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## Noble-Gas Hydrides: New Chemistry at Low Temperatures

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### CON SPECTUS

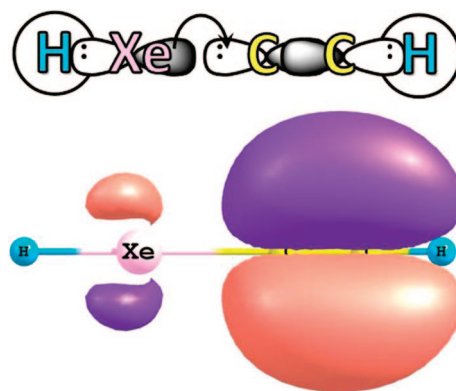
Noble-gas chemistry has been undergoing a renaissance in recent years, due in large part to noble-gas hydrides, HNgY, where Ng = noble-gas atom and Y = electronegative fragment. These molecules are exceptional because of their relatively weak bonding and large dipole moments, which lead to strongly enhanced effects of the environment, complexation, and reactions. In this Account, we discuss the matrix-isolation synthesis of noble-gas hydrides, their spectroscopic and structural properties, and their stabilities.

This family of species was discovered in 1995 and now has 23 members that are prepared in noble-gas matrices (HXeBr, HKrCl, HXeH, HXeOH, HXeO, etc.). The preparations of the first neutral argon molecule, HArF, and halogen-free organic noble-gas molecules (HXeCCH, HXeCC, HKrCCH, etc.) are important highlights of the field. These molecules are formed by the neutral  $H + Ng + Y$  channel. The first addition reaction involving HNgY molecules was  $HXeCC + Xe + H \rightarrow HXeCCXeH$ , and this led to the first hydride with two noble-gas atoms (recently extended by HXeOXeH). The experimental synthesis of HNgY molecules starts with production of H and Y fragments in solid noble gas via the UV photolysis of suitable precursors. The HNgY molecules mainly form upon thermal mobilization of the fragments.

One of the unusual properties of these molecules is the hindered rotation of some HNgY molecules in solid matrices; this has been theoretically modeled. HNgY molecules also have unusual solvation effects, and the H–Xe stretching mode shifts to higher frequencies (up to about  $150\text{ cm}^{-1}$ ) upon interaction with other species.

The noble hydrides have a new bonding motif: HNgY molecules can be represented in the form  $(H-Ng)^+Y^-$ , where  $(H-Ng)^+$  is mainly covalent, whereas the interaction between  $(HNg)^+$  and  $Y^-$  is predominantly ionic. The HNgY molecules are highly metastable species representing high-energy materials. The decomposition process  $HNgY \rightarrow Ng + HY$  is always strongly exoergic; however, the decomposition is prevented by high barriers, for instance, about 2 eV for HXeCCH. The other decomposition channel  $HNgY \rightarrow H + Ng + Y$  is endothermic for all prepared molecules.

Areas that appear promising for further study include the extension of argon chemistry, preparation of new bonds with noble-gas atoms (such as Xe–Si bond), and studies of radon compounds. The calculations suggest the existence of related polymers, aggregates, and even HNgY crystals, and their experimental preparation is a major challenge. Another interesting task, still in its early stages, is the preparation of HNgY molecules in the gas phase.



### Introduction

The history of noble-gas chemistry originates from the inspiring suggestions by Pauling<sup>1</sup> and pioneer-

ing preparation of the first noble-gas compound  $Xe^+[PtF_6]^-$  by Bartlett.<sup>2</sup> This was followed by a gradual development of the field<sup>3</sup> and by a recognized renaissance in recent years.<sup>4</sup>

In this Account, we describe a part of modern noble-gas chemistry, *noble-gas hydrides*, with the common formula HNgY where Ng = noble gas atom and Y = electronegative fragment. This family of species was started by Pettersson et al. in 1995,<sup>5</sup> and it now includes 23 members (see Table 1). We will discuss the matrix-isolation synthesis of these molecules, their spectroscopic and structural properties, and their stabilities. Examples such as HArF, the first neutral argon compound,<sup>6</sup> and organo-noble-gas compounds are discussed in more detail.<sup>7–9</sup> Quantum chemistry plays an important role in predicting new species and interpreting their peculiar properties. Even though we try to concentrate on facts that have been demonstrated experimentally, the theoretical view on the subject is carefully described.

The noble-gas hydrides are not only remarkable for exploring the frontiers of chemical reactivity. They are special in many other respects due to their relatively weak bonding and large dipole moments, which results in strongly enhanced effects of the environment, complexation and reactions. The results on these molecules shed light on photodissociation dynamics and atomic mobility in noble-gas solids. Thus, we extend our consideration beyond the existence of these molecules.

## Experimental Preparation and Identification

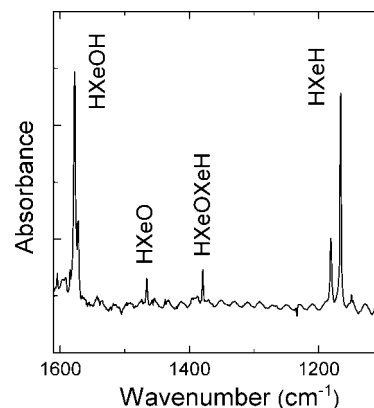
The synthesis of HNgY molecules starts with production of H and Y fragments in solid noble gas, prepared by UV photolysis of suitable precursors.<sup>10</sup> Major production of the HNgY molecules is activated by thermal mobilization of photogenerated fragments. Figure 1 presents the IR spectrum obtained by UV photolysis and annealing of a H<sub>2</sub>O/Xe matrix. The marked bands are the H–Xe stretching absorptions of various HXeY molecules.<sup>11–14</sup> These H–Ng stretching modes are very intense (typically >1000 km/mol) and useful for identification. Other modes are much weaker but detected in some cases (HArF, HKrF, etc.).<sup>6,15</sup>

The identified HNgY molecules are collected in Table 1, presenting the experimental and computational H–Ng stretching frequencies. The experimental frequencies can be very different, from 1119 and 1193 cm<sup>−1</sup> for HXeSH and HXeI to 1952 and 2016 cm<sup>−1</sup> for HKrF and HArF, respectively. The computational data follow this trend, the higher computational levels improving the agreement with experiment. The support from quantum chemistry calculations is essential to predict and identify novel species. The HNgY molecules form when the careful computational energetics of the H + Ng + Y → HNgY process is exothermic.<sup>16</sup> The first identified spe-

**TABLE 1.** Experimental and Theoretical H–Ng Stretching Frequencies (in cm<sup>−1</sup>) of Identified HNgY Molecules

molecule	frequency, experimental <sup>a</sup>	frequency, theoretical		ref
		MP2	CCSD(T)	
HArF	1970, 2016 <sup>b</sup>	2313	2053	6, 43
HKrCl	1476	1943		5
HKrCN	1497	2011	1781	17
HKrF	1925, 1952 <sup>b</sup>	2316	2174	15, 58
HKrCCH	1242	1575		20
HKrC <sub>4</sub> H	1290	1517		21
HKrC <sub>3</sub> N	1492	1692		22
HXeH	1166, 1181	1385	1216	10, 11
HXeI	1193	1514		5, 10
HXeBr	1504	1679		5, 10
HXeCl	1648	1740		5, 10
HXeCN	1624	1820		17
HXeNC	1851	1988		17
HXeSH	1119	1521	1148	18
HXeNCO	1788	1986		19
HXeOH	1578	1823	1678	12
HXeO	1466		1681	13
HXeCCH	1486	1736	1621	8, 9
HXeCC	1478		1754	8
HXeCCXeH	1301	1595		7, 8
HXeC <sub>4</sub> H	1532	1759		21
HXeC <sub>3</sub> N	1625	1777		22
HXeOXeH	1380	1572	1455	14

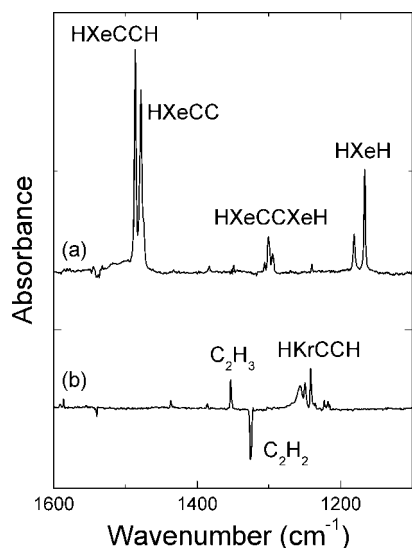
<sup>a</sup> Experiments in the corresponding Ng matrix. <sup>b</sup> Two values correspond to characteristic absorptions in unstable and stable configurations.



**FIGURE 1.** Noble-gas hydrides formed by 193 nm photolysis and 40 K annealing of a H<sub>2</sub>O/Xe matrix.

cies used hydrogen halides as the precursors (HCl, HBr, HI).<sup>5</sup> More complicated cases were examined later utilizing HCN, HNCO, H<sub>2</sub>S, and H<sub>2</sub>O.<sup>12,17–19</sup> The report on HArF enhanced the development in the field.<sup>6</sup> The first open-shell species was HXeO.<sup>13</sup>

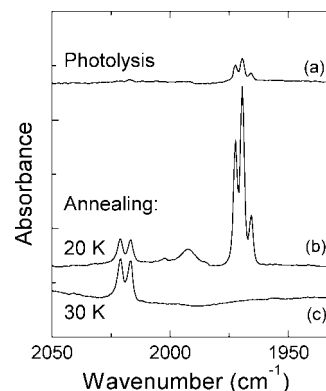
A group of noble-gas hydrides was prepared by insertion of Kr and Xe atoms into organic species. These studies were ignited by Lundell et al. who predicted HXeCCH, HXeCCXeH, and some other molecules.<sup>7</sup> This prediction was quickly verified, and a positive experimental result was obtained simultaneously in two groups on HXeCCH in solid xenon.<sup>8,9</sup> In addition to HXeCCH, Khriachtchev et al. identified in the same experiment HXeCC and HXeCCXeH (Figure 2a).<sup>8</sup> HXeCCXeH



**FIGURE 2.** Noble-gas hydrides formed by 193 nm photolysis and annealing of (a)  $\text{H}_2\text{C}_2/\text{Xe}$  and (b)  $\text{H}_2\text{C}_2/\text{Kr}$  matrices.

was the first hydride containing two noble-gas atoms, and HXeCC is an open-shell species. These three species were prepared using UV photolysis of a  $\text{H}_2\text{C}_2/\text{Xe}$  matrix and subsequent annealing at 40 K. Following this “organic” series, a Kr atom was reacted with acetylene producing HKrCCH (Figure 2b).<sup>20</sup> Such compounds as HKrCC or HKrCCKrH were not found, highlighting the lower reactivity of krypton compared with xenon. We suggested that more organo-krypton molecules could be prepared from other precursors containing the  $\text{H}-\text{C}\equiv\text{C}$  group, which was confirmed later. It also seemed that this approach could lead to the second argon molecule (in addition to HARF), but this challenge has not been realized yet.

The next progress in this direction was done with diacetylene ( $\text{H}_2\text{C}_4$ ), and new organic noble-gas compounds  $\text{HNgC}_4\text{H}$  ( $\text{Ng} = \text{Kr}$  and  $\text{Xe}$ ) were identified.<sup>21</sup> These species contain seven atoms, that is, they are the largest identified noble-gas hydrides. In addition to the strongest  $\text{H}-\text{Ng}$  stretching absorptions, some weaker bands ( $\text{C}-\text{H}$  stretching,  $\text{C}\equiv\text{C}$  and  $\text{C}\equiv\text{C}-\text{H}$  bending modes) were found. The IR absorption spectra indicate some stabilization of  $\text{HNgC}_4\text{H}$  compared with the  $\text{HNgC}_2\text{H}$  molecules; however, the argon compound ( $\text{HArC}_4\text{H}$ ) did not form. Most recently, Kr and Xe atoms have been inserted into cyanoacetylene ( $\text{HC}_3\text{N}$ ).<sup>22</sup> Photolysis and annealing of  $\text{HC}_3\text{N}/\text{Ng}$  matrices leads to the formation of  $\text{HNgC}_3\text{N}$  species for  $\text{Ng} = \text{Kr}$  and  $\text{Xe}$ , and bands from  $\text{H}-\text{Xe}$ ,  $\text{C}\equiv\text{N}$ , and  $\text{C}-\text{C}$  stretching modes are found for each species. The structural assignment was not straightforward here due to possible  $\text{HNgCCNC}$  isomers; however these isomers were less probable based on computations. No candidates for an argon compound were found. In addition to noble-gas hydrides, another group of noble-gas compounds ( $\text{HCCNgCN}$  and



**FIGURE 3.** Formation of HARF in solid argon. Shown are the spectra (a) after photolysis of an  $\text{HF}/\text{Ar}$  matrix, (b) after consequent annealing at 20 K, and (c) after annealing at 30 K.

$\text{HCCNgNC}$ ) was computationally predicted for  $\text{Ng} = \text{Ar}$ ,  $\text{Kr}$ , and  $\text{Xe}$ ; nevertheless, these molecules were not obtained experimentally, which can be explained by inefficient cage exit for the radical fragments (CCH and CN) upon photolysis.

## Formation Mechanisms

Photolysis and annealing are the two steps in matrix-isolation synthesis of  $\text{HNgY}$  molecules. Photodissociation of hydrogen-containing  $\text{HY}$  precursors produces matrix-isolated H and Y fragments. The high yields of the  $\text{HNgY}$  formation, which are often tens of percent of dissociated  $\text{HY}$  molecules, suggest low losses of H atoms during photolysis.<sup>10</sup> Photodissociation in solid noble gas is a local process demonstrated by the direct formation of some noble-gas hydrides (HARF, HKrCl, HXeNCO) during photolysis.<sup>6,19,23</sup> Figure 3a presents the direct formation of HARF in solid argon. A detailed experimental study of this phenomenon was done on HKrCl in solid krypton.<sup>23</sup> The HKrCl intermediate was shown to be the major channel (about 60%) for permanent dissociation of HCl in solid krypton with excess energy of 1.8 eV. The relatively small steady-state HKrCl concentration observed during photolysis is due to its low photostability.

The  $\text{HNgY}$  molecules can be formed in principle from either neutral  $\text{H} + \text{Ng} + \text{Y}$  or ionic  $(\text{HNg})^+ + \text{Y}^-$  fragments. The initial photolysis regularly produces some amounts of  $(\text{NgHNg})^+$  cations, and the ionic channels were considered by Pettersson et al. as a possible formation mechanism.<sup>5</sup> However, the  $(\text{NgHNg})^+$  decay does not correlate with the  $\text{HNgY}$  formation.<sup>22,24</sup> Moreover, two cases have been found when UV photolysis of  $\text{HY}$  does not produce cations but  $\text{HNgY}$  molecules are efficiently formed upon annealing.<sup>17,21</sup> Feldman and co-workers suggested that HXeH formed from H atoms rather than from charged precursors.<sup>25,26</sup> The first direct evidence of the neutral formation channel was obtained in exper-



iments with HXeI in solid xenon.<sup>27</sup> It was observed that  $\sim 3000\text{ cm}^{-1}$  light dissociated HXeI and released iodine atoms. After IR decomposition, HXeI recovers on a time scale of days in the dark at 15 K. This experiment indicates that HXeI is formed from neutral  $\text{H} + \text{Xe} + \text{Y}$  fragments since the IR photons are not energetic enough for ion formation. The formation of HXeCC from H and XeCC also indicates the neutral channel.<sup>28</sup> HXeCC decomposes by IR light above  $4500\text{ cm}^{-1}$ , which increases the XeCC concentration. The recovery of HXeCC was achieved in two ways. First, the HXeCC concentration slowly increased even at the lowest experimental temperatures ( $\sim 8\text{ K}$ ). Second, HXeCC could be efficiently formed by vibrational excitation of XeCC, which was explained by short-range mobility of the reagents promoted by vibrational energy redistribution near the absorbing XeCC molecules.

The HNgY formation upon annealing is controlled by thermal atomic mobility.<sup>29,30</sup> The thermal mobility of H atoms involved in the HNgY formation can be *global* and *local*.<sup>31</sup> Global mobility means a random walk across the matrix over large distances compared with the lattice parameter. Hydrogen atoms become globally mobile at  $\sim 30$  and  $40\text{ K}$  in krypton and xenon matrices. Local mobility is a short-range process when the H atom reacts with the parent  $\text{Xe} + \text{Y}$  center, and this may occur at relatively low temperatures. The formation of HARF found at  $8\text{ K}$  in solid argon is presumably a local process,<sup>24</sup> as well as the recovery of HXeCC and HXeI in solid xenon after their IR decomposition.<sup>27,28</sup>

The long-range mobility is a general case for the HNgY formation in krypton and xenon matrices. The HNgY formation ( $\text{Ng} = \text{Kr}$  and  $\text{Xe}$ ) upon annealing becomes slower for lower precursor concentrations in qualitative agreement with a simple kinetic model.<sup>30,32</sup> This observation indicates global mobility of H atoms because the formation time should be concentration-independent for local (geminate) formation. The long-range mobility is limited by lattice defects and impurities that can capture mobile H atoms. The most efficient formation of HXeBr was found in matrices with the best optical properties, that is, with the lowest defect concentration.<sup>32</sup>

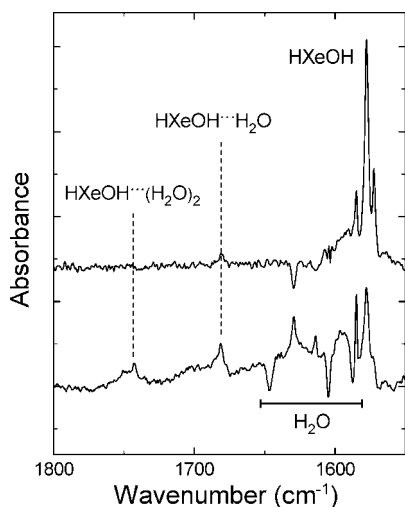
The HNgY molecules were used to study the temperature dependence of global hydrogen mobility. Formation rates of various H/D isotope analogs of HXeH and HXeOH were measured in solid xenon at temperatures from  $37$  to  $42\text{ K}$ , and the activation energy of  $\sim 110\text{ meV}$  was extracted.<sup>29</sup> Different mobilities for hydrogen isotopes were demonstrated (H faster than D) and their activation energies differed by  $\sim 4\text{ meV}$ . The

formation of HKrCl and DKrCl in solid krypton gave activation energies of  $\sim 64$  and  $68\text{ meV}$  for H and D atom mobilities.<sup>30</sup>

The chemical reactivity of HNgY molecules is another question to be addressed. Mobile H atoms can react with already formed HNgY molecules hence limiting the HNgY concentration. Indeed, the  $\text{HXeH} + \text{D}$  and  $\text{HKrCl} + \text{D}$  reactions were demonstrated.<sup>30,33</sup> The experimental method utilized the slower thermal mobility of D atoms compared with H atoms. It follows that D atoms become mobile after formation of the main part of HNgY molecules. If D atoms react with HNgY molecules, these kinetic distinctions should lead to a decrease of the HNgY concentration upon selective mobilization of D atoms, and this was found experimentally. The expected reaction products are hydrogen molecules and HY, but no experimental evidence of this was obtained.

The first reaction of a noble-gas molecule leading to another noble-gas molecule was  $\text{HXeCC} + \text{Xe} + \text{H} \rightarrow \text{HXeCCXeH}$ . Evidence for this was obtained from the formation kinetics of the products upon annealing of photolyzed  $\text{H}_2\text{C}_2/\text{Xe}$  matrices.<sup>34</sup> It was shown that HXeCC is the precursor for HXeCCXeH: when HXeCC was selectively photodecomposed during annealing, no formation of HXeCCXeH occurred. This addition reaction is not trivial because of the very large energy accumulated in the HXeCCXeH molecule with respect to acetylene (computationally  $9.3\text{ eV}$ ). A similar reaction of  $\text{HXeO} + \text{Xe} + \text{H}$  leads to HXeOXeH.<sup>14</sup>

Some experimental results suggest negligible barriers of the HNgY formation. HXeCl and HXeBr form in solid neon at  $10\text{ K}$ <sup>35</sup> and HXeCCH forms in argon and krypton matrices at  $\sim 20$  and  $30\text{ K}$ .<sup>36</sup> All known HNgY molecules form in matrices at similar temperatures ( $\sim 40$  and  $30\text{ K}$  for xenon and krypton) indicating that reaction barriers are not of major importance at these temperatures. On the other hand, indications of low formation barriers are also known, for example, for recovery of HXeI and HXeCC after their IR-induced decomposition.<sup>27,28</sup> HARF forms slowly but efficiently in a photolyzed HF/Ar matrix at  $8\text{ K}$ .<sup>24</sup> The formation of DARF at  $8\text{ K}$  is much slower, by a factor of  $\sim 50$ , than the formation of HARF. As a probable mechanism, the hydrogen atom tunnels to the  $\text{Ar}-\text{F}$  neutral center through a barrier that might be intrinsic and matrix-induced. Bihary et al. estimated the barrier of  $\sim 0.3\text{ eV}$  for the  $\text{H} + \text{Ar} + \text{F}$  reaction in solid argon, the barrier thickness being  $\sim 1.3\text{ \AA}$ .<sup>37</sup>



**FIGURE 4.** HXeOH–water complexes in solid xenon. The upper and lower traces present the spectra obtained for smaller and higher water concentrations.

## Complexes and Interaction with Matrix

The unusual properties of HNgY molecules are reflected in their interaction with other species and hosts. We concentrate here on the results demonstrated experimentally. Complexes of HArF, HKrF, and HKrCl with nitrogen were studied by Lignell et al.<sup>38</sup> Large blue shifts of the H–Ng stretching frequencies were induced by complexation, up to  $+113\text{ cm}^{-1}$  for HKrCl complexed with nitrogen. Based on computations, this shifted absorption was assigned to the linear hydrogen-bonded  $\text{N}_2 \cdots \text{HKrCl}$  complex. The bent complex was computationally more strongly bound, and it was also experimentally found with a shift of  $+32\text{ cm}^{-1}$  from the monomer. The computational interaction energies of the complexes between HNgY and  $\text{N}_2$  are between  $-4.8$  and  $-9.6\text{ kJ/mol}$  before zero-point energy (ZPE) correction. The electrostatic forces provide the most important contributions to the interaction energy of the linear  $\text{N}_2 \cdots \text{HNgY}$  complexes whereas the dispersion forces give a competing contribution in the bent structures. The observed blue shift means that the H–Ng covalent bond becomes stronger proposing that complexation could stabilize these species.

The  $\text{HXeOH} \cdots (\text{H}_2\text{O})_n$  structures were studied by Nemukhin et al.<sup>39</sup> Experimental evidence of the  $\text{HXeOH} \cdots (\text{H}_2\text{O})$  and  $\text{HXeOH} \cdots (\text{H}_2\text{O})_2$  complexes in solid xenon was presented, the shifts of the H–Xe stretching frequency being  $+103$  and  $164\text{ cm}^{-1}$  (Figure 4). In the computational  $\text{HXeOH} \cdots \text{H}_2\text{O}$  structure, a hydrogen atom of  $\text{H}_2\text{O}$  is bonded to the oxygen atom of  $\text{HXeOH}$ , and the binding energy is  $\sim 45\text{ kJ/mol}$ . The theory shows that interaction with water enhances charge separation in  $\text{HXeOH}$  and shifts the H–Xe stretching frequency by  $+107$ ,  $182$ , and  $276\text{ cm}^{-1}$  for  $n = 1, 2$ , and  $3$ , respectively,

indicating the stabilization of the H–Xe bond. However, the stabilization with respect to the stretching coordinate is accompanied with destabilization along the bending coordinate, and the bending barrier disappears for  $n = 4$ . This computational result casts doubts on the possibility to stabilize  $\text{HXeOH}$  in water hosts.

The  $\text{HXeCCH} \cdots \text{CO}_2$  complex in solid xenon was studied by Tanskanen et al.<sup>40</sup> The  $\text{HCCH} \cdots \text{CO}_2$  precursor of this species was prepared by UV photolysis of propiolic acid ( $\text{HCCCOOH}$ ). The  $\text{HCCH} \cdots \text{CO}_2$  complex is further decomposed to the  $\text{HCC} \cdots \text{CO}_2$  complex, and thermal mobilization of H atoms leads to the formation of  $\text{HXeCCH} \cdots \text{CO}_2$ . The experimental H–Xe stretching absorption of the  $\text{HXeCCH} \cdots \text{CO}_2$  complex is blue-shifted ( $+31.9$  and  $+5.8\text{ cm}^{-1}$ ) from the value of  $\text{HXeCCH}$  monomer. As the most recent example, Lignell et al. have studied the  $\text{HXeY} \cdots \text{HX}$  ( $\text{Y}, \text{X} = \text{Cl}$  and  $\text{Br}$ ) complexes in solid xenon and experimentally found large complexation-induced shifts (up to  $+150\text{ cm}^{-1}$ ).<sup>41</sup> It seems that the blue shift of the H–Ng stretching mode is a normal case for HNgY complexes.

The experiments with HNgY molecules reveal unusual solvation effects.  $\text{HXeCl}$  has the H–Xe stretching absorptions at  $1664$  and  $1649\text{ cm}^{-1}$  in krypton and xenon matrices, respectively,<sup>5</sup> and at  $1612\text{ cm}^{-1}$  in a neon matrix.<sup>35</sup> This matrix shift is “abnormal” because the H–Y stretching frequencies of “ordinary” molecules are usually highest in solid neon and decrease in more polarizable materials. The lower H–Xe stretching frequency in solid neon can be discussed in terms of a smaller  $\text{HXe}^+\text{Y}^-$  charge separation; however, it is unclear why solvation in solid krypton produces stronger charge separation than that in solid xenon. Complexation with single matrix atoms does not explain this solvation effect.<sup>36</sup> On the other hand, specific interactions with matrix atoms can explain the fine structure of absorption bands often observed experimentally, and detailed analysis was performed for  $\text{HXeCCH}$  and  $\text{HXeBr}$  interacting with xenon.<sup>36,42</sup>

Some efforts have been made to understand the matrix-site structure of HArF in solid argon. Annealing at  $16$ – $20\text{ K}$  of a photolyzed  $\text{HF/Ar}$  matrix produces the H–Ar stretching bands at  $1965.7$ ,  $1969.4$ , and  $1972.3\text{ cm}^{-1}$ .<sup>6</sup> This triplet absorption disappears at  $\sim 30\text{ K}$ , which is accompanied with a rise of the H–Ar stretching bands at  $2016.3$  and  $2020.8\text{ cm}^{-1}$  (Figure 3).<sup>43</sup> The blue-shifted doublet corresponds to a more stable configuration (matrix site) of HArF in solid argon, and its existence is limited only by degrading of argon matrix above  $40\text{ K}$ . This configuration is called “stable” HArF in order to distinguish from “unstable” HArF absorbing at  $\sim 1970\text{ cm}^{-1}$ . Theory confirmed the sensitivity of the H–Ar stretching fre-

quency to local matrix morphology.<sup>44–46</sup> Jolkkonen et al. connected the experimental blue shift of the stable HArF absorption bands with the tight  $\text{Ar} \cdots \text{HArF}$  complex formed in a loose matrix site.<sup>45</sup> Bochenkova et al. confirmed this assignment and found five different morphologies of an argon matrix around the HArF molecule,<sup>46</sup> in agreement with experiment. It is probable that these matrix sites differ by position of a vicinal lattice vacancy.<sup>47</sup> A similar matrix-site effect was experimentally found for HKrF upon annealing in solid krypton.<sup>15</sup>

Additional spectral features have been found for HNgY molecules that differ from the matrix-site effect. The spectra often show a satellite at higher energy from the main H–Ng stretching absorption. This satellite has a mirror counterpart at lower energies rising at elevated temperatures. These subbands were first studied for HXeBr and HKrCl.<sup>42</sup> The experimental and phenomenological theoretical results suggest that these satellites are connected with hindered rotation of the embedded molecule in matrix. Hindered rotation of HArF in solid argon was studied in detail later.<sup>48</sup> A theoretical model of rotation of HArF inside a large fragment of the fcc argon lattice with a cubooctahedral cavity for the trapped molecule was developed. A realistic rotational potential energy surface accounting for interaction of HArF with matrix atoms was constructed, and the rotational energy levels were estimated by numerical solution of the Schrödinger equation in the external adiabatic potential. These studies suggest that the band at  $1992\text{ cm}^{-1}$  (Figure 3) is due to combination of the H–Ar stretching and hindered rotation.

## The Nature of Chemical Bonding and Stability

In the first noble-gas compounds, the bonding mainly originates from ionic interactions. Very electronegative groups lead to ionization of the noble-gas atom. This is the bonding mechanism on which Pauling's predictions of  $\text{XeF}_n$  and  $\text{KrF}_n$  were based,<sup>1</sup> and it also prevails in Bartlett's compound  $\text{Xe}^+[\text{PtF}_6]^-$ .<sup>2</sup> Most of such noble-gas compounds involve bonding to fluorine, the most electronegative atom, or to fluorine-containing groups, although compounds of other strongly electronegative atoms are also known. The dominance of fluorinated groups has been pronounced in organic noble-gas chemistry.<sup>3</sup>

The noble-gas hydrides bring in a new bonding motif. They can be represented in the form  $(\text{H–Ng})^+\text{Y}^-$  where  $(\text{H–Ng})^+$  is mainly covalent, while the interaction between  $(\text{HNg})^+$  and  $\text{Y}^-$  is predominantly ionic.<sup>10,49</sup> To see a qualitative picture of the bonding mechanism, consider transfer of an electron from the

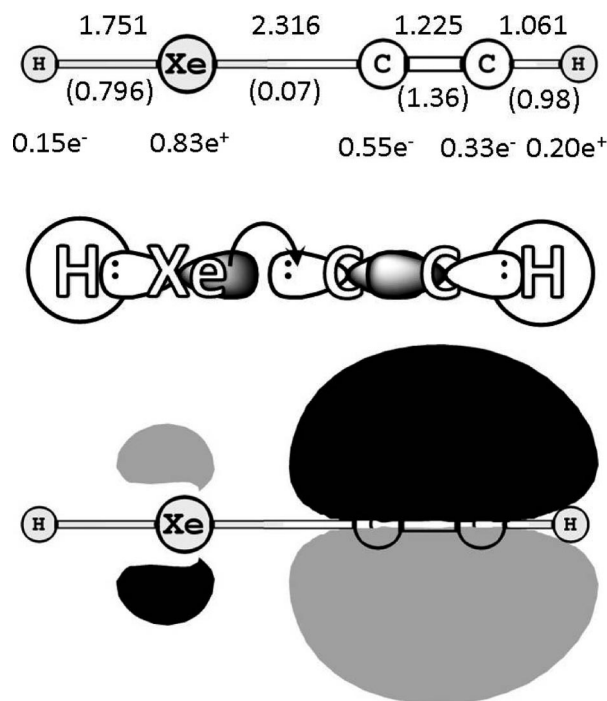


FIGURE 5. Bonding in HXeCCH.

closed-shell Ng atom to electronegative group Y. This involves a large expense of energy that is only partially compensated by the electron affinity of Y and Coulombic attraction between  $\text{Y}^-$  and  $\text{Ng}^+$ . However, the outer electronic shell of  $\text{Ng}^+$  is an open one, with an unpaired electron in a p-type orbital that forms a strong  $\Sigma$  bond with the unpaired s electron of the H atom. This provides an important additional energetic compensation for the removal of the electron from the Ng outer shell upon bonding. This bonding motif was found already years ago by Last and George, who employed the semiempirical DIM/DIIS method.<sup>50</sup>

Now we consider in more detail an example of HXeCCH. The acetylenic group is strongly electronegative leading to the  $(\text{H–Xe})^+(\text{CCH})^-$  ionic interaction. The structure of this species and the NBO partial charges, computed at the MP2/CERN-BLECP/6-311++G(2p,2d) level,<sup>51</sup> are presented in Figure 5 (upper part). The high partial charge  $0.83e^+$  on xenon indicates a powerful electron-withdrawing effect of CCH. The bond orders for HXeCCH are given in parentheses. The very small value of 0.07 for the bond between  $(\text{H–Xe})^+$  and  $\text{CCH}^-$  shows that this bond is mainly ionic, without significant covalent contribution. The bond order between the carbon atoms is much less than 2. In acetylene, this order is nearly 3, but when accepting the electron, the equivalent of more than one covalent bond disappears in  $\text{CCH}^-$ . On the other hand,  $n = 0.786$  in  $(\text{H–Xe})^+$  shows an essentially full two-electron covalent bond. The middle scheme in Figure 5 illustrates the bonding mechanism. The electron transferred from xenon to form



$\text{CCH}^-$  goes essentially into an  $sp$ -type orbital. Finally, Figure 5 (lowest scheme) shows that the highest occupied molecular orbital appears quite delocalized, mostly on the CCH group. This bonding mechanism is also valid for two molecules with multiple gas atoms characterized experimentally to date ( $\text{HXeCCXeH}$  and  $\text{HXeOXeH}$ ). An important example of HARF also corresponds to this bonding mechanism, and it seems that this is the only mechanism so far whereby a lighter noble-gas atom could be chemically bonded.

An important property of  $\text{HNgY}$  molecules is that they are metastable species. The decomposition process

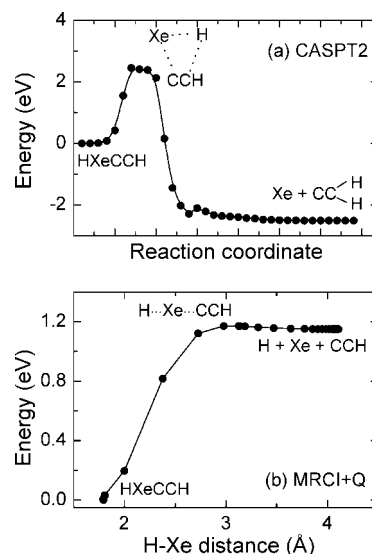


is always highly exoergic. We refer to this process as the two-body (2B) decomposition channel. The importance of the three-body (3B) decomposition channel is also recognized:



For all prepared  $\text{HNgY}$  molecules, the theoretical 3B channel is endothermic.<sup>16</sup> For HARF, it has small endothermicity of 0.182 eV (without ZPE correction).<sup>52</sup> The required endothermicity of reaction 2 is obvious for cases when the 3B potential surface has no substantial energy barrier. The hypothetical species, where reaction 2 is exoergic but has a substantial stabilization barrier, are of considerable interest and deserve future attention.

For triatomic HARF and HKrF, it was found that single-reference methods such as MP2 describe reasonably well the potential energy along the minimum energy path for the 2B process,<sup>53</sup> while for the 3B reaction, where two radicals are produced, multireference methods are required.<sup>52,53</sup> Various multireference methods have been employed, including the highest-level MRCI, and also CASPT2 and AQCC. CASPT2 is a reasonable semiquantitative approximation for the 3B channel, while AQCC is close to MRCI. The recent multireference CASPT2 calculations for the 2B decomposition of  $\text{HXeCCH}$  into  $\text{Xe} + \text{HCCH}$  yielded results different from those obtained by MP2,<sup>51</sup> in contrast with the previous experience with HARF and HKrF (Figure 6). The 2B reaction path computed from CASPT2 leads first to the production of xenon and vinylidene, and the latter subsequently goes into acetylene. In the MP2 calculation, the reaction path involves bending-like motions of the H atom toward the Xe of  $\text{HXeCCH}$ , and the vinylidene intermediate is not produced. Chemically, the 2B channel is unlikely to be important at practical temperatures since the barrier (over 2.0 eV) is very high. The main decomposition channel is then 3B, but also this channel has a high barrier of 0.96 eV (after ZPE corrections). The transition-state theory suggests the



**FIGURE 6.** Energetic stability of  $\text{HXeCCH}$  via (a) bending and (b) stretching coordinates.

kinetic stability of  $\text{HXeCCH}$  up to relatively high temperatures: the species is predicted to live for  $\sim 3$  h at 0 °C!

## Concluding Remarks

The  $\text{HNgY}$  molecules identified in noble-gas matrices exhibit quite a specific nature of bonding, which leads to unusual chemical and spectroscopic properties. The preparations of the first neutral argon molecule, HARF, and halogen-free organic noble-gas molecules are important achievements in the field.<sup>6,8</sup> The  $\text{HNgY}$  molecules are sensitive probes of local matrix structure and give information on various dynamical processes in solid matrices.<sup>23,29,30,43</sup> The H–Xe stretching frequency shifts upon interaction with other species to blue by up to  $\sim 150 \text{ cm}^{-1}$ .<sup>38–41</sup> These molecules exhibit strong anharmonic effects.<sup>54</sup>

Now we would like to take a brief look at perspectives of these compounds. Extension of argon chemistry is one direction because realistic predictions are known.<sup>49</sup> On the other hand, no clear candidates for neutral neon molecules are seen. The situation with He is slightly more optimistic because  $\text{HHeF}$  is computationally a short-lived species decaying in the gas phase by tunneling on a picosecond time scale.<sup>55,56</sup> The calculations suggest that  $\text{HHeF}$  can be stabilized in pressurized solid helium<sup>49</sup> or in polarizable medium.<sup>57</sup>

Preparation of new bonds with noble-gas atoms looks important, for instance, the Xe–Si bond in light of the geophysical missing-xenon problem. Considering the heaviest noble gas element radon, it is no surprise that calculations predict stability of  $\text{HRnF}$ ,<sup>58</sup> and other  $\text{HRnY}$  compounds are probable. No experimental studies of  $\text{HRnY}$  compounds exist, and the topic seems interesting.

More complex structures and even a bulk material of HNgY molecules are attractive issues. Calculations suggest the existence of oligomers and polymers with multiple XeCC groups.<sup>59</sup> Another open question is whether aggregates (HNgY)<sub>n</sub> of the noble-gas molecules can be stable, which is directly related to the possible existence of HNgY crystals. Crystalline HXeCCH compound is predicted.<sup>60</sup> There is no experimental work on these structures.

Besides being characterized in noble-gas matrices, some of these hydrides have been produced by Buck and co-workers by photodissociation of a suitable precursor on large Xe<sub>n</sub> clusters. In their experiments, the large anisotropy of the dipole polarizability and the large dipole moment of the molecules are utilized, and positive signals from HXeI and HXeCl and recently from HXeCCH were obtained.<sup>61</sup> However, the true gas-phase identification of a HNgY molecules has not been done yet, and this is another important challenge for experimentalists.

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## FOOTNOTES

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