Neutral rare-gas containing charge-transfer molecules in solid matrices. I. HXeCl, HXeBr, HXeI, and HKrCl in Kr and Xe

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Ultraviolet-irradiation of hydrogen halide containing rare gas matrices yields the formation of linear centrosymmetric cations of type (XHX)\(^+\), (X=Ar, Kr, Xe). Annealing of the irradiated doped solids produces, along with thermoluminescence, extremely strong absorptions in the 1700–1000 cm\(^{-1}\) region. Based on isotopic substitution and halogen dependence of these bands, the presence of hydrogen and halogen atom(s) in these species is evident. In the present paper we show the participation of rare gas atom(s) in these new compounds. The evidence is based on studies of the thermally generated species in mixed rare gas matrices. The new species are assigned as neutral charge-transfer molecules HX\(^+\)Y\(^-\) (Y=halogen), and their vibrational spectra are discussed and compared with those calculated with \textit{ab initio} methods. This is the first time hydrogen and a rare gas atom has been found to make a chemical bond in a neutral stable compound. The highest level \textit{ab initio} calculations on the existence of compounds of type HXY corroborate the experimental observations. The mechanism responsible for the formation of these species is also discussed. © 1995 American Institute of Physics.

INTRODUCTION

The rare gases make up about 1% of the earth’s atmosphere, the major component being Ar. Their inertness toward chemical bond formation has been attributed to the “stable octet” outer electronic structure, the criterion valid especially for the lighter group 18 elements. No stable neutral compounds of He, Ne, or Ar are known, and their computationally predicted chemical compounds are thoroughly discussed in the review article by Frenking and Cremer.\(^1\) Extensive search for rare gas compounds started in 1962 when Bartlett\(^2\) prepared for the first time the Xe-compound Xe\(^2\)[PtF\(_6\)]. The known chemistry of Xe today comprises several compounds, fluorine and/or oxygen atoms being typically involved in these compounds. The chemistry of Kr is confined to the difluoride and its derivatives.\(^3\) KrF\(_2\) is a linear molecule [the bond distance Kr–F being 1.875 Å (Ref. 4)], and it decomposes slowly at room temperature.

Matrix photogeneration of linear triatomic cations (XHX)\(^+\) (X=Ar, Kr or Xe) and anions (YHY)\(^-\) (Y=Cl, Br or I) is presently rather well understood.\(^5\) Spectroscopically these isoelectronic pairs show great similarities; their structure is D\(_{ab}\), and the large anharmonicity of the bonds leads to unexpectedly strong combination absorptions in the 700–1300 cm\(^{-1}\) spectral region.\(^6\) These \(v_3 + n v_1\) progressions are visible in the mid-infrared region up to \(n\) value of 5. The mechanism responsible for the formation of the rare gas cat-ionic species involves generation of hydrogen atoms and an electronegative center (for instance a halogen atom) in the matrix. Further irradiation of the matrix at ultraviolet wavelengths results in change separation in the Rg–electronegative center pair, and a delocalized hole is generated photolytically. The photophysics connected with these two-step processes is well understood on the basis of the pioneering studies of Fajardo and Apkarian.\(^10\)–\(^12\) In the case of photodissociation of hydrogen halides in rare gas matrices, one of the stabilization sites of the positive charge is in the form of the centrosymmetric (XHX)\(^+\) cations, while the electron is deeply trapped in the halogen atom. Other trapping sites besides (XHX)\(^+\) have not yet been experimentally characterized. The trapped holes can be thermally mobilized by increasing the matrix temperature to 30–50 K, and strong thermoluminescence is connected with this process.\(^5\) The most probable process occurring to the mobilized holes in the matrix is neutralization, and a large energy release by either nonradiative or radiative processes. The threshold temperature for thermoluminescence in Xe is typically 40 K.

Annealing of the system obtained from photodissociation of HY (Y=halogen) yields a number of extremely intense absorptions in the 1000–1700 cm\(^{-1}\) region.\(^7\) Figure 1 displays the infrared spectra of HI in Xe after different treatments pointing out the enormous intensity of the thermally activated species dealt with in this paper. Based on original measurements of photodissociation of hydrogen halides in different rare gases it has been possible to deduce only two of the atoms involved in these compounds. First, hydrogen is involved, the deuterium shift being typically about 1.34, displaying a strongly anharmonic potential. Additionally, the precursor dependence shows that also halogen atom(s) is involved. Due to the broadness of these bands it is quite difficult to make any detailed conclusions about the number of halogen atoms involved. Further, these absorptions also suggest the participation of rare gas atoms in these species. The characteristic thermal absorptions are experimentally obtainable in Xe matrices while photolyzing precursors containing Cl, Br or I atoms. However, in Kr matrices the thermal product can be detected only after photolysis of HCl. It must be noted also that we have not yet attempted to photolyze HF in rare gas matrices. A tentative assignment of the thermal products has been given by Kunttu and Seetula.\(^7\) This proposed assignment is based on the early experiment of Evans and Lo\(^13\) on the symmetrical and unsymmetrical (YHY)\(^-\)–anions (Y=halogen), strongly perturbed by the...
nearest-neighbor cation. Also the assignment of the thermal products as HXY\(^+\) cations was discussed.\(^7\)

Quite interestingly, Last and George\(^15\) in their computational studies for impurity centers in rare gases predicted the existence of an ionic molecule (HXe)\(^+\)Cl\(^-\). The calculation was based on the semiempirical diatomics-in-ionic-systems (DIIS) method. According to the calculation, the ground state (HXe)\(^+\)Cl\(^-\) molecule is linear and separated from the van der Waals complex HCl•••Xe by a barrier of 0.41 eV. The DIIS calculation suggests two strong bonds for this system, the (H–Xe)\(^+\) and Xe\(^+\)–Cl\(^-\), the former subspecies being iso-electronic with HI. Also, the calculations suggest quite extensive charge separation, leading to a very large dipole moment (15 D) for this molecule. From the experimental point of view it is of interest also to note that the DIIS results for the first excited state suggest a geometry of (XeH)\(^+\)Cl\(^-\). This leads to a considerable lowering of the barrier between the ionic molecule and its HCl•••Xe van der Waals complex in the electronically excited state.

**COMPUTATIONAL DETAILS**

All calculations were performed within the framework of the GAUSSIAN 92 (Ref. 16) package of computer codes. Electron correlation was considered via Møller–Plesset perturbation theory\(^17,18\) to the second order, including all electrons. The harmonic frequencies were calculated analytically at the UMP2 level of theory, and the high level UCCSD (Refs. 19–22) calculations were used to generate the HArF potential energy surface.

The applied basis sets display three different ways of describing the electronic structure of the atoms of concern. Effective core potentials (ECP) were introduced in the LANL1DZ presentation by Wadt and Hay\(^23–25\) and the relativistic presentation by Christiansen.\(^26–28\) Generally the CI and Ar atom basis sets are described with an explicit 7 or 8 electrons valence shell, respectively, while the chemically less active core electrons are pictured with effective potentials. For the heavier rare gas atoms (Kr and Xe) and halogen atoms (Br and I) the accuracy of calculations was improved in the ECP approach by inclusion of the underlying d-orbital in the valence space, resulting in a total of 18 or 17 valence electrons, respectively. Furthermore, for Ar and Cl the balanced atomic basis sets developed by Wallace et al.\(^29\) (WBP) were used within the Christiansen ECP approach.

The all-electron approaches are based on the standard, split-valence type, double-\(\zeta\) basis set augmented with a d-polarization function (6-31G\(^*\)) (Refs. 30–32) for Ar, F, and Cl, and the Huzinaga basis sets\(^33\) for heavier atoms. For Cl the Huzinaga 11s8p\(^1\) basis set was used contracted as (533/5111). In the case of Kr and Br the 13s10p4d basis sets were used contracted as (4333/4333/4). For Xe and I the basis set notation is 16s13p7d with a contraction of (4333/4333/43).

For the hydrogen basis the standard, split-valence type, double-\(\zeta\) basis sets, added with a single p-polarization function (3s1p and 3s1p1p) were chosen. However, the large 7s2p1d (contracted as 211111/111) by Rosmus,\(^34\) and the modified 3s1p basis (3s1s1p1p) by Latajka and Scheiner,\(^35\) denoted as +VP\(^2\)\(^p\), were also tested.

All calculations were carried out on CRAY X-MP EA/464, SGI Power Onyx, and Convex C3840 supercomputers at the Center for Scientific Computing (Espoo, Finland).

**EXPERIMENT**

HBr was synthesized from tetrahydroanaphtalene and bromine\(^36\) and was purified by low temperature distillation. HCl (Matheson) of technical purity was used without further purification. Xenon of 99.997% and krypton of 99.99% purity (Messer Griesheim) were used with their original purities. HBr was stored in a blackened glass bulb in order to reduce the decomposition of the gas. Gas mixtures were prepared in a glass manifold using standard manometric procedures. Premixed gas was sprayed through a 1/16 in. stainless steel capillary onto a CsI substrate. Substrate temperature of 30 K was used in most experiments. Typically ~4 mmol of the gas mixture was deposited at the rate of 2.7 mmol/h. After deposition the solids were slowly cooled to 15 K. A closed cycle helium refrigerator (Displex, DE-202A) was used for cooling. The matrix was warmed with a resistive heater and the temperature was measured with a silicon diode (accuracy 0.1 K) attached on the frame of the cold substrate. An excimer laser was used as the photolysis source. The laser (Estonian Academy of Sciences, ELI-76) was operated at 193 nm (ArF), and the pulse energies used were typically 5–20 mJ. The infrared spectra were recorded with a Nicolet 60SX Fourier transform spectrometer capable to a resolution of 0.25 cm\(^{-1}\), coadding typically 200 scans.

**RESULTS AND DISCUSSION**

193 nm irradiation of the ternary HCl/Xe/Kr and HBr/Xe/Kr solids at 15 K produces the ionic species, identified previously as Xe\(_2\)H\(^+\), Kr\(_2\)H\(^+\), Cl\(_2\)H\(^-\), and Br\(_2\)H\(^-\). The structure of all these species is linear centrosymmetric.\(^5,6,8,9,37–42\) Annealing of the extensively irradiated solids near 40 K causes the appearance of strong IR-absorptions in the 800–
1700 cm\(^{-1}\) region (cf. Fig. 1). It is also to be noted that careful kinetic measurements show that the disappearance of the centrosymmetric cations is not connected with the formation of the thermally generated species.\(^7\)

Table I lists the observed thermally induced peaks in different H(D)Y/X systems in various rare gas matrices (Y = Cl, Br, I, X = Xe, Kr), respectively. The data are adapted from Ref. 7. Importantly, HCl is the only hydrogen halide producing the thermally induced peaks both in Kr and Xe (experiments with HF precursor are underway in our laboratory). The large difference (173 cm\(^{-1}\)) between the wave numbers of the HCl/Xe (1649 cm\(^{-1}\)) and HCl/Kr (1476 cm\(^{-1}\)) annealing products would indicate that the peaks belong to different species rather than to the same species in different hosts. In order to verify which one of the cases is correct we have made photodissociation and annealing experiments with ternary HCl/Kr/Xe mixtures.

Figure 2 represents the spectrum obtained from a HCl:Xe:Kr\(=1:5:500\) sample which has been extensively irradiated by ArF-excimer laser and thereafter annealed to 50 K. There are two characteristic peaks in the spectrum in the region of 1800–1400 cm\(^{-1}\), which appear during the thermal treatment of the matrix. One of them (at 1475.7 cm\(^{-1}\)) corresponds to the HCl/Kr thermally induced peak and the other (at 1664.4 cm\(^{-1}\)) corresponds to the HCl/Xe thermally induced peak, shifted 15 cm\(^{-1}\) to higher wave numbers from its value in pure Xe. The lower wave number peak of the thermally generated species of HCl/Kr (544 cm\(^{-1}\)) is also observed in the mixed matrices but the corresponding peak of HCl/Xe is too weak to be observed. This simple experiment indicates that the thermally induced peaks belong to two different species. Moreover, it suggests that each of the species involved contains at least one rare gas atom.

Similar experiment was made with HBr and Xe doped krypton (HBr:Xe:Kr\(=1:5:500\)). As reported previously,\(^7\) the thermal product after photolysis of HBr doped matrices was obtained only in Xe, even though the trapped hole was present in Xe and Kr, as indicated by the (XHX)\(^+\) (X = Xe or Kr) absorptions. In accordance with this, in the present mixed matrix case only one thermally induced peak was observed, located close to the value of the thermally induced absorption in the pure HBr/Xe system (at 1504 cm\(^{-1}\)). The wave number of the peak is 1524 cm\(^{-1}\), which corresponds to a shift of +20 cm\(^{-1}\) compared to its value in pure xenon. Figure 3 shows the spectrum of the thermal product in two different Xe/Kr matrices, and we may note that the intensity of the thermal product corresponds qualitatively to the concentration of Xe in the mixture and that the only species forming is similar to that found in the case of photolysis of HBr in pure Xe. Additionally, the wave number of the thermally induced species in mixed matrices approaches at higher Xe concentrations that obtained in pure Xe.

Based on deuterium shift and halogen dependence the thermally induced species contain one hydrogen atom and at least one halogen atom\(^7\) and on the basis of the present experiments at least one rare gas atom. We have also good reasons to assume that the strong thermally generated absorptions in the HI/Xe system belong to a similar species containing hydrogen, iodine, and Xe. Assuming the simplest possible formula for the species leaves us with two candidates, a charged or a neutral HXY, where Y may be Cl, Br or I with X = Xe and Y is only Cl in the case of X = Kr. The cases of Y being F will be discussed below.
Our recent ab initio studies of ArHY⁺, KrHY⁺, and XeHY⁺ (Y=Cl, Br, I) suggest both linear and bent ground state structures for these ions. According to the MP2/ECP+VP5(2p)⁸ computational approach the bent structures appear to be the lowest-energy species in the cases of KrHCl⁺, XeHCl⁺, and XeHBr⁺, while the lowest-energy structure for the others is linear. The calculated spectra of the linear species resemble the spectra of the thermally induced species in matrices. This causes a controversy for assigning the products as cations on the basis of the computed spectra, since it would require that in HCl/Kr, HCl/Xe, and HBr/Xe only higher energy species could be generated, while in HBr/Xe and HI/Xe only lower energy species are obtainable. There are also quite large discrepancies between the calculated and observed spectra. For example, for KrHBr the calculated wave number for the ω₁ fundamental is more than 500 cm⁻¹ higher than the observed wave number of the thermally generated species in Kr matrix. Also according to the calculations the species KrHBr⁺ and KrH⁺ be stable but they have not been observed in matrices. Additionally, the energetics for the possible formation of XHY⁺ species deserves some discussion. For example, the calculated lowest energy dissociation asymptote of XeHCl⁺ is given as Xe²⁺ + HCl and it is predicted to lie 0.067 eV above the energy of the linear XeHCl⁺. However, dissociation of the cation in a xenon cage would immediately lead to the formation of a Xe₂⁺ or a Xe³⁺ rather than Xe⁺. Taking into account the dissociation energy of Xe₂⁺ of 1.08 eV,⁴⁴ the actual dissociation asymptote of XeHCl⁺ is ~1 eV lower in energy than the linear form of the cation. This makes the existence of the XeHCl⁺ species in xenon environment rather improbable.

The vibrational spectra of ions shift more than the spectra of neutral species in going from one rare gas environment to the other. In Table II we present the vibrational wave numbers for some ions and neutral molecules in xenon and krypton matrices. Included are also for comparison the wave numbers of the thermally induced peaks of HCl/Xe and HBr/Xe mixtures. The relative vibrational shifts of the thermally induced peaks are between those of ions and hydrogen halides and the shifts support the assignment of the thermal products as neutral species, possessing a relatively strong dipole.

At first, it would seem impossible to form a bound ground state molecule out of a closed shell rare gas atom with a hydrogen and a halogen atom. However, encouraged by the results of Last and George¹⁵ on HXe⁺Cl⁻ we have carried out ab initio calculations at different levels. Indeed, the bound ground state structure of neutral HXY molecules is reproducible. Table III shows the calculated properties of the HXY (X=Ar, Kr, Xe; Y=Cl, Br, I) species. All of the optimized structures are linear. In the optimizations it was of crucial importance to start with bond lengths which were near the optimized values because too large values led the system into the repulsive part of the surface. The calculated parameters change somewhat when different basis sets are used, but qualitatively the picture stays the same. One impor-

### Table II. Observed wave numbers for hydrogen stretching in Kr and Xe matrices for some anions and neutral species.

<table>
<thead>
<tr>
<th>Species</th>
<th>ν(Kr)/cm⁻¹</th>
<th>ν(Xe)/cm⁻¹</th>
<th>Δν/cm⁻¹</th>
<th>Δν(Δν(Kr))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl²⁻</td>
<td>663¹</td>
<td>644¹</td>
<td>19</td>
<td>2.9%</td>
</tr>
<tr>
<td>HBr²⁻</td>
<td>255²</td>
<td>253²</td>
<td>20</td>
<td>0.8%</td>
</tr>
<tr>
<td>HCl</td>
<td>287³</td>
<td>285³</td>
<td>20</td>
<td>0.7%</td>
</tr>
<tr>
<td>HBr/Xe thermally induced peak</td>
<td>152⁴</td>
<td>150⁴</td>
<td>20</td>
<td>1.3%</td>
</tr>
<tr>
<td>HCl/Xe thermally induced peak</td>
<td>1664⁵</td>
<td>1649⁵</td>
<td>15</td>
<td>0.9%</td>
</tr>
</tbody>
</table>

¹From Ref. 6.
²From Ref. 7.
³This work.

### Table III. Ab initio calculated properties of neutral HXY species at different levels.

<table>
<thead>
<tr>
<th>Method</th>
<th>Rg–H (Å)</th>
<th>Rg–Hal (Å)</th>
<th>qH⁻</th>
<th>qRg⁺</th>
<th>qHal⁺</th>
<th>μ (D)</th>
<th>E (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HXeF UMP2/43333/43333/43 (Xe)/6-31G** (F)/6-311G**(H)</td>
<td>1.6687</td>
<td>2.1393</td>
<td>-0.073</td>
<td>+0.799</td>
<td>-0.707</td>
<td>6.1</td>
<td>-7 362 809 579 4</td>
</tr>
<tr>
<td>HXeCl UMP2/LANL1DZ</td>
<td>1.8085</td>
<td>2.7844</td>
<td>-0.041</td>
<td>+0.693</td>
<td>-0.652</td>
<td>8.9</td>
<td>-30 388 300 3</td>
</tr>
<tr>
<td>UMP2/ECF (Xe)/WBP (Cl)/6-31G**(H)</td>
<td>1.8098</td>
<td>2.8226</td>
<td>-0.016</td>
<td>+0.520</td>
<td>-0.504</td>
<td>6.9</td>
<td>-141 138 256 7</td>
</tr>
<tr>
<td>UMP2/43333/43333/43 (Xe)/5335111 (Cl)/6-31G**(H)</td>
<td>1.6736</td>
<td>2.8519</td>
<td>+0.040</td>
<td>+0.664</td>
<td>-0.704</td>
<td>10.7</td>
<td>-7 686 661 758 6</td>
</tr>
<tr>
<td>HXeBr UMP2/LANL1DZ</td>
<td>1.8690</td>
<td>2.9775</td>
<td>-0.036</td>
<td>+0.626</td>
<td>-0.590</td>
<td>8.8</td>
<td>-28 609 107 7</td>
</tr>
<tr>
<td>UMP2/ECP (Xe,Br)/6-31G**(H)</td>
<td>1.8490</td>
<td>3.0130</td>
<td>-0.004</td>
<td>+0.464</td>
<td>-0.460</td>
<td>6.9</td>
<td>-279 504 569 5</td>
</tr>
<tr>
<td>UMP2/43333/43333/43 (Xe)/43333/43 (Br)/6-31G**(H)</td>
<td>1.7801</td>
<td>2.9780</td>
<td>-0.011</td>
<td>+0.528</td>
<td>-0.518</td>
<td>7.7</td>
<td>-9 797 318 977 1</td>
</tr>
<tr>
<td>HXeI UMP2/LANL1DZ</td>
<td>2.0426</td>
<td>3.2391</td>
<td>-0.024</td>
<td>+0.512</td>
<td>-0.487</td>
<td>7.9</td>
<td>-26 836 799 6</td>
</tr>
<tr>
<td>UMP2/ECF(Xe,J)+VP5(2p)²</td>
<td>1.9157</td>
<td>3.2594</td>
<td>+0.002</td>
<td>+0.384</td>
<td>-0.386</td>
<td>6.3</td>
<td>-235 871 557 4</td>
</tr>
<tr>
<td>HXF UMP2/43333/43333/43 (Kr)/6-31G**(F)/6-311G**(H)</td>
<td>1.5256</td>
<td>2.0383</td>
<td>+0.026</td>
<td>+0.627</td>
<td>-0.652</td>
<td>6.2</td>
<td>-2 849 494 813 1</td>
</tr>
<tr>
<td>HXCl UMP2/ECF (Kr)/WBP (Cl)/6-31G**(H)</td>
<td>1.7348</td>
<td>2.6629</td>
<td>+0.040</td>
<td>+0.365</td>
<td>-0.405</td>
<td>5.5</td>
<td>-192 066 222 4</td>
</tr>
<tr>
<td>UMP2/43333/43333/43 (Kr)/5335111 (Cl)/6-31G**(H)</td>
<td>1.5337</td>
<td>2.6866</td>
<td>+0.135</td>
<td>+0.530</td>
<td>-0.665</td>
<td>10.2</td>
<td>-3 209 338 929 5</td>
</tr>
<tr>
<td>HArF UMP2/6-31G**</td>
<td>1.3928</td>
<td>1.9409</td>
<td>+0.045</td>
<td>+0.526</td>
<td>-0.571</td>
<td>5.1</td>
<td>-626 857 992 9</td>
</tr>
<tr>
<td>HArCl UMP2/6-31G**</td>
<td>1.3939</td>
<td>2.5013</td>
<td>+0.123</td>
<td>+0.450</td>
<td>-0.573</td>
<td>7.8</td>
<td>-986 902 985 4</td>
</tr>
</tbody>
</table>

⁴Partial atomic charges based on Mulliken population analysis.
tant result during the optimizations appeared; neither HKrBr nor HKrI could be optimized at any of the levels used in the calculations. This suggests that such molecules do not exist. This is in accordance also with the experiments, because in HBr doped krypton or in HI doped krypton no thermally induced peaks have been observed. Knowing these facts no attempts to optimize HArBr or HArI were made.

Inspection of the data given in Table III shows that these species are charge-transfer molecules. In all of them the rare gas has donated electron density to the halogen atom. As a consequence of a charge transfer the properties of the rare gas atom should approach those of the corresponding isoelectronic halogen atom. Also, at the extreme of charge separation the system looks like a HX$^-\!\!$-cation (which are strongly bound),$^{34,45,46}$ connected to a Y$^-\!\!$-anion. The calculations indicate that stretching the X–Y coordinate from its equilibrium value yields HX$^+$ and Y$^-$ as the dissociation asymptote. The existence of HXY charge-transfer molecules can be rationalized in terms of HX$^+$ and X$^+\!\!$Y$^-\!\!$ pair potentials which are both strongly bound.$^{34,47}$ As an example the HXe$^+$ and XeCl$^+$ potentials are displayed in Fig. 4. The difference in energy between ionic Xe$^-\!\!$Cl$^+$ and neutral XeCl at Xe$^-\!\!$Cl$^+$ equilibrium structure is given as

$$\Delta E(R=R_{e,ionic}) = IP(Xe) - EA(Cl) - D_e(Xe^+Cl^-)$$

Ignoring the last term as small compared with the other values gives

$$\Delta E = IP(Xe) - EA(Cl) - D_e(Xe^+Cl^-).$$

Inserting the following values: IP (Xe) = 12.130 eV, EA (Cl) = 3.613 eV, $D_e(Xe^+Cl^-) = 4.53$ eV (Ref. 51) gives the energy difference the value of 3.99 eV. Interaction of a hydrogen atom with Xe$^-\!\!$Cl$^+$ yields (Xe–H)$^+$-type of bond, which lowers the energy of the molecule by the value, which maximally could be the dissociation energy of XeH$^+$ [$D_{e}(XeH^+)=3.90$ eV (Ref. 34)]. Assuming that the H–Xe bond length in HXeCl charge-transfer molecule is only slightly larger than the equilibrium value of the HXe$^+$ bond length we are led to a situation where the HXeCl molecule could be lower in energy than a repulsive H$+$Xe$+$Cl$^-$ configuration. The reason for this is the shape of the neutral H–Xe potential which raises the energy of the repulsive configuration when Xe–H separation approaches the equilibrium value of (XeH)$^+$. These considerations suggest that when H, Xe, and Cl atoms are forced to approach each other, the charge-transfer molecule becomes a minimum energy configuration. In order to check the idea we have calculated the minimum energy dissociation path for HXeCl by stretching the H–Xe coordinate and optimizing the Xe–Cl coordinate at each H–Xe value. The results are shown in Fig. 5. It can be seen that at the minimum energy configuration ionic HXeCl is lower in energy than the repulsive triplet state. At larger values for H–Xe and Xe–Cl bond distances the triplet state becomes lower in energy. Thus, once formed, the HXeCl charge-transfer molecule is stable at a local minimum configuration. The possible stabilizing consequences of solution in the solid environment will be discussed later.

![Fig. 4. Energetics of different diatomic combinations for HXeCl. The energy of the XeH$^+$ surface in the upper panel is scaled to 12.13 eV at infinite separation (ionization energy of Xe). The data for construction of the graphs is taken from Ref. 47 for XeH$^+$, and Refs. 48 for XeCl$^+$, from Ref. 49 for Xe$+$H, and from Refs. 34 and 45 for XeH$^+$](image-url)
which are 1.6028 Å, 1.4212 Å, and 1.2804 Å for XeH

on neon compounds have not been attempted.

The computed hydrogen-rare-gas bond length is quite

sensitive to the basis set used. For example in HXeI it re-

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sensitive to the basis set used. For example in HXeI it re-

duces 0.2286 Å in going from LANL1DZ basis set to the

TABLE IV. Ab initio calculated harmonic wave numbers of neutral HXY species at different levels. Numbers in parentheses are intensities (km/mol).

<table>
<thead>
<tr>
<th>Method</th>
<th>$v_{Xe-Hal}$</th>
<th>$\delta_{H-Xe-Hal}$</th>
<th>$v_{H-Xe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HXeF</td>
<td>495.7(121)</td>
<td>738.6 (14)</td>
<td>2059.7 (649)</td>
</tr>
<tr>
<td>HXeCl</td>
<td>262.0 (26)</td>
<td>503.4 (5)</td>
<td>1246.2 (313)</td>
</tr>
<tr>
<td>HXeBr</td>
<td>177.7 (2)</td>
<td>455.1 (3)</td>
<td>1008.4 (4177)</td>
</tr>
<tr>
<td>HKrF</td>
<td>101.7 (89)</td>
<td>355.7 (3)</td>
<td>536.0 (3885)</td>
</tr>
<tr>
<td>HKrCl</td>
<td>131.7 (23)</td>
<td>404.5 (0.1)</td>
<td>899.8 (7595)</td>
</tr>
<tr>
<td>HArF</td>
<td>535.6(105)</td>
<td>782.7 (0)</td>
<td>1973.7 (1563)</td>
</tr>
<tr>
<td>HArCl</td>
<td>235.0 (83)</td>
<td>492.6 (1.6)</td>
<td>977.4 (4581)</td>
</tr>
</tbody>
</table>

$^a$Experimental relative intensities based on integrated peak areas. Higher intensity has been given a value of 1000.
MECHANISTIC ASPECTS

The HXY species are metastable with respect to dissociation into hydrogen halides and rare gas atoms, and also with respect to dissociation into neutral atoms, as discussed previously. In order to get a qualitative insight of the formation route, we have calculated the energetics of the possible precursors \([(\text{HXe}^+ + \text{Cl}^-), (\text{HCl} + \text{Xe}), \text{and} (\text{H} + \text{Xe} + \text{Cl})]\) of HXeCl at the UMP2/LANL1DZ-level. The results are presented in Fig. 6. It can be seen that HXeCl is higher in energy than the infinitely separated atoms. However, in a solid rare gas environment the energy of a strong dipole HXeCl is lowered due to solvation in the dielectric medium. This is probably a very important effect when considering the stability of HXY-charge-transfer molecules. As a numerical example we can take the difference of the B→X transition of XeCl in gas phase and in solid Xe, yielding a value of 0.53 eV attributable to solvation of Xe\(^{+}\)Cl\(^{-}\) in Xe.\(^{10}\) Knowing that HXeCl is formed by annealing the matrix it seems clear, that it cannot be formed from neutral atoms. Warming up the matrix should drive the reaction into the direction in which lower energy species are formed. Also considering the repulsive nature of neutral H–Xe and Xe–Cl potentials leaves us with the conclusion, that ions must take part in the formation process of HXeCl and related species.

One possible formation route could be the following: After extensive irradiation of a hydrogen-halide doped rare-gas matrix there are several neutral and ionic species present in the matrix, including halogen ions, hydrogen atoms and trapped Rg\(_n^+\)-centers.\(^{12}\) The range of migration of hydrogen atom from the site of photodissociation is not known but some of the hydrogen atoms may be located near the halogen ions, which are surrounded by rare-gas atoms. The charge-transfer excitation may provide the hole with enough kinetic energy to escape the precursor site.

\[
\begin{align*}
Y^− \cdots X \cdots H \cdots (X)_m \cdots X_n^+ \\
\text{or} \\
Y^− \cdots (X_m) \cdots (XHY)^+.
\end{align*}
\]

Annealing the matrix would then result in mobilization of the trapped holes and subsequent neutralization of charges. Consequently, a reaction of a thermally mobilized hole (MH) with a \(Y^− \cdots X \cdots H\)-center could result in the formation of a high energy neutral YXY-species.

\[
Y^− \cdots X \cdots H + MH \rightarrow YXH.
\]

The formation temperature of HXY-species correlates well with the temperature in which thermoluminescence from the matrix is detected, resulting from mobile holes neutralizing negative ions.\(^{12}\) Another reaction which could produce HXY is a reaction of \(X^+Y^−\) with a hydrogen atom

\[
X^+Y^− + H \rightarrow HXY.
\]

Fajardo and Apkarian\(^{10}\) have demonstrated that Xe\(^+\)Cl\(^−\) in Xe forms readily the triatomic configuration Xe\(^2+\)Cl\(^−\), which then relaxes radiatively,

\[
\text{Xe}^+\Cl^- + \text{Xe} \rightarrow \text{Xe}^2+\Cl^- \xrightarrow{573 \text{ nm}} 2\text{Xe} + \Cl^-.
\]

X\(^+\)Y\(^−\) is formed by UV-irradiation and it is possible that also HXY is formed simultaneously. However, this reaction cannot produce HXY in significant amounts because irradiation also destroys it.\(^7\) One more possible formation route for HXY would be the reaction of a proton with a XY\(^−\) center,

\[
H^+ + Y^− \rightarrow XHY.
\]

This mechanism has to be rejected because in the rare gas matrices proton is stabilized in the form of (XHY)^+\(^\cdot\), and the disappearance of these cationic centers is not correlated with the formation of the HXY charge-transfer molecules.

Because the HXY species are metastable with respect to dissociation to atoms or HY and X, it is important to investigate the potential barrier heights in order to find out how stable the species are. It is known from annealing experiments, that in xenon and krypton matrices HXeCl, HXeBr, HXeI, and HKrCl are stable up to the sublimation temperature at the solid. We have scanned the potential energy surface of the linear molecule is presented in Fig. 7. In order to find the height of the potential barrier we have calculated the minimum energy path to dissociation by stretching the Ar–H bond and optimizing the Ar–F bond length at each fixed value of Ar–H. The results are given in Fig. 8 indicating a barrier of \(-0.18\) eV. We have also calculated a few points of the minimum energy path with respect to the bending coordinate of HArF. The results indicate the barrier height of at least 0.48 eV, which is larger than the barrier height with respect to stretching of the linear configuration. The highly correlated calculations of barrier heights for other HXY species is beyond the scope of this paper.
In this paper we have shown that the strong infrared absorbers in Kr and Xe matrices, originating from photodissociation of hydrogen halides and subsequent annealing of the matrix, are neutral charge-transfer species of type \( \text{HX}^+\text{Y}^- \). The four compounds observed so far are \( \text{HXeI}, \text{HXeBr}, \text{HXeCl}, \text{and HKrCl} \). The identification is based on experiments where \( \text{HX} \text{Y} \) species are systematically generated in mixed rare gas matrices, as well as on extensive \textit{ab initio} calculations. Agreement between the stabilities of the calculated \( \text{HX} \text{Y} \) species and the observed thermally generated species is excellent. Also, the computed spectra (including intensities) agree with the experimental ones. The high-energy \( \text{HX} \text{Y} \) species possess extensive ionic nature in the \( \text{HX}^+\text{Y}^- \) bond, making these molecules very strong absorbers in the infrared. These species are formed from ionic precursors.

**CONCLUSIONS**

Given a dissociation barrier height of 0.18 eV for \( \text{HArF} \) it is expected that krypton and xenon compounds are even more stable than the heavier rare gas atoms have lower ionization potentials and are more polarizable than Ar. Lower ionization potential leads to more efficient charge separation between X and Y which in turn strengthens the H–X bond. Finally, if the potential barrier were very low it would lead to tunneling to the repulsive surface. However, tunneling effects are not observed (all the species are stable at 15 K), which indicates significant height for the barrier between the bound and repulsive configurations. Theoretical, computational, and experimental work considering the new rare gas compounds is strongly encouraged.

**ACKNOWLEDGMENTS**

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17. C. Möller and M. S. Plesset, Phys. Rev. 46, 618 (1934).