Neutral Xenon Hydrides in Solid Neon and Their Intrinsic Stability[†]

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Halogen xenon hydrides ClXeH and BrXeH, their deuterated analogues, and tentatively the HXeH dihydrides were generated in solid neon matrices and characterized by infrared absorption spectroscopy. Preparation of these interesting species in the weakly interacting neon matrix, as well as extensive density functional theory calculations, suggests that their observation is not solely due to stabilization by the matrix but that they should be capable of independent existence.

Introduction

Even though several small ions or metastable species involving rare gases were known for a long time, until fairly recently, their rare gas elements were generally regarded as chemically inert. In 1962, Bartlett showed in his trailblazing study[1,2] that they are capable of forming what one could consider as normal chemical compounds, compelling chemists to readjust considerably their thinking regarding these elements. In a burst of activity in the years that followed, a number of compounds of noble gases have been reported.[3−7] While many of these can be regarded as metastable species, several are actually thermodynamically stable compounds and can be obtained commercially. For example, xenon difluoride has found a relatively widespread use as a fluorinating agent and has useful applications in semiconductor processing for etching silicon.

Very shortly after the discovery of rare gas compounds, matrix isolation specialists made considerable contributions to the understanding of their chemistry, with, for instance, xenon dichloride,[8] krypton difluoride,[9] and mixed xenon chlorofluoride[10] having been characterized. Infrared spectra of the HAr_2^+ and HKr_2^+ species have also been observed, although initially their structure and ionic nature were in doubt;[11] however, recent calculations helped to clarify the exact structure.[12,13] Progress in the following 20−30 years was then relatively slow, with the chemistry of rare gases being effectively restricted to a few compounds of xenon involving the most electronegative elements, fluorine or oxygen. Quite recently, a new breakthrough in this direction occurred in the laboratory of Räsänen, when a whole group of novel neutral rare gas compounds was observed. These included not only several hydrido-halogenides of the type HRgX with both a halogen (Cl, Br, or I) and a hydrogen (or deuterium) atom bound to Kr or Xe[14] but also the symmetric dihydrides[15] as well as several compounds with CN, SH, and other groups bound directly to the rare gas.[16,17]

While these species were carefully characterized, the question remained as to the ability of the molecules to exist outside the stabilizing environment of the polarizable xenon or krypton host matrix.[18] To address this question, we explore in the present paper the properties and the chemistry of these species in solid neon, where any stabilization due to the solvent will be appreciably diminished with respect to the heavier rare gases. We also explore the question of solvent stabilization by extending our earlier theoretical computations with additional rare gas atom interactions with the HRgY species. We believe that the results show clearly that solvent stabilization is not essential, at least in the case of HXeCl and HXeBr, and that once prepared, the species should be capable of existence as free gas-phase molecules.

Experimental Section

To produce the samples in our experiments, commercially available HBr and HCl gases (Aldrich, purity >99.8%) were used. HI was produced in a standard way by reduction of the halogen by red phosphorus and water. The corresponding deuterated halides could be generated by substituting D_2O for regular water. After extensive passivation of the gas system was performed, mixtures of the neon matrix gas (Messer-Griesheim, purity >99.999%) with xenon (Messer-Griesheim, purity >99.998%) and the hydrogen halides were prepared by standard volumetric techniques. Concentrations of the hydrogen halides relative to the matrix gas were in the range of 1:1000−1:20000, while the xenon:hydrogen halide ratio varied from 0.5:1 to 10:1.

Samples were deposited on a copper mirror substrate cooled by a Leybold RGD 580 closed-cycle refrigerator. While it should be nominally capable to attain 6 K, currently its base temperature is only about 8 K. The premixed gas was expanded via a pulsed valve through a 1-mm orifice using a backing pressure of about 2 bar and condensed on the 8 K substrate. The samples could then be irradiated by means of an excimer ArF laser, operating at 10 Hz and delivering ≈10 mJ/pulse at 193 nm. Following the irradiation procedure, the samples could be annealed by carefully raising the substrate temperature to 10−12 K, but attempts to increase the temperature much beyond 12 K usually resulted in an irreversible loss of the matrix.

The samples were investigated spectroscopically using a Bruker IFS 120 HR Fourier transform spectrometer equipped with beam splitters and detectors for the 500−30 000 cm^{-1} spectral range. In most experiments, a background infrared spectrum was first recorded using a MCT (mercury−cadmium telluride) detector in the spectral range of 500−4000 cm^{-1} with

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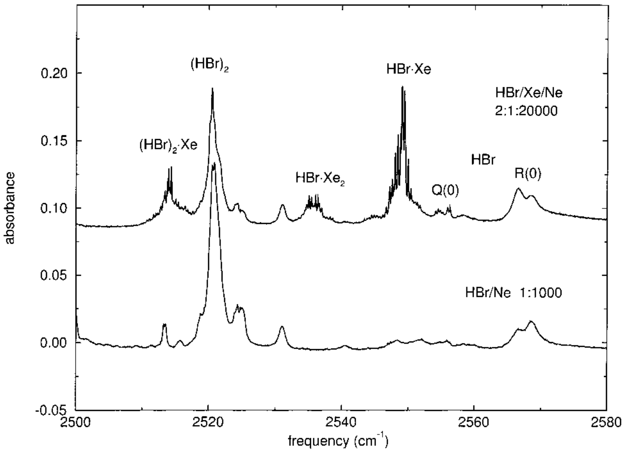

Figure 1. IR absorption spectra of hydrogen bromide in neon matrices. The bottom trace shows a sample of HBr:Ne = 1:1000, the upper trace shows a more dilute sample with a very minor amount of added xenon. The former spectrum shows only the Q(0) and R(0) lines of HBr, as well as bands due to (HBr)$_n$ aggregates. The latter spectrum exhibits clearly additional bands due to the HBr complexes with xenon.

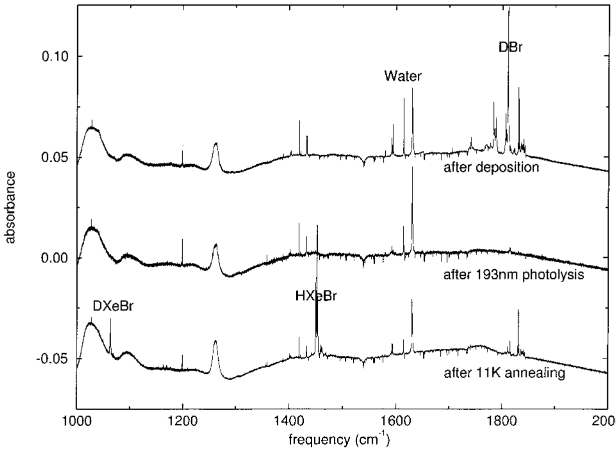

Figure 2. Series of spectra of an HBr/DBr:Xe:Ne mixture showing the xenon compound formation process. DBr (and HBr) bands present in the top trace right after deposition disappear completely after extended 193-nm irradiation (middle trace). Annealing of the sample at 12 K allows H atom diffusion and leads to appearance of bands of the HXeBr and the DXeBr products.

0.06 cm^{-1} resolution. Subsequently, the spectra were recorded after sample deposition, after different periods of 193-nm photolysis, and finally again after careful annealing of the sample by raising its temperature to the desired value, typically 10−12 K, for times ranging from 5 to 20 min.

Results and Discussion

In the previous studies, the HRgY species were in most cases prepared by photolyzing hydrogen halides HY in a matrix of a rare gas Rg and by subsequent annealing of the samples.[14,15] Irradiation of the samples results in a permanent dissociation of the HY species and presumably in the formation of halogen and hydrogen atoms. The presence of halogen atoms is evidenced by the infrared absorption bands due to the $Y_{3/2} \leftrightarrows Y_{1/2}$ transition between the ground-state spin−orbit components that appear in the irradiated samples near 3600 cm^{-1} in Br and ≈7600 cm^{-1} in I.[19] Subsequent controlled annealing of the matrices results then in diffusion of hydrogen and is accompanied by the growth of strong absorption bands of the products, assigned to the HRgY species. In several investigations of these species, it was suggested that they are strongly ionic structures of the type HRg^+Y^-.[14,18] We have recently investigated proton solvation in rare gases and have shown that the effectively dimensionless proton will always be solvated by two rare gas atoms.[20] This naturally raised the question of whether the stability of the HRgY species could be due to the stabilization by the rare gas solvent, that is, if they could actually be considered to be the four-atom species $(RgHRg)^+Y^-$. We use here two approaches to test this question: we examine the solvation of the HRgY species by rare gases and the stability of the $(RgHRg)^+Y^-$ four-atom species by density functional calculations, and we try to prepare the HRgY species in solid neon, where, in view of the much lower polarizability and high ionization potential of neon atoms, the stabilizing effect of the rare gas solvent should be negligible.

The infrared spectra of even the most diluted HY/Xe/neon samples measured immediately after deposition contained not only the monomeric HY bands but also rather strong dimer and trimer absorptions (see Figure 1). This is in part due to formation of the complexes in the supersonic expansion and during deposition on the matrix surface and may also be contributed to the relatively high 8 K temperature of the matrix substrate. The spectra are, however, somewhat misleading, since hydrogen bonding greatly enhances the oscillator strength of the YH absorptions, in some cases by more than an order of magnitude.[21]

In the presence of xenon, additional strong and sharp bands appear in the spectrum, which can be identified as YH−Xe species, complexes of the hydrogen halide with a xenon atom. The complex formation results in a red shift of the HY infrared absorption and again in a considerable enhancement of its intensity.

From the experimental point of view, it was most expedient to study the photolysis of HBr since its absorption overlaps well the 193-nm line of the argon fluoride laser. When exposed to the 193-nm line, the HBr samples are bleached quite effectively, so that after some 60 min the absorptions of both the $(HBr)_n$ aggregates and the monomeric hydrogen bromide disappear almost completely. Although BrH−Xe photolyzes less efficiently than the free species, even these complexes are bleached after an extended irradiation. The photochemistry of hydrogen halides in rare gas matrices, as well as the effect of hydrogen bonding, was studied in detail in a recent publication.[21]

More dilute samples (HBr:Xe:Ne = 1:1:10000) immediately after UV irradiation show little evidence of any new rare gas compound formation. When, however, the samples are carefully annealed to temperatures above ≈9.5 K, allowing hydrogen atom diffusion, a group of strong, sharp bands appears near 1450 cm^{-1}, as shown in the lowest trace of Figure 2. Specifically, new bands grow in at 1436.61, 1442.61, 1450.49, and 1452.57 cm^{-1}, with the latter two being favored with increasing dilution of the samples. Prolonging the sample annealing and increasing the annealing temperature results in a gradual disappearance of the lower frequency absorptions, and the intensity shifts in favor of the 1452.57 cm^{-1} band. In more concentrated samples, some absorption in this region, and in particular the 1442.61 cm^{-1} band, appears immediately after the sample irradiation, but the intensity again increases drastically upon annealing, with intensity shifting to the higher frequency 1450.49 and 1452.57 cm^{-1} absorptions.

These bands clearly correspond to the H−Xe stretching frequency of the HXeBr molecule. With increasing xenon concentration, additional bands probably due to species involving more than one Xe atom appear at higher energies, and when the concentration of xenon is increased to 1%, the 1452 cm^{-1}

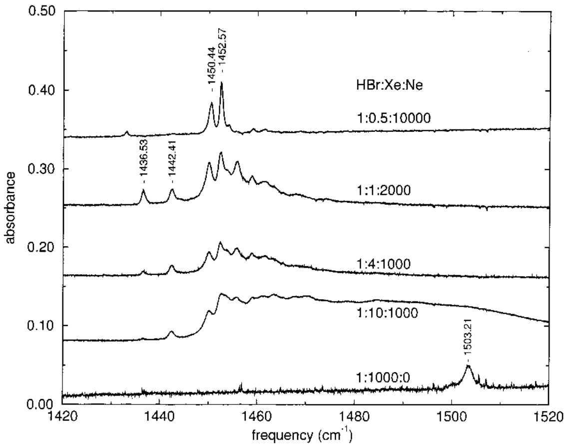

Figure 3. Hydrogen stretching vibration of HXeBr in solid neon in samples with different Xe concentrations. As the Xe concentration is increased, the absorptions broaden and shift toward blue. The lowest trace shows the HXeBr band in a pure xenon matrix.

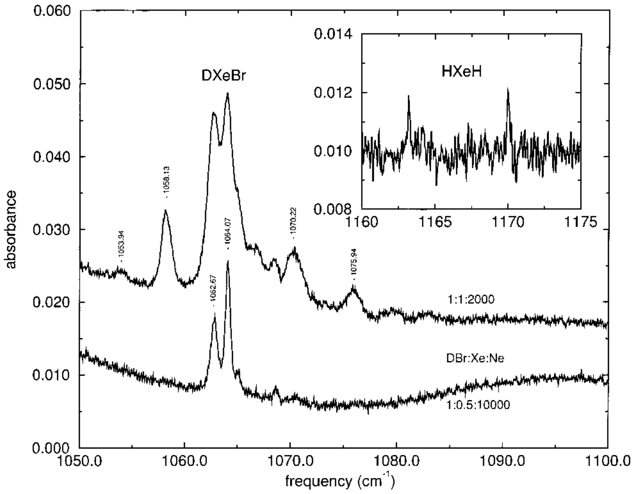

Figure 4. Hydrogen stretching vibration of DXeBr in solid neon using two different xenon concentrations. The inset shows the very weak absorptions at 1163.19 and 1169.98 cm^{-1} of a highly diluted HBr:Xe:Ne = 1:0.5:10000 matrix after photolysis and annealing at 12 K. These absorptions are assigned tentatively to the asymmetric stretch of HXeH (two sites).

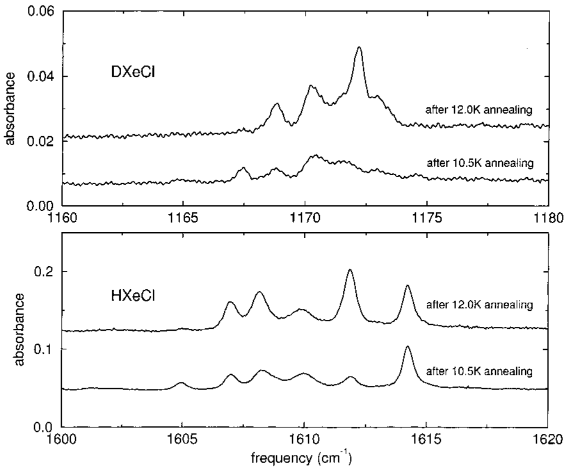

Figure 5. Effect of annealing upon site distribution. Spectra show the hydrogen stretching vibrations of HXeCl and DXeCl in a sample of H(D)Br:Xe:Ne = 1:0.5:10000.

absorption is followed by a broad structured absorption extending to beyond 1503.2 cm^{-1}, the position of the corresponding HXeBr absorption in a pure xenon matrix.[14] This dependence on the xenon concentration is shown in Figure 3.

The HXeBr bands shift appropriately in deuterated samples, as can be seen in Figure 4. A nearly identical pattern of bands appears near 1050 cm^{-1}, with the DXeBr bands at 1053.94, 1058.13, 1062.67 and 1064.07 cm^{-1} mirroring the four major sharp bands in the HXeBr region. Increasing the sample dilution and annealing the sample more thoroughly again favor the highest frequency 1064.07 cm^{-1} band. In neon, the frequencies are again considerably red-shifted as compared with the 1100 cm^{-1} absorption band in a pure xenon matrix. Besides the xenon hydrogen bromide, in the most dilute experiments, the diffusion also produced absorptions bands at 1163.19 and 1169.98 cm^{-1} (see insert of Figure 4), very close to bands assigned in solid xenon to the xenon dihydride. Accordingly, we assign these neon matrix bands somewhat tentatively also to the HXeH species.

Irradiation of the samples using a tungsten lamp was found to photolyze very efficiently the HXeBr species. This confirmed their relatively labile nature but also prevented meaningful measurements of their visible and near-IR absorption spectra. After these species were decomposed and their absorptions were bleached, only a very minor amount could be regenerated by additional annealing and diffusion. This suggests that the reaction involved is probably not dissociation to H + XeBr (or HXe + Br) but more likely to bromine−hydrogen recombination and presumably conversion to the BrH−Xe “isomer”. Similar photoinstability has also been observed in pure xenon matrices.[14]

It is interesting to note that around 9 K, where we observe the onset of long-range hydrogen diffusion in solid neon and formation of the HXeY molecules, changes in the matrix Raman spectrum were previously observed and interpreted in terms of a partial hcp-fcc phase transition.[22] If this is accepted, it is conceivable that the onset of global hydrogen mobility is connected with such a phase transition.

Hydrogen chloride absorption occurs at considerably higher energies than those of hydrogen bromide and are therefore not efficiently excited by the 193-nm laser. Only after a very prolonged irradiation there is a minor photolysis of the HCl monomer, with basically no change in the sharp, spectrally shifted absorptions of the ClH···Xe complexes. Annealing of such irradiated samples leads to growth of absorptions due to the HXeCl species (see Figure 5). These, like the corresponding bromine compound, exhibit in solid neon several distinct trapping sites, all of them again considerably red-shifted as compared with their positions in pure xenon. In samples thoroughly annealed to 11−12 K, the HXeCl absorptions concentrate into a quintet at 1607.03, 1608.25, 1609.88, *1611.80*, and 1614.22 cm^{-1}, with the italicized fourth component being the strongest. Using a deuterated sample, the corresponding DXeCl absorptions appear at 1167.40, 1168.75, 1170.33, *1172.14*, and 1172.96 cm^{-1}.

When an HBr impurity was added to the HCl/Ne sample, this of course could be photolyzed very efficiently, as did the mixed HBr−HCl complexes, and annealing of such irradiated mixed samples led also to an enhanced formation of the HXeCl species. This may be due to the reaction HCl + H → H_2 + Cl, followed by reactions of the Cl atom with Xe and eventually with another hydrogen atom. Interestingly, even though the 193-nm laser line overlaps ideally with the HI absorption, and indeed HI is easily photolyzed in solid neon, we had no success trying to generate the corresponding HXeI compound by annealing of the photolyzed matrices. This may either be due to an intrinsic instability of the iodine compound, which needs the stabilizing environment of solid xenon, or perhaps due to the dynamics of

TABLE 1: $\nu_{\mathrm{H-Rg}}$ (cm^{-1}) for H(D)RgY Molecules in Solid Xe and Ne

species	xenon[a]	neon after 12 K annealing
HKrCl	1476	−[b]
DKrCl	1106	−
HXeCl	1648	1607.03, 1608.25, 1609.88, *1611.80*,[c] 1614.22
DXeCl	1198	1167.40, 1168.75, 1170.49, *1172.14*, 1172.96
HXeBr	1504	1436.61, 1442.61, *1450.49*, *1452.57*
DXeBr	1100	1053.94, 1058.13, *1062.67*, *1064.07*
HXeI	1193	−
DXeI	893	−
HXeH	1166, 1181	1163.19, 1169.98

[a] From refs 14 and 15. [b] Tried to observe but failed. [c] Strongest absorptions are italicized.

the matrix diffusion and reaction, which do not favor the compound formation in solid neon. In this connection, it is appropriate to note that theoretical calculations also predict the HXeI molecules to be bound considerably more weakly than the corresponding bromide or chloride.[18] The lower stability of the HXeI species is also evidenced by the observation that in solid xenon it can be readily photolyzed by infrared excitation near 3000 cm^{-1}, caused by the low dissociation energy $D_0 = 2950$ cm^{-1}.[23]

If one considers more closely the problem of the mechanism of their formation, it is, in fact, remarkable that the HRgY compounds form in solid neon with an efficiency comparable to that in solid xenon. They are undoubtedly formed when lighter and more mobile hydrogen atoms diffuse through the matrix and eventually approach an RgY, e.g., XeBr, complex. The substitutional Br atom will presumably have 12 nearest neighbor xenons, and regardless of the direction of approach, when the hydrogen reaches the second solvation shell, there will be a quasi-linear H−Xe−Br configuration appropriate for HXeBr formation.[18] The situation is quite different in solid neon, where even if a XeBr complex is already present, only one of the bromine nearest neighbors is xenon, and the approaching hydrogen would thus appear to have a less than 10% chance of arriving exactly from the right direction. One might thus expect that, in more than 90% of events, the hydrogen will encounter the halogen and find the global minimum on the potential surface, that is, the BrH−Xe complex rather than the shallow, much less stable HXeBr local minimum.

To explain the experimental observation that this does apparently not occur, that the hydrogen bromide recombination is relatively minor, and that the HXeBr forms efficiently, we have proposed that each matrix-isolated atom can be viewed as being surrounded by a protective solvation shell of the matrix atoms. Since the interaction of the guest atom with the rare gas atoms is usually stronger than the interaction between two rare gas atoms themselves, such a shell may be relatively stable, and the activation energy for penetrating it may be considerably higher than that for diffusion through the pure matrix. If the barrier for penetrating such a solvation shell around Cl or Br atoms in neon were too high to overcome at 10−11 K, where the H atom diffusion takes place, this would explain why the hydrogen halide recombination is relatively inefficient. The hydrogen would then preferentially have to attack the Xe−Br complex from the xenon side—supposing such a solvation shell around the xenon atom is easier to penetrate than that around the halogen—explaining the efficient HXeBr formation. Extending this idea, in the case of the large iodine atom, the neon solvation shell might be less stable and more penetrable, and this could lead to efficient HI recombination and provide an alternative explanation for our failure to observe the HXeI species in solid neon.

The vibrational frequencies of the HXeY and the DXeY species observed in this work are listed in Table 1 and compared with the values previously found in solid xenon. The comparison reveals a rather large matrix effect, with the frequencies being appreciably blue-shifted when going from neon to xenon. The guest−host interactions are quite complex, and their magnitude and direction depend on the nature of the trapping site, polarizabilities of both the guest and the host, and a number of other factors. Very large matrix shifts are, in general, indicative of ionic or strongly polar bonds. The bonds in the HXeY molecules indeed have a partial ionic character, and the relatively large blue shifts observed could be rationalized by stabilization of the polar structures by the polarizable xenon solvent.

Theoretical Calculations

As explained in the Introduction, the considerable stability of the linear RgHRg$^+$ ions led to the question of whether the HRgY compounds in the matrix could be viewed as RgHRg$^+$Y$^-$ species, rather than as HRg$^+$Y$^-$ species as previously proposed and whether they owe their stability to the stabilizing effect of the matrix. To explore this idea, we have carried out density functional calculations on these systems using the Gaussian 94 program package.[24] Most of the calculations were carried out by the hybrid B3LYP method, although several results were checked by other methods. On the light atoms (H and F), all electrons were explicitly treated with the 6-311++G(3df,3pd) basis sets. For the heavier halogens, Kr and Xe, the quasi-relativistic effective core potential 6s6p1d/4s4p1d basis sets of the Stuttgart/Dresden groups were used.[25]

Some of the results are summarized in Table 2. The calculated geometries and vibrational frequencies for the HRgY species are in good agreement with the previous theoretical results,[14] and they overestimate somewhat the frequencies observed in solid neon. To check the effect of additional solvation, we have optimized the four-atom RgHRgY species, starting from the geometry one might expect for the RgHRg$^+$Y$^-$ species, that is, from the optimized geometry of RgHRg$^+$, with the halogen at a relatively large distance from one of the rare gas atoms. As one can see in Figure 6, the optimization smoothly converged to a Rg⋯HRgY geometry, yielding the HRgY species with an

TABLE 2: Computational Properties of Different (Xe)HXeY Molecules at the B3LYP/6-311++G(3df,3pd)/SECP Level[a]

	r(Xe⋯H)	r(H−Xe)	r(Xe−Y)	ν(Xe−Y)	δ(HXeY)	ν(H−Xe)
HXeF		1.6915	2.1670	434.0 (153)	603.2 (0.9)	1882.8 (401)
Xe⋯HXeF	4.5082	1.6914	2.1670	433.9 (160)	610.3 (1.1)	1883.7 (403)
HXeCl		1.7252	2.6884	246.8 (64)	523.2 (0.5)	1698.0 (1148)
Xe⋯HXeCl	4.0798	1.7248	2.6898	246.2 (68)	531.0 (0.5)	1699.5 (1133)
HXeBr		1.7437	2.8437	172.5 (30)	499.4 (0.6)	1616.9 (1518)
Xe⋯HXeBr	4.1961	1.7431	2.8449	172.1 (33)	509.0 (0.5)	1618.5 (1524)
HXeI		1.7749	3.0756	137.1 (17)	468.0 (0.5)	1491.3 (2163)
Xe⋯HXeI	4.4708	1.7744	3.0763	136.9 (18)	477.0 (0.5)	1493.2 (2210)

[a] Bond lengths are given in Å, and harmonic vibrational frequencies are given in cm^{-1}, with the corresponding intensities (km/mol) in parentheses.

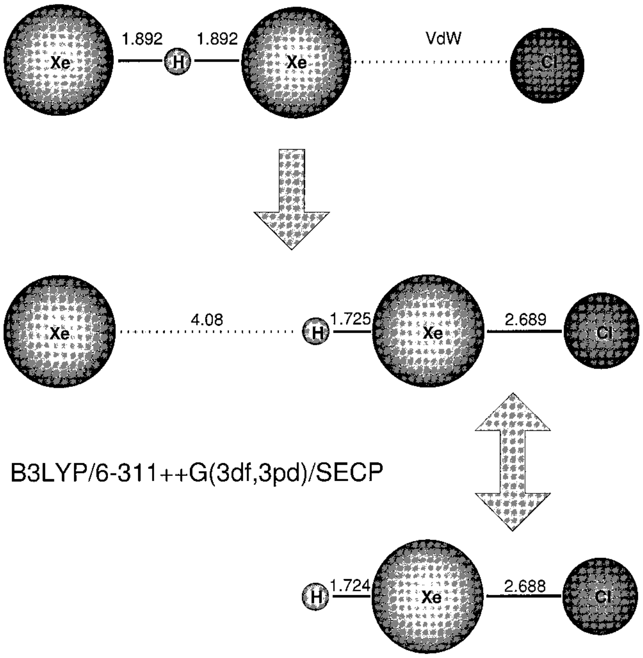

Figure 6. Schematic representation of the DFT (B3LYP) geometry optimization of XeHXeCl. Starting from a linear $(XeHXe)^+$ cation and a Cl^- anion at a large distance, the calculation smoothly converges to an HXeCl molecule, with the second Xe atom being pushed left to a distance appropriate for a weak van der Waals bond. The resulting geometry of the HXeCl "perturbed" by the second Xe atom is almost identical to that of the "free" HXeCl.

almost identical geometry and frequencies as obtained from the triatomic calculations. The remaining rare gas atom was pushed away to a comfortably large van der Waals distance. This result, coupled with the ability of the HRgY compounds to exist in the weakly interacting neon matrix, provides a strong evidence that these do not owe their existence solely to the stabilization by the matrix but should be capable of independent existence as free gas-phase molecules.

Summary

The infrared spectra of the noble gas compounds HXeCl, HXeBr, and their deuterated analogues, and possibly also of the xenon dihydride molecules were observed in solid neon. Their detection in the weakly interacting neon suggests that they should be capable of existence as free molecules even without the stabilization effect of the matrix, a conclusion supported also by density functional theory (DFT) calculations. A mechanism for the formation of these xenon compounds is proposed, explaining the observation that they form in the highly diluted neon matrices with similar efficiencies as in solid xenon.

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