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Destabilization of noble-gas hydrides by a water environment: calculations for HXeOH@(H₂O)ₙ, HXeOXeH@(H₂O)ₙ, HXeBr@(H₂O)ₙ, HXeCCH@(H₂O)ₙ

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HNgY molecules are chemically-bound compounds of a noble-gas atom (Ng) with a hydrogen and with an electronegative group Y. There is considerable current interest in the stability of these species in different types of media. The kinetic stability of several compounds, HXeOH, HXeOXeH, HXeBr and HXeCCH, in water clusters is explored by *ab initio* calculations. It is found that the kinetic stability of the compounds is reduced by the water environment, generally falling off with the number of H₂O molecules. For a relatively modest number of water molecules, the compounds decompose spontaneously. Implications of the results for storage of HNgY in molecular media are discussed.

1. Introduction

Several families of new noble-gas compounds have been discovered in recent years. One of these interesting families is the HNgY compounds, representing a formal insertion of a noble-gas atom (Ng) into a hydride molecule (HY), which were discovered by Räsänen and coworkers.[1,2] The HNgY compounds, the nature of their bonding, formation mechanisms and their properties have been discussed in recent reviews.[3–5]

In nearly all cases, HNgY compounds are prepared and studied in cryogenic Ng-matrices in which they are stable. However, these compounds are not always completely "isolated" by the matrix and often form complexes with other species inhibiting the matrix. HNgY compounds are experimentally known to form complexes with their precursor HY molecules[6–9] with N₂[10,11] and CO₂.[12] The interaction between HNgY molecules and neighboring species can be substantial: the estimated interaction energy of HXeCCH and acetylene is 0.15 eV, half of the energy of a typical hydrogen bond. These strong interaction energies imply that a condensed form of HNgY compounds along with other molecules can exist, for instance, HXeCCH and acetylene are expected to form clusters with liquid-like behavior in which HXeCCH is "solvated" by the acetylene molecules.[13] HXeCCH is also expected to be able to

form complexes with other HXeCCH molecules and possibly even neat crystals.[14]

The effect of complexation on the electronic structure of HNgY molecules is observable in experiments by measuring the shift in the IR spectra of the H–Ng stretch vibration. Usually, a blue shift of this vibration is measured which originates from the enhanced (HNg)⁺ Y⁻ ion-pair character upon complexation[15] and is related to the shortening of the H–Ng bond. The blue shifted H–Ng stretch can therefore imply stabilization with respect to dissociation through the H–Ng stretch coordinate. However, stabilization with respect to a certain dissociation coordinate does not necessarily imply an overall increase in the intrinsic molecular lifetime since destabilization with respect to other dissociation coordinates may take place.[6]

Since water is the most important solvent in nature and water vapor is abundant in the atmosphere, it is essential to consider the influence of water on the stability of HNgY molecules.[16] Whether water stabilizes or destabilizes HNgY molecules, understanding the processes governing the solvent–solute interactions, may provide important insights into the search for HNgY materials with increased stabilities.

In this paper we show, for several HNgY molecules, that there is significant evidence of a common destabilization mechanism when solvated (complexed) in water, which is likely to be general for all HNgY compounds due to their common structure and binding motif. The instability of HNgY in water is demonstrated for four experimentally known compounds: HXeBr,[1] HXeCCH,[17–19] HXeOH[20] and HXeOXeH.[21] A detailed analysis for the destabilization mechanism and comparison to experimental results are given for the water based HXeOH and

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HXeOXeH molecules. Although we demonstrate this effect only for 4 out of 28 currently known HNgY molecules, analysis of the destabilization mechanism will demonstrate that this phenomenon is likely to be general for all HNgY compounds, regardless of the specific Ng and Y groups.

The paper is organized as follows: Section 2 discusses the model, methods and computational details. Section 3 describes the results and Section 4 is for discussion and conclusion.

2. Model systems, methods and computational details

To understand the stabilization mechanisms of HNgY compounds it is useful to consider their dissociation pathways as an isolated species in the gas phase. This was the topic of recent computational studies.[22–24] There are two uni-molecular dissociation channels for HNgY compounds:[22,23,25]

$$HNgY \rightarrow Ng + HY \qquad (1)$$

$$HNgY \rightarrow H + Ng + Y \qquad (2)$$
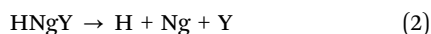
Reaction (1), known as the 2-body (2B) decomposition, can be described as a bending motion of the H atom around the Xe atom. This reaction is exoergic, for all studied HNgY species.[17,23–28] HNgY compounds are thus metastable molecules. However, the energy barrier for process (1) is quite high, of the order of 2 eV.[24] Therefore the half-life of HNgY compounds is actually dominated by channel (2) except at extremely low temperatures where dissociation is practically negligible. Channel (2), the 3-body (3B) dissociation, is endoergic, but the energy barrier is much lower than the energy barrier of the 2B reaction. Computationally, it was demonstrated that the 3B reaction can only be described correctly by multi-reference calculations, while the 2B reaction can be described by single-reference methods.[22,23]

The barriers for the 3B dissociation reaction for isolated HXeCCH, HXeOH and HXeOXeH were calculated previously[23,28] and were found to be 0.96, 0.59 and 0.4 eV, respectively, much lower than the 2B barrier of ~2 eV. The corresponding intrinsic half-lives, governed by the 3B reaction, were found to be 1 h at 253, 170 and 120 K for HXeCCH, HXeOH and HXeOXeH respectively. Previous calculations on HXeCCH$\cdots$(C$_2$H$_2$)$_n$ (ref. 13) and HXeOH$\cdots$(H$_2$O)$_n$ (ref. 6) show that the complexation reaction with solvent molecules tends to strengthen the Xe–H bond. In this work we generally assume that bond strengthening has only a small effect on the 3B reaction and does not change significantly the expected lifetimes. Explicit evaluation of the complexation effect on stability with respect to the 3B reaction requires a suitable multi-reference treatment and remains a subject for future investigation.

Nemukhin and coworkers[6] have studied HXeOH$\cdots$(H$_2$O)$_n$ complexes, where n = 0, 1, 2, 3. They found that the 2B reaction barrier is gradually lowered with the addition of water molecules. The clusters then become unstable for n = 4. They have also found that the H–Xe stretch vibration is blue shifted with addition of water molecules, which can also imply the elevation of the 3B reaction barrier. Our work goes beyond the results of Nemukhin *et al.* by showing that the phenomenon of

destabilization in water is apparently general for all HNgY compounds. Also, an analysis of expected lifetimes is given for HXeOH and HXeOXeH where experimental data exist.

In this manuscript we examine the effect of the clusters of water molecules on the stability of four HXeY molecules: HXeOH, HXeOXeH, HXeCCH and HXeBr. The Ng–water clusters HXeOH$\cdots$(H$_2$O)$_n$ and HXeOXeH$\cdots$(H$_2$O)$_n$ for n = 0, 1, 2, 3 where experimental data exist are studied in detail: for each cluster we optimize the equilibrium structure (ES), the corresponding 2B reaction transition structure (TS) and products. The partition function is calculated for the ES and TS and used, along with the barrier heights, to obtain the reaction rate k_{2b} utilizing Transition State Theory (TST). IR-spectroscopic data are calculated for the equilibrium structures. For HXeCCH and HXeBr, the stability with respect to the 2B decomposition in the presence of water is tested: for the corresponding complexes with water, we evaluate the 2B barrier by calculating the ES, TS and partition function. It is assumed that the HXeBr and HXeCCH clusters share the same behavior with respect to spectroscopic and bonding characteristics as the Ng–water compounds.

It is of considerable interest to simulate HNgY in a more realistic, full solvation shell. However, such a simulation at a reasonable *ab initio* level is beyond our computational capabilities, especially when considering the optimization of the transition structure and Hessian matrix evaluations.

All calculations were carried using the ORCA package,[29] which was found to provide good efficiency and accuracy. Since intermolecular interactions are important for the study of complexes, the SCS-MP2 electronic structure method,[30] which provides improved results for noncovalent interactions over MP2,[31] was used along with the aug-cc-pVDZ[32] basis set (cc-pVDZ augmented with diffused functions, necessary for an at least qualitatively reliable calculation of conformational energies).[33] For the larger clusters of HXeCCH$\cdots$(H$_2$O)$_n$ where n = 3, 4 where computations become prohibitive, "resolution of the identity" approximated SCS-MP2[34–36] was used along with the RI-MP2 auxiliary basis set.[37,38]

Our results for the HXeOH molecule are in excellent agreement with the results reported by Nemukhin and coworkers[6] who have used the larger aug-cc-pVTZ basis along with the MP2 method. Our results for barrier heights are higher by an average of 0.67 kcal mol^{-1} while IR frequency shifts are in agreement within 8 cm^{-1}. The striking agreement between MP2/aug-cc-pVTZ results of Nemukhin *et al.* and our SCS-MP2/aug-cc-pVDZ results is strong evidence for the robustness of our calculation. It also demonstrates that BSSE has little importance on the determination of barrier heights of the systems, or alternatively, that the SCS approach is able to predict accurate barrier heights using smaller basis sets. All studied compounds have been studied previously using double-zeta quality bases, and shown to yield good results compared to spectroscopic data.[6,21,23,39]

3. Results

HXeOH and HXeOXeH

Equilibrium structures. The calculated equilibrium and corresponding 2B transition structures for the HXeOH$\cdots$(H$_2$O)$_n$

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and HOXeOH$\cdots$(H$_2$O)$_n$ clusters where $n \leq 3$ are shown in Fig. 1. Above $n = 3$ the noble-gas compounds become unstable and spontaneously decompose into the 2B products. The driving force in the formation of the complexes which also determines the equilibrium structures is the hydrogen bonding between the negatively charged oxygen atoms and the positively charged hydrogen atoms. The water molecules form a hydrogen bonded chain which itself is hydrogen-bonded to the oxygen atom on the Xe-compound.

The structure of the Xe-compound determines the structure of the water-chain. For the HXeOH molecule, with each addition of a water molecule, the water-chain will evolve gradually, forming an arch "connecting" the O and H atoms of HXeOH. The case of HXeOXeH is different: since HXeOXeH has C_{2V} symmetry the water-chain remains perpendicular and does not connect the O and H atoms of HXeOXeH, with the exception of structure 3(a).

For HXeOXeH there are two different conformations for $n = 3$ that differ in the spatial arrangement of the water molecules. Both conformations have very close energies with a negligible difference of 0.02 eV, 3(b) having slightly lower energy. However, under experimental conditions the matrix environment may impose the preference of one conformation over the other.

Spectroscopic IR data and chemical bonding. The calculated spectroscopic data used for experimental identification of the Xe-compounds, along with H–Xe distance and the HXe group NPA[40] (NBO) charge, are shown in Table 1. The data are provided for the H–Xe stretch vibration which are usually employed for the identification of HNgY compounds in the matrix, due to its strong absorption.

It can be seen that as the number of water molecules increases: (a) the H–Xe distance is shortened, (b) the positive charge on the HXe group increases towards (HXe)$^{+1}$ (isoelectronic with HI) with decreasing intensity, and (c) the H–Xe stretch frequency is blue shifted. These observations may imply the strengthening of the H–Xe bond with respect to the 3B dissociation reaction which proceeds through the same stretch coordinate. This phenomena was also observed for HXeCCH$\cdots$(C$_2$H$_2$)$_n$.[9,13]

Transition structures and catalytic properties of the hydrogen chain. What is the origin of the catalytic properties of the water chain with regard to dissociation? It can be assumed that the energy barrier of the 2B dissociation reaction is proportional to the degree of geometrical distortion (frustration) of the Ng-compound at the transition geometry. This geometrical distortion is essential for enabling the transfer of the hydrogen-atom bound to the Xe atom and its re-attachment to the oxygen atom (i.e. the 2B reaction). The hydrogen chain catalyzes the 2B reaction by mediating the hydrogen transfer, therefore easing the frustration of the Ng-compound at the TS and lowering the reaction barrier. As the number of water molecules in the cluster increases and a longer chain is formed, the frustration of the Ng-compound and the corresponding 2B reaction barrier decrease. This is a clear example of specific catalytic action of water molecules acting on the 2B decomposition channel. We were not able to find evidence for the formation of a hydronium ion as a distinct species in either of the reactions.

The structure of the hydrogen chain has an important effect on its catalytic properties. For conformation 3(a) of the
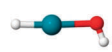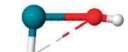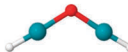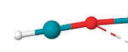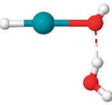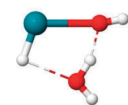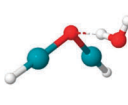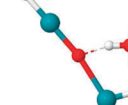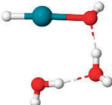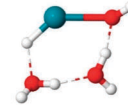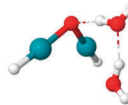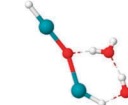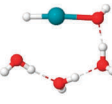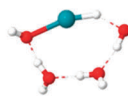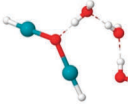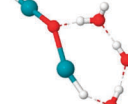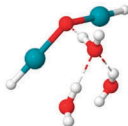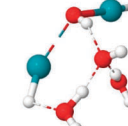

n	ES	TS	ΔE (eV)	n	ES	TS	ΔE (eV)
0			1.78	0			1.94
1			1.17	1			1.45
2			0.51	2			0.72
3			0.02	3(a)			0.13
				3(b)			0.31

Fig. 1 Equilibrium structures (ES) and transition structures (TS) for the 2B reaction of HXeOH$\cdots$(H$_2$O)$_n$ and HOXeOH$\cdots$(H$_2$O)$_n$.

Table 1 Spectroscopic and bonding data for HXeOH$\cdots$(H$_2$O)$_n$ and HXeOXeH$\cdots$(H$_2$O)$_n$. Since HXeOXeH contains two H–Xe units, data are shown only for the unit mostly affected by the presence of water

	HXeOH$\cdots$(H$_2$O)$_n$				HXeOXeH$\cdots$(H$_2$O)$_n$				
Water mol. (n)	0	1	2	3	0	1	2	3(a)	3(b)
Xe–H stretch (cm^{-1})	1771	1881	1959	2056	1498	1561	1582	1585	1609
Shift (cm^{-1})	0	109	187	285	0	63	84	87	112
Intensity (T^2)	806	494	346	119	5332	3867	3365	2772	2798
Relative intensity	1	0.61	0.43	0.15	1.00	0.73	0.63	0.52	0.52
H–Xe distance (Å)	1.72	1.7	1.68	1.66	1.77	1.75	1.74	1.71	1.73
HXe charge (e)	0.75	0.80	0.83	0.86	0.67	0.71	0.72	0.78	0.74

HXeOXeH$\cdots$(H$_2$O)$_3$ complexes, the water molecules form an ordered arch and the corresponding TS has a three membered water ring. In conformation 3(b), the hydrogen chain does not form an arch and the corresponding TS has only a two membered water ring. A smaller ring requires a larger geometric distortion – it is therefore expected that the dissociation barrier of conformation 3(a) will be somewhat lower than the barrier of conformation 3(b).

As already mentioned, the results for the HXeOH molecule are in excellent agreement with the results reported by Nemukhin and coworkers:[6] Our results on barrier heights are higher by an average of 0.67 kcal mol^{-1} (*i.e.* within chemical accuracy) while IR frequency shifts are in agreement within 8 cm^{-1}.

Dissociation reactions and lifetimes. The results on the energetics of the dissociation reactions and lifetimes of HXeOH$\cdots$(H$_2$O)$_n$ and HXeOXeH$\cdots$(H$_2$O)$_n$ are shown in Table 2. All previous studies on the stability of experimentally known HNgY compounds have shown that the 3B dissociation is the favorable dissociation mechanism. This also seems to be the case for HXeOH clusters of n = 0, 1 and HXeOXeH clusters of n = 0, 1, 2 where the 3B barrier is 0.59 eV for HXeOH and 0.4 eV for HXeOXeH,[24] which is much lower than the corresponding 2B dissociation.

However, for HXeOH clusters of n = 2, 3 and HXeOXeH clusters of n = 3, water molecules reduce the 2B reaction barrier below the barrier of the 3B reaction which becomes the dominant dissociation mechanism. This change of the preferred dissociation mechanism is a phenomenon unique for the presence of solvent (water) molecules.

In the case of the HXeOXeH$\cdots$(H$_2$O)$_3$ complex where two conformers exist, the lifetime is calculated for each individual conformer. Although both conformers are close in energy, they are quite different in spatial organization and also in their electronic structure, as evident from the differences in IR shifts.

It is therefore reasonable to assume that there exists a significant barrier of conformational shift between the two, so that the more stable 3(b) population is not affected by the relatively fast decay of the 3(a) conformation.

Another significant observation is that, unlike the cases of the isolated molecule and of the smaller clusters, for n = 3, the expected lifetime of HXeOXeH is longer than HXeOH as observed by experiment.[21] The extended computational model, which enhances the isolated gas-phase Ng–water molecules with complexed water molecules, is therefore able to reproduce certain qualitative behaviors observed by experiment and not predicted by the gas-phase model.

The equilibrium structures and corresponding 2B transition structures and barriers for the HXeBr$\cdots$(H$_2$O)$_n$ are shown in Fig. 2. For the isolated HXeBr molecule, we were not able to locate a barrier of the 2B reaction for HXeBr. It seems that due to the large distance between the Xe atom and the Br atom of 2.84 Å, the barrier of the 2B reaction becomes very high and the TS could not be located using conventional transition structure optimization algorithms. For cases other than the isolated HXeBr molecules, the HXeBr$\cdots$(H$_2$O)$_n$ clusters show an expected behavior of reduction of the 2B barrier with increasing number of water molecules. With $n \geq 3$, HXeBr loses stability and decomposes spontaneously.

The equilibrium structures and corresponding 2B transition structures and barriers for the HXeCCH$\cdots$(H$_2$O)$_n$ are shown in Fig. 3. Other conformers may exist for the HXeCCH$\cdots$(H$_2$O)$_n$ clusters, as for HXeOXeH$\cdots$(H$_2$O)$_n$, especially for clusters with a large number of water molecules, however, only the structures assumed to be the global energetic minima are shown and analyzed. Although other structural minima may exist and could have different stabilities, the evidence shown here establishes the existence of the dissociation mechanism. Since other conformations are expected to have almost the same or higher

Table 2 Energetics and half-lives of HXeOH$\cdots$(H$_2$O)$_n$ and of HXeOXeH$\cdots$(H$_2$O)$_n$ clusters. The geometric distortion is measured as the change in the OXeH angle: $\Delta \angle$OXeH = $\angle$OXeH (ES) − $\angle$OXeH (TS). T (K) is the temperature at which the half-life is 1 hour. Where the 2B barrier is significantly higher than 3B barrier, lifetime was taken from ref. 24 and is marked by an asterisk

	HXeOH$\cdots$(H$_2$O)$_n$				HXeOXeH$\cdots$(H$_2$O)$_n$				
Water mol. (n)	0	1	2	3	0	1	2	3(a)	3(b)
2B barrier (eV)	1.78	1.17	0.51	0.02	1.94	1.45	0.72	0.13	0.31
TS distortion $\Delta \angle$OXeH (°)	92	68	40	11	82	70	42	16	24
Δ reaction (eV)	−4.68	−4.50	−4.46	−4.51	−4.53	−4.50	−4.50	−4.51	−4.55
T (K)	170*	170*	150	7	120*	120*	120*	35	95
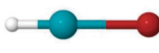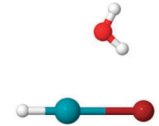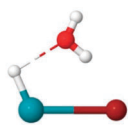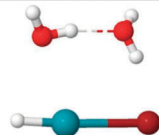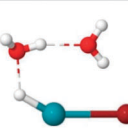
Fig. 2 Equilibrium structures (ES), 2B transition structures (TS) and corresponding barriers of the HXeBr$\cdots$(H$_2$O)$_n$ clusters.

energies, it is expected that under cryogenic non-matrix conditions the crossover between conformations would result in the dissociation of the HNgY molecule. A full investigation of all possible conformations is beyond the scope of this study.

The HXeCCH$\cdots$(H$_2$O)$_n$ clusters show the same behavior with respect to stability of the HXeCCH: as water molecules are added, the barrier for the 2B reaction decreases gradually from 2.01 eV for the isolated molecule ($n = 0$) until spontaneous decomposition occurs for $n \geq 4$. An interesting anomaly is the case of $n = 4$ where the barrier unexpectedly increases to 1.1 eV instead of dropping to below 0.07 eV, the barrier for $n = 3$. The origin of the anomaly can be traced to the formation of a very stable water tetramer structure. In order to catalyze the 2B reaction this tetramer undergoes substantial geometric rearrangement along the reaction path, which results in the elevation of the
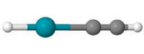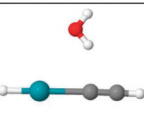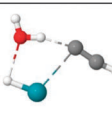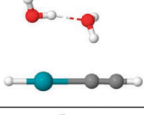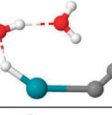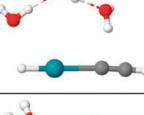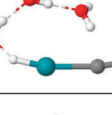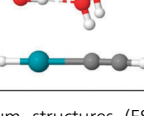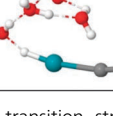

Fig. 3 Equilibrium structures (ES), 2B transition structures (TS) and corresponding barriers of the HXeCCH$\cdots$(H$_2$O)$_n$ clusters.

reaction barrier. This exceptional stability of the $n = 4$ case is somewhat reminiscent of the "magic" number phenomena in hydrated water clusters where certain water cluster ions (H$_2$O)$_n$H$^+$ exhibit enhanced structural stability.[41]

This tetramer structure does not occur for the case of HXeOH$\cdots$(H$_2$O)$_4$, due to the very strong electrostatic interaction between the HXeOH and the water molecule, due to the electron lone-pairs of the (HO) unit in HXeOH. For HXeCCH the electrostatic interaction with the water molecules is considerably weaker and thus stable only-water structures can form.

4. Discussion and conclusion

Environmental effects can have significant implications for the stability of HNgY compounds. A thorough understanding of the interactions of HNgY species with other molecules in their environment and related dissociation mechanisms is essential for devising HNgY compounds that would be able to persist in a realistic environment.

HNgY compounds suffer from two predicted instabilities: one due to mostly intrinsic properties and another due to interaction with adjacent species. All experimentally known HNgY compounds are metastable species, protected by the kinetic barrier for their intrinsic decomposition, and therefore exist only at the cryogenic temperatures. Also, HNgY are ionic species and have a large dipole moment between their two electrostatic units: (HNg)$^+$ and Y$^-$, making them a target for charged species or other species with significant polarities. Thus, understanding of their decomposition processes is essential for devising new HNgY molecules or materials that would have sufficient stability to enable existence under ambient conditions and perhaps their utilization for practical purposes.

Extension of the HNgY stability range is an important challenge. One approach for stabilizing and prolonging the HNgY lifetimes could be the utilization of complexed or adjacent molecules in environments such as molecular solids, liquids or aerosols. Mechanisms of stabilization could be steric, in which complexed molecules could provide steric protection, or electronic, in which electronic interactions with complexed molecules (such as charge transfer, for instance) would influence the electronic structure of the HNgY molecule and affect its stability.

Water molecules can catalyze the 2B decomposing reaction of HNgY molecules by mediating the 2B related proton shift. By their virtue, all known HNgY compounds can decompose by the 2B reaction (HNgY → Ng + HY), which can also be thought of as a shift of the hydrogen atom. Despite being energetically favorable, this reaction is prevented only by the high barrier for this reaction, which requires a significant bending distortion of the molecule. Since water can very effectively transport protons, they can very effectively assist in shifting the hydrogen atom, reducing the strain of the transition structure and dissociation of the HNgY molecule. The formation of a catalytically effective water chain is guaranteed by the ionic character (HNg)$^+$ Y$^-$ of all the HNgY compounds, to which the polar water molecules arrange to optimize the electrostatic interaction.

Therefore, all HNgY compounds are expected to share the "weakness" characteristics with respect to interaction with water.

Another important aspect that is shown is the importance of the inclusion of solvent molecules in the computational model. For the Ng–water compounds, the inclusion of solvent molecules suggests important insights and a new mechanism for their dissociation mechanisms, not predicted by the "isolated molecule" model. In particular, the solvated complex model suggests a possible mechanism that may resolve the discrepancy between experiment and calculation, where the computational "isolated molecule" model predicted longer lifetime for HXeOH[24] while experiments show that HXeOXeH persists longer[21] in the matrix. This predicted mechanism for the "inversion of stability" may well take place under experimental matrix conditions.

Due to the highly transitive character of the precursor molecules (H and Y radicals or ions) which react with the noble-gas to form HNgY compounds, it is very likely that isolation-by-solvation is an essential strategy for their preparation. HNgY–solvent interactions are also capable of stabilizing the H–Ng covalent bond with respect to the 3B dissociation reactions. Therefore, a thorough understanding of the HNgY–solvent chemistry is required for devising new preparation and stabilization strategies. In this respect, the dissociation of HNgY compounds in water raises several important questions: would HNgY molecules also dissolve in other protic or polar solvents? Are there solvents which stabilize HNgY molecules with respect to both 2B and 3B dissociation channels? Answers for these questions may suggest new strategies for the preparation and stabilization of HNgY compounds and are therefore an important direction for future investigations.

Complexation of water–Ng molecules with up to two water molecules does not seem to affect the stability of the water–Ng molecules, which is determined by the 3B reaction. Given the stability range of these special species, it may be interesting to speculate on the possibility that they may be found in natural systems, particularly, interstellar clouds or comets may be relevant. A search for the possible existence of these species in space and planetary systems may be of considerable interest.

Acknowledgements

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