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American Institute of Physics

2002-07-15

Journal of Chemical Physics July 15, 2002 Volume 117, Issue 3, pp. 961-964

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COMMUNICATIONS

Large blueshift of the H–Kr stretching frequency of HKrCl upon complexation with N₂

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(Received 30 April 2002; accepted 15 May 2002)

Interaction between HKrCl and N₂ is investigated in a low temperature Kr matrix and by using *ab initio* calculations. Two configurations of the HKrCl··N₂ complex are found both computationally and experimentally. The complexes show large monomer-to-complex blueshifts (+112.9 and +32.4 cm⁻¹ experimentally) of the H–Kr stretching vibration mode. The large blueshifts are attributed to the enhanced (HKr)⁺Cl⁻ ion-pair character of complexed HKrCl resulting in stronger H–Kr covalent bonding. © 2002 American Institute of Physics. [DOI: 10.1063/1.1491403]

Several years ago, it was found that solid rare gas (Rg) matrices become reactive when they are doped with hydrogen atoms (H) and suitable electronegative fragments (Y).¹ Upon thermal mobilization of hydrogen atoms, chemically bound HRgY molecules are formed.² Vibrational properties of the HRgY molecules are sensitive to their local environment as evidenced by the large site splittings of the H–Rg stretchings of HArF (~50 cm⁻¹, 2.5%) and HKrF (~25 cm⁻¹, 1.2%).^{3,4} The strong environmental effects are most probably connected with the large polarity of the HRgY molecules as well as with their relatively weak bonding. The HRgY compounds show (HRg)⁺Y⁻ ion-pair character, resulting in large computational dipole moments (4.5–9.4 D, 1 D≈3.34×10⁻³⁰ C m),² comparable with salt molecules such as NaCl (9.00 D).⁵

Until now, the experimental investigations of HRgY molecules have concentrated on the properties of monomers isolated in rare gas matrices. Computationally, complexes of XeH₂ with water have previously been studied.⁶ In this work, we investigate both computationally and experimentally interaction between HKrCl and N₂. An intriguing question is how much the intermolecular interaction can stabilize or destabilize HRgY molecules, and to what extent the complexation influences the properties of these molecules.

A large number of various N₂ complexes of hydrogen containing molecules have been studied. Typically, complexation with N₂ induces a monomer-to-complex redshifts in the hydrogen stretching vibrational mode. As a representative example, the HCl··N₂ complex shows a complexation-induced redshift of -19.1 cm⁻¹ (-0.7%) in solid krypton.⁷ According to our best knowledge, no blueshifts of the hydrogen stretching modes have been reported upon complexation with N₂. Recently, several examples of blueshifting hydrogen bonds have been found between different complex partners.⁸

In the experiments, HCl (99%, CIL), N₂ (99.9999%,

Aga) and Kr (99.95%, Air Liquide) gases were mixed in various proportions in a glass bulb. The matrix ratios used were HCl:N₂:Kr=1:(0–10):1000. The samples were deposited onto a CsI substrate kept at 27 K in a closed-cycle helium cryostat (APD, DE 202A). The typical matrix thickness was 100–200 μm. The spectra were measured at 7.5 K by a Nicolet 60 SX Fourier-transform infrared (FTIR) spectrometer with 0.25 cm⁻¹ resolution in the middle infrared region.

In the HCl/Kr matrices, the HCl monomer bands at 2872.9 and 2870.5 cm⁻¹ dominate in the spectra (see the lower spectrum in Fig. 1).⁹ HCl molecules were photodecomposed at 7.5 K with 193 nm radiation from an ArF-eximer laser (MPB, MSX-250) by using ~10⁴ pulses with a pulse energy density of ~10 mJ/cm², which led to decomposition of >90% of HCl. As reported previously, HKrCl appears as an intermediate during photolysis.¹⁰ Annealing of the photolyzed HCl/Kr matrix leads to the additional formation of HKrCl molecules, as shown in Fig. 2(a) in the lowest trace. The H–Kr stretching (1476.1 cm⁻¹) and H–Kr–Cl bending (543.7 and 542.1 cm⁻¹ with the overtone at 1069.3 and 1067.9 cm⁻¹) absorptions are observed, in agreement with the literature data.^{1,2}

In the HCl/N₂/Kr matrices, the known bands of the HCl··N₂ complex at 2853.6 and 2851.2 cm⁻¹ are seen (the upper spectrum in Fig. 1).⁷ Taking into account the four times larger computational IR absorption intensity of N₂-complexed HCl compared with the HCl monomer and integrated experimental absorptions, the [HCl]/[HCl··N₂] ratio is estimated to be ~2.5 for HCl:N₂:Kr=1:2:1000. Additionally, we observed the N–N stretch of the HCl··N₂ complex at 2327.4 cm⁻¹. The 193 nm radiation decomposed the HCl··N₂ complex with a somewhat smaller rate than monomeric HCl. Annealing of the photolyzed HCl/N₂/Kr matrix generated, in addition to HKrCl, a set of new bands due to N₂ doping. In the H–Kr stretching region the N₂-induced bands are at 1480.2 (s), 1497.7 (w), 1508.5 (s), 1514.5 (w) and 1589.0 cm⁻¹ (w) [see the upper spectrum in Fig. 2(a)]. In the H–Kr–Cl bending region, we observed a

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FIG. 1. FTIR spectra of HCl and HCl/N₂ in solid Kr at 7.5 K. The HCl...N₂ complex in the lower spectrum originates from the N₂ impurity present in a matrix.

band at 541.5 cm⁻¹ (w) and in the bending overtone region a band at 1067.0 cm⁻¹ (w) [see the upper spectrum in Fig. 2(b)]. These N₂-induced bands are in the middle trace of Fig. 2 where HKrCl monomer bands are subtracted from the complex bands. These additional nitrogen-induced bands are proposed to belong to the HKrCl...N₂ complex.

The experimental assignment is based on the following arguments. Upon annealing, the efficient increase of the complex bands starts at ~25 K and the formation saturates at ~30 K, similarly to the monomer bands.⁴ This temperature dependence fits well the mobility of atomic hydrogen in solid krypton lattice.¹¹ Both monomer and complex bands are thermally stable below the matrix sublimation temperature (~40 K). The HKrCl...N₂ bands are observed as intermediate during photolysis, qualitatively similar to the behavior of the monomeric HKrCl bands.¹⁰ Photostability of HKrCl and the nitrogen-induced species are similar to each other as checked with 193 nm and 350 nm irradiation (see Ref. 10 for the HKrCl photodecomposition profile). Importantly, the decomposition upon irradiation at 350 nm suggests that the complex contains HKrCl, since HCl, N₂, or natural matrix impurities do not decompose at this wavelength. We excluded the complexation with impurity water as the origin of the complex bands by additional experiments using water doping. The ternary N₂ complex of HKrCl was also ruled out by the experiment with the extensive N₂ doping.

We employed *ab initio* calculations to study the HKrCl...N₂ complex. The calculations were carried out within the framework of the GAUSSIAN 98 (revision A.9) package of computer codes.¹² The local minima on the intermolecular potential energy surface were preliminary computed at the Hartree-Fock level and using relatively small but computationally cost-effective basis sets. For the final calculations we employed the Møller-Plesset second order perturbation theory (MP2) including all electrons explicitly into the correlation calculation. The Berny optimization was used with the tight convergence criteria. The basis set was

FIG. 2. FTIR spectra of monomeric and complexed HKrCl in solid Kr at 7.5 K: (a) H-Kr stretching region and (b) H-Kr-Cl fundamental and overtone bending regions. In the middle trace, HKrCl monomer bands are subtracted. The species are prepared by using HCl/Kr and HCl/N₂/Kr matrices, irradiating them at 193 nm and annealing at 34 K. Bands labeled A and B are proposed to originate from the linear and bent N₂ complexes of HKrCl, respectively. A band marked with C is proposed to originate from a longer-range interaction of HKrCl with N₂.

the standard split-valence 6-311++G(2d,2p) which has been found to yield reasonable results for weakly bound complexes.¹³ The vibrational frequencies and IR intensities were calculated by using harmonic force fields.

Two true energy minima of the HKrCl...N₂ complex are found and we call them (a) linear and (b) bent (see Fig. 3). Computationally, the HKrCl monomer has a dipole moment of 7.4 D. According to the natural population analysis (NPA) at the MP2 level, HKrCl induces a small dipole moment in the N₂ molecule with partial charges of (+0.061, -0.042) and (+0.020, -0.026) for the linear and bent configurations, respectively. Due to the small induced dipole moment of N₂, some IR absorption intensity of the N-N stretch is activated in the complexes. The basis set superposition error (BSSE) corrected electronic interaction energies for the HKrCl...N₂ complexes are -471.5 and -495.1 cm⁻¹ for the linear and bent configuration, respectively. The vibrational zero-point energy (ZPE) corrected interaction energies are -234.2

FIG. 3. Computational [MP2(full)/6-311++G(2d,2p)] structures for two configurations of the HKrCl $\cdots$ N $_2$ complex: (a) linear configuration and (b) bent configuration. The distances are in Å and the angles in degrees.

cm $^{-1}$ for the linear complex and -366.8 cm $^{-1}$ for the bent complex. For comparison, the electronic interaction energies for HF $\cdots$ N $_2$ and HCl $\cdots$ N $_2$ complexes are -812.5 cm $^{-1}$ and -334.4 cm $^{-1}$, respectively.^{14,15}

In order to discuss the nature of interaction in the HKrCl $\cdots$ N $_2$ complex, a simple energy component analysis was done. We assume that the major part of the interaction energy is contributed by dipole-quadrupole, dipole-induced-dipole, dispersive and repulsive interactions. The multipole moment expansion terms were used to calculate the dipole-quadrupole and dipole-induced-dipole interaction.¹⁶ The experimental values of the quadrupole moment (-1.468 D Å) and the polarizability (1.740 Å 3) of N $_2$ are taken from the literature,⁵ and the dipole moment of HKrCl (7.4 D) is taken from our *ab initio* computations. The dispersion energy and the repulsive part is estimated with an anisotropic Lennard-Jones (6–12) potential function,¹⁷ determined for the N $_2\cdots$ Kr system.¹⁸ For the energy component analysis we used MP2(full)/6-311++G(2d,2p) geometries of complexes. In both complexes, the interaction is mainly of dipole-quadrupole (39% in linear, 45% in bent) and dispersion (54% in linear, 45% in bent) origins. A smaller part of the interaction energy is found to originate from the dipole-induced-dipole interaction (7% in linear, 10% in bent). Ac-

cording to this energy component analysis, the total interaction energies of -317 cm $^{-1}$ (linear) and -581 cm $^{-1}$ (bent) are in reasonable agreement with our *ab initio* data.

We assign the bands labeled A and B in Fig. 2 to the linear and bent configurations of the HKrCl $\cdots$ N $_2$ complex, respectively. The harmonic vibrational frequencies and the IR absorption intensities are presented in Table I. For the linear complex, an exceptionally large blueshift of the H–Kr stretching mode is found computationally ($+145.7$ cm $^{-1}$) and observed experimentally ($+112.9$ cm $^{-1}$). The calculation for the linear complex predicts a large blueshift of the bending mode ($+29.4$ cm $^{-1}$), but a corresponding band was not experimentally observed. For the bent complex, a large blueshift is obtained for the H–Kr stretching mode both computationally ($+31.0$ cm $^{-1}$) and experimentally [$+32.4$ cm $^{-1}$, band B in Fig. 2(a)]. In the H–Kr–Cl bending region, a small redshift is found computationally (-5.4 cm $^{-1}$ and -2.7 cm $^{-1}$) in agreement with the experimental value [-2.2 cm $^{-1}$, band B in Fig. 2(b)]. The experimental shift for bending overtone of the bent complex (-2.3 cm $^{-1}$) is close to that for the bending fundamental, which indicates higher harmonicity for the complex bending mode compared with the monomer. A slightly blueshifted ($+4.1$ cm $^{-1}$) band marked C in Fig. 2(a) and corresponding bands at bending region [Fig. 2(b)] are proposed to belong to the HKrCl perturbed by N $_2$ molecule from a longer distance. The origin of the perturbation can be (1) an additional site connected with nitrogen-induced perturbation of the local matrix morphology or (2) the longer-range (loose) HKrCl $\cdots$ N $_2$ complex. Analogous loose complexation or longer-range interactions are noticed in the experiments with hydrogen peroxide and water.^{19,20}

The formation of the bent HKrCl $\cdots$ N $_2$ complex follows linearly the amount of the photolyzed HCl $\cdots$ N $_2$. This indicates that the bent complex originates from the Cl $\cdots$ N $_2$ complexes formed in photolysis. The linear complex does not correlate directly with the amount of photolyzed HCl $\cdots$ N $_2$ but shows linear dependence with the product of [photolyzed HCl][N $_2$], indicating that the linear complex is formed from the photolyzed HCl monomer having N $_2$ as a close neighbor.

The large spectral blueshifts of the H–Kr stretching mode are attributed to the enhanced (HKr) $^+Cl^-$ ion-pair character of complexed HKrCl, resulting in stronger H–Kr covalent bonding. According to the NPA, the partial charge of the HKr entity of the HKrCl monomer is $+0.673$. Upon

TABLE I. Computational and experimental vibrational data of the HKrCl $\cdots$ N $_2$ and HCl $\cdots$ N $_2$ complexes and HKr $^+$ ion. The experimental monomer-to-complex shifts are calculated from the strongest monomer and complex bands. The IR absorption intensities are marked in parentheses. Frequencies are in cm $^{-1}$ and intensities are in km mol $^{-1}$. The calculations correspond to the ^{35}Cl isotope.

N $_2$ + HKrCl	ν (H–Kr)	δ (H–Kr–Cl)	ν (Kr–Cl)	ν (N–N)	N $_2$ + HCl ν (H–Cl)	HKr $^+$ ν (H–Kr)
MP2(full)/6-311++G(2d,2p)						
Monomer	1828.4(2412)	600.3(38)	278.5(122)	2179.4(0)	2998.1(51.8)	2600.4(401)
Bent complex	+31.0(2189)	$-5.4(19)$; $-2.7(21)$	$-3.3(119)$	$-0.4(0.3)$		
Linear complex	+145.7(907)	+29.4(21); +29.4(21)	$-11.3(141)$	$-1.6(2.7)$	$-24.1(199)$	
Experimental						
Monomer	1476.1	543.7, 542.1, 1069.3 ^a , 1067.9 ^a	-	-	2872.9	2429.2 ^b
Bent complex	+32.4	-2.2 , -2.3^a	-	-		
Linear complex	+112.9	-	-	-	-19.3	

^aOvertone.

^bReference 21.

complexation with N_2 , the corresponding partial charges are +0.709 and +0.685 for the linear and bent configurations, respectively. We can speculate that, while the $(HKr)^+Cl^-$ ion-pair character increases, the H–Kr vibrational frequency and absorption intensity approach the corresponding values of the HKr^+ ion with higher frequency and lower absorption intensity (see Table I).²¹ The computational value for the H–Kr stretching frequency of HKr^+ [MP2(full)/6-311++G(2d,2p)] is 2600.4 cm^{-1} with intensity of 401 km mol^{-1} . As a comparison, the corresponding values of the $HKrCl$ monomer obtained at the same level are 1828.4 cm^{-1} and 2412 km mol^{-1} .

In summary, two $HKrCl \cdots N_2$ configurations are characterized experimentally in solid krypton and by *ab initio* calculations. The computational structures are presented in Fig. 3. Due to the complexation-enhanced ion-pair character of $(HKr)^+Cl^-$, the complexes have large spectral blueshifts of the H–Kr stretching mode compared with the monomer. The experimental shifts are in agreement with the computations. The interaction energy of the complexes originates mostly from dipole-quadrupole and dispersive interactions.

This work was supported by the Academy of Finland. The CSC-Center of Scientific Computing Ltd. (Espoo, Finland) is thanked for providing computer facilities. Dr. Jan Lundell is gratefully thanked for very useful discussions. A. L. is a member of the graduate school LASKEMO (Academy of Finland).

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