

NEW CHEMISTRY OF THE NOBLE GAS ELEMENTS: NOVEL MOLECULES, POLYMERS AND CLUSTERS

R.B. Gerber, Department of Physical Chemistry, the Hebrew University of Jerusalem and Department of Chemistry, University of California, Irvine, CA, U.S.A.

I. Introduction

Since the discovery of the noble gases, well over a century ago, these elements have been a challenge to chemistry and to the understanding of chemical bonding. For many years after they were discovered, the chemical inertness of the noble gas elements was believed to be absolute. The advent of quantum chemistry in the 1930's and beyond led to first-principles understanding of the chemical inactivity. This was interpreted in terms of the remarkable stability of the closed-shell electronic structure of the noble gas atoms in the ground state. Pauling conjectured in 1933⁽¹⁾ that for the heavier noble gas atoms such as xenon, where the outermost electronic shell is less stable due to its relatively large distance from the nucleons, chemical bonding may be possible. The breakthrough came in 1962 when Bartlett prepared experimentally $\text{Xe}^+[\text{PtF}_6]^-$, xenon hexafluoro platinate, the first noble gas compound^{(2),(3)}. This was followed by a period of steady growth, in which a good number of xenon compounds, and much fewer krypton and radon compounds were obtained⁽⁴⁻⁷⁾. There was also a significant development in the quantitative theoretical understanding of the chemical bonding of the heavier noble gases⁽⁸⁾. In the last several years, the field of noble gas chemistry has gone through a phase of rapid development in several different directions. A recent article by Christie⁽⁹⁾, highlighting some of the developments, is entitled "A Renaissance in Noble Gas Chemistry", which seems to reflect current impressions in the field. Some of these developments are described in several recent reviews⁽¹⁰⁻¹³⁾.

The results described in this paper are related to and motivated by the pioneering work done in recent years by Räsänen and coworkers in Helsinki⁽¹⁴⁻²¹⁾. These authors were able to obtain a range of molecules of the type HNgY , where Ng is a noble gas atom and Y an electronegative group, by photo dissociation of the hybrid HY in the noble gas Ng matrix⁽¹⁴⁻²¹⁾. Examples of molecules prepared in these experiments include HXeH , HXeOH , HXeBr , HKrCN and HArF , the latter being the first chemically bound compound of argon⁽²¹⁾. The importance of these results is twofold: First, many new chemical bonds of the noble elements were discovered, including Xe-H, Xe-I, Xe-Br, Xe-S, Kr-H, Ar-H and Ar-F. Second, for the first time one of the light noble gas elements was harnessed into chemical bonding.

The results overviewed in the present paper include several contributions: (1) Theoretical simulations are used to yield understanding of the formation mechanisms of the HNgY compounds in the matrix. (2) HHeF is predicted to be stable in pressurized solid helium. This is a first chemically bound compound of helium. (3) A new family of organic noble gas compounds are found, the prototype of which is HXeCCH . These compounds, predicted by our calculations were already prepared experimentally. This is a rapidly growing area, and we discuss further extensions and possible future directions. (4) A first polymer made of xenon and carbon is predicted. The search for polymers opens exciting prospects in noble gas chemistry. (5) Stable aggregates and crystals of certain HNgY molecules are found to exist, suggesting an interesting new class of noble gas materials.

II. Formation Mechanisms of HNgY Noble Gas Compounds

A. Direct formation dynamics

Potential energy surfaces developed by the author and coworkers⁽²²⁾, combined with Molecular Dynamics simulations, indicate direct formation of HNgY products in an ultrafast process following photo dissociation of HY in the matrix, in a number of cases^{(13),(22)}. In modeling the potential surfaces⁽²²⁾, the Diatomics In Molecules (DIM) approach⁽²³⁾ was used to describe the interactions between the H and the Y atoms with the matrix atoms, but this treatment was augmented by the introduction of an additional interaction, representing the HNgY triatomic, obtained by fitting ab initio calculations for HNgY .⁽²²⁾ This

description of the electronic states is similar in part to the DIIS model of Last and George⁽²⁴⁾. As it turns out, there is a whole manifold of excited states pertinent to the photochemical process, with crossings between some of the potential energy surfaces involved. Thus, nonadiabatic transitions between different electronic states must be incorporated in the dynamics, and this was done by the semiclassical Surface Hopping method^{(25),(26),(22)}. The essential picture that emerges from this model is described qualitatively in Figures 1 and 2. Upon photoexcitation, the HY molecule is promoted to the repulsive manifold of states in the Franck-Condon region. As the H atom moves away from the Franck-Condon region, it ultimately

Photochemical synthesis of HKrCl

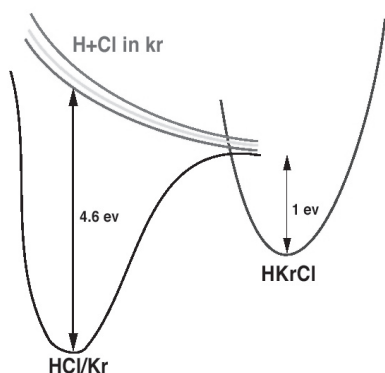


Fig 1. Potential energy curves for the HKrCl formation in solid Kr

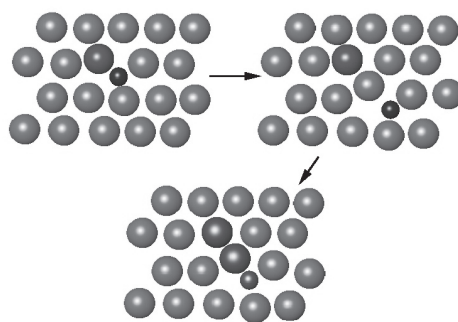


Fig 2. Snapshots showing the HKrCl formation in photodissociation of HCl in solid Kr

reaches a crossing with a state representing the bound molecule HNgY (Fig. 1). The molecule undergoes fast vibrational relaxation once HNgY is formed. As Fig. 1 shows, HNgY is much higher in energy than Ng+HY, but there is a barrier protecting the HNgY molecule which at cryogenic temperatures is practically insurmountable. Fig.2 shows snapshots from the formation dynamics. As the picture shows, the formation involves exit of the H atom from the cage⁽²²⁾. Upon photolysis the H atom exits the original cage, recoils from the second layer of noble gas atoms, and hits an Ng atom which on the other side is adjacent to the Y atom (Cl in this case). The H·Ng·Y arrangement at this point corresponds essentially to the crossing in Fig. 1. HNgY is formed, and is stabilized by vibrational relaxation. We estimate that after a timescale of ~ 10 picoseconds the relaxation is already sufficient in most cases to prevent the back reaction to HY+Ng. Obviously, the formation yield is a key issue, and there is insufficient data as yet from the simulations on that. Moreover, this modeling was hitherto applied only to a couple of cases: HKrCl and HXeCl. There is evidence from the matrix experiments of Räsänen for such a direct mechanism in several cases (including HKrCl)⁽²⁷⁾. Furthermore, HXeI was recently produced in gas phase (cluster) experiments⁽²⁸⁾, which support the direct formation mechanism. However, ultrafast time-resolved experiments to demonstrate the picosecond timescale formation have not been carried out yet. Such an investigation of the formation is a very interesting challenge for photochemical reaction dynamics in matrices.

B. Delayed formation by H diffusion

Experimental evidence shows that for most systems studied so far, the HNgY molecules are formed mainly by a delayed mechanism. This is the case, for example, for the formation of HArF following photolysis of HF in argon⁽²¹⁾, and in the formation of HXeOH in solid xenon⁽¹⁶⁾. In these experiments, there is no evidence for the presence of HNgY directly after the photo dissociation of HY in the matrix. Only upon a procedure of annealing, involving successive steps of heating and cooling, are the noble gas molecules found. Räsänen and coworkers have suggested that the formation involves H atom migration, induced thermally by the heating. Bihary et al.⁽²⁹⁾ were able to support this qualitative mechanism by simulations. This requires above all accurate potential energy surfaces for the motion of the H atom in the matrix, in sites at the proximity of a Y atom. Such potentials were obtained by fitting ab initio calculations. The relevant geometries and potential energy landscape are shown in Fig. 3. After photo dissociation

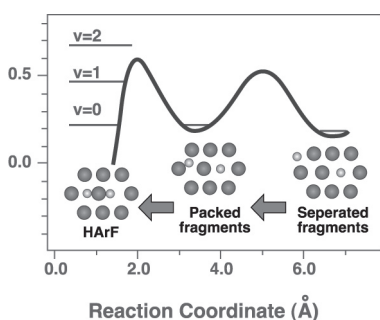


Fig 3. Potential energy landscape for the delayed formation of HArF

all atoms including the H are immobilized in their sites at low temperatures. Upon heating, thermally induced migration sets in. In the case of HArF, the most demanding barrier is the actual formation of the molecule by “hopping” of the H atom into the required geometry. Bihary, Chaban and Gerber⁽²⁹⁾ carried out Monte Carlo Transition State calculations, and were able to obtain threshold temperatures for the formation of HArF, HKrF in good accord with experiment.

It seems very important to pursue such calculations also for other systems, and to determine the relative yields of the direct and delayed mechanisms, which is a major open issue. There is no doubt that with better understanding of the formation mechanisms, yields can be increased and optimized, and pathways for formation of new molecules can be engineered.

III. HHeF in Pressurized Solid Helium

With the first harnessing of argon into chemical bonding in the preparation of HArF, two elements are left in the periodic table for which no neutral, chemically bound molecule is known: helium and neon. It is obviously an exciting challenge to search for the possible existence of the helium and neon compounds. Wong found by ab initio calculations that HHeF, with a linear structure, corresponds to a local minimum on the potential energy surface⁽³⁰⁾, and Lundell et al.⁽³¹⁾ computed the unharmonic vibrational energy spectrum of these species. However, Chaban et al.⁽³²⁾ showed that HHeF, isolated in the gas phase, is not a stable molecule but a very short lived species, with a lifetime in the picosecond range. The difference between HArF (that is apparently of indefinitely long lifetime in the laboratory) and HHeF is that for the latter species the barriers against decomposition are much lower. Consequently, HHeF is predicted to decay by tunneling even in its lowest vibrational state. Bihary et al.⁽³³⁾ investigated the dynamical stability of HHeF in pressurized solid helium. They found that at pressures of 15 GPa or higher, which are experimentally feasible, HHeF is predicted to have an indefinitely long lifetime. The effect of the pressure is to practically eliminate the decay of the species by tunneling, and to leave it intact. At the same time, the calculations of Bihary et al.⁽³²⁾ show that also at the pressures mentioned the nature of the species itself is unaltered, and it is a chemically bound molecule, with vibrational frequencies very close to those of the gas phase species.

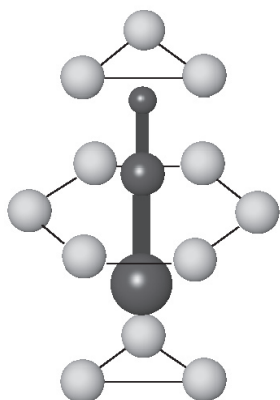


Fig 4. Local structure of HHeF in solid helium at pressure of 15 GPa

In summary, the theoretical results suggest two experimental approaches to the exploration of the species HHeF: (a) Using ultrafast femtosecond pulsed laser techniques, it may be possible to prepare the species and explore it as a transient of short lifetime. (b) It may be possible to prepare the species in pressurized solid helium (by photo dissociation of HF trapped in the solid). In these conditions, the species should have an indefinitely long lifetime.

IV. Organic HNgY Molecules: Noble Gas Atoms into Hydrocarbons

The author and coworkers have explored the existence of organic molecules of the type of HNgY. The question of compounds made of noble gas atoms and hydrocarbons is particularly challenging, since such molecules, if found to exist, will not include any strongly electronegative atom. Approximately two years ago Lundell, Cohen and Gerber⁽³⁴⁾, using ab initio calculations, predicted the existence of the noble gas/hydrocarbon compounds HXeCCH and HXeCCXeH, shown in Fig. 5. In the inorganic HNgY compounds, an approximate model of the bonding is that the species correspond to $\text{H-Ng}^+\text{Y}^-$, thus the $\text{Ng}^+\cdots\text{Y}^-$ bond is dominantly ionic, while the H-Ng^+ bond is essentially covalent. This picture applies

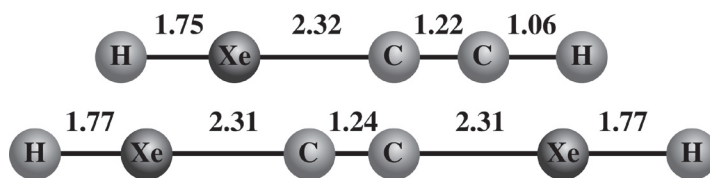
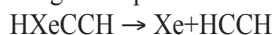
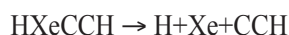


Fig 5. Equilibrium structures of HXeCCH and HXeCCXeH

also to HXeCCH (and HXeCCXeH): The bonding corresponds roughly to the model $\text{H-Xe}^+ \text{-CCH}$, with a large fractional charge on the acetylenic group, while the H is covalently bound to the Xe^+ . Indeed, the high electron affinity of the acetylenic group was the motivating factor for the authors of Ref. (34) in pursuing these compounds. The ab initio calculations predict that HXeCCH is in fact expected to be much more stable than most known inorganic HNgY compounds. The barrier for the decomposition channel:



has a height of 2.18 eV, and is very wide⁽³⁴⁾. The decomposition channel



is highly endothermic (nearly 1.5 eV)⁽³⁴⁾. This should suffice for kinetic stability well above the cryogenic

range of temperatures. The analogy with the electronic structure of inorganic HNgY suggests also a corresponding mode of preparation: Photolysis of acetylene in solid xenon. Shortly after our predictions were made, and with this motivation, two groups were able to prepare the noble gas/hydrocarbons. Räsänen et al.⁽³⁵⁾ made both HXeCCH and HXeCCXeH, while Feldman and coworkers⁽³⁶⁾ independently prepared HXeCCH. Shortly afterwards, Räsänen and coworkers have also prepared HKrCCH⁽³⁷⁾. In the short period since these first preparations, the topic of noble gas/hydrocarbon compounds has developed rapidly, and several interesting new molecules were obtained. Some of the noble gas/hydrocarbon compounds originally predicted in Ref. (34), were not made yet. These include the insertion compound of xenon into benzene, HXeC₆H₅, which is indeed by the calculations less stable kinetically than the acetylene derivatives. In any case, the noble gas/hydrocarbon compounds seem to offer a very large number of options for future developments, and we expect that they may become a major sub-field of noble-gas chemistry.

V. A Polymer Made of Xenon and Carbon

We extended the calculations on HXeCCH and HXeCCXeH, to explore the energetic stability of the species HXeCCXeCCXeH and HXeCCXeCCXeCCXeH. They were predicted to be stable by the ab initio calculations, with structures as shown in Fig. 6. This suggests the existence of a polymer with the repeat unit -(CCXe)-.

Since for the finite molecules the H-Xe bond makes a significant contribution to the stability, the

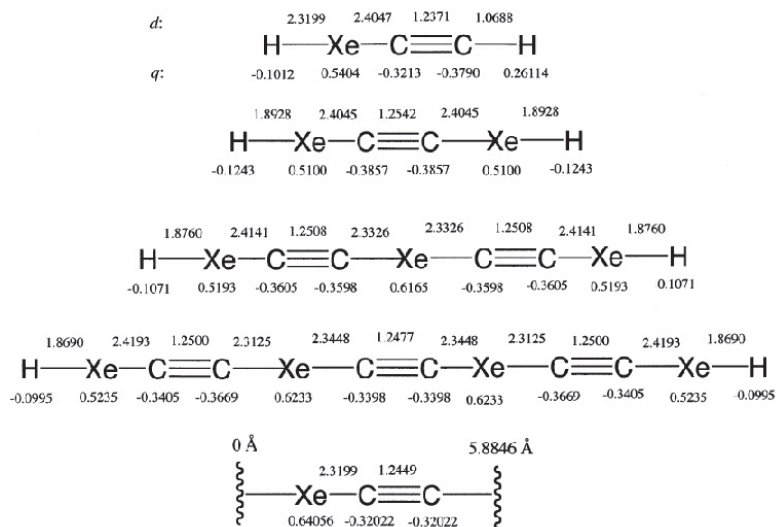


Fig 6. Computed structures for the HXe(CCXe)_nH, and for the (Xe-CC)_n

existence of the extended polymer was established by electronic structure calculations (DFT/B3LYP) using periodic boundary conditions⁽³⁸⁾. The predicted polymer is a highly interesting and novel type of compound, no longer of the HNgY type. Indeed, it is unusual in many respects as a polymer. Our search for other noble gas polymers is continuing, and we believe there are some very interesting prospects. We note that the di-acetylenic bonding of xenon -CC-Xe-CC- is expected to be stable also in finite molecules. In recent ab initio calculations, the molecule HCCXeCCH was found to be very stable⁽³⁸⁾. It seems that in

these di-acetylide compounds of the noble gases, the CC groups provide both covalent and ionic bonding contributions. We expect these molecules to have some potentially very useful properties as relatively very stable noble gas molecules, but these molecules are still to be prepared, and the main challenge on this is to develop suitable preparation strategies.

VI. Organic and Silico Compounds of Argon

Obtaining new molecules of the lighter noble gases: Ar, Ne, He remains an outstanding challenge. Since HArF was prepared, no additional compound of argon was found experimentally. According to theory, however, there is ground for optimism. Fig. 7 shows a first organic molecule of argon and a first molecule with a silicon-argon bond, predicted in ab initio calculations⁽⁴⁰⁾. No argon/hydrocarbon compound was predicted to be stable so far.

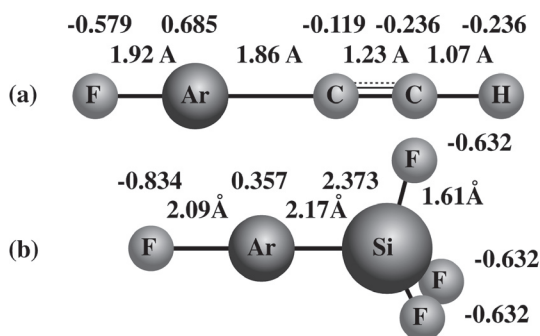


Fig 7. Structures of (a). FArCCH and of (b). FArSiF₃

VII. Crystals of HNgY Molecules

So far, the HNgY molecules were obtained as isolated species in rare gas matrices. Some complexes of these molecules with other molecules such as N₂ in the matrix are also known. However, can neat aggregates of HNgY, or even crystals or liquids be stable? Simulations show that this is not always the case. For example, the dimer (HArF)₂ was found to be chemically unstable, decomposing spontaneously into HF and argon⁽¹³⁾. Also on this issue, however, there is strong theoretical ground for optimism. Fig. 8 shows a predicted structure for the molecular crystal of HXeH⁽⁴¹⁾. Small clusters of this molecule were shown to be stable by ab initio calculations⁽⁴²⁾.

It is not yet known if HXeH is expected to melt into a stable molecular liquid.

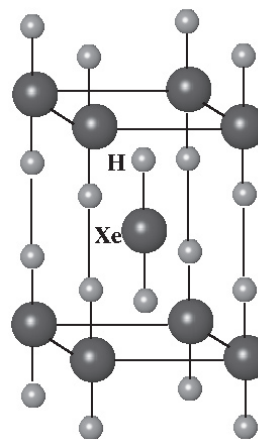


Fig 8. Proposed structural model for the molecular HXeH compound

VIII. Concluding Remarks

Recent developments have greatly expanded the field of noble gas chemistry. Novel species of interesting types of bonding and unusual properties have been obtained. Theoretical predictions have made a contribution to these developments both in the interpretation of experimental findings, and in predicting new compounds and their properties and in suggesting mechanisms.

Above all, the extensive recent experimental and theoretical results seem to indicate an exciting future for the field in the next several years.

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Prof. Robert Benny Gerber

was born in 1944. He received his B.Sc. in Chemistry (1965) from the Hebrew University of Jerusalem. He carried out his doctoral research in Theoretical Chemistry with Prof. C.A. Coulson at the University of Oxford, obtaining the D.Phil. in 1968. He was then a Postdoctoral Research Fellow with Prof. Martin Karplus at Harvard University. He joined the Weizmann Institute of Science in 1969, and from 1976 has been on the Faculty of Science at the Hebrew University of Jerusalem, where he holds the Saerree K. and Louis P. Fiedler Chair in Chemistry. From 1990, he also spends part of his time at the University of California at Irvine, where he is Professor of Chemistry.

Benny Gerber's research is in theoretical and computational chemistry, and his main current research interests include: (1) Molecular photochemistry in low-temperature matrices and clusters; (2) Prediction of new compounds of the noble gas elements, and their formation dynamics; (3) Vibrational spectroscopy methods for large molecules, and using spectroscopy for the development of new force fields for biological molecules; (4) Mechanisms and dynamics of molecular processes in atmospheric systems.

He has trained over 50 doctoral and postdoctoral researchers.

Prof. Benny Gerber is the recipient of the Israel Chemical Society Prize for 2004.