New Rare-Gas-Containing Neutral Molecules

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Keywords: Ab initio calculations / Matrix isolation / Rare-gas compounds / Solid-state chemistry / Photochemistry

The synthesis of novel neutral rare-gas-containing molecules of type HXY, where X = Xe or Kr and Y is an electronegative atom or fragment, is discussed. The molecules are characterised experimentally by their vibrational spectra and computationally by extensive ab initio calculations. They are formed in low-temperature rare-gas solids from neutral reagents and their bonding consists of both covalent and ionic contributions. Our recent studies add to the previously known class of rare-gas chemical bonds in neutral ground-state molecules the new bonds Xe–H, Xe–I, Xe–Br, Xe–S, Kr–H, Kr–C, and Kr–Cl.

Introduction

The rare gases form one of the most abundant classes of constituents of our Universe. The beautiful octet rule led scientists to accept the nonreactivity of rare gases until 1933, when Linus Pauling suggested[1] from considerations of ionic radii of different elements that molecules like XeF_6 and KrF_6, and perhaps unstable compounds XeF_8 and H_4XeO_6, should be preparable. However, attempts to synthesize rare-gas-containing molecules were not successful at that time.[2]

It took about 30 years until the first rare-gas-containing chemical compound was found. Neil Bartlett reported[3a] first a solid compound with a structure $Xe^+[PtF_6]^-$, which was later shown to consist most probably of a mixture of $XeF^+PtF_6^-$ and $XeF^+Pt_2F_{11}^-$.[3b] The key idea for this discovery was the similar ionisation potentials of O_2 and Xe. Almost simultaneously independently of Bartletts results, Hoppe et al.[4] synthesized XeF_2, and slightly later, Claassen et al.[5] reported XeF_4. After these first findings a number of compounds, where Xe is bound to fluorine and/or oxygen, were characterised. The extent of rare-gas chemistry in its early stages accounted, in addition to the species

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Jan Lundell (left, bottom), born in 1966, received his Ph.D. in 1995 from the Laboratory of Physical Chemistry, University of Helsinki. After his Ph.D. he spent a postdoctoral year at the Fritz Haber Research Institute for Molecular Dynamics, The Hebrew University of Jerusalem with professor Robert B. Gerber. In 1996 he returned to University of Helsinki, where he is now as a postdoctoral researcher of the Academy of Finland. He focuses his interest on hydrogen-bonded complexes, weak chemical interactions, and photochemical processes of small molecules in low-temperature matrices.

Markku Räsänen (right), born in 1949, received his Ph.D. in 1983 from the Laboratory of Physical Chemistry, University of Helsinki. After this he spent a postdoctoral year at the AT&T Bell Laboratories, Murray Hill, NJ with professor Vladimir E. Bondybey. He was a senior researcher of the Academy of Finland and received in 1992 the position of Associate Professor in Physical Chemistry, University of Helsinki (the title was changed to Professor in 1998). His general interests are in spectroscopy (vibrational and time-resolved luminescence) and photochemistry of small impurity molecules in simple solids, e.g. rare gases at low temperatures. The light-induced processes of interest are bond dissociation with UV/Vis photons and conformational changes induced by vibrational excitations.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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mentioned above, for example molecules XeF_6, $XeOF_4$ and XeO_2F_2, $XeF_2 \cdot 2\,SbF_5$ and $XeF_6 \cdot AsF_5$ salts, and the XeF radical.[6–11] These species have been reviewed by several authors.[12–16] In addition, the theory of binding in the Xe compounds has been authoritatively reviewed by Coulson.[17]

These findings promoted an active search for the extent of chemical bonds between rare gases and other elements. In this search, carbon played an important role and the first reports on Xe–C bonds date in the early 1970s when the bond strength of CH_3Xe^+ was measured[18] (its value is 231.0 ± 10.5 kJ mol^{-1}[19]). Also, an unstable $FXeCF_3$[20] species has been suggested as a reaction intermediate and for $Xe(CF_3)_2$ a lifetime of ca. 30 min has been reported[21] even though the compound has not been characterised spectroscopically. A stable Xe–C-bonded molecule, pentafluorophenylxenon(II) fluoroborate, was found almost simultaneously by two groups in 1989.[22][23] After this, a number of novel organoxenonium compounds have been synthesized.[24][25]

Before the advent of Xe–C chemistry, some other elements were found to bond chemically to Xe. In an Xe matrix, Nelson and Pimentel[26] prepared $XeCl_2$ and also compound $FXeBF_2$ was reported.[27] In addition, in condensed phases xenon is found to form readily a dixenon cation (Xe_2^+).[28] The first Xe–N bond was found in fluoro[imidobis(sulphuryl fluoride)]xenon, $FXeN(SO_2F)_2$.[29] After this, a number of xenon–nitrogen bonds were characterised in complex molecules.[30–38]

Chemistry related to the lighter rare gases is naturally much more sparse than that of Xe. The first reports dealt with fluorine–krypton compounds, molecules KrF_4[39] and KrF_2[40–42] being analogous to the fluorinated xenon compounds. Discoveries of Kr bonding to N and O have been done especially by the Schrobilgen group.[43–46]

The only serious candidate for Ar compounds, ArBeO, was prepared in low-temperature matrices by Thompson and Andrews.[47] The considerable spectral shifts suggested rather strong binding between Ar and BeO, and computational results give 0.29 eV for the interaction energy,[48] which is caused by induced dipole interactions. Various possible bonds between rare-gas atoms and other elements have been extensively studied theoretically by Frenking and Cremer.[49]

As referenced above, the early stages of rare-gas chemistry benefitted also of low-temparature matrix-isolation studies.[26,40,42,47] This method was originally developed for trapping unstable species and reaction intermediates at low temperatures.[50–52] The novel compounds described in this microreview have been up to now prepared in solid rare gases. In brief, the starting point for the preparation is the selection of a suitable hydrogen-containing precursor followed by photodissociative generation of hydrogen atoms and electronegative fragments and trapping them in the low-temperature solid for further reactions. The typically used precursors include hydrogen halides, HCN, H_2S etc. In solid rare gases, the photodissociation is often prevented by the strong cage effect.[53–58] However, the barrier for cage exit of hydrogen atoms during photodissociation in solid rare gases is relatively low, 1–2 eV[59][60], allowing photogeneration and isolation of H atoms. After preparation of the neutral reactants, hydrogen atoms are selectively mobilised by annealing the matrix at a suitable temperature (ca. 30 K for Kr and ca. 50 K for Xe). HXY-type rare-gas compounds (X = Kr or Xe; Y = Cl, Br, I, CN, ...) are then formed in a concerted reaction $H + X + Y \rightarrow HXY$.

In this article we describe the solid-state synthesis of several HXY-type rare-gas molecules shown in Figure 1. It is to be noted that the present species *are not* van der Waals systems but truly chemically bound molecules. We give the spectral characteristics of these new compounds, describe their formation mechanism from neutral constituents as well as their stabilities. This review is based on original articles and a PhD Thesis during years 1995–1998.[61–67] Additionally, we connect ab initio results with the experimental data to aid the understanding of the bonding and charge distribution of the new molecules.

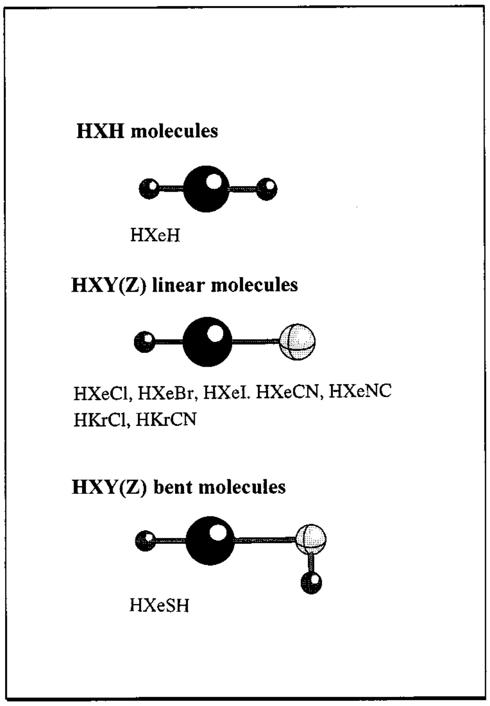

Figure 1. The HXH, HXY, and HXY(Z) molecules

Preparation of the HXY Molecules

In the following we describe shortly the solid-state experiments for preparing the new rare-gas-containing molecules. Solid rare gases (5–50 K) are used as the medium for synthesis and for spectroscopic identification of the formed species. The precursor molecules HY (hydrogen halides, HCN, H_2S, etc) are mixed with rare gases in the gas phase and isolated in a typical 1000-fold excess of the host atoms in a polycrystalline solid deposited onto an optically transparent substrate. The isolated species and their photoproducts can be monitored by measuring their infrared absorption spectra or by measuring the time-resolved luminescence spectra.

In order to promote the isolated precursor to photodissociative repulsive states different light sources can be used. The dissociation energies (D_0) of the hydrogen halides HCl, HBr, and HI are 4.43, 3.75, and 3.05 eV, respectively,[68] and various UV lamps work well for decomposing these precursors. For H_2S, photodissociation at 193 nm (ArF laser) is very efficient,[69] since the absorption maximum of the precursor is near this wavelength. Also HCN can be photodissociated at 193 nm in solid Kr and Xe even though the efficiency is low. Additionally, water, which is always present as an impurity, produces H atoms into the solid host upon 193 nm excitation.

Upon photolysis the IR absorptions of the precursor disappear and isolated H atoms and electronegative fragments Y are formed. This can be seen for instance from the appearance of the spin-orbit ($^2P_{1/2} \leftarrow {}^2P_{3/2}$) absorption at ca. 7600 and 3600 cm^{-1} for iodine and bromine atoms, respectively.[66] Both the H atoms and Y fragments are stable below the mobilisation temperature of hydrogen atoms (30−50 K). In very diluted matrices (M/A ratio > 1000), it is possible to convert a major part of the precursor molecules into hydrogen atoms and Y fragments. In more concentrated matrices, other processes like clusterization and photoinduced reactions of hydrogen atoms produce more complicated products and hydrogen molecules.[66,70]

The next step in the synthesis is the raising of the temperature to the point at which the photogenerated hydrogen atoms start to diffuse. In solid Xe, several separate experiments have shown that hydrogen atoms diffuse at around 45 K.[59,70−73] Randomly distributed hydrogen atoms diffuse until they find a Xe atom which has a fragment Y as a nearest neighbour. At this stage, these three fragments H, Xe, and Y react and form an HXY molecule. This process is described in Figure 2. Another possibility is a reaction of two hydrogen atoms with an Xe atom between them. This reaction produces xenon dihydride (HXeH) and it happens in any Xe matrix which contains hydrogen atoms. Most importantly, since HXY molecules are formed from H and Y which are too far from each other to be able to re-form the precursor HY, species HXY and HXeH are the major trapping sites for H atoms and Y fragments in solid rare gases after the mobilisation of hydrogen atoms.[67]

The formed HXY molecules are easily detected by IR spectroscopy since they have extremely intensive X−H stretching absorptions,[61,62,64,65] and the position of the stretching band is very characteristic for each Y. The Xe−H stretching bands of different HXeY molecules are presented in Figure 3. In addition to these absorptions, weaker bending absorptions can be detected for some of the compounds. Characteristic for HXeNC is also an intensive N−C stretching absorption. All vibrational bands of the HXY compounds observed thus far are collected in Table 1 including the deuterated compounds.

As can be seen from Table 1 and Figure 3, the position of the Xe−H stretching band (or more generally the X−H stretching band) changes considerably by varying the Y fragment. This property is rationalised in the following sections where the origin of the bonding is discussed. It will be shown that the position of the stretching band reflects both the Xe−H bond length as well as the charge distribution of the compounds. A striking example of this sensitivity of the ν_{Xe-H} absorption can be found by comparing the two isomers of HXeCN. For the more stable HXeCN the ν_{Xe-H} absorption is at 1624 cm^{-1} and it shifts +227

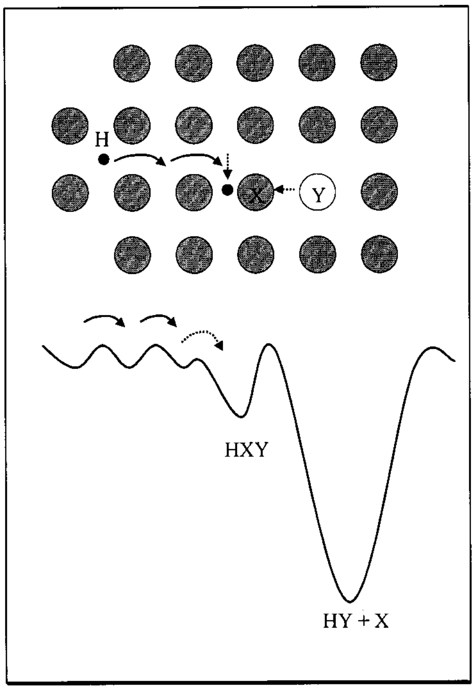

Figure 2. A schematic picture of the generation of the HXY (X = Kr, Xe; Y = Cl, Br, I, CN, ...) molecules in solid rare gases; the lower curve describes the potential energy

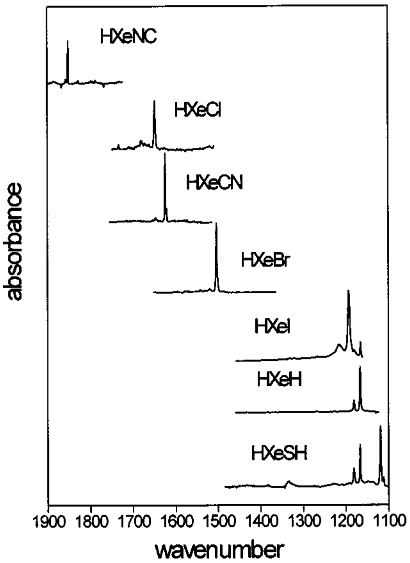

Figure 3. The Xe−H stretching absorptions of different HXeY compounds in solid Xe; note that the absorptions of HXeH at 1166 and 1181 cm^{-1} appear in the spectra of HXeI and HXeSH as well

cm^{-1} for HXeNC to 1851 cm^{-1}. This also measures the anisotropicity of the CN pseudohalogen.

The data in Table 1 also collects the observed overtones. At first it can be noted that HXeI, HXeBr, and HXeH show measurable intensity in the first overtone of Xe−H stretching vibration originating from anharmonic effects. Furthermore, this anharmonicity influences the fundamental wavenumber by several percent, which must be kept in mind while comparing the experimental and calculated (harmonic) wavenumbers.

Table 1. The observed IR absorptions [cm^{-1}] of different HXY(Z) compounds

Compound	ν[Xe−H(D)]	2ν[Xe−H(D)]	δ	2δ	ν(Y−Z)
HXeCl	1648				
DXeCl	1198				
HXeBr	1504	2869	489	965	
DXeBr	1100				
HXeI	1193	2190	450		
DXeI	893	1693			
HXeCN	1624				
DXeCN	1178				
HXeNC	1851				2044
DXeNC	1339				
HXeSH(D)	1119				
DXeSH(D)	833				
HXeH	1166, 1181	2003[a]	701		
HXeD	1093 ν(Xe−H) 753 ν(Xe−D)		621		
DXeD	846, 856		514		
HKrCl	1476		544	1070	
DKrCl	1106				
HKrCN	1497		618		
DKrCN	1109				

[a] Combination of symmetric and asymmetric Xe−H stretches or 2ν(Xe−H).

Mechanism of Formation

Before going into the details of bonding it is important to discuss the mechanism of formation of the rare-gas molecules. UV photolysis of halogen-doped rare gases may induce permanent charge separation as was shown by Fajardo and Apkarian,[74−76] which results in trapped ionic centers like X_2H^+, Y_2H^-, and X_n^+ (X = rare gas, Y = halogen).[77−80] Thus, thermal activation of the photolysed solids may also induce ionic reaction channels, which should not be neglected when considering the mechanism of formation of the HXY molecules. However, for HXeI we could experimentally show that the molecule originates from neutral atoms. The ν_{Xe-H} frequency of HXeI is 1193 cm^{-1}, $2\nu_{Xe-H}$ is 2190 cm^{-1}, and around energies $3\nu_{Xe-H} \approx$ 3000 cm^{-1} the molecule decomposes (see Figure 4). The HXeI photodissociation experiment[63] also yields the absorption profile for the $3\nu_{Xe-H}$ transition with an onset at 2950 cm^{-1} which can be taken as an approximate value for the D_0 dissociation energy of HXeI. After this IR decomposition the molecular form can be restored *quantitatively.* Important is that the quantitative restoration of the molecular form occurs at considerably lower temperatures than the global mobilisation of H atoms after initial UV photodissociation of the precursor. This means that the IR decomposition of HXeI produces atoms, which are in a dissociated form in close contact with each other and HXeI can be recovered by slight warming or even at the lowest temperatures by tunneling.[63] The low energy of the $3\nu_{Xe-H}$ infrared photons is not sufficient to produce ionic centers into the crystal and the only effect is bond breaking with the resulting neutral atoms being located at their van der Waals distances from each other. The final proof in favour of the formation of the HXeI molecule from neutral atoms was obtained by following the concentrations of HXeI and I atoms simultaneously by IR measurements. The increase of the spin-orbit absorption ($^2P_{1/2} \leftarrow {}^2P_{3/2}$) of I atoms[66] at 7457 cm^{-1} correlated with the decrease of HXeI and vice versa.[63]

In addition to this direct evidence on formation of HXeI from neutral atoms supporting information is available from Feldman and co-workers.[81,82] By combined infrared and ESR-spectroscopic studies on electron-irradiated hydrocarbon-containing Xe matrices these authors found that the decrease of hydrogen atoms correlated with the growth of HXeH. Also, addition of electron scavengers which enhanced the ion formation decreased the yield of xenon dihydride.[81,82] It can also be mentioned that these authors found indications of possible reactions of HXeH with hydrocarbons.

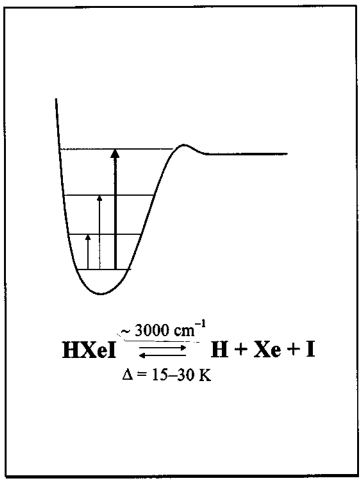

Figure 4. Photodissociation of the HXeI molecule with infrared light at ca. 3 μm

The result that the HXY compounds are formed from neutral atoms is very important because neither ions nor complex intermediates are needed to synthesize these molecules. Solid rare gases form an ideal environment for synthesis since one of the reactants is present as a solvent. Additionally, one needs only to find a suitable precursor molecule which can be photodissociated to hydrogen atoms and Y fragments. In most cases, hydrogen atoms can be selectively mobilised after photolysis, the Y fragments being immobile. This reduces the number of unwanted side reactions and only HXeH is a major "side product".

Considering the possible preparation of HXY in the gas phase, the major requirement appears to be the simultaneous production of H and X atoms, and the Y fragments. This can be achieved, for example, by microwave discharge. In preliminary attempts we have obtained HXeCl directly in the matrix by depositing a mixture of HCl and Xe through a discharge.[83] Unfortunately, it was impossible to determine whether HXeCl was produced in the gas phase or on the surface of the matrix. In any case, this positive result prompts for further gas-phase experiments.

A Simple Model for the Bonding

The origin of bonding in the HXY compounds can be understood on the basis of a simple ionic model. In this model, the HXY molecule is best described as an ion pair HX^+Y^-, which contains a covalently bound HX^+ interacting with Y^- mainly due to Coulombic attraction. This idea was presented by Last and George predicting the existence of HXe^+Cl^- in 1988 by their semiempirical DIIS method.[84] It is also interesting to note that the ionic $(HXe)^+$ and $(HKr)^+$ constituents of the new rare-gas molecules are isoelectronic with HI and HBr, respectively.

On the basis of this charge-transfer model it is informative to determine the main factors which affect the existence and stability of HXY. Figure 5 explains the model of HXY compounds in a simple manner. According to this model, HXY has ionic nature at the equilibrium structure which originates from the ionic $HX^+ + Y^-$ diabatic surface. However, when the bonds are stretched the system dissociates to the neutral H + X + Y limit due to the avoided crossing between the two diabatic surfaces. The ionization potential (*IP*) of X, electron affinity (*EA*) of Y and the dissociation energy (D_e) of XH^+ determine the energetics between the ionic and neutral limits. Low ionization potential of X and large electron affinity of Y are favourable with respect to the stability of HXY. The D_e values of XeH^+ and KrH^+ are about 4.05 and 4.8 eV, respectively.[85–88] These large values tend to bring the ionic limit low in energy and this explains partially the existence of the HXY compounds. Moreover, small Y^- fragments stabilise HXY more than the larger ones because they can approach closer to the HX^+ fragment and thus produce larger Coulombic stabilisation. Altogether, there is rather subtle balance between different factors affecting the energetics of HXY compounds and their properties depend strongly on Y as observed in experiments from the position of the X−H stretching band.

In terms of resonance structures, HXY should be described as a resonance hybrid between several possible structures from which the most important is HX^+Y^-. Other important structures are neutral H−X−Y and ionic H^-X^+Y. The ionic structures tend to stabilise the compound and the neutral structure destabilises it. HXeH is best described similarly as a resonance hybrid between HXe^+H^- and H^-Xe^+H.

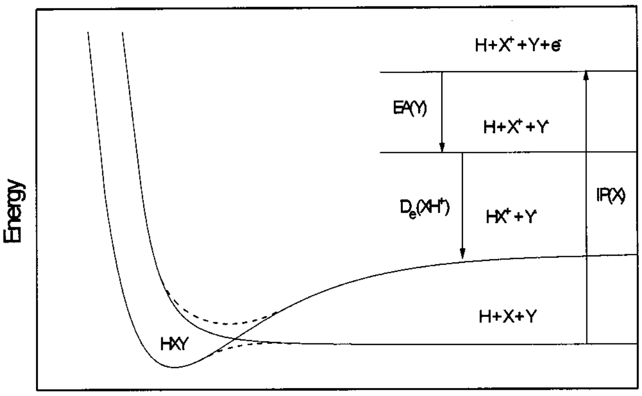

Figure 5. Schematic picture of the origin of bonding in the HXY molecules; the *x* axis describe the sum of the X−H and X−Y distances in a linear geometry

The bonding of the HXeH molecule can be considered qualitatively within the Molecular Orbital (MO) theory also by a three-center four-electron model[12,17,89,90] in accordance to the fluorinated Xe compounds. The highest occupied orbital (σ_g) of HXeH is practically centered around the H atoms, being non-bonding.[90] The lowest σ_u molecular orbital, responsible for the covalent bonding, consists of a collinear set comprising one 5p orbital of Xe and the hydrogen 1s orbitals, being occupied by the two other electrons. Similar simple linear model should be valid also for other HXY molecules by replacing the other 1s hydrogenic orbital by the proper orbital of the Y fragment.

Computational Properties of the HXY Compounds

In order to understand the nature of bonding and spectral characteristics of the rare-gas molecules, ab initio methods have been applied extensively.[61,62,64,65,67,90] The computational results support strongly the bonding model presented above and they corroborate the experimental spectroscopic features as well as give insight to the stabilities of these molecules. The basis set and electron-correlation dependencies of the various properties are discussed separately in the following.

Selection of Computational Methods

From the computational point of view the HXY(Z) molecules are a challenging task. The ion-pair nature of these compounds, interaction of different neutral and ionic configurations, as well as relatively weak bonds and relativistic effects establish a test for the performance of the standard computational approaches. All-electron basis sets become unfeasibly large when rare-gas atoms are considered. Therefore, most of the studies on the HXY molecules have applied effective core potentials (ECP) to describe the rare-gas atoms while first- and second-row atoms are dealt with standard all-electron Gaussian-type basis sets. The use of ECPs diminishes the size of the calculation by the accounted number of electrons, for example, reducing the number of electrons in Xe from 54 to 8 or 18 in the valence space. This enables also application of higher level correlation in the calculations. As an example, the calculated bond lengths and spectra of HXeH have been collected at various levels of theory in Table 2. Most of these calculations would not be feasible using all-electron basis sets on xenon.

Table 2. The calculated bond lengths [Å] compared with the calculated and experimentally observed vibrational frequencies [cm^{-1}] of linear HXeH

	r(H−Xe)	$\nu_1(\sigma_g)$	$\nu_2(\pi_u)$ [a]	$\nu_3(\sigma_u)$	Ref.
MP2/LANL1DZ	2.0193	1007	706	1221	[62]
MP2/LJ18[b]	1.8607	1559	876	1384	
Becke3-LYP/LJ18[b]	1.8789	1523	857	1334	
CCSD(T)/LJ18[c]	1.892	1281	777	1272	[90]
CCSD(T)/LJ18[c] + BSSE + SO	1.916	1216	773	1279	[90]
CCSD(T)/N8[d]	1.929	1028	735	1199	[90]
CCSD(T)/N8[d] + BSSE +SO	1.958	1018	708	1187	[90]
Experimental			701	1166/1181	[62]

[a] Doubly degenerate. − [b] 18-VE ECP basis on xenon and the 6−311++G(2d,2p) standard basis set on hydrogen. − [c] Modified 18-VE ECP basis on xenon and an aug-cc-pVTZ basis added with one f-function on hydrogen. − [d] Modified 8-VE ECP on xenon and an aug-cc-pVTZ+f basis on hydrogen.

Aiding the first observations of the HXY molecules HXeI, HXeBr, HXeCl, HKrCl, and HXeH the MP2/LANL1DZ level was used as the preliminary theoretical method.[61][62] This very inexpensive approach was observed to give a stable minimum for all the observed 5 molecules, whereas the HKrI and HKrBr molecules were unstable computationally and have, in fact, despite attempts, never been experimentally observed. The failure of the MP2/LANL1DZ calculations was that they predicted the HXY molecules to be energetically *above* the atomic dissociation limit. However, these calculations were able to predict the properties around the equilibrium structure reasonably well and the harmonic vibrational frequencies of the new HXY molecules were satisfactory. As can be seen in Table 2, the discrepancy between the MP2/LANL1DZ-calculated and the observed wavenumbers is quite small especially when taking into account the anharmonic effects. This is actually accidental as pointed out by Runeberg and co-workers.[90] These authors showed that increasing the level of correlation requires also a larger and more flexible basis set to work properly for the HXY molecules. Increasing only the basis set using the perturbation theory (MPn) shortens the Xe−H bond length thereby also increasing the harmonic vibrational frequency. If higher correlation levels are used the Xe−H bond length increases decreasing the harmonic frequencies. The most appropriate levels of theory seem to be the CCSD(T) and multireference-CI (MR-CI) levels when connected with extensive basis sets.[90] It must be noted, however, that even though the CCSD(T) theory, coupled with large basis sets and taking into account BSSE and spin-orbit effects, results in a qualitatively correct picture, it failed to reproduce a deep enough potential well to be consistent with the observed overtone/combination band of HXeH. Therefore, in most cases the low-level calculations are sufficient to help the interpretation of experimental data while obtaining an accurate potential energy surface is very demanding.

Computed Structures of the HXY Molecules

The observed new rare-gas molecules can roughly be divided into three groups: the centrosymmetric HXH molecule, the linear HXY(Z) molecules, and the bent HXYZ molecules (see Figure 1). In all of these cases, linear bonding around the rare-gas atom is found. The only new centrosymmetric molecule HXeH resembles its fluorine analog FXeF. Concerning the structures of these novel rare-gas molecules we have to rely on calculated values, experimental data being nonexistent so far. The calculated structural parameters, Mulliken charges and dipole moments of the various HXY(Z) molecules, are collected in Table 3. For comparison the experimental bond lengths of XeH^+ and KrH^+ are included.

It can be noted that the calculated parameters follow a general trend. The H−Xe bond length decreases with the increasing partial positive charge on xenon. The positive charge residing on xenon is largest (+0.88) for the HXeNC molecule resulting in the shortest H−Xe bond length (1.659 Å). This trend finally approaches the XeH^+ cation at the limit of complete ionic bonding. Similarly, in the Kr compounds the larger charge on Kr results in a shorter bond length converging towards the KrH^+ cation. It is also worth mentioning that these molecules have very large dipole moments due to the extent of charge separation.

To rationalize the difference of the HXY molecules from the van der Waals geometries of the constituents we can inspect the HXeI system. Figure 6 displays the molecular and van der Waals distances showing that chemical bond formation between the atoms results in more than two-fold decrease of the Xe−H distance and in almost 30% contraction of the Xe−I distance.

HXeSH is an interesting bent molecule representing the first example of an Xe−S bond. The Xe−S−H angle of ca. 91 degrees is very close to the angle of H_2S. Also the S−H bond length of HXeSH (calculated 1.334 Å) is almost the same as the experimental value for H_2S (1.336 Å).[91] Therefore it seems that the rare-gas atom is inserted into the covalent hydrogen−sulphur bond and has a negligible effect on the residing molecule. Also, for the linear HXeCN, HXeNC, and HKrCN molecules the rare-gas molecules restore the precursor structure, the novel molecules being linear and having C≡N bond lengths close to the HCN precursor.

Vibrational Spectra of the HXY Molecules

The Xe−H stretching motion is an essential part of the vibrational calculation of the HXY molecules. As discussed above, highly correlated calculations with large basis sets

Table 3. The computational properties of different HXY(Z) compounds at the MP2 level[a]; for comparison, values for KrH^+ and XeH^+ have been included

	r(H−X) [Å]	r(X−Y) [Å]	r(Y−Z) [Å]	q(H)	q(X)	q(Y)	q(Z)	μ [D]
HXeH	1.861			−0.344	0.688			0.0
HXeSH[b]	1.774	2.729	1.334	−0.226	0.671	−0.435	−0.009	4.458
HXeI	1.747	3.095		−0.178	0.645	−0.467		6.405
HXeCN	1.707	2.392	1.178	−0.203	0.847	−0.401	−0.242	7.432
HXeBr	1.694	2.837		−0.156	0.802	−0.647		7.331
HXeCl	1.685	2.663		−0.165	0.816	−0.651		7.246
HXeNC	1.659	2.342	1.187	−0.161	0.880	−0.424	−0.295	9.263
XeH^+[c]	1.596			+0.091	0.909			
HKrCN	1.466	2.349	1.177	−0.206	0.886	−0.488	−0.193	9.205
HKrCl	1.435	2.666		−0.178	0.887	−0.709		9.351
KrH^+[d]	1.382			+0.061	0.939			

[a] For Kr and Xe 18-VE ECPs and for I 17-VE ECP (denoted as LJ18, see ref.[93]) were used while the standard 6−311++G(2d,2p) basis set was applied for the first- and second-row atoms. – [b] This is the only bent molecule of the HXY(Z) molecules with the H−S−Xe angle being 91.02°. – [c] Experimental value 1.603 Å, ref.[94]. – [d] Experimental value 1.421 Å, ref.[85].

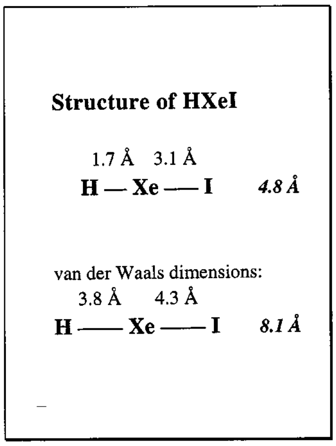

Figure 6. Structure of HXeI; the molecular bond lengths are taken from MP2/LJ18 calculations; the van der Waals dimensions are deduced from Xe−H[95] and Xe−I[96] pair potential minima

result in a good agreement with the experimental values.[90] This is especially important when the HXY molecule is relatively weakly bound, and the potential energy surface near the dissociation limit is not described accurately with modest computational methods like the perturbation theory. For instance, such examples are HKrCN[64] and HXeSH.[65] For HKrCN the MP2/LJ18-calculated Kr−H stretching wavenumber is 2011 cm^{-1}, while the largest correlation level, CCSD(T)/LJ18, gives a harmonic ν_{Kr-H} frequency of 1781 cm^{-1} for HKrCN, still being ca. 300 cm^{-1} above the experimental value of 1497 cm^{-1}.[64] As discussed previously, anharmonic effects explain partially the difference. In addition, the solid host red-shifts the observed wavenumber from its gas-phase value and the remaining discrepancy can mostly be attributed to the underestimated basis set used. For HXeSH the situation is similar: The MP2/LJ18 calculations predict the Xe−H stretching at 1521 cm^{-1}, while the CCSD(T)/LJ18 calculation reduces this value to 1148 cm^{-1}, the experimental value being 1119 cm^{-1}.

Increasing the size of the HXY molecules beyond three-atomics makes the use of state-of-art computational methods unfeasible. In the course of our work with the HXY-type molecules we have found that even the moderate MP2/LJ18 level gives reasonable qualitative results for structures, charge separation, and vibrational frequencies. In addition, the extreme intensities of the X−H stretching absorptions are well predicted. Therefore, we have collected the MP2/LJ18-calculated characteristic X−H bond lengths and vibrational frequencies, including IR intensities in Table 4 for comparison. Also the Becke3-LYP/LJ18-calculated values are included, since the DFT methods are becoming more attractive for larger molecular systems due to their computational efficiency.

The experimental Xe−H stretching wavenumbers shift to higher values when going from the HXeSH molecule to HXeNC. Even though the computational vibrational frequencies are generally overestimated the systematic trend among the present HXY molecules is correctly predicted as discussed in more details in ref.[67] Therefore, using a low-level, economical computational approach, quite useful approximations on the structures and especially on the ν_{X-H} wavenumbers and intensities of new HXY molecules can be done.

Energetics of the HXY Molecules

Even though the structure and vibrational frequencies appear to be reachable also with low-level computational methods, the energetics of the new HXY molecules is more challenging. As demonstrated in the simple bonding model derived earlier (see Figure 5), the HXY molecules possess both neutral (HXY) and ionic (HX^+Y^-) character. This means also that the closer the ionic surface lies to the neutral molecular surface, the larger interaction between the two surfaces is expected. The preliminary MP2/LANL1DZ calculations indicated that the H + X + Y atomic dissociation limit would be *below* the HXY molecular en-

Table 4. The calculated harmonic H−Xe stretching frequencies [cm^{-1}] of HXY(Z) molecules at the MP2 and Becke3-LYP levels; the numbers in the parentheses are the calculated intensities [km mol^{-1}], and the bond lengths are given in Å

	MP2/LJ18		Becke3-LYP/LJ18		Experimental
	r(H−Xe)	ν (I)	*r*(H−Xe)	ν (I)	ν
HXeSH	1.774	1523.1 (3100)	1.798	1556.5 (1800)	1119
HXeI	1.747	1514.8 (5500)	1.786	1559.9 (2200)	1193
HXeCN	1.707	1874.9 (1300)	1.740	1817.3 (800)	1624
HXeBr	1.694	1830.6 (2400)	1.747	1729.9 (1400)	1504
HXeCl	1.685	1904.6 (1700)	1.733	1799.0 (1000)	1648
HXeNC	1.659	2010.5 (500)	1.704	1935.8 (800)	1851
HKrCN	1.468	2010.6 (1700)	1.547	1738.0 (1400)	1497
HKrCl	1.435	2177.8 (2900)	1.543	1757.7 (1800)	1476

ergy[61][62] However, increasing the basis set *and* the correlation level the situation is reversed and the HXY configuration becomes *lower* in energy than the atomic dissociation limit. A dissociation energy of 0.32 eV was estimated for HXeH according to the dissociation limit Xe + 2 H.[90] This result was obtained at the CCSD(T) level, using a large 18-VE ECP basis for Xe and all-electron basis for hydrogen, and correcting the value for both BSSE and spin-orbit coupling effects. However, taking into account the observed overtone/combination transition at 2003 cm^{-1} and assuming this vibrational level to lie below the dissociation limit, and estimating the symmetric stretch wavenumber from the calculations (ca. 1100 cm^{-1}) we end up with a value of at least 0.48 eV for the experimental dissociation energy (D_e) of HXeH. The origin of the present discrepancy ($\geq$ 0.16 eV) between the calculated and experimental dissociation energies may be technical since also the stabilising role of the solid host has been estimated to be small (0.033 eV for quadrupole interaction of HXeH in Xe[90]).

For HXeI an experimental D_e value of about 0.42 eV has been deduced from IR pumping experiments.[63] These molecules together with HXeSH are the weakest bound of all the HXY molecules found up to now. They also have the lowest lying Xe−H stretching bands. The $\nu_{\mathrm{Xe-H}}$ for HXeCl at 1648 cm^{-1} suggests a larger binding energy than for HXeH, HXeSH, and HXeI. Indeed, a preliminary high-level computational study at the CISD level estimates the binding energy of HXeCl to be 0.9 eV.[92] The computationally strongest bound molecule is HXeCN, which has a D_e of 1.43 eV[64] with respect to the dissociation limit H + Xe + CN. In general, the observed HXY molecules feature dissociation energies between 0.4 and 1.4 eV, and the corresponding fluorine compound HXeF is expected to be much more strongly bound but it has not yet been experimentally observed.

An additional interesting aspect of the calculation of the stabilization energy of the HXY molecules is that all calculations are performed for molecules in vacuo whereas the experimental evidence up to now is from low-temperature solid rare gases. This rises the question of the role of the rare gas lattice in stabilizing the HXY molecules. First, as found out in the IR pumping experiments on HXeI, the lattice traps the atomic fragments. Secondly, except HXeH, the HXY molecules possess strong dipole moments which could induce long-range interactions with the surrounding rare gases. Especially the xenon environment could be an important, additional stabilizing factor due to its large polarizability compared to argon and krypton. Anyhow, as was shown experimentally in ref.[61], HXeCl can be easily produced also in Kr surroundings and in this case the Xe−H stretch was shifted only by 16 cm^{-1} from its value in pure Xe. Corresponding shifts for HXeBr and HXeCN are 26 and 20 cm^{-1}, respectively,[61][64] indicating a relatively small environmental effect.

Conclusions

Rare-gas atoms X (Xe and Kr) are shown to react with a hydrogen atom and a neutral electronegative fragment Y in a concerted reaction to produce neutral ground-state HXY molecules. The very strong X−H stretching absorption is the most characteristic spectral feature of these molecules, its wavenumber reflecting sensitively the electron distribution in the HXY molecule. The present ab initio calculations show that the bonding comprises both covalent and ionic contributions. A bonding model based on avoided crossing of the neutral H + X + Y and ionic $(HX)^+ + Y^-$ surfaces is presented. This model is applicable for qualitative understanding of bonding in all of the new compounds: HXeI, HXeBr, HXeCl, HXeH, HXeCN, HXeNC, HXeSH, HKrCl, and HKrCN. At the present time these species are produced in solid rare gases by photodissociation of the HY precursor and thermal mobilisation of the fragments. The dissociation energies vary from 0.4 to over 1 eV, and warrant observation of these molecules also in the gas phase. Future computational studies will deepen our understanding in the bonding details as well as suggest the existence of further similar compounds.

Acknowledgments

Financial support from the Academy of Finland and the University of Helsinki are gratefully acknowledged.

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[1] L. Pauling, *J. Am. Chem. Soc.* **1933**, *55*, 1895.
[2] [2a] H. Käding, N. Riehl, *Naturwiss.* **1933**, *21*, 479. − [2b] D. M. Yost, A. L. Kaye, *J. Am. Chem. Soc.* **1933**, *55*, 3890. − [2c] O. Ruff, W. Menzel, *Z. Anorg. Chem.* **1938**, *213*, 206. − [2d] A.v.

Antropoff, *Z. Angew. Chem.* **1933**, *46*, 23. – [2e] A.v. Antropoff, *Z. Anorg. Chem.* **1933**, *213*, 208.

[3] [3a] N. Bartlett, *Proc. Chem. Soc.* **1962**, 218. – [3b] F. O. Sladky, P. A. Bulliner, N. Bartlett, *J. Chem. Soc. A* **1969**, 2179.

[4] R. Hoppe, W. Dähne, H. Mattauch, K. H. Rödder, *Angew. Chem.* **1962**, *74*, 903.

[5] H. H. Claassen, H. Selig, J. G. Malm, *J. Am. Chem. Soc.* **1962**, *84*, 3593.

[6] F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. DeBoer, A. Zankin, *Chem. Comm.* **1968**, 1048.

[7] V. M. McRae, R. D. Peacock, D. R. Russell, *Chem. Comm.* **1969**, 62.

[8] J. H. Holloway, J. G. Knowles, *J. Chem. Soc. A* **1969**, 756.

[9] N. Bartlett, M. Gennis, D. D. Gibler, B. K. Morrell, A. Zalkin, *Inorg. Chem.* **1973**, *12*, 1717.

[10] D. E. McKee, C. J. Adams, N. Bartlett, *Inorg. Chem.* **1973**, *12*, 1722.

[11] J. R. Morten, W. E. Falconer, *J. Chem. Phys.* **1963**, *39*, 427.

[12] J. G. Malm, H. Selig, J. Jortner, S. A. Rice, *Chem. Rev.* **1965**, *65*, 199.

[13] N. Bartlett, F. O. Sladky in *Comprehensive Inorganic Chemistry*, Pergamon Press, New York, **1973**, vol. 3, pp. 213–330.

[14] E. Tommila, *Suom. Kemistil. A* **1963**, *36*, 209.

[15] K. Seppelt, D. Lentz, *Prog. Inorg. Chem.* **1982**, *29*, 167.

[16] J. H. Holloway, *J. Fluor. Chem.* **1986**, *33*, 149.

[17] C. A. Coulson, *J. Chem. Soc.* **1964**, 1442.

[18] D. Holtz, J. L. Beauchamp, *Science* **1971**, 1237. They reported the bond strength as 180 ± 33 kJ mol^{-1}.

[19] J. K. Hovey, T. B. McMahon, *J. Am. Chem. Soc.* **1986**, *108*, 528.

[20] M. Wechsberg, P. A. Bulliner, F. O. Sladky, R. Mews, N. Bartlett, *Inorg. Chem.* **1972**, *11*, 3063.

[21] L. J. Turbini, R. E. Aikman, R. J. Lagow, *J. Am. Chem. Soc.* **1979**, *101*, 5833.

[22] D. Naumann, W. Tyrra, *J. Chem. Soc., Chem. Commun.* **1989**, 47.

[23] H. J. Frohn, S. Jacobs, *J. Chem. Soc., Chem. Commun.* **1989**, 625.

[24] V. V. Zhdankin, P. J. Stang, N. S. Zefirov, *J. Chem. Soc., Chem. Commun.* **1992**, 578.

[25] D. Naumann, W. Tyrra, R. Gnann, D. Pfolk, T. Gilles, K. F. Tebbe, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1821.

[26] L. Y. Nelson, G. C. Pimentel, *Inorg. Chem.* **1967**, *6*, 1758.

[27] C. T. Goetschel, K. R. Loos, *J. Am Chem. Soc.* **1972**, *94*, 3018.

[28] [28a] L. Stein, J. R. Norris, A. J. Down, A. Minihan, *J. Chem. Soc. Chem. Comm.* **1978**, 502. – [28b] T. Drews, K. Seppelt, *Angew. Chem. Int. Ed.* **1997**, *36*, 273.

[29] R. D. LeBlond, D. D. DesMarteau, *J. Chem. Soc., Chem. Commun.* **1974**, 555.

[30] D. D. DesMarteau, *J. Am. Chem. Soc.* **1978**, *100*, 6270.

[31] D. D. DesMarteau, R. D. LeBlond, S. F. Hossain, D. Nothe, *J. Am. Chem. Soc.* **1981**, *103*, 7734.

[32] A. A. A. Emara, G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.* **1987**, 1644.

[33] A. A. A. Emara, G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.* **1988**, 257.

[34] G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.* **1988**, 1506.

[35] J. Foropopoulos, Jr., D. D. DesMarteau, *J. Am. Chem. Soc.* **1982**, *104*, 4260.

[36] J. F. Sawyer, G. J. Schrobilgen, S. J. Sutherland, *Inorg. Chem.* **1982**, *21*, 4064.

[37] G. A. Schumacher, G. J. Schrobilgen, *Inorg. Chem.* **1983**, *22*, 2178.

[38] R. Faggiani, D. K. Kennepohl, C. J. L. Lock, G. J. Schrobilgen, *Inorg. Chem.* **1986**, *25*, 563.

[39] A. V. Grosse, A. D. Kirschenbaum, A. G. Streng, L. V. Streng, *Science* **1963**, *139*, 1047.

[40] J. J. Turner, G. C. Pimentel, *Science* **1963**, *140*, 975.

[41] D. R. MacKenzie, *Science* **1963**, *141*, 1171.

[42] W. F. Howard, L. Andrews, *J. Am. Chem. Soc.* **1974**, *96*, 7864.

[43] G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.* **1988**, 863.

[44] J. C. P. Sanders, G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.* **1989**, 1576.

[45] R. J. Gillespie, G. J. Schrobilgen, *Inorg. Chem.* **1976**, *15*, 22.

[46] G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.* **1988**, 1506.

[47] C. A. T. Thompson, L. Andrews, *J. Am. Chem. Soc.* **1994**, *116*, 423.

[48] A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1994**, *226*, 11.

[49] G. Frenking, D. Cremer, in *Structure and Bonding*, *Noble Gas and High Temperature Chemistry* (Eds.: M. J. Clarke, J. B. Goodenough, J. A. Ibers, C. K. Jørgensen, D. M. P. Mingos, J. B. Neilands, G. A. Palmer, D. Reinen, P. J. Sadler, R. Weiss, R. J. P. Williams), Springer, Berlin, **1990**, p. 17–95.

[50] E. Whittle, D. A. Dows, G. C. Pimentel, *J. Chem. Phys.* **1954**, *22*, 1943.

[51] I. Norman, G. O. Porter, *Nature* **1954**, *174*, 508.

[52] H. Broida, J. R. Pellam, *Phys. Rev.* **1954**, *95*, 845.

[53] L. Andrews, G. C. Pimentel, *J. Chem. Phys.* **1967**, *47*, 3637.

[54] L. E. Brus, V. E. Bondybey, *Chem. Phys. Lett.* **1975**, *36*, 252.

[55] L. E. Brus, V. E. Bondybey, *J. Chem. Phys.* **1976**, *65*, 71.

[56] V. E. Bondybey, L. E. Brus, *J. Chem. Phys.* **1976**, *64*, 3724.

[57] V. E. Bondybey, L. E. Brus, *J. Chem. Phys.* **1975**, *62*, 620.

[58] V. E. Bondybey, C. Fletcher, *J. Chem. Phys.* **1976**, *64*, 3615.

[59] R. Schriever, M. Chergui, N. Schwentner, *J. Chem. Phys.* **1991**, *95*, 6124.

[60] K. H. Gödderz, N. Schwentner, M. Chergui, *J. Chem. Phys.* **1996**, *105*, 451.

[61] M. Pettersson, J. Lundell, M. Räsänen, *J. Chem. Phys.* **1995**, *102*, 6423.

[62] M. Pettersson, J. Lundell, M. Räsänen, *J. Chem. Phys.* **1995**, *103*, 205.

[63] M. Pettersson, J. Nieminen, L. Khriachtchev, M. Räsänen, *J. Chem. Phys.* **1997**, *107*, 8423.

[64] M. Pettersson, J. Lundell, L. Khriachtchev, M. Räsänen, *J. Chem. Phys.* **1998**, *109*, 618.

[65] M. Pettersson, J. Lundell, L. Khriachtchev, E. Isoniemi, M. Räsänen, *J. Am. Chem. Soc.* **1998**, 7979.

[66] M. Pettersson, J. Nieminen, *Chem. Phys. Lett.* **1997**, *283*, 1.

[67] M. Pettersson, Ph.D. Thesis, University of Helsinki, **1998**; available upon request from the author.

[68] H. Okabe, *Photochemistry of Small Molecules*, Wiley, New York, **1978**.

[69] L. Khriachtchev, M. Pettersson, E. Isoniemi, M. Räsänen, *J. Chem. Phys.* **1998**, *108*, 5747.

[70] D. LaBrake, E. T. Ryan, E. Weitz, *J. Chem. Phys.* **1995**, *102*, 4112.

[71] D. LaBrake, E. Weitz, *Chem. Phys. Lett.* **1993**, *211*, 430.

[72] J. Eberlein, M. Creutzburg, *J. Chem. Phys.* **1997**, *106*, 2118, and references therein.

[73] H. Muto, K. Nunome, M. Iwasaki, *J. Phys. Chem.* **1980**, *84*, 3402.

[74] M. E. Fajardo, V. A. Apkarian, *J. Chem. Phys.* **1986**, *85*, 5660.

[75] M. E. Fajardo, V. A. Apkarian, *J. Chem. Phys.* **1988**, *89*, 4102.

[76] M. E. Fajardo, V. A. Apkarian, *J. Chem. Phys.* **1988**, *89*, 4124.

[77] H. Kunttu, J. Seetula, M. Räsänen, V. A. Apkarian, *J. Chem. Phys.* **1992**, *96*, 5630.

[78] M. Räsänen, J. Seetula, H. Kunttu, *J. Chem. Phys.* **1993**, *98*, 3914.

[79] H. Kunttu, J. Seetula, *Chem. Phys.* **1994**, *189*, 273.

[80] T. F. Fridgen, J. M. Parnis, *J. Chem. Phys.* **1998**, *109*, 2155.

[81] V. I. Feldman, F. F. Sukhov, *Chem. Phys. Lett.* **1996**, *255*, 425.

[82] V. I. Feldman, F. F. Sukhov, A. Yu. Orlov, *Chem. Phys. Lett.* **1997**, *280*, 507.

[83] M. Pettersson, J. Nieminen, unpublished results.

[84] I. Last, T. F. George, *J. Chem. Phys.* **1988**, *89*, 3071.

[85] J. W. C. Johns, *J. Mol. Spectrosc.* **1984**, *106*, 124.

[86] H. E. Warner, W. T. Connor, R. C. Woods, *J. Chem. Phys.* **1984**, *81*, 5413.

[87] K. A. Peterson, R. H. Petrmichl, R. L. McClain, R. C. Woods, *J. Chem. Phys.* **1991**, *95*, 2352.

[88] R. Klein, P. Rosmus, *Z. Naturforsch.* **1984**, *39a*, 349.

[89] R. E. Rundle, *J. Am. Chem. Soc.* **1963**, *85*, 112.

[90] N. Runeberg, M. Seth, P. Pyykkö, *Chem. Phys. Lett.* **1995**, *246*, 239. N. Runeberg, Doctoral Dissertation, University of Helsinki, **1996**.

[91] W. C. Lane, T. H. Edwards, J. R. Gillis, E. S. Bonomo, F. J. Murcray, *J. Mol. Spectrosc.* **1982**, *95*, 365.

[92] M. Johansson, M. Hotokka, M. Pettersson, M. Räsänen, *Chem. Phys.*, accepted for publication.

[93] L. A. LaJohn, P. A. Christensen, R. B. Ross, T. Atashroo, W. C. Ermler, *J. Chem. Phys.* **1987**, *87*, 2812.

[94] S. A. Rogers, C. R. Brazier, P. F. Bernath, *J. Chem. Phys.* **1987**, *87*, 159.

[95] R. W. Bickes, Jr., B. Lantzsch, J. P. Toennies, K. Walaschewski, *Faraday Discuss. Chem. Soc.* **1973**, *55*, 167.

[96] P. Casavecchia, G. He, R. K. Sparks, Y. T. Lee, *J. Chem. Phys.* **1982**, *77*, 1878.

Received October 22, 1998
[I98370]