

# Kr–Cl stretching vibration of HKrCl: Matrix-isolation and anharmonic *ab initio* study

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The Kr–Cl stretching vibration of HKrCl molecule is studied. The absorption shows  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopic splitting due to natural abundance of the Cl isotopes. The observed Kr–Cl stretching vibrations of the HKrCl are at 253.1 ( $^{35}\text{Cl}$ ) and 248.3  $\text{cm}^{-1}$  ( $^{37}\text{Cl}$ ). Deuteration of the HKrCl does not cause experimentally a shift of the Kr–Cl stretching frequency. In addition to the Kr–Cl stretching mode, the bending mode of DKrCl is observed at 397.7  $\text{cm}^{-1}$ . The vibrational analysis suggests that the Kr–Cl bond show, in addition to ionic, some covalent character. Anharmonic *ab initio* calculations are employed to verify vibrational properties of various isotopologues of HKrCl.

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## 1. Introduction

A number of hydrogen-containing rare gas molecules HRgY (H is hydrogen, Rg is a rare gas atom, and Y is an electronegative fragment) have been synthesized and studied in low-temperature matrices within the last several years [1,2]. Preparation of these HRgY molecules consists of photodecomposition of the HY precursor followed by thermal mobilization of atomic hydrogen in a low-temperature rare gas matrix. Infrared absorption spectroscopy is a useful method for detecting these molecules due to the large intensity of the H–Rg stretching vibration absorption [2]. In addition to the H–Rg stretching modes, bending vibrations for many of the HRgY molecules have been observed. The heavy-atom stretching vibration modes  $\nu(\text{Rg–Y})$  have been observed only for HArF and HKrF [3–5]. The indirect observation of the Xe–I stretching frequency of HXeI, calculated as a difference between combination and fundamental vibration, has been previously reported [6]. Since there are a variety of Rg–Y bonds in these HRgY compounds, it would be very interesting to learn more about the nature of the bonding via direct observation of the Rg–Y stretching vibration. In this work, we study experimentally and computationally the Kr–Cl stretching modes of the H/D and  $^{35}\text{Cl}/^{37}\text{Cl}$  isotopologues of

HKrCl. The experimental data is compared with our previous experimental measurements for HKrF [5].

## 2. Experimental and computational details

In the HCl/Kr experiments, HCl (99%, CIL) and Kr (99.995% Aga) gases were mixed in a glass bulb. The gas mixture was deposited onto a CsI window kept at 27 K in a closed-cycle helium cryostat (APD, DE 202A). The typical matrix thickness after the 30-minute deposition was 100–200  $\mu\text{m}$ . Deuteration of HCl was achieved by passing premixed gas over the deuterated sulphuric acid (>99%  $\text{D}_2$ , Merck) in the deposition line. The resulting HCl/DCl ratio was typically  $\sim 1$ . The samples were photolysed through a  $\text{MgF}_2$  window at 7.5 K by an 193 nm ArF-excimer laser (MPB, MSX-250) using  $\sim 10^4$  pulses with a pulse energy density of  $\sim 10 \text{ mJ}/\text{cm}^2$ . The infrared (IR) spectra were measured with a Nicolet SX 60 FTIR spectrometer. In the mid-IR spectral region, the spectrometer was operated with a Ge–KBr beam splitter (BS) and a MCT detector and resolutions of 0.25 and 1  $\text{cm}^{-1}$  were used, while in the far-IR region ( $< 400 \text{ cm}^{-1}$ ) a 6  $\mu\text{m}$  mylar BS with a DTGS detector and 1  $\text{cm}^{-1}$  resolution were used.

In the computational description of the potential energy surface of HKrCl, electron correlation was

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considered via Møller-Plesset perturbation theory to the second order (MP2), and all electrons were accounted for in the calculations (MP2 = FULL). The correlation consistent double-zeta quality all-electron basis set, aug-cc-pVDZ, was employed for all atoms. The equilibrium structure and harmonic vibrational frequencies of HKrCl were also studied by the higher-level coupled cluster [CCSD(T)] approach. The anharmonic vibrational frequencies were obtained from the vibrational self-consistent field (VSCF) and its extension by corrections via second-order perturbation theory (CC-VSCF) [7–10]. A pairwise coupling approximation was made to the potential in the normal mode representation [8]. Further details of CC-VSCF combined with an *ab initio* electronic structure code are given in Refs. 9 and 10. All *ab initio* calculations at the MP2 and CC-VSCF levels were performed in the framework of the GAMESS electronic structure program on dual PIII/500MHz workstations [11]. The CCSD(T) calculations were performed on a SGI Origin 2000 computer at the CSC-Center for Scientific Computing Ltd. (Espoo, Finland) using the «Gaussian 98» package of programs [12].

### 3. Experimental results

The HCl/Kr samples were highly monomeric with respect to HCl and DCl precursors and the known absorption bands of HCl at 2872.9 and 2870.5  $\text{cm}^{-1}$ , and DCl at 2078.6 and 2075.6  $\text{cm}^{-1}$  dominate in the spectra [13]. A small amount of HCl and DCl was complexed with  $\text{N}_2$  due to natural nitrogen impurity in the matrices. Interestingly, the complexation efficiency of DCl was observed to be significantly higher than that of HCl. Typically, >90% of HCl was decomposed upon 193 nm photolysis, and the decomposition of DCl was somewhat slower than that of HCl.

HKrCl and DKrCl appeared already during photolysis as reported previously [14]. Annealing of the sample at  $\sim 30$  K led to an increase of the amount of HKrCl and DKrCl due to mobilization of atomic hydrogen in a Kr matrix [15]. The observed H–Kr stretching (1476.1  $\text{cm}^{-1}$ , see Fig. 1) and H–Kr–Cl bending vibration bands (543.7 and 542.1  $\text{cm}^{-1}$  with the overtone at 1069.3 and 1067.9  $\text{cm}^{-1}$ ) are in a good agreement with the previous experimental data [1]. The Kr–Cl stretching vibrations of HKrCl were observed at 253.1 and 248.3  $\text{cm}^{-1}$ , the splitting (4.8  $\text{cm}^{-1}$ ) being due to the natural  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopes (see Fig. 1). The intensity ratio between the HKr $^{35}\text{Cl}$  and HKr $^{37}\text{Cl}$  bands is  $\sim 3.2$  in accordance with the natural isotope ratio of 3.1. In addition to the previously reported band of the D–Kr stretching mode of DKrCl at 1105.6  $\text{cm}^{-1}$  [1], the D–Kr–Cl bending

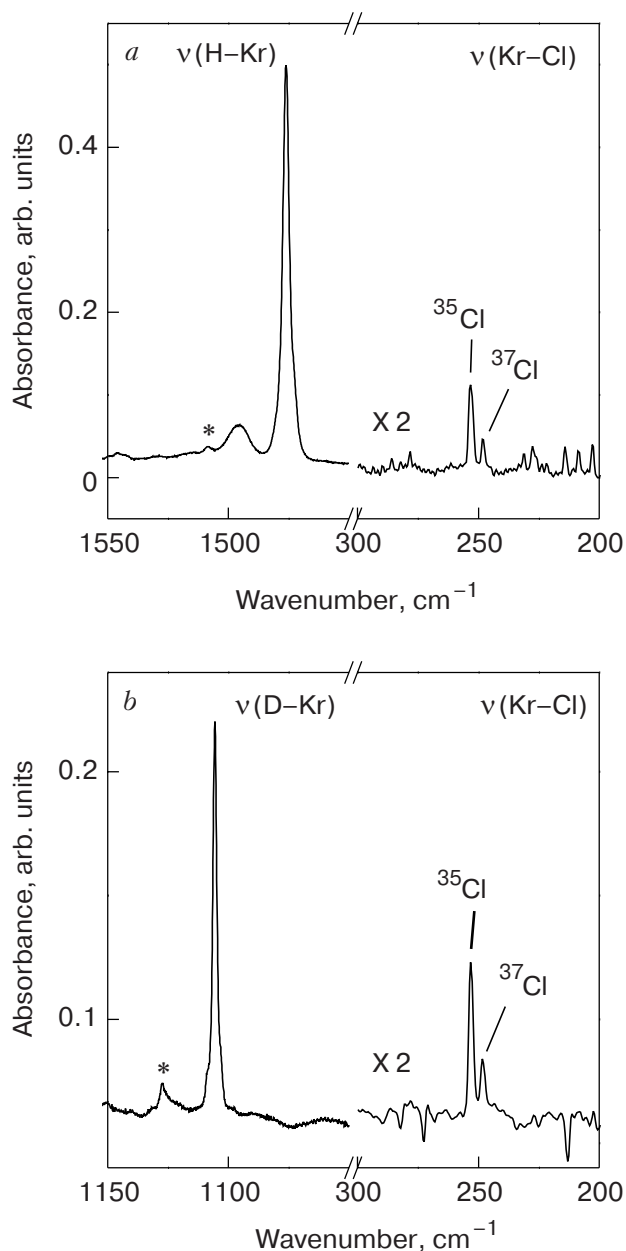


Fig. 1. FTIR spectra of HKrCl (a) and DKrCl (b) in the middle and far infrared regions.  $^{35}\text{Cl}/^{37}\text{Cl}$  isotopes cause a splitting (4.8  $\text{cm}^{-1}$ ) of the bands in the Kr–Cl stretching vibration mode. A band marked with asterisk belongs to  $\text{N}_2$  complex of HKrCl and DKrCl (see Ref. 23) induced by small nitrogen impurity present in the matrix. In plot (b), the bands of HKrCl are subtracted.

vibration band was found at 397.7  $\text{cm}^{-1}$ , which is the new spectroscopic data obtained here. The Kr–Cl stretching vibrations of DKrCl were practically unshifted from the corresponding HKrCl bands (see Fig. 1). The experimental assignment of the Kr–Cl stretching bands of HKrCl and DKrCl are based on the following arguments. They increase synchronously with the known HKrCl and DKrCl bands upon annealing. Photostability of the bands are similar as

checked with ArF-excimer laser (193 nm). The  $^{35}\text{Cl}/^{37}\text{Cl}$  isotopic shift and intensity ratio show proper values. Finally, the computations (see later) agree with the observed experimental findings.

#### 4. Computational results and discussions

The optimized H-Kr and Kr-Cl bond distances of the linear HKrCl molecule, calculated at the MP2/aug-cc-pVDZ computational level, are 1.500 and 2.563 Å, respectively. The harmonic vibrational frequencies obtained at this computational level are 1943.1, 604.2, and 275.7  $\text{cm}^{-1}$ . The increase of electron correlation to the CCSD(T) level gives longer H-Kr and Kr-Cl distances of 1.545 and 2.580 Å, respectively, and the frequency of H-Kr stretching mode shifts down to 1512.8  $\text{cm}^{-1}$ , which is close to the experimentally observed H-Kr stretching frequency (1476.1  $\text{cm}^{-1}$ ). Increasing the electron correlation affects less the bending and Kr-Cl stretching modes. At the CCSD(T) level of theory the predicted frequencies are at 569.9 and 273.0  $\text{cm}^{-1}$ , respectively, which are very similar to the values obtained using the MP2 calculations.

The high-level harmonic calculations neglect anharmonicity of the potential energy surfaces. However, there is experimental and theoretical evidence for important anharmonic effects for HRgY molecules [6,16–18]. The anharmonic MP2 vibrational frequencies of the HKrCl isotopologues are shown in Table.

The H-Kr stretching ( $\nu_3$ ) is predicted at 1691.0  $\text{cm}^{-1}$ ,  $\sim 250 \text{ cm}^{-1}$  below the corresponding harmonic value. Clearly, both electron correlation and anharmonicity are important for the adequate description of this molecule. The H-Kr-Cl bending ( $\nu_2$ ) and Kr-Cl stretching ( $\nu_1$ ) modes appear to be less anharmonic than the H-Kr stretching. In the anharmonic calculations, the bending vibration mode is reduced to 575.2  $\text{cm}^{-1}$ , i.e.,  $\sim 30 \text{ cm}^{-1}$  below its harmonic value. The  $\nu(\text{Kr-Cl})$  mode is relatively insensitive to the inclusion of anharmonicity and the vibration is predicted to be at 274.3  $\text{cm}^{-1}$ , shifted only by +1.4  $\text{cm}^{-1}$  from the harmonic prediction.

The computational overtone spectrum of HKrCl is rather rich and several bands are predicted to be promising for experimental detection. The experimentally observed first overtone of the H-Kr-Cl bending mode offers a good benchmark for the anharmonic calculations. The first overtone is predicted to lie at 1149.8  $\text{cm}^{-1}$  whereas the experimentally observed overtone is at 1069.4  $\text{cm}^{-1}$  [1]. Computationally the infrared intensity of the first overtone is 10% from its fundamental intensity whereas the experimental value is  $\sim 30\%$ . The first and second overtones of the H-Kr stretching mode and the first overtone of the Kr-Cl stretch are predicted to be intense enough to be experimentally searched for, however, they were not observed in this work experimentally.

The HRgY molecules have  $(\text{HRg})^+\text{Y}^-$  ion-pair character. The stronger electronegative moiety  $\text{Y}^-$  causes

Table

Anharmonic computational (MP2/CC-VSCF) and experimental frequencies (in  $\text{cm}^{-1}$ ) of HKrCl and its isotopologues. The computational IR intensities (in  $\text{km}/\text{mol}$ ) calculated at HF level are given in parentheses. The experimental IR intensities are in arbitrary units

Level	HKr $^{35}\text{Cl}$ Computational	HKr $^{37}\text{Cl}$ Computational	Experimental	DKr $^{35}\text{Cl}$ Computational	DKr $^{37}\text{Cl}$ Computational	Experimental
$3\nu_3$	4627.2 (1.0)	4627.1 (1.0)	–	3496.9 (0.2)	3496.8 (0.2)	–
$2\nu_3$	3207.1 (3.9)	3207.0 (3.9)	–	2410.1 (1.2)	2410.0 (1.2)	–
$3\nu_2$	1723.7 (0.4)	1723.3 (0.4)	–	1267.6 (0.1)	1267.0 (0.1)	–
$\nu_3 \nu(\text{H-Kr})$	1691.0 (680.9)	1691.0 (681.3)	1476.1 (1.00)	1250.9 (351.6)	1250.8 (352.1)	1105.6 (1.00)
$2\nu_2$	1149.8 (3.3)	1149.5 (3.3)	1069.4, 1067.9 (0.01)	844.1 (1.0)	843.7 (1.0)	–
$3\nu_1$	817.3 (0.0)	801.7 (0.0)	–	817.0 (0.0)	801.4 (0.0)	–
$\nu_2 \delta(\text{H-Kr-Cl})$	575.2 (33.1)	575.0 (33.3)	543.7, 542.1 (0.03)	421.6 (13.3)	421.4 (13.5)	397.7 (0.02)
$2\nu_1$	546.7 (1.1)	536.3 (1.1)	–	546.5 (1.1)	536.0 (1.0)	–
$\nu_1 \nu(\text{Kr-Cl})$	274.3 (137.7)	269.0 (132.4)	253.1 (0.05) $^{35}\text{Cl}$ 248.3 (0.05) $^{37}\text{Cl}$	274.2 (137.1)	268.9 (131.9)	253.1 (0.17) $^{35}\text{Cl}$ 248.3 (0.17) $^{37}\text{Cl}$

larger charge separation between the  $(\text{HRg})^+$  and  $\text{Y}^-$  moieties shortening the H–Rg distance and enhancing its vibrational frequency. This leads to stronger covalent bonding of the  $(\text{HRg})^+$  entity, while covalent character of the Rg–Y bond is reduced lowering the activation energy of dissociation via bending motion. According to the experimental data, the quadratic force constant ( $f_2$ ) for Kr–Cl stretch of HKrCl is 0.93 N/cm as calculated from equation  $f_2 = 4\pi^2 c^2 \omega^2 \mu$ , where  $\omega$  is the vibrational wavenumber,  $c$  is the light velocity, and  $\mu$  is the reduced mass. For comparison,  $f_2$  for Kr–F stretch of HKrF is 1.57 N/cm [5], and the force constants for asymmetric stretches of KrF<sub>2</sub> and XeCl<sub>2</sub> are 2.59 N/cm and 1.32 N/cm [19,20], respectively. These data indicate a stronger Kr–F chemical bonding than Kr–Cl bonding in accordance with the electron localization studies of Berski and co-workers [21]. Similar trend can be seen for the H–Kr moiety when its covalent character is enhanced from HKrCl to HKrF as judged by the increase of the H–Kr stretching frequency. As a reference, the harmonic wavenumbers for the  $\text{Kr}^+\text{Cl}^-$  and  $\text{Kr}^+\text{F}^-$  exciplexes are  $(208\pm 20)$  and  $(284\pm 27)$   $\text{cm}^{-1}$  deduced from their electronic emission spectrum [22], resulting in force constants of  $f_2(\text{Kr}^+\text{Cl}^-) = 0.63$  N/cm and  $f_2(\text{Kr}^+\text{F}^-) = 0.74$  N/cm. Since the exciplexes are ionic in nature, the higher frequency of the Kr–Y stretch in HKrY molecules suggest that the Kr–Y bonding in HKrY molecules is not purely ionic but contains also some covalent contribution between the Kr and Y fragments. The covalent contribution between Rg–Y fragments is essential for the existence of a bending barrier in HRgY molecules and thus important for the intrinsic stability of HRgY molecules.

## 5. Conclusions

The Kr–Cl stretching vibration mode for various isotopologues of HKrCl is studied experimentally and compared with the previous measurements on the Kr–F stretching mode of HKrF. Anharmonic vibrational calculations are done on the HKrCl molecule and show good agreement with the experiments. According to the vibrational analysis, it is suggested that the Kr–Cl and Kr–F bonds of HKrCl and HKrF molecules have, in addition to ionic, some covalent contributions.

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