University of Helsinki
Faculty of Science
Department of Chemistry

Novel Organo-Noble-Gas Hydrides

Hanna Tanskanen

ACADEMIC DISSERTATION

To be presented, with the permission of the Faculty Science of the University of Helsinki, for public criticism in the Main lecture hall A110 of the Department of Chemistry (A. I. Virtasen aukio 1, Helsinki) on September 26th 2009, at 12 noon.

Helsinki 2009
Abstract

Noble gases are mostly known as inert monatomic gases due to their limited reactivity with other elements. However, the first predictions of noble-gas compounds were suggested by Kossel in 1916, by von Antropoff in 1924, and by Pauling in 1930. It took many decades until the first noble-gas compound, XePtF$_6$, was synthesized by Neil Bartlett in 1962. This was followed by gradual development of the field and many noble-gas compounds have been prepared. In 1995, a family of noble-gas hydride molecules was discovered at the University of Helsinki. These molecules have the general formula of HNgY, where H is a hydrogen atom, Ng is a noble-gas atom (Ar, Kr, or Xe), and Y is an electronegative fragment. The first molecular species made include HXeI, HXeBr, HXeCl, HKrCl and HXeH. Nowadays the total number of prepared HNgY molecules is 23 – including both inorganic and organic compounds. The first and only neutral ground-state argon compound, HArF, was synthesized in 2000. Helium and neon are the only elements in the periodic table that do not form neutral, ground-state molecules.

In this Thesis, experimental preparation of eight novel xenon- and krypton-containing organo-noble-gas hydrides made from acetylene (HCCH), diacetylene (HCCCCH) and cyanoacetylene (HCCCN) are presented. These novel species include the first organic krypton compound, HKrCCH, as well as the first noble-gas hydride molecule containing two Xe atoms, HXeCCXeH. Other new compounds are HXeCCH, HXeCC, HXeC$_4$H, HKrC$_4$H, HXeC$_3$N, and HKrC$_3$N. These molecules are prepared in noble-gas matrices (krypton or xenon) using ultraviolet photolysis of the precursor molecule and thermal mobilization of the photogenerated H atoms. The molecules were identified using infrared spectroscopy and ab initio calculations.

The formation mechanisms of the organo-noble-gas molecules are studied and discussed in this context. The focus is to evidence experimentally the neutral formation mechanisms of HNgY molecules upon global mobility of H atoms. The formation of HXeCCXeH from another noble-gas compound (HXeCC) is demonstrated and discussed.

Interactions with the surrounding matrix and molecular complexes of the HXeCCH molecule are studied. HXeCCH was prepared in argon and krypton solids in addition to a Xe matrix. The weak HXeCCH···CO$_2$ complex is prepared and identified. Preparation of the HXeCCH···CO$_2$ complex demonstrates an advanced approach to studies of HNgY complexes where the precursor complex (HCCH···CO$_2$) is obtained using photolysis of a larger molecule (propiolic acid).
Acknowledgements

This research was carried out in the Laboratory of Physical Chemistry at the University of Helsinki during years 2003-2007. I would like to express my gratitude to our group leader and my supervisor Professor Markku Räsänen for introducing me to the field of matrix isolation and giving me an opportunity to work in his group. My second supervisor, Dr. Leonid Khriachtchev is greatly acknowledged and appreciated for his encouragement and invaluable guidance during the research. I am very grateful to Professor Jan Lundell for guidance in the field of computational chemistry and for many useful scientific and non-scientific discussions.

I would like to express my gratitude towards co-authors in Papers I-IX for their contribution to the research. I would also like to acknowledge the reviewers of this Thesis, Dr. Austin Barnes and Professor Helge Lemmetyinen, for their work. Head of Laboratory, Professor Lauri Halonen, and all other present and former members of the Laboratory of Physical Chemistry are thanked for making the laboratory a pleasant working environment. Especially I would like to thank my colleagues, Dr. Antti Lignell and Dr. Susanna Pehkonen for sharing the days in the lab and making the days brighter. I want also warmly thank Professor Maija Aksela for her encouragement and support.

Magnus Ehrnrooth Foundation, University of Helsinki, Emil Aaltonen Foundation, and Assosiation of Finnish Chemical Societies are thanked for the financial support during this research.

Finally, I thank my family. My mom and my sisters are thanked for their continuous support and encouragement. My beloved Arto and our son Aarni are thanked for their love, support and patience during the work.

Tusen takk!

Hanna
Tromsø, June 2009
List of original publications

This Thesis is based on the following publications which are referred to by the Roman numerals I-IX:

I  L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen, and M. Räsänen, 
Fluorine-free Organoxenon Chemistry: HXeCCH, HXeCC, and HXeCCXeH 

II L. Khriachtchev, H. Tanskanen, A. Cohen, R. B. Gerber, J. Lundell, M. Pettersson, H. Kiljunen, and M. Räsänen, 
A Gate to Organokrypton Chemistry: HKrCCH 

III H. Tanskanen, L. Khriachtchev, J. Lundell, H. Kiljunen, and M. Räsänen, 
Chemical Compounds Formed from Diacetylene and Rare-Gas Atoms: HKrC₄H and HXeC₄H 

IV H. Tanskanen, L. Khriachtchev, J. Lundell, and M. Räsänen, 
Organo-noble-gas hydride compounds HKrCCH, HXeCCH, HXeCC, and HXeCCXeH: Formation mechanisms and effect of ¹³C isotope substitution on the vibrational properties 

V H. Tanskanen, L. Khriachtchev, J. Lundell, and M. Räsänen, 
HXeCCH in Ar and Kr matrices 

VI L. Khriachtchev, A. Lignell, H. Tanskanen, J. Lundell, H. Kiljunen, and M. Räsänen, 
Insertion of Noble Gas Atoms into Cyanoacetylene: An ab initio and Matrix Isolation Study 

VII L. Khriachtchev, H. Tanskanen, and M. Räsänen 
Selective and reversible control of a chemical reaction with narrow-band infrared radiation: HXeCC radical in solid xenon 
<table>
<thead>
<tr>
<th>Page</th>
<th>Authors</th>
<th>Title and Details</th>
</tr>
</thead>
</table>

The candidate, Hanna Tanskanen, has done most of the experimental work in publications I-IX where she prepared samples, measured FTIR spectra, and performed excimer laser photolysis. She has also participated in the Ar⁺ laser and OPO photolysis together with Dr. Leonid Khriachtchev. The candidate has also taken part in the syntheses of diacetylene, cyanoacetylene, and deuterated acetylene in guidance of M.Sc. Harri Kiljunen. She has performed all calculations in publication V and together with Dr. Antti Lignell and M.Sc. Susanna Johansson in publication VIII. Other calculations were provided by Prof. Jan Lundell (Papers I-IV, VI) and Dr. Antti Lignell (Paper VI). The candidate has been the corresponding author in Papers III-V, VIII and IX and the coauthor in Papers I, II, VI, and VII.
3.3.2 HXeCCH⋯CO₂ complex

4 Conclusions

4.1 Main results briefly

4.2 Future perspectives

References
1 Introduction

Noble gases are mostly known as inert monatomic gases, and seldom chemical reactivity is connected with them. Nevertheless, a number of ground-state noble-gas compounds of radon, xenon, krypton and argon are known. Only for helium or neon no neutral chemical compounds have been found so far.\textsuperscript{1-9}

The noble-gas atoms were discovered around the turn of 20\textsuperscript{th} century.\textsuperscript{10,11} The first predictions of noble-gas compounds were suggested in 1916 by Kossel and in 1924 by von Antropoff,\textsuperscript{12-14} but only in the 1960’s the finding of the first noble-gas compound led to rich experimental xenon and krypton chemistry.\textsuperscript{15} Novel noble-gas compounds (noble-gas hydrides) were found by using matrix isolation techniques in 1990’s.\textsuperscript{2,7,16} One of the recent matrix isolation achievements includes the finding of the first argon containing molecule.\textsuperscript{17,18} The general description of noble-gas chemistry can be found elsewhere.\textsuperscript{19}

This introduction mainly focuses on the history of neutral noble-gas compounds. It should be noted that ions, excited states and weak complexes of noble gases have been also studied extensively, broadening the field of noble-gas chemistry.\textsuperscript{20}

1.1 A glance to the history of noble-gas compounds

All noble gases were discovered before the 20\textsuperscript{th} century and they were considered chemically inert for quite a long time.\textsuperscript{10,11} Kossel, von Antropoff and Pauling suggested that noble-gas atoms could form compounds with halogens.\textsuperscript{12-14,21} However, attempts were unsuccessful at that time.\textsuperscript{22-24} The breakthrough in noble-gas chemistry was achieved in 1962 when Neil Bartlett reported a successful synthesis of the first noble-gas compound, xenon hexafluoroplatinate $\text{Xe}^+\text{[PtF}_6^-]$, which was later found to be a mixture of $\text{XeF}^+\text{PtF}_6^-$ and $\text{XeF}^+\text{PtF}_{11}^-$.\textsuperscript{15,25,26} Almost simultaneously with Bartlett’s work, Hoppe \textit{et al.} synthesized $\text{XeF}_2$ and Claassen \textit{et al.} reported $\text{XeF}_4$.\textsuperscript{27,28} After these discoveries, several compounds where xenon is bound to fluorine and oxygen have been made (for example, $\text{XeF}_6$, $\text{XeOF}_4$ and $\text{XeO}_2\text{F}_2$).\textsuperscript{29-34} The fluorine and oxygen chemistry of xenon has been extensively reviewed by several authors.\textsuperscript{35-38} The theory of chemical binding of xenon is interesting and it has been discussed thoroughly by Coulson.\textsuperscript{39}

Even though most of the known noble-gas compounds possess Xe-O or Xe-F bonds, there are examples where xenon is bound to other elements. The first Xe-Cl bond in $\text{XeCl}_2$ was reported by Nelson and Pimentel in 1967, and this molecule was prepared in a low-temperature xenon matrix.\textsuperscript{40} The first experimental example of the Xe-B bond in F$\text{XeBF}_2$ was demonstrated by Goetschel and Loos in 1972.\textsuperscript{41} The first Xe-N bond was reported in 1979, the formation of $\text{Xe(CF}_3)_2$ was reported presenting the first Xe-C bond, but it has not been spectroscopically characterized.\textsuperscript{43} Besides this species, several other compounds containing a Xe-C bond have been synthesized since 1989 like fluorophenylxenon (II) fluoroborate ($\text{[C}_6\text{H}_5\text{Xe}][\text{B(C}_6\text{H}_5)_3\text{F}]$) and a number of other organoxenonium compounds.\textsuperscript{44-47} The first bulk compound containing a noble-gas-noble-metal bond, [AuXe$_4$]$_2$Sb$_2$F$_{11}$, was
reported by Seidel and Seppelt in 2000. An extensive review of chemistry of xenon derivatives was written by Brel et al.

Krypton chemistry was launched in 1963, one year later than the discovery of the first xenon molecule. Turner and Pimentel reported the first krypton compound, KrF$_2$. The importance of KrF$_2$ is emphasized by the fact that practically all following synthetic krypton chemistry is based on this species. In 1988, Schrobilgen prepared (HCNKrF)$_+$(AsF$_6$)$^-$, which represents the first Kr-N bond. One year later, Schrobilgen and Sanders synthesized Kr(OTeF$_5$)$_2$ which was the first example of a Kr-O bond.

In comparison with xenon, organic compounds containing krypton are very exceptional, and no neutral Kr-containing organic molecule was known before HKrCCH. The other known species with a Kr-C bond are the CH$_3$Kr$^+$ cation, the inorganic HKrCN molecule, and the organo-noble-gas species HKrC$_4$H and HKrC$_3$N prepared later.

Recent research on chemical reactivity of noble gases has benefited from studies in solid noble gases at low temperatures. The matrix isolation technique was originally developed for studies of reactive and unstable species. Most of the matrix isolation studies have been performed in solid argon and neon (see more information on matrix isolation in Experimental section 2.1.1). However, krypton and xenon matrices appear to react with many isolated species and this can be used for synthetic purposes. Examples of such reactivity at low temperatures is evidenced by noble-gas containing molecules like KrF$_2$, XeCl$_2$, and XeClF. An important development in noble-gas chemistry taking advantage of the reactivity of the surrounding was the preparation of noble-gas hydrides HNgY, where Ng is a noble-gas atom and Y is an electronegative fragment. This family of molecules was experimentally introduced at the University of Helsinki in 1995 and the experiments employed the matrix isolation technique. The first molecular species were HXeI, HXeBr, HXeCl, HKrCl and HXeH. Nowadays the total number of prepared HNgY molecules is 23 – including the first neutral ground-state argon compound, HArF.

### 1.2. Noble-gas hydrides

The first noble-gas hydride molecules, HNgY, were found more than ten years ago and at present over twenty HNgY species are known. The HNgY molecules are high-energy metastable species with respect to the HY + Ng asymptote, and they are formed from the neutral H + Ng + Y fragments. Most of the significant studies on these molecules have been performed in noble-gas matrices. However, HXeI, HXeH, HXeCl and HXeCCH have also been reported in the gas-phase Xe clusters. For the HNgY molecules, the synthetic procedure in matrices is quite straightforward and has produced many compounds exhibiting previously unknown chemical bonds such as Xe-S, Xe-I, Kr-Cl, Kr-C, H-Ar, and Ar-F. Additionally, a novel group of halogen-free organo-noble-gas molecules has been introduced, that is the main subject at the research presented in this Thesis.
photolysis of HY produces hydrogen atoms and electronegative\(^{(1)}\) fragments (Y). Next, H atoms are thermally mobilized at 20-45 K depending on the matrix to promote their reactions with neutral Ng + Y centers.\(^7,^{16}\) There are examples of HNgY molecules (HArF, HKrCl, HXeNCO) which also form directly during photodissociation.\(^{17,66,67}\)

HNgY molecules have been attributed to possess a strong (HNg)\(^+\) Y\(^-\) ion-pair character, and their large dipole moments make them attractive systems to investigate electrostatic interactions with surrounding.\(^ {16,68,69}\) HNgY molecules can be easily detected by IR spectroscopy due to their very strong H-Ng stretching absorption with characteristic spectral positions.\(^7,^{16}\) The experiments show that the vibrational properties of the HNgY molecules are sensitive to the local environment.\(^{18,70}\)

The structural and energetic properties of the HNgY molecules are known only from quantum chemical computations. Electronic structure methods such as perturbation theory (mostly MP2, but MP3 and MP4 as well) and coupled cluster [CCSD, CCSD(T)] calculations have been employed. From the computational point of view, the noble-gas compounds are challenging due to a large number of electrons. The \textit{ab initio} calculations provide information on equilibrium structures and computational vibrational spectra, energetics and stability, and also on partial charges of HNgY molecules. The studies of HNgY molecules provide a good example where the computational and experimental approaches are combined successfully.

1.2.1 Nature of bonding and energetics of the HNgY molecules

The origin of bonding in HNgY molecules can be understood based on the model where both ionic (HNg\(^+\) Y\(^-\)) and neutral (HNgY) bonds contribute.\(^ {2,7,16,59}\) This type of bonding was first suggested in a computational study by Last and George in 1988 when semiempirical DIIS (Diatomics In Ionic System) method predicted the existence of HXe\(^+\) Cl\(^-\).\(^71\) The HNgY molecules have a strong ionic nature in their equilibrium structure and the molecule may be viewed as an ion-pair consisting of HNg\(^+\) and Y\(^-\). This model means that the bonding in the H-Ng fragment is mostly covalent and the Ng-Y bond is mainly ionic. When the HNgY molecules are stretched along the molecular axis (H-Ng-Y) the ionic potential surface describing the motion is crossed by a repulsive electronic surface leading to the neutral fragments H + Ng + Y. This has been shown for HXeI and HXeCC,\(^ {61,\text{VII}}\) and theoretically for HArF and recently for HXeCCH.\(^ {72,73}\) The dissociation limit of the HNgY molecules corresponds to the neutral fragments due to the avoided

---

\(^{(1)}\) Electronegative Describing elements that tend to gain electrons and form negative ions. The halogens are typical electronegative elements. There are various ways of assigning values for the electronegativity of an element. Mulliken electronegativities are calculated from E= \((I+A)/2\), where I is ionization potential and A is electron affinity. More commonly, Pauling electronegativities are used. These are based on bond dissociation energies using a scale in which fluorine, the most electronegative element, has a value 4.

crossing between the neutral and ionic potential energy surfaces. For HArF, these contributions have been verified by MRCI (Multireference configuration interaction) yielding an energy barrier of 0.33 eV for HArF dissociation to H + Ar + F fragments.\(^7\) In a qualitative literature model, the ionization potential (IP) of Ng, electron affinity (A)\(^2\) of Y and the dissociation energies of NgH\(^+\) can be used to construct the energetics between ionic and neutral dissociation limits.\(^2\) Low ionization potentials for Ng and high electron affinities for Y are favourable to the stability of HNgY molecules enhancing the HNg\(^+\)Y\(^-\) ion-pair Coulombic attraction.\(^2\) Two factors make this electronic structure energetically favorable: the NgH\(^+\) ions are strongly bound\(^74-77\) and the Y fragments in all the found HNgY molecules have high electron affinities. Also, the small Y\(^-\) fragments stabilize HNgY more than the larger ones, because they allow a closer approach of the HNg\(^+\) fragment, which leads to stronger Coulombic attraction between the charged species. It should be remembered, that the ionic model is simplified and other electronic configurations contribute also to the wavefunction describing the HNgY molecule. Other important resonance structures are neutral HNgY and ionic H\(^+\)X\(^-\)Y.\(^2,7,16\) For HArF, Avramopoulos et al. calculated the resonance structures of H-Ar\(^+\)F ↔ H Ar\(^2\)F ↔ H\(^+\)ArF.\(^78\) Berski et al. have studied bonding and delocalization of electron density in these chemical systems using topological analysis of the electron localization function (ELF).\(^79\) The calculations reveal that all molecules included in their study (HXeCN, HKrCN, HXeSH and HXeOH) are charge-transfer systems with the approximate formulas [HKr]\(^{0.65}\) [CN]\(^{-0.65}\), [HXe]\(^{0.66}\) [CN]\(^{-0.66}\), [HXe]\(^{0.45}\) [SH]\(^{-0.45}\), and [HXe]\(^{0.57}\) [OH]\(^{-0.57}\). It was shown that the Ng-C, Ng-N, Xe-S, and Xe-O bonds are of the unshared electron type and are mainly of electrostatic origin, i.e. the interaction is mainly ionic but with non-negligible fraction of a covalent character. This conclusion is in agreement with the simple model where both neutral and ionic potential surfaces contribute to the HNgY molecule.

Recently, the bonding of HXeCCH was studied.\(^1,73\) In this molecule, the acetylenic group is strongly electronegative leading to the (H-Xe)\(^+\)(CCH)\(^-\) ionic interaction. The structure, the NBO partial charges and the bond orders are presented in Fig. 1. The large partial charge +0.83e on Xe indicates a powerful electron-withdrawing effect of CCH. Between (H-Xe)\(^+\) and CCH\(^-\), the bond order is very small (0.07) showing that the bond is mainly ionic without significant covalent contribution. The bond order value of 0.796 in (H-Xe)\(^+\) shows an essentially full two-electron covalent bond. The electron transferred from Xe to form CCH\(^-\) goes to an sp-type orbital in the bonding mechanism of HXeCCH and the highest occupied molecular orbital appears quite delocalized, mostly on the CCH group.\(^1,73\)

All HNgY molecules are highly metastable species. The decomposition process for HNgY → HY + Ng is always strongly exoergic; however, the decomposition is prevented

---

\(^2\) Electron affinity Symbol A. The energy change occurring when an atom or molecule gains an electron to form a negative ion. For an atom or molecule X, it is the energy released for the electron-attachment reaction \(X(g) + e \rightarrow X^-(g)\). Often this is measured in electronvolts.

by high barriers. The other decomposition channel HNgY → H + Ng + Y is endothermic for all experimentally prepared molecules. For HXeCCH (see Fig. 2), the barrier for the HXeCCH → HCC + Xe reaction is over 2 eV and the barrier for the HXeCCH → H + Xe + CCH is 0.98 eV. However, the backward reaction (H + Xe + CCH → HXeCCH) has a small barrier of 0.022 eV implying the formation of the molecule by this process is very efficient.

Computing the H + Ng + Y dissociation path is extremely difficult due to involvement of several electronic configurations. All experimentally observed HNgY molecules are computationally below the neutral H + Ng + Y dissociation limit and the existence of this barrier is not the determining factor for their stability. The DFT and MP2 calculations are able to give reasonable estimates especially for the bending barrier, but for the H+ Ng + Y stretching coordinate, the MP2 method can give spurious results and more sophisticated methods are required. The MP2 method has been widely used in computing energies of HNgY molecules and many of the theoretical predictions were experimentally realized. However, the MP2 is often inaccurate with respect to the relative energies of the HNgY molecule and the H + Ng + Y reagents, especially for larger open-shell species.
1.3 Organo-noble-gas chemistry

In organic chemistry of noble-gas compounds, $\text{XeF}_2^{27}$ and $\text{XeF}_4^{28}$ and their related cations $[\text{XeF}]^+$ and $[\text{XeF}_3]^+$, have been widely used in synthesis. The $[\text{FXe}]^+$ cation is the basis for preparation of new xenon-carbon bonds due to its strong oxidation potential. Additionally, organoxenonium salts offer a promising route to the Xe-C compounds due to their lower oxidation potential in comparison with the $[\text{FXe}]^+$ cation. The stability and reactivity of organoxenonium salts $[\text{RXe}]^+[\text{Y}^-]$ depends on the nature of the organic group R and counteranion $[\text{Y}^-]$. At the present time, various types of organoxenon compounds are known: mononuclear xenonium(II) salts $[\text{RXe}]^+[\text{Y}^-]$ (where R = aryl, polyfluoroalkenyl, alkynyl and Y = a counteranion), binuclear xenonium(II) salts $[(\text{C}_6\text{F}_5\text{Xe})_2\text{Z}]^+[\text{AsF}_6]^- \text{ (where Z = F or Cl)}$, arylxenonium(IV) salt $[\text{C}_6\text{F}_5\text{XeF}_2]^+[\text{BF}_4]^{-}$, covalent xenon(II) compounds $\text{C}_6\text{F}_5\text{XeZ}$ [where Z = F, Cl, CN or OC(O)C$_6$F$_5$], symmetric and asymmetrical diorganoxenon(II) compounds, $\text{R}_2\text{Xe}$ (where $\text{R} = \text{C}_6\text{F}_5$ or 2,4,6-C$_6$H$_2$F$_3$), and $\text{RXeR'}$ (where $\text{R} = \text{C}_6\text{F}_5$, and $\text{R'} = 2,4,6-$C$_6$H$_2$F$_3$), respectively. Recently, Frohn and Bardin have reported the preparation of an alkynylxenon(II) compound $[\text{CF}_3\text{C}==\text{CXe}][\text{BF}_4]$. Recent reviews on organoxenon chemistry have been written by Brel et al. and by Frohn and Bardin.

In 2000, it was predicted that Xe could be inserted into carboxylic acids, and chemical binding of xenon to proteins was hypothesized. However, no experimental verification of these results has been reported. In 2002, Lundell et al. presented the first prediction on fluorine-free alkynylxenon derivatives. They reported computational predictions of $\text{HXeCCH}$ and other organic molecules such as Xe-insertion compounds of benzene and phenol. These calculations also described molecules with more than one xenon atom such as $\text{HXeCCXeH}$ and $\text{HXeCCXeCCXeH}$. It was suggested that such xenon-insertion molecules could form a new class of possible precursors and intermediates for synthetic and organoelement chemistry. These predictions have been realized for $\text{HXeCCH}$ and $\text{HXeCCXeH}$ which were prepared experimentally briefly after the computational prediction. The existence of the larger systems quoted by Lundell et al. and shown in Fig. 3 remains still an open question. Feldman and coworkers have reported failed attempt to insert Xe into benzene.

![Figure 3](https://via.placeholder.com/150)

**Figure 3** Computationally predicted and characterized compounds with Xe inserted to acetylene, benzene and phenol. The structural models of molecules are adapted from Ref. 83.
1.4 Aim of this study

In this Thesis, experimental preparation of eight novel xenon- and krypton-containing organo-noble-gas hydrides made from acetylene (HCCH), diacetylene (HCCCCH) and cyanoacetylene (HCCCN) are presented.

The main focus of this Thesis at the first stage was to test experimentally the hypothesis of fluorine-free organo-noble-gas compounds. The first experimental target was the stoichiometrically simplest species, HXeCCH in solid xenon and HKrCCH in solid krypton. Once it was clear that HXeCCH and HKrCCH could be made, the chemistry of HXeC\textsubscript{2n}H and HKrC\textsubscript{2n}H compounds were studied further. A promise for larger molecules originates from the increasing electron affinities of longer carbon chains. The electron affinities (EA) are 2.956 eV for CCH, 3.558 eV for C\textsubscript{4}H, 3.809 eV for C\textsubscript{6}H, and 3.996 eV for C\textsubscript{8}H. Therefore, insertion of Ng atoms into HC\textsubscript{2n}H (where n = 1, 2, 3, …) is a realistic idea providing an experimental test for the simple model of bonding described in Chapter 1.2.1. The experiments with diacetylene were a step to increase the electronegativity of the Y fragment. The HXeC\textsubscript{4}H and HKrC\textsubscript{4}H seem to be more strongly bound than HXeC\textsubscript{2}H and HKrC\textsubscript{2}H. The preparation of HArC\textsubscript{4}H was tried because EA of C\textsubscript{4}H radical is larger than that of a F atom (~3.4 eV). However, this compound did not form in experiment. Additionally, the formation mechanisms of organo-noble-gas molecules and the matrix effects are studied and discussed in this context. The focus is to evidence experimentally the neutral formation mechanisms of HNgY molecules upon global mobility of H atoms. The formation of HXeCCXeH from another noble-gas compound (HXeCC) is demonstrated and discussed. Finally, the weak complex of HXeCCH--CO\textsubscript{2} is prepared and identified.
2 Methods

2.1 Experimental methods

2.1.1 Matrix isolation

The matrix isolation technique was originally introduced in the 1950’s as a method to investigate reactive intermediates and unstable species, for example radicals.\textsuperscript{55,56} In this approach, the studied species are trapped at low temperatures (typically between 4 and 80 K) in an inert solid matrix. These conditions considerably increase the lifetime of the trapped unstable species and decrease its interaction with other atomic or molecular species. The matrix isolation technique has been widely and successfully used for decades with different detection techniques including infrared (IR), laser-induced fluorescence (LIF), Raman, and electron paramagnetic resonance (EPR) spectroscopy.\textsuperscript{96,97} Most of the matrix isolation studies nowadays utilises noble gases as matrix materials, mainly argon and neon, but xenon and krypton solids have been used as well. The noble-gas solids do not absorb in the IR region and for most purposes they are chemically inert.\textsuperscript{96} Nitrogen, hydrogen or oxygen as well as other molecular solids can also be used as a matrix material.

2.1.2 Experimental procedure

In this research, acetylene (HCCH), diacetylene (HCCCCH), cyanoacetylene (HCCCN) and propiolic acid (HCCCOOH) have been used as precursor molecules. The diacetylene and cyanoacetylene molecules were synthetized by M.Sc. Harri Kiljunen.

Gaseous mixtures of the studied molecule and noble gas were prepared in various proportions in a glass bulb. The typical absorber to matrix (A/M) ratios varied between 1:300 and 1:2000. The mixtures were deposited onto a CsI window cooled with a closed-cycle helium cryostat (DE-202, ADP) at typically 10-30 K, depending on the matrix gas. The selection of the deposition temperature was always a compromise between the monomeric absorber and the optical matrix properties. A typical matrix thickness was \( \sim 100 \) \( \mu \text{m} \). After deposition of the gaseous sample onto the cold window, the matrix is cooled to the lowest operation temperature (7-9 K). The photolysis of the matrix was carried out at this temperature. Then the photolyzed matrix was annealed up to \( \sim 30 \) K (krypton) or 40-45 K (xenon) to mobilize hydrogen atoms.\textsuperscript{98-101} After annealing the matrix spectra were measured at 7-9 K.

The infrared (IR) absorption spectra (4000-400 cm\(^{-1}\)) were measured with a Nicolet 60SX Fourier-transform (FTIR) spectrometer typically with 1 cm\(^{-1}\) resolution coadding 200-1000 scans. Photolysis of the precursor molecules was performed mainly with an excimer laser (MPB, MSX-250) operating at 193 nm or with an optical parametric
oscillator (OPO) at 250 nm. Other radiation sources were also used, for example 488 nm (Ar\(^+\)) radiation was used to decompose some of the annealing-induced products. Detailed information of the sample preparation and experimental condition employed in these studies can be found in Papers I-IX.

### 2.2 Computational methods

In this section, only short introduction to \textit{ab initio} methods is given. The detailed information on the methods, approximations, procedures and applicabilities can be found elsewhere.\(^{102}\)

The \textit{ab initio} methods are based on solving the time-independent Schrödinger equation.

\[
H \Psi(\mathbf{r}, \mathbf{R}) = E \Psi(\mathbf{r}, \mathbf{R})
\]  

(1)

In this equation, \(H\) is the Hamiltonian operator; \(E\) is the energy (eigenvalue) of the stationary state representing by the wavefunction (eigenfunction, \(\Psi\)) in the electronic (\(\mathbf{r}\)) and nuclear (\(\mathbf{R}\)) coordinates. It is impossible to solve Schrödinger equation (1) analytically for molecular systems and various approximations are needed to solve the equation. The Born-Oppenheimer approximation separates electronic and nuclear motions. The Schrödinger equation is separated into one part which describes the electronic wavefunction for a fixed nuclear geometry, and another part for the nuclear wavefunction where the energy from the electronic wavefunction plays the role of potential energy. Schrödinger equation is solved depending only on the electronic coordinates and handling the nuclear coordinates as parameters. Using the Born-Oppenheimer approximation provides the effective electronic energy of the molecule in static field of the nuclei.

\[
H \Psi(\mathbf{r}; \mathbf{R}) = E^{\text{eff}}(\mathbf{R}) \Psi(\mathbf{r}; \mathbf{R})
\]  

(2)

This approximation allows construction of potential energy surface (PES) which describes the changes of molecular electronic properties when the nuclear coordinates are changed. The electronic Schrödinger equation has to be solved for large number of nuclear geometries until the PES is known.

However, even with the Born-Oppenheimer approximation the Schrödinger equation is difficult to solve for molecular systems containing many atoms. Another useful approximation is the Hartree-Fock approximation where the energy of the electron depends on the electric field generated by the nuclei and the other electrons. By using the Fock operator, the \(n\)-electron equation is separable into \(n\) one-electron equations. There, the electron-electron repulsion is treated as an electrostatic energy between one electron and the charge density created by all other electrons. The total wavefunctions are described as products of the one-electron wavefunctions and when electron spin is included they are called spin-orbitals. The antisymmetrized product of the total wavefunction is called a Slater determinant. The Hartree-Fock equation is solved by using the self-consistent field (SCF) method employing an approximation where wavefunctions
are generated iteratively. However, the Hartree-Fock approximation does not take into account the Coulombic electron-electron correlation because each orbital is a solution of the one-electron Schrödinger equation. For a better result, it is necessary to correct the motions of the electrons. One of the methods that include the effects of electron correlation is the perturbation theory where the total Hamiltonian operator is written as a sum of the Hartree-Fock Hamiltonian \( H_0 \) and the perturbation term \( V \)

\[
(H_0 + \lambda V)\Psi = E\Psi.
\] (3)

The \( \lambda \) is the strength parameter. When the eigenfunctions and eigenenergies are expanded in a Taylor series and grouped to the order of the strength parameter, the linear combinations of different orders of perturbation are obtained. The Møller-Plesset perturbation method to the second order is referred for example as MP2 and coupled cluster method as CCSD(T).

The molecular orbitals are generated from a linear combination of atomic orbitals. These functions constitute the basis set. The Gaussian-type functions are mostly used in general QM programs. The Gaussian primitives \( g_p \) are given as

\[
g_p = c(\alpha) x^n y^m z^l e^{-a r^2}.
\] (4)

where the orbital exponent \( \alpha \) is a parameter describing the radial extent of the function, \( c \) is the normalizing constant, \( n, m, \) and \( l \) are the powers of \( x, y, \) and \( z \) coordinates.

In this work, \textit{ab initio} calculations have been used to support the experimental work. The \textit{ab initio} calculations were carried out with the GAUSSIAN98 (Revision A.11.4) and GAUSSIAN03 (Revision B.02) packages of computational codes.\textsuperscript{103,104} The electron correlation methods were the Møller-Plesset second order (MP2) perturbation theory where all electrons were taken explicitly into correlation calculations (full). For HXeCC, the coupled cluster CCSD(T) method was employed. The standard split valence 6-311++G(2d,2p) basis set was applied for H, C, N, Kr, and Ar atoms. For Xe atoms, an effective core potential (ECP) was used for economical reasons because of the large number of electrons. In ECP, the core electrons are modelled by a suitable function and only valence electrons are treated explicitly.\textsuperscript{102} The relativistic pseudopotential by LaJohn \textit{et al.} was employed for Xe and it is denoted as LJ18 throughout this work. This ECP include the \( d \) subshell in the valence space resulting in 18 valence electrons. The valence basis set combined with ECP was used in a decontracted form.\textsuperscript{105} In some calculations, the effective core potential of LaJohn \textit{et al.} (LJ18) was combined with Runeberg and Pyykkö’s valence space and employed for Xe atoms.\textsuperscript{106} In Paper VI, the anharmonic computations on Kr-containing molecules were performed with the vibrational self-consistent field (VSCF) method and its extensions by correlations via the second-order perturbation theory.\textsuperscript{107-110} All anharmonic calculations based on the VSCF method were performed with the GAMESS (version R4, 2004) electronic structure program.\textsuperscript{111} The C, N, and H atoms were described by the cc-pVDZ all electron basis set, whereas for krypton the cc-pVDZ-PP basis set were used.\textsuperscript{112}
3 Results and discussion

3.1 Identification of new organo-noble-gas hydrides

This section focuses on the preparation and identification of novel organo-noble-gas compounds in experiments with various precursor molecules $\text{C}_2\text{H}_2$, $\text{C}_4\text{H}_2$, and $\text{HC}_3\text{N}$ in solid noble gas matrices.

The characterization of the novel noble-gas molecules is based on the isotope substitution experiments and on the computed IR spectra. A detailed discussion of the assignments of the organo-noble-gas molecules can be found in Papers I-VI.

The calculated spectra are in most cases in good agreement with the observed spectra. All computationally strong bands are usually found in the experiments. The harmonic MP2 H-Ng stretching frequencies are overestimated, but this is typical in the case of the HNgY molecules. This overestimation is mainly due to anharmonicity not being taken into account in the calculations. The MP2 method is used as a standard method for economical reasons but for the energy calculations more accurate methods should be used.

The HNgY molecules have characteristic properties that can be used in their identification. They are formed upon annealing of the photolyzed HY/Ng matrix at $\sim 40$ K in solid xenon and at $30$ K in solid krypton. The H-Ng stretching absorption is the most intense and very characteristic for the HNgY molecules. The noble-gas molecules usually decompose easily upon irradiation by light due to excitation to repulsive states.

3.1.1 HXeCCH, HXeCC, HXeCCXeH, and HKrCCH

The infrared (IR) spectra of acetylene in Ng (Ng = xenon, krypton and argon, $\text{C}_2\text{H}_2$/Ng) matrices and in argon matrix doped with xenon ($\text{C}_2\text{H}_2$/Xe/Ar) are presented in Fig. 4. Acetylene can be photolyzed in solid xenon with UV light (for example, 193 nm) producing isolated H atoms, $\text{C}_2\text{H}$ radicals, $\text{Xe-CC}$ complexes, and $\text{XeHXe}^+$ ions. The $\text{C}_2\text{H}$ radicals are further photolyzed to $\text{C}_2$ molecules. 250 nm photolysis is used in some experiments with $\text{C}_2\text{H}_2$/Xe. The 193 and 250 nm photolysis products are similar, but the $\text{C}_2/\text{C}_2\text{H}$ ratio is larger upon irradiation at 250 nm than at 193 nm. The larger $\text{C}_2/\text{C}_2\text{H}$ ratio leads upon annealing to more efficient formation of HXeCC radicals as compared with HXeCCH. In solid krypton, the most prominent photolysis products of acetylene are $\text{C}_2\text{H}$ radicals, $\text{KrHKr}^+$ ions, as well as $\text{C}_2$. $\text{C}_2$ are IR-inactive in a Kr matrix. Some formation of $\text{C}_4$ clusters was observed especially in samples with a higher initial acetylene concentration. The photodecomposition of acetylene is more efficient in solid xenon (typically $\sim 50-80\%$) than in solid krypton ($\sim 20-30\%$) for similar light exposures at 193 nm (typically up to 5000 pulses with pulsed energy density of 20 mJ/cm$^2$). This is probably connected with the fact that UV photolysis in noble-gas solids is often self-limited due to rising absorbers. 193 nm photolysis of $\text{C}_2\text{H}_2$/Ar sample generates $\text{C}_2\text{H}$ radicals as the main product. In mixed matrices [$\text{C}_2\text{H}_2$/Xe/Ng (Ng = Kr or Ar)], the
CCH::Xe and Xe-CC complexes are visible upon 193 nm photolysis. The IR-active photolysis products in various solids are collected in Table I.

![Figure 4](image)

**Figure 4**  IR absorption spectra of acetylene in solid xenon, krypton and argon at 8 K. The lower trace shows the effect of Xe atoms on the acetylene absorption bands in an Ar matrix. The experimental absorptions of acetylene in various matrices can be found in Paper V.

**Table I**  193 nm photolysis products (absorption wavenumbers in cm\(^{-1}\)) of acetylene in Ar, Kr and Xe matrices. The dominating photolysis products are highlighted in bold.
Subsequent annealing of the photolyzed matrix at 30 K (Kr) and at 45 K (Xe) mobilizes H atoms and leads to the formation of various noble-gas molecules with characteristic H-Ng stretching bands: HKrCCH in solid krypton, and HXeCCH, HXeCC, HXeCCXeH, and HXeH in solid xenon. Vinyl radicals, C$_2$H$_3$, are also formed upon annealing. Annealing of photolyzed C$_2$H$_2$/Xe/Kr (at 30 K) and C$_2$H$_2$/Xe/Ar (at 20 K) matrices produces vinyl radicals and HXeCCH in solid krypton (in addition to HKrCCH) and argon. The absorption wavenumbers are collected in Table II. The spectra of these molecules in C$_2$H$_2$/Xe, C$_2$H$_2$/Kr and C$_2$H$_2$/Xe/Kr matrices in the H-Ng stretching region are presented in Fig. 5. In experiments with C$_2$H$_2$/Ar, no noble-gas molecules are produced.

**Table II**

Annealing products of (absorption wavenumbers in cm$^{-1}$) acetylene (C$_2$H$_2$/Ng and C$_2$H$_2$/Xe/Ar) samples in Ar, Kr and Xe matrices. The strongest absorptions are marked with (s).

<table>
<thead>
<tr>
<th></th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKrCCH</td>
<td></td>
<td></td>
<td>1241.6 (s)</td>
</tr>
<tr>
<td>HXeCCH</td>
<td>1531.3</td>
<td>1517.4</td>
<td>1478.3 (s)</td>
</tr>
<tr>
<td></td>
<td>1518.7</td>
<td>1505.6</td>
<td>1474.7</td>
</tr>
<tr>
<td></td>
<td>1482.2</td>
<td>1479.9</td>
<td>1486.4 (s)</td>
</tr>
<tr>
<td>HXeCCXeH</td>
<td></td>
<td></td>
<td>1305.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1300.9 (s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1294.3</td>
</tr>
<tr>
<td>HXeH</td>
<td></td>
<td></td>
<td>1180</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1166</td>
</tr>
<tr>
<td>HKrCCH</td>
<td></td>
<td>1256.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1249.6</td>
<td>1241.6 (s)</td>
</tr>
<tr>
<td>C$_2$H$_3$</td>
<td>1356.7</td>
<td>1353.2</td>
<td>1348.9</td>
</tr>
<tr>
<td></td>
<td>900.8</td>
<td>896.6</td>
<td>891</td>
</tr>
<tr>
<td>C$_4$H</td>
<td></td>
<td>2055</td>
<td></td>
</tr>
</tbody>
</table>

21
Figure 5  Annealing-induced formation of Xe- and Kr-containing noble-gas compounds in different matrices. The IR spectra are measured at 8 K. (a) Difference spectrum showing the result of annealing at 45 K of a photolyzed C$_2$H$_2$/Xe (~1/1000) matrix. (b) Result of annealing at 30 K of a photolyzed C$_2$H$_2$/Kr (~1/2000) matrix. (c) Result of annealing at 30 K of a photolyzed C$_2$H$_2$/Xe/Kr (~1/2/1000) matrix. All samples were photolyzed using 193 nm (~ 1800-2400 pulses, 10-20 mJ/cm$^2$) before annealing. The absorption bands of vinyl radical are marked with asterisk.

The assignment of HXeCCH in a Xe matrix is based on several facts. The amount of the absorber HXeCCH with the H-Xe stretching band 1486 cm$^{-1}$ correlates with the C$_2$H concentration after photolysis, and its bands at 3273 and 626 cm$^{-1}$ fit well the H-C stretching and H-CC bending modes. The deuteration and $^{13}$C experiments fully support this assignment. The harmonic MP2 calculations agree reasonably with the experimental values. The assignment of HKrCCH in solid krypton is done similarly to HXeCCH, and the formation of HKrCCH needs C$_2$H radicals in the matrix. Such compounds as HKrCC or HKrCCKrH were not found, highlighting the lower reactivity of krypton compared to xenon.

Formation of HXeCC is enhanced by longer 193 nm or 250 nm initial photolysis which produce larger amounts of C$_2$ molecules. C$_2$ is an electronegative fragment and H atoms can react with the Xe-C$_2$ center. The selective photodissociation of HXeCC leads to an increase of the Xe-C$_2$ concentration. HXeCC is also very photolabile compared to HXeCCH, HXeH and HXeCCXeH molecules. The absorption bands of the H-Xe
stretching mode of HXeCC and HXeCCH partially overlap with each other, and the absorptions of both molecules are doublets. By using the selective photolysis, it is possible to separate the absorptions of HXeCC and HXeCCH from each other.

The assignment of HXeCCXeH at ~1301 cm\(^{-1}\) is based on \textit{ab initio} calculations and deuteration experiments. The \textit{ab initio} calculations show the stability of the species and predict a decrease (by ~140 cm\(^{-1}\)) of its H-Xe stretching frequency as compared to HXeCCH. This is in agreement with the measured difference of 177 cm\(^{-1}\). The experiments with partially deuterated acetylene provide a conclusive method to identify HXeCCXeH. For HXeCCXeD, two absorptions corresponding to the H-Xe and D-Xe stretching modes are expected and these bands should be shifted from the corresponding bands belonging to HXeCCXeH and DXeCCXeD. The MP2 calculations predicted blue shifts for the H-Xe and D-Xe stretching absorptions (+40 and +24 cm\(^{-1}\), respectively) of HXeCCXeD from the corresponding bands of HXeCCXeH and DXeCCXeD. These shifts are experimentally determined to be +41 and +27 cm\(^{-1}\), respectively (see Fig. 6).\(^1\)

The experimental and calculated vibrational frequencies of HXeCCH, HXeCC, HXeCCXeH and HKrCCH are collected in Tables VI and VII (Chapter 3.2).\(^{11,16}\)

![Figure 6](image_url)

**Figure 6**  
Difference IR absorption spectra demonstrating results of photodissociation of HXeCCXeH isotopologues (a) without deuteration and (b) with deuteration (degree of deuteration ~70%). The species were obtained by 250 nm photolysis (1.5x10\(^4\) pulses, ~2 mJ/cm\(^2\)) of acetylene in solid xenon and annealing at 45 K.
3.1.2 HXeC₄H and HKrC₄H

The IR absorption spectra of C₄H₂ and C₄D₂ in a Kr matrix are presented in Fig. 7 and the recorded spectra indicate mainly monomeric trapping of the precursor molecule. The diacetyle-d₂ sample contains practically no diacetylene-d. Similar results were obtained for Xe matrices.

![IR absorption spectra of diacetylene (~ 1:1000) in solid krypton at 8 K. Spectra for C₄H₂ and C₄D₂ are shown by the upper and lower traces, respectively. The absorptions of diacetylene are presented in Paper III.](image)

Photolysis at various wavelengths (193, 235, 240 and 250 nm) was used. The photolysis products of diacetylene in noble-gas matrices are C₄H radicals,¹²² carbon clusters such as C₄,¹¹⁷ and C₈,¹¹⁷ and NgHN²⁺ (see Table III). The C₄H concentration achieves in the initial stage of photolysis reaches its maximum, and decreases upon longer photolysis. The C₄ concentration increases monotonically. It should be noted, that the KrHKr⁺ ions¹¹⁶,¹²³ were not detected after photolysis at 240 and 250 nm, whereas this species was seen after photolysis at 235 and 193 nm.

<table>
<thead>
<tr>
<th>Absorbance</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄H₂/Kr</td>
<td>3000</td>
</tr>
<tr>
<td>C₄D₂/Kr</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>1000</td>
</tr>
</tbody>
</table>

**Table III**  *The main photolysis products of diacetylene in Kr and Xe matrices.*

<table>
<thead>
<tr>
<th></th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄H</td>
<td>2055</td>
<td>2050</td>
</tr>
<tr>
<td>C₄</td>
<td>1539.5</td>
<td>1536</td>
</tr>
<tr>
<td>C₈</td>
<td>2065.5</td>
<td>2057</td>
</tr>
<tr>
<td>KrHKr⁺</td>
<td>852</td>
<td>1008</td>
</tr>
<tr>
<td>XeHXe⁺</td>
<td>730.5</td>
<td>842.5</td>
</tr>
</tbody>
</table>
Thermal annealing of photolyzed C₄H₂/Ng matrices mobilizes the H atoms and they can react with the Ng + C₄H centers, which yields new molecules. The strongest bands are assigned to the H-Ng stretching modes of the HKrC₄H and HXeC₄H molecules (see Table IV and Fig. 8). In a Xe matrix, the formation of HXeH is also observed.⁶⁰ At higher-temperature annealing (above 40 and 55 K in krypton and xenon solids, respectively), a decrease of some lower-frequency H-Ng stretching bands and an increase of the higher-frequency bands components were observed. In experiments with C₄H₂/Ar, there was no detection of similar absorptions of HArC₄H.

Table IV  Main annealing products (in cm⁻¹) of diacetylene in Kr and Xe matrices. The (h) mark refers to the absorption bands observed after higher-temperature annealing.

<table>
<thead>
<tr>
<th></th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKrC₄H</td>
<td>1275.5</td>
<td></td>
</tr>
<tr>
<td>(H-Kr str.)</td>
<td>1290</td>
<td>1290</td>
</tr>
<tr>
<td></td>
<td>1307.5</td>
<td>1307.5</td>
</tr>
<tr>
<td></td>
<td>1317 (h)</td>
<td>1326</td>
</tr>
<tr>
<td>HXeC₄H</td>
<td>1503.5</td>
<td></td>
</tr>
<tr>
<td>(H-Xe str.)</td>
<td>1521.5</td>
<td>1521.5</td>
</tr>
<tr>
<td></td>
<td>1532</td>
<td>1532</td>
</tr>
<tr>
<td></td>
<td>1545 (h)</td>
<td>1555 (h)</td>
</tr>
<tr>
<td></td>
<td>1558.5 (h)</td>
<td>1560</td>
</tr>
<tr>
<td>HXeH</td>
<td>1180</td>
<td>1180</td>
</tr>
<tr>
<td></td>
<td>1166</td>
<td></td>
</tr>
</tbody>
</table>

The identification of HNgC₄H molecules is straightforward. The obtained IR spectra strongly depend on the matrix medium. The new species exhibit typical properties of HNgY species such as strong H-Ng stretching absorptions with extensive matrix-site splitting. The noble-gas molecules usually decompose easily upon irradiation by light due to excitation to the repulsive states and this behaviour was found for both HKrC₄H and HXeC₄H molecules. By using this property, weaker absorptions belonging to these respective species were identified. All computationally strong absorptions (the H-Ng stretch, the H-C stretch, and the C-C-H and C-C-C bendings) were experimentally identified. The deuteration experiments also support the assignment and the calculated spectra are in agreement with experiment.
Figure 8  Difference IR absorption spectra of HXeC$_4$H in solid xenon. The spectra are measured at 8 K. Shown are the result of annealing at 45 K of the photolyzed sample (the upper trace), the result of annealing at 65 K (the middle trace), and the result of 250 nm irradiation of the annealed sample (the lower trace). The absorption band marked with asterisk (*) is not assigned here to HXeC$_4$H molecule because this is not supported by the deuterization experiments and calculations.

3.1.3 HXeC$_3$N and HKrC$_3$N

The deposited HCCCN/Ng (Ng = Xe, Kr, and Ar) samples were quite monomeric with respect to cyanoacetylene. The IR absorption bands of the HCCCN precursor in argon, krypton, and xenon solids can be found in Paper VI. Similarly to our experiments with acetylene and diacetylene, photolysis and annealing of cyanoacetylene/Ng matrices evidence the formation of noble-gas hydrides. Accordingly, the strongest IR absorption bands are found to be at 1492.1 and 1624.5 cm$^{-1}$ for Ng = Kr and Xe, respectively (see Fig. 9). Deuteration of cyanoacetylene leads to a proper down-shift of the H-Ng stretching frequency with the H/D ratios of 1.349 and 1.380 for Ng = Kr and Xe, respectively. The experiments with $^{15}$N/$^{14}$N-substitution were also performed to increase the confidence of the assignment. The annealing-induced vibrational bands are efficiently bleached by UV light, which is also characteristic for noble-gas hydrides. The band fine structure of the Kr-containing molecule, which is most probably due to the matrix-site effect, is very similar to the H-Kr stretching bands of HKrCCH and HKrC$_4$H.$^{3,4}$ New absorptions were observed in three spectral regions (H-Ng, C=N, and C-C stretching modes) that belong to the HNgC$_3$N molecules (see Tables VI and VII). The observed bands are also the strongest in the computed spectrum. The structural assignment was not straightforward due to possible HNgCCNC isomers possessing similar vibrational properties. However, the computational spectra of
HKrCCCN and HXeCCCN fit most closely the experimental data, which is the basis for the assignment. The identified species also have the H-Ng stretching absorptions at quite similar frequencies to the known HKrCN and HXeCN molecules, which is in agreement with the theoretical predictions. No strong candidates for an Ar compound were found in the experimental data.

Figure 9  Spectra of (a) HKrCCCN and (b) HXeCCCN in the H-Ng stretching region. The spectra were obtained by 193 nm photolysis of cyanoacetylene in noble-gas matrices and annealing at 30 K (Kr) and 45 K (Xe). The insert in panel (b) shows the correlation of the main band at 1624.5 cm⁻¹ with the weaker bands at 896 (triangles) and 2233 (circles) cm⁻¹ obtained by using photodissociation at 250 nm. The data points shown in the insert correspond to a different duration of photodissociation.
3.1.4 Experimental and computational properties of organo-noble-gas molecules

In this section, the properties of new organo-noble-gas molecules are compared. The focus is on comparison of the stability of the observed organo-noble-gas molecules. Various computational properties of the molecules are also presented.

The H-Ng (Ng = Kr or Xe) stretching absorptions of the molecules are presented in Fig. 10. The H-Ng stretching absorption for HNgC\textsubscript{3}N is at higher wavenumbers than HNgC\textsubscript{4}H and HNgC\textsubscript{2}H indicating that HNgC\textsubscript{3}N is more strongly bound than the two other ones. The trend is similar for both Xe and Kr containing molecules. The H-Ng bond lengths support this trend. The computed H-Xe bond for HXeC\textsubscript{3}N molecule is \(~0.01\) and \(~0.02\) Å shorter than for HXeC\textsubscript{4}H and HXeC\textsubscript{2}H. The H-Kr bond length for HKrC\textsubscript{3}N is \(~0.04\) and \(~0.06\) Å shorter than for HKrC\textsubscript{4}H and HKrC\textsubscript{2}H. The calculated equilibrium structures of the novel organo-noble-gas compounds are collected in Fig. 11.

Figure 10  (A) Spectra of xenon insertion molecules: (a) HXeCCH, HXeCC, and HXeCC\textsubscript{2}HeH, (b) HXeC\textsubscript{2}H, and (c) HXeC\textsubscript{3}N in the H-Xe stretching region. (B) Spectra of krypton insertion molecules: (a) HKrC\textsubscript{3}H, (b) HKrC\textsubscript{2}H, and (c) HKrC\textsubscript{3}N in the H-Kr stretching region. The matrices were first UV photolyzed and then annealed at 45 K (Xe) and 30 K (Kr). The spectra are measured at \(~8\) K. Broad spectral features originate from background fluctuations.
Figure 11  Ab initio structures of HNgCCH, HNgC,N, HXeCC, and HXeCCXeH (Ng = Xe or Kr). The bond lengths are in Å. For calculations, the MP2/LJ18(Xe), 6-311++G(2d,2p) level was used. For HXeCC, the computational level is CCSD(T)/LJ18[Xe],6-311++G(2d,2p).
The correlation of the computational H-Ng bond length and the experimental H-Ng stretching absorption of organo-noble-gas molecules is presented in Fig. 12 and the calculated partial charges [natural orbital analysis (NBO)] of the studied molecules are collected in Table V. When HNgY molecule is strongly bound, the H-Ng bond distance is shorter, and this is reflected as a blue shift of the H-Ng stretching vibration. In this image, the HNgC3H molecules are most bound of the organo-noble-gas molecules. With these criteria, the most bound molecule of HXeY molecules is the HXeNC molecule. In organo-noble-gas molecules, the noble-gas atom has most of the positive charge. In the carbon chains of these molecules, the carbon atom vicinal to Ng atom has most of the negative charge. For HNgC3N, the carbon atom vicinal to the N atom has a positive partial charge.

![Figure 12](image)

**Figure 12** Correlation between the experimental H-Ng stretching wavenumbers and the calculated H-Ng bond length of organo-noble-gas compounds. The calculations were done using the MP2/LJ18(Xe), 6-311++G(2d,2p) level.

**Table V** Calculated NBO partial charges of the organo-noble-gas molecules. The computational level is MP2/LJ18(Xe), 6-311++G(2d,2p). The notation of atoms is shown in Fig. 10.

<table>
<thead>
<tr>
<th></th>
<th>HXeCC</th>
<th>HXeCC*</th>
<th>HXeCCXeH*</th>
<th>HXeC2H</th>
<th>HXeC2N</th>
<th>HKrCCH</th>
<th>HKrC2H</th>
<th>HKrC2N</th>
</tr>
</thead>
<tbody>
<tr>
<td>q (H1)</td>
<td>-0.12</td>
<td>-0.17</td>
<td>-0.20</td>
<td>-0.15</td>
<td>-0.12</td>
<td>-0.02</td>
<td>+0.01</td>
<td>+0.06</td>
</tr>
<tr>
<td>q (Ng/Xe1)</td>
<td>+0.78</td>
<td>+0.77</td>
<td>+0.75</td>
<td>+0.77</td>
<td>+0.76</td>
<td>+0.55</td>
<td>+0.56</td>
<td>+0.58</td>
</tr>
<tr>
<td>q (C1)</td>
<td>-0.69</td>
<td>-0.49</td>
<td>-0.55</td>
<td>-0.43</td>
<td>-0.37</td>
<td>-0.40</td>
<td>-0.32</td>
<td>-0.30</td>
</tr>
<tr>
<td>q (C2)</td>
<td>+0.03</td>
<td>-0.31</td>
<td>-0.55</td>
<td>-0.15</td>
<td>-0.22</td>
<td>-0.33</td>
<td>-0.19</td>
<td>-0.27</td>
</tr>
<tr>
<td>q (C3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.06</td>
<td>+0.21</td>
<td>-</td>
<td>-0.10</td>
<td>+0.21</td>
</tr>
<tr>
<td>q (C4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.20</td>
<td>-</td>
<td>-</td>
<td>-0.18</td>
<td>-</td>
</tr>
<tr>
<td>q (Xe2)</td>
<td>-</td>
<td>-</td>
<td>+0.75</td>
<td>-0.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>q (H2)</td>
<td>-</td>
<td>+0.20</td>
<td>-0.20</td>
<td>+0.22</td>
<td>-</td>
<td>+0.20</td>
<td>+0.22</td>
<td>-</td>
</tr>
<tr>
<td>q (N1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.27</td>
<td>-</td>
<td>-</td>
<td>-0.28</td>
</tr>
</tbody>
</table>

* Values from Ref. 83
In Tables VI and VII, the experimental and calculated vibrational frequencies of organo-noble-gas molecules with isotopic substitutions are presented. For HNgCCH, HNgC₃H and HNgC₃N, at least three different vibrational modes have been experimentally characterized, which is in agreement with the calculated spectra and isotopic substitution experiments.

**Table VI** Experimental and calculated MP2/6-311++G(2d,2p) vibrational frequencies (in cm⁻¹) and IR intensities [in parentheses (in km mol⁻¹)] of Kr-containing organo-noble-gas molecules. The strongest absorptions are marked with (s). The (h) mark refers to the absorption bands observed after higher-temperature annealing. Calculated values are in italics. Only the most intense and experimentally observed absorptions are presented.

<table>
<thead>
<tr>
<th></th>
<th>H(D)-Kr str.</th>
<th>C-H(D) str.</th>
<th>C-C-H(D) bend</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HKrCCH</strong></td>
<td>1256.6</td>
<td>3290.0</td>
<td>610.2</td>
</tr>
<tr>
<td></td>
<td>1249.6</td>
<td>3454.9(34)</td>
<td>651.8(44)*</td>
</tr>
<tr>
<td></td>
<td>1241.6 (s)</td>
<td></td>
<td>608.2</td>
</tr>
<tr>
<td><strong>DKrCCD</strong></td>
<td>936</td>
<td>2555.5</td>
<td>482.5</td>
</tr>
<tr>
<td></td>
<td>1140.5(1194)</td>
<td>2645.3(26)</td>
<td>507.6(20)*</td>
</tr>
<tr>
<td></td>
<td>929</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>920</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>HKr¹²C¹³CH</strong></td>
<td>1255.6</td>
<td>3274.8</td>
<td>605.2</td>
</tr>
<tr>
<td></td>
<td>1464.1(2372)</td>
<td>3438.1(32)</td>
<td>645.9(45)*</td>
</tr>
<tr>
<td></td>
<td>1246.5</td>
<td></td>
<td>603.5</td>
</tr>
<tr>
<td></td>
<td>1238.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>HKrCCCH</strong></td>
<td>1317 (h)</td>
<td>1517.2(3174)</td>
<td>892</td>
</tr>
<tr>
<td></td>
<td>1307.5</td>
<td>3484.7(100)</td>
<td>931.2(133)</td>
</tr>
<tr>
<td></td>
<td>1290</td>
<td></td>
<td>592.5</td>
</tr>
<tr>
<td></td>
<td>1275.5</td>
<td></td>
<td>590.3(49)*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>587</td>
</tr>
<tr>
<td><strong>DKrCCCD</strong></td>
<td>977 (h)</td>
<td>1080.2(1498)</td>
<td>871 (h)</td>
</tr>
<tr>
<td></td>
<td>961.5</td>
<td>2582</td>
<td>914.5(225)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2670.4(85)</td>
<td>455.8(27)*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>869</td>
</tr>
<tr>
<td><strong>HKrCCCN</strong></td>
<td>1498</td>
<td>1692.3(2606)</td>
<td>894</td>
</tr>
<tr>
<td></td>
<td>1492</td>
<td>2234</td>
<td>912.3(163)</td>
</tr>
<tr>
<td></td>
<td>1482</td>
<td>2230</td>
<td>892</td>
</tr>
<tr>
<td></td>
<td>1478</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1453?</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>DKrCCCN</strong></td>
<td>1108</td>
<td>1204.1(1256)</td>
<td>891</td>
</tr>
<tr>
<td></td>
<td>1105</td>
<td>2233</td>
<td>910.7(205)</td>
</tr>
<tr>
<td></td>
<td>1099</td>
<td>2230</td>
<td>890</td>
</tr>
<tr>
<td><strong>HKrCCC¹⁵N</strong></td>
<td>1498</td>
<td>1692.3(2607)</td>
<td>885</td>
</tr>
<tr>
<td></td>
<td>1492</td>
<td>2217</td>
<td>902.1(164)</td>
</tr>
<tr>
<td></td>
<td>1482</td>
<td>2213</td>
<td>884</td>
</tr>
<tr>
<td></td>
<td>1478</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1453?</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Doubly degenerate

a For HKrC₄H, the C-H stretching absorption could not be detected because it was most probably overlapping with the strong C-H stretch of diacetylene.

b The low sensitivity of the apparatus in spectral range below 500 cm⁻¹ did not allow to detect the C-C-D bending vibration.
Table VII  Experimental and computational IR absorption spectra (in cm\(^{-1}\)) of Xe-containing organo-noble-gas compounds. The calculated vibrational frequencies are in italics and IR intensities are given in parentheses (in km mol\(^{-1}\)). Only experimentally observed vibrations are presented. The calculations have been done using MP2/LJ18[Xe],6-311++G(2d,2p) level. For HXeCC, the computational level is CCSD(T)/LJ18[Xe],6-311++G(2d,2p). The strongest absorptions are marked with (s). The (h) mark refers to the absorption bands observed after higher-temperature annealing.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H(D)-Xe str.</th>
<th>C-H(D) str.</th>
<th>C-C-H(D) bend</th>
</tr>
</thead>
<tbody>
<tr>
<td>HXeCCH(^a)</td>
<td>1486.4 (s) 1735.9(1515)</td>
<td>3273.0 3462.3(31)</td>
<td>627.6 640.6(27)*</td>
</tr>
<tr>
<td></td>
<td>1480.7</td>
<td></td>
<td>625.7</td>
</tr>
<tr>
<td>DXeCCD</td>
<td>1077.5 1231.8(765)</td>
<td>2545 2650.7(20)</td>
<td>491.5 503.4(28)*</td>
</tr>
<tr>
<td>HXe(^{13})C(^{13})CH</td>
<td>1486.5 1735.8(1517)</td>
<td>3257.0 3445.5(30)</td>
<td>623.3 634.9(28)*</td>
</tr>
<tr>
<td></td>
<td>1480.9</td>
<td></td>
<td>621.5</td>
</tr>
<tr>
<td>HXeCCCCH</td>
<td>1558.5 (h) 1759.2(1998)</td>
<td>3316 3482.3(99)</td>
<td>897.5 (h) 949.4(113)</td>
</tr>
<tr>
<td></td>
<td>1545 (h)</td>
<td></td>
<td>896</td>
</tr>
<tr>
<td></td>
<td>1532</td>
<td></td>
<td>590.5 (h) 664.0(11)*</td>
</tr>
<tr>
<td></td>
<td>1521.5</td>
<td></td>
<td>588.5 (h)</td>
</tr>
<tr>
<td></td>
<td>1503.5</td>
<td></td>
<td>587.5 591.2(49)*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>586</td>
</tr>
<tr>
<td>DXeCCCD</td>
<td>1127.5 (h) 1248.9(931)</td>
<td>2582.5 (h) 2668.9(83)</td>
<td>869.5 (h) 933.8(134)</td>
</tr>
<tr>
<td></td>
<td>1120.5 (h)</td>
<td></td>
<td>863.5</td>
</tr>
<tr>
<td></td>
<td>1111.5</td>
<td></td>
<td>b 496.7(18)*</td>
</tr>
<tr>
<td></td>
<td>1103.5</td>
<td></td>
<td>458.6(18)*</td>
</tr>
<tr>
<td></td>
<td>1093</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HXeCCCN</td>
<td>1624.5 1634.4(1596)</td>
<td>2232 2182.6(26)</td>
<td>896 919.3(139)</td>
</tr>
<tr>
<td>DXeCCCN</td>
<td>1177.5 1302.3(781)</td>
<td>2232 2162.6(29)</td>
<td>898 918.6(154)</td>
</tr>
<tr>
<td>HXeCC(^{15})N</td>
<td>1624.5 1634.4(1597)</td>
<td>2215 2171.5(24)</td>
<td>893 909.1(141)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2213</td>
</tr>
<tr>
<td>HXeCCXeH</td>
<td>1305.8 1594.7(5451)</td>
<td></td>
<td>1300.9 (s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1294.3</td>
</tr>
<tr>
<td>DXeCCXeD</td>
<td>1342 1634.9(2469)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>972 1156.9(1590)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HXe(^{13})C(^{13})XeH</td>
<td></td>
<td></td>
<td>c</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1301.1 1594.5(5467)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1294.4</td>
</tr>
<tr>
<td>HXeCC</td>
<td>1478.3(s) 1754.7</td>
<td>1748 1599</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1474.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DXeCC</td>
<td>1081.5 1244.7</td>
<td>1748 1599.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1474.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Doubly degenerate
\(^{b}\) Computational data from Ref. 83
\(^{c}\) The low sensitivity of the apparatus in spectral range below 500 cm\(^{-1}\) did not allow to detect the C-C-D bending vibration.
\(^{c}\) Partially overlaps with a strong band of acetylene at 1306.5 cm\(^{-1}\).
3.2 Formation mechanisms

In this section, the formation mechanisms of HNgY molecules are considered. The focus is on the experimental evidence of neutral formation mechanisms and global mobility of H atoms. The case of formation of HXeCCXeH from another noble-gas compound is emphasized.

3.2.1 Neutral formation mechanism

The HNgY molecules can be formed in principle from either neutral H + Ng + Y or ionic (HNg)+ + Y ion fragments. The initial photolysis of the precursor molecules of the HNgY compounds regularly produces some amounts of (NgHNg)+ ions, and Pettersson et al. considered the ionic channels as a possible formation mechanism. Feldman et al. suggested that HXeH molecules are formed from H atoms rather than from charged precursors. The first direct evidence of the neutral H + Ng + Y formation channel was obtained for HXeI and later for HXeCC. Pettersson et al. observed that IR light at ~ 3000 cm⁻¹ decomposed HXeI and released iodine atoms. After IR decomposition, HXeI recovers on a time scale of days in the dark at 15 K indicating that HXeI is formed from neutral H + Xe + I fragments since the IR photons are not energetic enough for ion formation.

For HXeCC, the light-induced H + XeCC ↔ HXeCC reaction was studied in solid xenon. HXeCC radicals were decomposed to a local metastable configuration and then selectively recovered by resonant excitation of the XeCC vibrations by using IR narrow-band light. The experiments show that HXeCC radical is formed in the reaction of a neutral XeCC molecule, and ionic channels are negligible. First, the decomposition rate of HXeCC was studied as a function of the excitation photon energy using tunable IR radiation (see Fig. 13). The decomposition starts at ~ 4500 cm⁻¹ and reaches the maximum efficiency at ~ 7000 cm⁻¹. The profiles are similar for HXeCC and DXeCC, which indicates that the decomposition of these species occurs via photodissociation continuum or broad excited states. This mechanism is different from the earlier studied HXeI where its photodissociation involved the second H-Xe stretching overtone and hence had a relatively narrow profile.
Figure 13  Photodecomposition spectrum of HXeCC and DXeCC in solid xenon at 8 K. With a pulse energy density of ≈1 mJ/cm$^2$, 200 pulses at 8000 cm$^{-1}$ decompose about a half of HXeCC radicals, which estimates a photodecomposition cross-section of $\sim 10^{-18}$ cm$^2$.

HXeCC radicals decomposed by IR light slowly recover in dark even at the lowest experimental temperature (8 K), and the recovery rate is temperature dependent. The temperature dependence is practically the same for HXeCC and DXeCC, and it shows a flat region below 18 K and a fast recovery rate for higher temperatures (see Fig. 14). These temperatures ($\sim 20$ K) are much lower than the temperatures required for thermal diffusion of hydrogen atoms in solid xenon (＞35 K). It follows that this recovery process involves short-range (local) atomic mobility, which needs lower activation energies. The rise of the HXeCCH recovery rate above 18 K is characterized by an activation energy of $\sim 400$ cm$^{-1}$. In experiments with HXeI, activation energy of 688 cm$^{-1}$ was obtained. No essential losses of the HXeCC concentration upon numerous decomposition-recovery cycles were observed, which further supports the idea of local mobility.

Figure 14  Dark-recovery time of HXeCC and DXeCC as a function of 1/T. In the beginning, the molecules were partially decomposed by IR light. The recovery time was found by fitting the kinetics data with a single exponent.
After decomposition of HXeCC by IR light, the recovery of HXeCC was also achieved by resonant excitation of the first and second C-C stretching overtone of XeCC [at 3510.5 cm\(^{-1}\) (assigned from IR spectra) and 5231.8 cm\(^{-1}\)]. This recovery process takes place similarly for HXeCC and DXeCC, i.e. with the same photon energy and similar efficiency. This light-induced formation is many orders of magnitude faster than the thermal reaction at 8 K.\(^{VI}\) These cycles of light-induced decomposition and light-induced recovery can be repeated many times without sufficient losses. This IR irradiation does not produce HXeCC prior to annealing at 45 K. Thus, this phenomenon is explained based on local activation of the lattice promoted by vibrational excitation of XeCC molecules. These experiments with narrow-band IR excitation demonstrate that the formation of HXeCC from XeCC molecules and H atoms is due to local atomic mobility, which is promoted by vibrational energy redistribution near the absorbing molecule. It should be remembered that global mobility of H atoms leads to the formation of HXeCC at 40-45 K.

The formation of HNgY molecules from neutral fragments has not been a trivial case because most of such experiments show the presence of NgHNg\(^+\) ions after UV photolysis and because the noble-gas hydrides have a strong ion-pair character (HNg)\(^+\)Y\(^-\). However, two examples are known when HNgY molecules are efficiently formed in annealing and no NgHNg\(^+\) ions are observed after photolysis.\(^{III,54}\) In experiments with C\(_4\)H\(_2\) in solid krypton, no KrHKr\(^+\) ions are observed after photolysis at 240 and 250 nm whereas HKrC\(_4\)H efficiently form upon annealing.\(^{III}\) Similarly, 193 nm photolysis of HCN in solid krypton produces no KrHKr\(^+\) ions, but HKrCN molecules appear upon annealing.\(^{54}\) These observations confirm that the HNgY molecules originate from the neutral fragments instead of ionic channels involving the NgHNg\(^+\) cations. Involvement of the NgHNg\(^+\) ions to the formation of HNgY molecules have been extensively studied. Khriachtchev \textit{et al.} studied the low-temperature formation of HArF and role of ArHAr\(^+\) ions in this process.\(^{127}\) They concluded that the formation process of HArF molecules is mainly independent of the decay of ArHAr\(^+\) ions at low temperatures (8 K) and the decay of NgHNg\(^+\) cations in general can occur via neutralization of solvated protons by electrons. This electron mechanism for proton neutralization process is also supported by the results of Lignell \textit{et al.} on the decay of the (NgHNg)\(^+\)···N\(_2\) complexes.\(^{128}\) In experiments with organo-noble-gas molecules, the XeHXe\(^+\) decay and HXeY formation were found to have very different temperature dependences.\(^{IX}\) In experiments with HCN in solid krypton, the long-term decrease of the KrHKr\(^+\) concentration at 8 K did not lead to any detectable formation of noble-gas hydride.\(^{VI}\) Thus, the decay of the NgHNg\(^+\) ions can be disregarded to be connected with the main formation of the HNgY species.
3.2.2 Global mobility of H atoms and kinetic scheme

The annealing-induced formation of HNgY molecules is controlled by H atom mobility.\textsuperscript{98,99} Mobility of H atoms involved in the formation of HNgY molecules can be global (long-range) or local (short-range). In this terminology, the global mobility means random motion across the matrix lattice over large distances (compared to the lattice parameter) when the reaction position is not determined by the initial position. In contrast, the local mobility is a short-range process occurring in a perturbed matrix morphology, which generally changes the activation energy of the process.\textsuperscript{126} Hydrogen atoms become globally mobile at \( \sim 30 \) and \( 40 \) K in Kr and Xe matrices, respectively.\textsuperscript{100} Local mobility is short-range process when hydrogen atom reacts with the parent Xe + Y center, and this may occur at relatively low temperatures. The reported examples of local processes involve the low-temperature formation of HArF,\textsuperscript{127} as well as formation of HXeNCO, HKrCl and HArF directly during UV photolysis of the HY precursor.\textsuperscript{17,66,67} Pettersson \textit{et al.} demonstrated that the formation of HXeI is a combination of short-range and long-range mobilities of H atoms and their relative contribution depends on the precursor photolysis time.\textsuperscript{129} The recovery of HXeCC and HXeI in solid xenon after their IR decomposition is a local process.\textsuperscript{VII,61}

The formation of noble-gas hydrides in C\(_2\)H\(_2\)/Xe, C\(_2\)H\(_2\)/Xe/Kr and HBr/Xe matrices allows distinguishing the local and global mobility and losses of H atoms.\textsuperscript{IX} Different precursor concentrations control the averaged distance between reacting species influencing the reaction kinetics, and different deposition temperatures change the amount of lattice imperfections and, hence, the amount of traps for H atoms. A simple kinetic scheme is used to analyze the results. The annealing-induced formation of the products (HXeCCH, HXeH, C\(_2\)H\(_3\), etc.) depends on the Xe/C\(_2\)H\(_2\) matrix ratio and slows down for lower C\(_2\)H\(_2\) concentration. The experimental formation time of HXeCCH, HXeH and C\(_2\)H\(_3\) is presented as a function of the Xe/C\(_2\)H\(_2\) ratio in Fig. 15.

![Figure 15](image)

\textit{Figure 15} Characteristic formation times (at the 0.63 level) of HXeCCH, HXeH and C\(_2\)H\(_3\) as a function of the Xe/C\(_2\)H\(_2\) ratio obtained upon annealing at 38 K. The IR absorption spectra are measured at 8 K.

The kinetic approach is described in Paper IX in detail and it has been successfully used for a number of other noble-gas molecules such as HXeH, HXeOH, HKrCl and
In this kinetic model, the global random mobility of H atoms is assumed. The following reactions are considered:

\[
\begin{align*}
H + Xe + Y & \rightarrow HXEY \quad (1) \\
H + Xe + H & \rightarrow HXeH \quad (2) \\
H + HXEY & \rightarrow H_2 + Xe + Y \text{ or } H + Xe + HY \quad (3) \\
H + HXeH & \rightarrow H_2 + Xe + H \quad (4) \\
H + T & \rightarrow HT \quad (5)
\end{align*}
\]

The first two reactions (1) and (2) describe the formation of noble-gas hydrides HXEY and HXeH, whereas reactions (3) and (4) describe the decomposition of these molecules, which has been demonstrated experimentally. The last reaction (5) is the loss channel for H atoms describing the capture of the mobile H atoms by various traps (for example matrix defects, impurities, etc.) and T is the effective concentration of the loss centers. The formation kinetics of HXEY and HXeH obtained from this model is in agreement with all experimental data. The simulated formation time is three times shorter for HXeH than for HXEY, which is in good agreement with the experimental ratio obtained for HXEH and HXECH (~ 2.7 for C2H2/Xe = 1/1000). In Fig. 16, the formation time for HXEH and HXEY calculated at 0.63 level of the kinetic curves as a function of the inverse precursor concentration are present and it is comparable with Fig. 15. Formation time becomes longer for smaller H and Y concentrations because more jumps are needed for H atoms to meet an H-Xe or Y-Xe center. The global mobility leads to reaction of H atoms mainly apart from the parent cage. In experiments, the formation of HXECH and HXeH becomes slower for smaller precursor concentrations, which is in qualitative agreement with the simulations featuring global mobility of H atoms upon annealing. In the case of local formation, the formation time should be essentially concentration-independent. The present data indicate that the previous annealing-induced mobility formation studies with HXEOH and HKrCl apply mainly to global mobility of H atoms. The local processes can generally be possible due to locality of primary photolysis in noble-gas solids.

Figure 16 Modelling of annealing-induced formation of HXEH and HXEY in a Xe matrix. Formation time of HXEH and HXEY is shown versus the inverse H and Y concentration. The solid symbols correspond to the formation without losses, and the open symbols show the result with traps ([T] = 0.5). Notice the multiplication factor of 2.5.
Formation of HXeBr and HXeH was experimentally studied as a function of the deposition temperature (from 10 to 40 K). The obtained HXeBr concentrations are presented in Fig. 17. The maximal formation of HXeBr is obtained for deposition at 30 K and the formation efficiency is 5 times lower for deposition at 10 K. As it can be seen from Fig. 17(b), the deposition temperature influences the proportion of annealing-produced HXeBr and HXeH. The largest HXeH/HXeBr ratio is observed for deposition at 30 K, and it decreases by an order of magnitude for deposition at 10 K.

**Figure 17** Formation of noble-gas species as a function of the deposition temperature. (a) HXeBr concentration after annealing at 35 K (for 5 min) and at 45 K (for 5 min). Notice the multiplication factor $\times 5$ for the lower-temperature annealing. (b) HXeH/HXeBr absorption ratio after annealing at 45 K for 5 min (solid squares). The average slope of the IR spectrum baseline (after photolysis) in the 5000 to 6000 cm$^{-1}$ is shown by open triangles. The width of the 2531 cm$^{-1}$ absorption band of HBr after deposition is presented by open circles. The experiments were performed with HBr/Xe mixtures (~1/1000). The samples were first irradiated at 193 nm, which decomposed the main part of HBr molecules. The annealing was first done at 35 K in steps for 155 min and then at 45 K for 5 min. Annealing at 45 K stabilized the processes connected with hydrogen mobility.

In Fig. 17, the formation of HXeBr observed after 5 min at 35 K can be connected mostly to short-range mobility of hydrogen atoms because H atoms have insufficient time to move extended distances at this rather low temperature. It can be deduced from the data that the short-range formation of HXeBr is equally efficient for matrices deposited at different temperatures from 10 to 30 K. The matrix morphology does not influence much the short-range formation efficiency. The deposition temperatures are more important for long-range formation processes. Annealing at 45 K leads to an order of magnitude more efficient formation of HXeBr for the sample deposited at 30 K than deposited at 10 K. We
can conclude that long-range hydrogen mobility is substantially suppressed in matrices deposited at 10 K. This fact can be connected with efficient H atom losses upon long-range mobility. The presence of such traps is supported by the low optical quality of samples deposited at low temperature and the broad absorption band of HBr reflecting lattice imperfections. This is shown in Fig. 17(b) where the average slope of the IR spectrum baseline in the 5000-6000 cm\(^{-1}\) interval (down triangles) is presented. The slope characterizes the optical properties of the sample with respect to light scattering. The scattering is most probably connected to the number and size of lattice imperfections. Smaller slopes correspond to less scattering matrices with lower amounts of lattice imperfections. The baseline slope anticorrelates with the HXeH/HXeBr ratio and the HXeBr concentration. The width of the HBr absorption behaves similarly to the baseline slope. For 40 K deposition, the long-range mobility is also suppressed correlating again with the lower optical quality and the broader HBr band.

The obtained results show that the most efficient formation of noble-gas hydrides is connected with global (long-range) mobility of H atoms leading to the H + Xe + Y reaction. The highest concentration of noble-gas hydrides was obtained in matrices of highest optical quality which probably have the lowest concentration of defects. In matrices with a high amount of defects, the HXeY formation is inefficient and dominated by a local (short-range) process.

### 3.2.3 Formation of HXeCCXeH from HXeCC

In principle, the formation mechanism of HXeCCXeH in solid xenon may occur via two possible reactions:

\[
\begin{align*}
\text{HXeCC + Xe + H} & \rightarrow \text{HXeCCXeH} \quad (1) \\
\text{H + Xe + CC + Xe + H} & \rightarrow \text{HXeCCXeH} \quad (2)
\end{align*}
\]

Reaction (1) involves HXeCC as a precursor and reaction (2) occurs via a “triple collision” of two mobile hydrogen atoms with an immobile CC molecule in a Xe lattice. These two situations were modelled based on kinetic equations for diffusion of H atoms in the lattice and the H + Ng + Y formation reactions described in the previous section. The result of modeling is presented in Fig. 18. As seen in plot (a), HXeH exhibit the fastest formation whereas HXeCCXeH is the slowest one to form, which is connected with the assumed formation of HXeCCXeH from HXeCC [reaction (1), model A]. Fig. 18(b) presents the formation kinetic based on reaction (2), i.e. model B, which indicates very fast formation of HXeCCXeH from the beginning. This originates from the assumption of triple collisions that are the most efficient at the early annealing stage when the H and CC concentrations are the highest. Comparison with experiments supports the HXeCC + Xe + H formation channel (model A). Formation kinetics of the HXeH, HXeCC and HXeCCXeH species was measured upon annealing (see Fig. 19). As a fingerprint, the experimental HXeCCXeH formation is the slowest among the products.
Figure 18  Modeling of the HXeCCXeH formation mechanism. Plot (a) presents concentrations of HXeCC, HXeCCXeH, and HXeH as a function of annealing time using model A based on reaction (1). The concentrations are normalized by their values after a long annealing. The plot (b) describes the formation process based on model B relaying on reaction (2), and the normalized concentrations of the annealing products are shown. These results are obtained neglecting the HXeCCH formation, which corresponds to very efficient decomposion of CCH radicals.

Figure 19  Formation kinetics of HXeCC, HXeCCXeH and HXeH at 39 K and 40 K in solid xenon. Before annealing the acetylene/Xe samples were photolyzed at 250 nm which produced CC molecules in large amounts and CCH radicals in minor amounts. The relative concentrations of HXeCC, HXeCCXeH and HXeH are obtained by integrating the 1478.3, 1300.9 and 1180, 1166 cm\(^{-1}\) absorption bands and they are normalized by the values obtained after additional annealing at 45 K. In this experiment, HXeCCH is formed in relatively small amounts. The spectra are measured at 8 K.

The validity of the reaction mechanism based on reaction (1) (model A) can be confirmed by a direct experiment. The idea of this experiment is to decompose HXeCC selectively upon annealing and see if HXeCCXeH molecules still form. HXeCC is very photolabile and it can be efficiently bleached by 488 nm irradiation of an Ar\(^+\) ion laser (in timescale of \(~ 1\) min for laser intensity of \(~ 10\) mW/cm\(^2\)). The other annealing products
(HXeCCH, HXeCCXeH and HXeH) are practically stable upon this irradiation. Based on model A, the irradiation at 488 nm should prevent formation of the HXeCCXeH molecules because of the absence of the HXeCC intermediate. This is exactly what is seen in experiments (see Fig. 20). The 488 nm irradiation totally stops the formation of HXeCCXeH indicating that it requires the HXeCC intermediate. In contrast, model B predicts an increase of the HXeCCXeH concentration upon selective decomposition of HXeCC. These results show that the formation of HXeCCXeH needs HXeCC as a precursor.

![Figure 20](image)

**Figure 20**  IR absorption spectra of Xe-containing compounds prepared from C$_2$H$_2$/Xe. The samples were photolyzed at 250 nm and then annealed for ~60 min at 40 K and for ~3 min at 45 K [spectrum (a)]. Spectrum (b) was prepared in a similar way, but the sample was irradiated at 488 nm during annealing. The 488 nm radiation efficiently destroys HXeCC, but it does not essentially decompose HXeCCH and HXeCCXeH. The absence of HXeCCXeH in spectrum (b) features reaction (1). The spectra were measured at 8 K.

The HXeCC + Xe + H → HXeCCXeH reaction offers the first example of an additive chemical reaction involving HNgY molecules. In this case, a reaction of one noble-gas molecule (HXeCC) produces another noble-gas molecule (HXeCCXeH). This reaction is not trivial because of the very large energy accumulated in the HXeCCXeH molecule with respect to acetylene (computationally 9.3 eV). It is a remarkable case of low-temperature chemical synthesis of noble-gas compounds, i.e. it is possible to react a HNgY molecule and form another metastable noble-gas species. Recently, the experimental preparation of the second example of noble-gas molecule with two xenon atoms (HXeOXeH) has been reported. The formation mechanism of the HXeOXeH molecules is similar to HXeCCXeH. The HXeOXeH molecule is formed in the HXeO + Xe + H reaction, where the HXeO radical is an intermediate precursor.
3.3. Interactions

In this section, the matrix effects on the H-Xe stretching absorption of HXeCCH are reported and the interaction of the host with the embedded molecule is analyzed using calculations on 1:1 HXeCCH--Ng complexes (Ng = Xe, Kr or Ar). The weak complex between HXeCCH and CO$_2$ in solid xenon is identified and discussed.

3.3.1 Matrix effect on HXeCCH

The matrix effects generally include not only relatively small matrix-site splittings but also larger matrix-induced shifts due to interactions with the matrix material described as solvation effects.\textsuperscript{132} The HNgY molecules are embedded in a solid matrix and they interact with the surrounding atoms. Most of the HNgY molecules have been prepared in noble-gas matrices, however, HXeI, HXeH, HXeCl, and HXeCCH have also been reported in the gas-phase Xe clusters.\textsuperscript{62-64} The first HNgY molecules prepared in a "different" matrix media were the HXeCl and HXeBr molecules in a Kr matrix.\textsuperscript{59} Lorenz \textit{et al.} reported HXeCl and HXeBr in a neon matrix and concluded from these results that these molecules are intrinsically stable.\textsuperscript{133}

Recently, HXeCCH has been prepared in Kr and Ar matrices (see Fig. 21) (Paper VIII). This is the first example of an organo-noble-gas compound prepared in an Ar matrix. When the solid state synthesis was attempted in solid argon and krypton, several new absorptions close to those observed in Xe matrices for HXeCCH was found. Three annealing-induced absorptions were identified in solid krypton at 1518.7, 1505.6 and 1498 cm$^{-1}$. In solid argon, four new absorptions at 1531.3, 1517.4, 1482.2, and 1479.9 cm$^{-1}$

![Figure 21](image_url)  \textit{IR absorption spectra of HXeCCH in the H-Xe stretching region measured in Xe, Kr and Ar matrices at 8 K. The samples were first photolyzed at 193 nm and then annealed at 45 K [C$_2$H$_2$/Xe (1:1000), the upper trace], at 40 K [C$_2$H$_2$/Xe/Kr (1:2:1000), the middle trace] and at 25 K [C$_2$H$_2$/Xe/Ar (1:2:1000), the lowest trace].}
cm\(^{-1}\) were found. All bands are connected to the H-Xe stretching mode of HXeCCH. The H-Xe stretching absorptions of HXeCCH in Ar and Kr matrices are blue-shifted up to +44.9 and +32.3 cm\(^{-1}\) compared to the Xe matrix, respectively. This indicates that the H-Xe bond is stronger in krypton and argon compared to xenon matrices. Ab initio calculations of the 1:1 HXeCCH---Ng (Ng = Ar, Kr, or Xe) complexes were used to model the interaction of the hosts with the embedded molecule. The calculations show that the interaction energies for these systems are small (max. -444.7 cm\(^{-1}\)) and the computational complexation-induced shifts are different from the experimentally observed solvation effect. The calculations generate the largest blueshift for the HXeCCH---Kr complex (up to +9.4 cm\(^{-1}\)), whereas the largest experimental blueshift is observed in solid argon. The 1:1 interactions are therefore unable to describe the observed shifts of HXeCCH between various matrix materials, even though, they are able to reproduce the upward shift of the H-Xe vibrational band upon complexation with a Ng atom. Calculations on larger cluster should be considered.

The calculations on the 1:1 complexes can probably explain the matrix-site structure of HXeCCH in different solids. The HXeCCH molecule has two H-Xe stretching bands in solid xenon (see Fig. 20, lower trace).\(^{IV}\) The doublet matrix-site splitting of the H-Ng stretching mode is a characteristic feature for the HNgY molecules (e.g. HXeI, HXeBr, HXeCN, HXeSH, HKrCN and HKrCl).\(^{7,16,54,59,65}\) In addition, a number of organo-noble-gas molecules (HXeCCXeH, HKrCCH, HXeC\(_4\)H, and HKrC\(_4\)H) show a more extensive H-Ng stretching band fine structure, which has been explained by the matrix-site effect.\(^{II,III,IV}\) The most detailed study has been recently done for doublet structure of the HXeBr molecule.\(^{70}\) The spectral feature was described as matrix sites due to specific interactions with noble-gas atoms. For HXeCCH, the splitting between H-Xe stretching components is 5.7 cm\(^{-1}\). Our calculations on the 1:1 HXeCCH---Xe complexes show that the H-Xe vibration frequency can vary by several cm\(^{-1}\) (up to 5.3 cm\(^{-1}\)) in different HXeCCH---Xe structures. A similar doublet structure is found for HXeCCH in Kr and Ar matrices (see Fig. 21, middle and lower traces, respectively). The experimental splittings are 13 cm\(^{-1}\) in solid krypton and 14 cm\(^{-1}\) in solid argon. The calculations on the H-Xe stretching mode of the 1:1 HXeCCH---Kr and HXeCCH---Ar complexes give spectral shifts up to 10.8 and 7.6 cm\(^{-1}\) depending on complex structure, respectively. This correspondence between experiments and calculations is fairly good and the calculations support the matrix-site model where the band splitting is caused by specific interaction of the HXeCCH molecule with the Ng atoms in certain local morphologies. The obtained results are similar to HXeBr discussed previously.\(^{70}\) Results of HXeCCH and HXeBr are in accordance with the computational simulations of HArF. Jolkkonen \textit{et al.} suggested the large band splitting of HArF is caused by a specific interaction between one argon atom and the HArF molecule.\(^{134}\) Bihary \textit{et al.} and Bochenkova \textit{et al.} have also studied the matrix-site splitting of HArF.\(^{135,136}\) It seems that the most successful method for studying and explaining the band structure of HArF is the DIM based QM/MM method. By using this method, however, Bochenkova \textit{et al.} did not find evidence for specific interaction between HArF and argon compounds.\(^{136}\) More computational studies are required to understand details of matrix-site splitting and the question of specific interaction in noble-gas matrices.
3.3.2 HXeCCH···CO₂ complex

Complexation of HNgY molecules provides valuable information on intermolecular interactions. In the literature, various computational and experimental studies on complexation of HNgY molecules can be found. The first works include a computational study of HXeH···H₂O system and experimentally studied the complexes of HXeOH with water molecules and of HKrCl with N₂ where the complexation produced a large experimental blue shift of > 100 cm⁻¹ for the H-Ng (Ng = Xe or Kr) stretching. A few computational complexation studies of organo-noble-gas molecules are known. These include HKrCCH complexes with the HCl, HF and NH₃ molecules, 1:1 HXeCCH···Ng (Ng = Ar, Kr, or Xe) complexes, and the dimer and tetramer of HXeCCH. The complexation typically increases the H-Ng stretching frequency and the blue shift of this mode seems to be the normal case for HNgY complexes, especially for structures where the interacting species locates at the H-Ng end (X···HNgY). The red shift was computationally shown for the HXeBr···Xe and HArF···P₂ complexes.

UV photolysis of propiolic acid (HCCCCOOH) in solid xenon leads to the formation of the HCCH···CO₂ complex, higher energy cis conformer of propiolic acid, complexes of ethynol and carbon monoxide (HCCOH···CO), and water and C₃O (H₂O···C₃O). The HCCH···CO₂ complex is further photolyzed to the HCC···CO₂ complex. Thermal annealing of the photolyzed sample leads to formation of HXeCCH complexed with CO₂. The H-Xe stretching absorption of the HXeCCH···CO₂ complex has two blueshifted bands (+31.9 and +5.8 cm⁻¹) compared with the HXeCCH monomer band in solid xenon (see Fig. 22).

Figure 22  Annealing-induced IR absorption spectra of Xe-containing organo-noble-gas compounds in the H-Xe stretching region. Shown are the results of experiments with two different precursors in solid xenon. The H₂C₂/Xe (1:1000) and HCCCCOOH(PA)/Xe (1:1000) samples (the upper and lower traces, respectively) were first irradiated at 193 nm and then annealed at 45 K. The spectra were measured at 9 K. Note that the lower trace is multiplied by a factor of 5.
The HXeCCH...CO$_2$ complex is identified by IR absorption spectroscopy and *ab initio* calculations. The calculations give three HXeCCH...CO$_2$ structures: one parallel and two linear structures (see Fig. 23). For the H-Xe stretching modes, the calculations predict for parallel and linear (1) complexation structures blueshifts of $+19.2$ and $+19.4$ cm$^{-1}$ at the MP2/6-311++(2d,2p) level of theory and $+19.5$ and $27.9$ cm$^{-1}$ at the MP2/aug-cc-pVDZ level of theory. For linear structure (2), the computations predict redshifts of $-8.6$ and $-9.4$ cm$^{-1}$ at these computational levels. Based on the calculations, the experimental band shifted by $+5.8$ cm$^{-1}$ (1492.2 cm$^{-1}$) most likely corresponds to the HXeCCH...CO$_2$ parallel structure. The band with larger blueshift of $+31.9$ cm$^{-1}$ (1518.3 cm$^{-1}$) fits better to linear structure (1). It should be noted, that the linear structure has a very small binding energy (see Table VIII), which makes it doubtful candidate for experimental detection. Most probably, two bands at 1492.2 and 1518.3 cm$^{-1}$ originate from two matrix sites of the parallel structure which is the most stable and strongly bound (see Table VIII). The present results give an additional case of blue-shifting interactions. Good review of the topic is recently published where is demonstrated that the blue shift is a normal effect for these complexes which originates from the enhanced (HNg)$^+$Y$^-$ ion-pair character upon complexation.$^{145}$

![Figure 23](image)

*Figure 23*  *Computational structures of the HXeCCH...CO$_2$ complexes.*
Table VIII  Electronic interaction energies and BSSE and ZPVE-corrected electronic interaction energies of the HXeCCH···CO₂ complexes obtained at two computational levels. The values are in cm⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>6-311++G(2d,2p)</th>
<th>aug-cc-pVDZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parallel</td>
<td>Linear (1)</td>
</tr>
<tr>
<td>$E_{\text{int}(\text{MP2})}$</td>
<td>−1412</td>
<td>−229</td>
</tr>
<tr>
<td>$E_{\text{int}(\text{MP2}),\text{ZPVE}^a}$</td>
<td>−1202</td>
<td>−98</td>
</tr>
<tr>
<td>$E_{\text{int}(\text{MP2}),\text{CP}^b}$</td>
<td>−1099</td>
<td>−123</td>
</tr>
<tr>
<td>$E_{\text{int}(\text{MP2}),\text{CP-ZPVE}}$</td>
<td>−889</td>
<td>+8</td>
</tr>
<tr>
<td>$E_{\text{int}[\text{CCSD(T)}]}^c$</td>
<td>−1320</td>
<td>−250</td>
</tr>
<tr>
<td>$E_{\text{int}[\text{CCSD(T)}],\text{CP}^,}^{a,b}$</td>
<td>−979</td>
<td>−125</td>
</tr>
</tbody>
</table>

^a) Zero-point vibrational energy corrected interaction energy
^b) Counterpoise corrected interaction energy taking into account the BSSE energy contribution
^c) MP2-computed equilibrium structures are used in calculations.
4 Conclusions

4.1. Main results briefly

In this work, eight novel neutral organo-noble-gas compounds have been identified. These include the first organic krypton compound, HKrCCH, as well as the first noble-gas hydride molecule containing two Xe atoms, HXeCCXeH. The new compounds were prepared from acetylene (HXeCCH, HXeCC, HXeCCXeH, and HKrCCH), diacetylene (HXeC$_4$H and HKrC$_4$H) and cyanoacetylene (HXeC$_3$N and HKrC$_3$N) in krypton and xenon matrices using UV photolysis of the precursor molecule and thermal mobilization of the photogenerated H atoms. The organo-noble-gas molecules were identified using IR spectroscopy and supported by \textit{ab initio} calculations.

The formation mechanisms of the organo-noble-gas compounds have been studied. These molecules are formed from the neutral H + Ng + Y fragments in conjunction with long-range mobility of hydrogen atoms. It was also demonstrated that the decay of NgHN$_{+}$ ions was not connected with the main formation channel of these organic noble-gas species. The formation of HXeCCXeH involves HXeCC radicals as an intermediate, and it is formed in secondary reactions.

Interactions with the surrounding matrix and molecular complexes of the HXeCCH molecule have been studied. HXeCCH was prepared in argon and krypton solids in addition to a Xe matrix. The H-Xe stretching absorption of HXeCCH in Ar and Kr matrices is blueshifted from the value measured in solid xenon indicating stabilization of the H-Xe bond. The H-Xe stretching band of HXeCCH is split into doublets in Xe, Kr and Ar matrices. The HXeCCH matrix-site splitting has been modelled with computational 1:1 HXeCCH···Ng (Ng = Ar, Kr, Xe) complexes. The correspondence between experiments and calculations is fairly good and the calculations support the matrix-site model where the band splitting is caused by specific interaction of the HXeCCH molecule with the Ng atoms in certain local morphologies. However, more computational studies are required to understand details of matrix-site splitting. The weak HXeCCH···CO$_2$ complex is prepared from propiolic acid in solid Xe. The H-Xe stretching absorption of the HXeCCH···CO$_2$ complex is blueshifted from the value of the HXeCCH monomer in a xenon matrix and the structural assignment is done according to the \textit{ab initio} calculations. The preparation of the HXeCCH···CO$_2$ complex demonstrates an advanced approach to studies of HNgY complexes where the precursor complex (HCCH···CO$_2$) is obtained using photolysis of a larger molecule (propiolic acid).

4.2 Future perspectives

A number of interesting questions concerning the future of the HNgY molecules can be mentioned. These concern the existence and preparation of HNgY molecules without the stabilizing environment of polarizable matrix, their existence above cryogenic...
temperatures, and their preparation as bulk materials. Also expanding the organic noble compounds to argon chemistry and bio-noble-gas compounds are future challenges.

The HXeCCH molecule has been the most studied compound of the novel organo-noble-gas molecules, mostly due to its simplicity and stability. Here, it is demonstrated that the HXeCCH molecule can exist in an argon matrix, VIII and recently Poterya et al. has prepared it in the gas-phase xenon clusters. 64 Extensive computational work on properties of HXeCCH and its clusters have been done. 73,83,146,147 Computational studies indicate that even HXeCCH crystals could exist. 146 Similarly, computational crystal structure for the HXeH molecule was been reported. 148 Moreover, kinetic stability of the HXeCCH molecule was studied by multi-reference ab initio methods by Gerber and co-workers. 73 They reported that the calculated lifetime of HXeCCH implies its stability at non-cryogenic conditions. 73

HArF is still the only experimentally prepared neutral argon compound and the only example of a neutral molecule containing a lighter noble gas atom. 17,18 Up to now, no argon-containing organo-noble-gas compounds have been prepared, even though, many experimental attempts and computational predictions have been published. III,VI,87,149-151 These computationally predicted organo-argon compounds include FArCCH, 150 HArC₄H, 149 HArC₆H, 149 HArCCCN, VI HArCCNC, VI HCCArCN, VI HCCArNC, VI FArCCF, 151 ClArCCCl, 151 FArCCArF, 151 and ClArCCArCl 151. It has been found that at least HArC₄H, HArCCCN, and HArCCNC are not experimentally feasible. III,VI It has been also found that the high level of computations are important for reliable theoretical predictions of new noble-gas hydrides. 87,88

The novel group of organo-noble-gas hydrides has encouraged researchers to computational predictions of noble-gas polymers and bio-noble-gas chemistry. For example, the calculations predict large molecules like HXeCCXeCCXeH and HXeCCXeCCXeCCXeH with the -(Xe-CC)- building blocks. 152 Even larger noble-gas polymers have been computationally introduced. 153 Few steps towards bio-noble-gas chemistry has been done by calculations of molecules where Xe is inserted in formic and aspartic acids, 91 and where Ng (Ng = Xe, Kr and Ar) is inserted into the O-H bond of glycine. 154
References


112. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact Karen Schuchardt for further information.