2 and the wave number for the ν_3 mode of HXeD is near the HXeH stretching modes. For this reason the ν_1 and ν_3 modes of HXeD can be approximated as localized Xe–D and Xe–H stretching modes, respectively. Similar situation is reported for HgH_2, HgD_2, and DHgH molecules by Legay-Sommaire and Legay.[17] The agreement between the calculated and experimental spectra in Table II support strongly the assignment of the new species as xenon dihydride. Furthermore, this finding finally closes the assignment of infrared bands resulting from annealing the UV-irradiated hydrogen halide doped xenon matrices. The new findings indicate that thermal activation of some intermediate

TABLE II. The calculated (MP2/LANL1DZ) and experimental wave numbers of XeH_2, HXeD, and XeD_2. The numbers in parentheses are the calculated intensities (km/mol).

Species	ν_1 (cm^{-1})	ν_2[a] (cm^{-1})	ν_3 (cm^{-1})
XeH_2	1006.9 (0)	706.4 (94)	1221.2 (701)
Experiment	⋯	700.8	1165.9, 1180.6
HXeD	766.5 (67)	613.4 (71)	1139.1 (461)
Experiment	753.0	621.0[b]	1093.4, 1120.6
XeD_2	712.2 (0)	503.4 (48)	870.4 (355.9)
Experiment	⋯	513.5[b]	845.8, 856.2

[a]Doubly degenerate.
[b]Weak peaks observed only in matrices where large amounts of the products are generated.

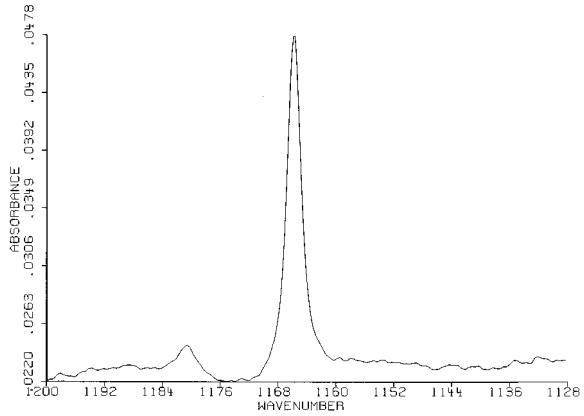


FIG. 7. A HBr:Ar:Xe=1:25:460 sample in which the 1181/1166 cm^{-1} ratio is markedly different from that presented in other figures. This sample was prepared by depositing the mixture at 40 K and irradiating the matrix with the ArF laser (~14 mJ/pulse, 400 pulses) at 15 K. After photolysis the sample was annealed first to 40 K and then recooled to 15 K. In a second cycle the sample was annealed to 70 K and cooled to 15 K before recording the spectrum.

generated during photolysis (hole, electron, hydrogen, atom, ...) results in competing formation of HXeH, in addition to formation of HXY (Y=halogen atom).

There is one interesting feature connected with the structure of the stretching absorptions of xenon dihydride; the peaks are doublets. The difference between the two components is 15, 10, and 28 cm^{-1} for XeH_2, XeD_2, and HXeD, respectively. These differences seem too large to be explained by a difference between peaks belonging to molecules in different trapping sites. The intensity ratio of the two components is not constant although the example in Fig. 1 represents the most typical situation. An example of a different ratio between the components is presented in Fig. 7 which represents a HBr:Ar:Xe=1:25:460 sample which has been deposited at 40 K, irradiated with the ArF laser and annealed to 70 K. The spectra in Figs. 1 and 7 are recorded at the same temperature (15 K). Therefore it seems that the splitting is not caused by intrinsic properties of the molecule but rather arises from specific interactions of the molecule with its environment. The extent of the splittings indicate strong interactions between the molecule and its environment. However, definite assignment of the fine structure of the stretching absorptions of HXeH in Xe requires further investigations.

C. Energetics and mechanism of formation

In our previous paper[1] we showed that the HXY-type molecules are higher in energy than the separated atom H+X+Y limit. The stability of those molecules is possible because at *their equilibrium geometries* the HXY molecules are the lowest energy configurations. When the distance of the atoms is increased the repulsive surface yielding neutral atoms becomes lower in energy. In the case of XeH_2 the situation is similar. Our MP2/LANL1DZ calculations indicate that at the equilibrium geometry the XeH_2 molecule is 0.55 eV lower in energy than the first repulsive triplet state. However, according to the MP2/LANL1DZ calculations the

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infinitely separated neutral atoms are 2.04 eV lower in energy than the XeH_2 molecule. The accuracy of the calculations at this level is not expected to be very high but qualitatively the picture should be right. Detailed investigation of the potential energy surfaces for these molecules requires more sophisticated methods and they are beyond the scope of this paper. The lowest energy configuration for the two hydrogen atoms and one xenon atom is clearly H_2+Xe and according to the MP2/LANL1DZ treatment this asymptote lies 6.08 eV lower in energy than XeH_2. Nevertheless, once produced in the matrix XeH_2 molecule is stable at 15 K at least for hours (detailed investigations on the thermal and photostability have not yet been done). This high energy-storing efficiency of XeH_2 is quite interesting and XeH_2 might be a suitable molecule for some special applications.

The true formation mechanism of XeH_2 cannot be deduced from the present experiments. However, we propose a mechanism which explains the formation of the HXY species as well.[1] When HY doped xenon matrix is irradiated with UV light a large number of different species are produced including hydrogen atoms, halogen atoms, and anions, YHY^-, $XeHXe^+$, and also possibly Xe_2^+ or Xe_3^+ centers. Further irradiation may detach the electrons from the halogen atoms and as a consequence the electrons may be retrapped by the hydrogen atoms forming H^- surrounded by Xe atoms,

$$H^-\cdots Xe_m\cdots Xe_n^+/XeHXe^+. \tag{1}$$

There may also be centers where a hydrogen atom is located near the hydrogen anion,

$$H^-\cdots Xe\cdots H\cdots Xe_m\cdots Xe_n^+/XeHXe^+. \tag{2}$$

Annealing of the matrix mobilizes the holes[7] which can result in a reaction of the mobile hole (MH) with a $H^-/Xe/H$ center,

$$H^-\cdots Xe\cdots H+MH\rightarrow HXeH. \tag{3}$$

Alternatively the neutral hydrogen atom in reaction (3) could be a thermally mobilized atom. Other possibilities of the formation mechanisms are discussed in Ref. 1.

D. The bonding nature of the rare-gas molecules

The first rare-gas compound ever made was ionic $Xe^+[PtF_6]^-$ prepared by Bartlett[18] in 1962. Since those days a vast range of rare-gas compounds have been prepared. Typically rare-gas compounds are ionic complexes of xenon. Other examples are XeO_3 and the fluorine compounds XeF_2, XeF_4, XeF_6, and KrF_2, which are all well known molecules. Different theoretical descriptions of the bonding nature in these compounds have been proposed.[19] For instance the valence bond method can be applied. Accordingly XeF_2 can be described as a resonance hybrid between the forms F^-Xe^+-F and $F-Xe^+F^-$. The same description explains the bonding also in XeH_2, HXeCl, HXeBr, HXeI, and HKrCl. This reasoning suggests that the chemistry of rare gases is actually chemistry of rare-gas ions. This is a consequence of the fact that in order to achieve bonding between a rare-gas atom and another atom one has to take ionic forms into account (weak van der Waals complexes are another category of molecular systems and they are not included in this discussion).

Keeping these facts in mind we can derive certain rules which should be helpful in search of new rare-gas compounds. In order to make a bound triatomic molecule from fragments A and B and from a rare-gas atom X one can argue that X^+A and X^+B^- or alternatively X^+B and X^+A^- should be strongly bound. If both $X^+A(B)$ and $X^+A(B)^-$ are bound then symmetric AXA or BXB should be potential candidates for rare-gas molecules. In general the charge-transfer states X^+A^- are always bound due to the Coulombic attraction. However, the important parameter of fragment A is electron affinity (EA) making the charge-transfer state energetically more favorable with increasing electron affinity. Another important parameter is the ionization potential (IP) of the rare-gas X. Xenon is the most potential candidate for new compounds because of its low IP. Examination of the HXY type molecules reveals that the criteria mentioned above are fulfilled; the rare-gas hydride cations are strongly bound (see Ref. 4, and references therein) and likewise the rare-gas halogen charge-transfer states,[15] which are energetically stabilized by the large electron affinities of the halogen atoms. In the case of XeH_2 the same arguments hold except that EA of hydrogen is quite small. As an example of xenon fluorides, the existence of XeF_2 is justified since in addition to the strongly bound Xe^+F^- also XeF^+ is bound by 2.03 eV.[20] By this reasoning it is possible to justify the existence of several known rare-gas molecules and furthermore to make predictions of a large number of yet unknown species. These predictions can then be tested by *ab initio* calculations and/or experimentally. For example we have predicted that species like HXeCN, HXeNC, HKrCN, and HKrNC should be available in rare-gas matrices and the search of them is under way in our laboratory.

It is also interesting to find out if these new molecules can be made in large quantities or even crystallize them. For this purpose it is informative to look at the stability of the AB molecule (or AA or BB). If this fragment is strongly bound then we can expect that the crystalline form of AXB (AXA,BXB) is unlikely to exist. This is because bringing AXB molecules close to each other makes it possible for A and B to react and AXB decomposes to AB and X. The Xe–fluorine compounds can be solidified and this seems natural because the dissociation energy of F_2 is quite small[16] (1.6 eV) and the formation of F_2 does not lower the energy of the system sufficiently to make the formation of the crystal unfavorable. In contrast, the bond energies of hydrogen halides and hydrogen molecule are quite large[16] varying from 3.1 eV for HI to 5.9 eV for HF. Based on these arguments we do not expect the crystalline forms of the HXY molecules or XeH_2 to be stable. The arguments mentioned above are of course only a qualitative tool which can help one to make predictions of some properties of rare-gas molecules. Detailed investigations are needed in order to get quantitative results.

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V. CONCLUSIONS

We have shown that the infrared peaks appearing in UV-irradiated and annealed xenon matrices, doped with hydrogen halides or some other hydrogen containing molecules, belong to xenon dihydride. According to *ab initio* calculations the XeH_2 molecule is linear and centrosymmetric. The vibrational spectra of HXeH, HXeD, and DXeD are presented and the *ab initio* calculated spectra agrees very well with the experimental ones. The bonding nature of the molecule is proposed to be a resonance hybrid of the two ionic forms H^-Xe^+H and HXe^+H^-.

ACKNOWLEDGMENT

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