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Leonid Khriachtchev, Mia Saarelainen, Mika Pettersson, and Markku Räsänen

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# H/D isotope effects on formation and photodissociation of HKrCl in solid Kr

Leonid Khriachtchev,<sup>a)</sup> Mia Saarelainen, Mika Pettersson, and Markku Räsänen Laboratory of Physical Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland

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The HCl (DCl)/Kr matrixes were irradiated at 193 nm, which produced matrix-isolated H (D) and Cl atoms as permanent photolysis products. The annealing-induced formation of HKrCl and DKrCl was used as a measure of atomic hydrogen (H and D) mobility at various annealing temperatures (from 24 to 30 K). The temperature dependencies of the HKrCl and DKrCl formation rates yield  $\sim$ 64 and 68 meV for the corresponding activation energies estimating the isotope effect on atomic hydrogen mobility in solid Kr (D slower than H). The difference in mobility of H and D atoms allowed us to demonstrate a reaction between D atoms and HKrCl molecules, and the suggested kinetic model is in good agreement with experiment. In addition, the H/D isotope effects on the solid-state photodissociation of HCl and HKrCl are studied and discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1560635]

# I. INTRODUCTION

The family of HRgY molecules (Rg=rare gas atom, Y = electronegative fragment) introduced in 1995 by the Helsinki group contains now 13 members (HXeI, HKrCl, HArF, etc.).<sup>1–3</sup> These molecules show a charge transfer  $(HRg)^+Y^$ character, and they are easily detected due to very strong absorption intensity of the H-Rg stretching vibration. The HRgY molecules can be prepared in rare-gas matrixes using photolysis of the HY precursor and subsequent thermal mobilization of H atoms to promote their reactions with neutral Rg+Y centers. In some cases, the HRgY molecules (HKrCl, HXeNCO, and HArF) were detected already during solidstate photolysis of the HY precursor featuring a quite limited light-induced travel distance of dissociating H atoms in raregas lattices.<sup>2,4,5</sup> This local formation of the HRgY intermediates in photolysis of HY in a rare-gas host was studied theoretically as well.<sup>6</sup>

Thermally induced motion of atomic hydrogen in raregas solids, in addition to the common interest, is of particular importance for the formation of the HRgY molecules. Eberlein and Creuzburg studied thermal mobility of atomic hydrogen in Xe and Kr matrixes and extracted activation energies of 123 and 66 meV, respectively.<sup>7</sup> Vaskonen *et al.* obtained considerably larger activation energy for H atom thermal mobility in solid Kr (90-140 meV).8 No H/D isotope effect was found in those two studies for hydrogen mobility in solid Kr. We have recently suggested that the diffusion-controlled formation of the HRgY molecules is a productive approach to investigate accurately thermal mobility of atomic hydrogen in rare-gas solids, and the method has been successfully employed for the case of HXeH and HXeOH in solid Xe.<sup>9</sup> That study definitely distinguished the mobilities of atomic H and D isotopes in solid Xe featuring a difference of  $\sim 4$  meV between the corresponding activation energies. The modeling of thermally activated jumps of hydrogen atoms in a relaxed Xe lattice agreed reasonably with experiment with respect to the isotopic effects but it underestimated the jump rate.

The annealing-induced formation of HRgY consumes a large part of H atoms generated during photolysis of HY.<sup>1</sup> Moreover, the experimental data reveal further reactions of the HRgY molecules with mobile H atoms as demonstrated for HXeH molecules in solid Xe.<sup>10</sup> A simple kinetic model including reactions of HRgY molecules with mobile H atoms described the experimental observations. It was proposed that these reactions limited the amounts of HXeH molecules upon annealing and presumably resulted in formation of H<sub>2</sub> molecules, hence the proposed reaction scheme formed a buffering mechanism stabilizing the HXeH concentration in solid Xe.

The HRgY molecules are known to decompose easily while exposed to UV and, in some cases, to visible light, which features the transition to electronically excited repulsive states. The wavelength dependence of the photodissociation efficiency was studied for matrix-isolated HKrCl, HArF, HKrF, HXeOH, and HXeH molecules showing large differences between their photodissociation profiles.<sup>3,5,11</sup> However, no clear H/D isotope effect on the solid-state photodissociation efficiency was found in those studies. Direct measurements of UV absorption spectra were also performed for a number of HRgY molecules.<sup>11–13</sup> For HXeH, the measured photodecomposition and absorption profiles are very similar,<sup>13</sup> which shows that this photodecomposition method can be successfully applied to probe electronically excited states of HRgY molecules.

In this work, we investigate H/D isotope effects on formation and photodissociation of HKrCl in solid Kr. The formation kinetics of HKrCl and DKrCl reveals the isotope effect on thermally activated mobility of atomic hydrogen. The difference between the H and D mobilities allowed us to

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<sup>&</sup>lt;sup>a)</sup>Electronic mail: Leonid.Khriachtchev@Helsinki.Fi



FIG. 1. IR absorption spectra of HCl and DCl in an as-deposited Kr matrix (the lower trace) and HKrCl and DKrCl prepared by irradiating the deposited sample at 193 nm and consequent annealing at 30 K (the upper trace). The IR absorption spectra were measured at 8 K.

show that a reaction of D atoms with HKrCl is taking place. The HKrCl and DKrCl photodecomposition rates are compared.

#### **II. EXPERIMENT**

The gaseous HCl (DCl)/Kr mixtures were deposited onto a CsI window. The deposition temperature was 20 K, the deposition time was  $\sim 20$  min, and the typical matrix thickness was 50–100  $\mu$ m. Efficient deuteration (up to 75%) was achieved by passing the HCl/Kr gaseous mixture through a tube with  $D_2SO_4$  droplets. The experiments were performed at temperatures down to 8 K provided by a closed-cycle cryostat (DE-202A, APD). The infrared (IR) absorption spectra in the 4000 to 400 cm<sup>-1</sup> region were recorded with a Nicolet 60 SX FTIR spectrometer using resolution of 1 cm<sup>-1</sup>. In order to decompose HCl and DCl molecules, the samples were irradiated with an excimer laser (MPB, MSX-250) operating at 193 nm. Typically, we used in photolysis up to  $\sim 10^4$  pulses with a pulse energy density of  $\sim 10$  mJ/cm<sup>2</sup>. Most of the experiments were performed using samples with similar HCl/Kr ratios of  $\sim$ 1:1000. We decomposed HCl molecules to a similar level of  $\sim 0.3$ , which produced similar concentrations for hydrogen atoms in various experiments. The photodecomposition of HKrCl and DKrCl was done with the second harmonic of tunable signal radiation of an optical parametric oscillator (Continuum).

# **III. EXPERIMENTAL RESULTS**

The IR absorption spectrum of HCl and DCl in solid Kr measured at 8 K is presented in Fig. 1 (the lower trace), and it is in agreement with the literature data.<sup>14,15</sup> The sample is quite monomeric with respect to HCl and, in particular, complexation with nitrogen is negligible. Upon irradiation at 193 nm, HCl and DCl decompose and the Kr<sub>2</sub>Cl emission rises around 355 nm.<sup>5,16</sup> For longer irradiation, clear features of self-limited photolysis due to the rising Kr–Cl charge-



FIG. 2. Photolysis kinetics of the HCl and DCl precursors and the HKrCl and DKrCl intermediate products. The data were obtained by integrating the corresponding IR absorption bands in the same experiment with a HCl/DCl/Kr sample ( $\sim$ 1:1:2000). The data for HKrCl and DKrCl are normalized by the initial integrated absorptions of HCl and DCl, respectively, and multiplied by a factor of 2.5 for better presentation. The 193 nm photolysis was performed at 8 K, the pulse energy density being  $\sim$ 10 mJ/cm<sup>2</sup>.

transfer absorption is observed for the present case of relatively thick samples.<sup>17</sup> The typical 193 nm photolysis kinetics is presented in Fig. 2. The DCl photodissociation is essentially slower, by a factor of  $\sim 2.0$ , as compared with HCl. Both HKrCl and DKrCl are formed during photolysis, and this evidences the locality of the primary photolysis event as discussed elsewhere for the case of HKrCl.<sup>5</sup> In Fig. 2, the HKrCl and DKrCl absorptions are normalized by the initial amounts of HCl and DCl, respectively, which allows their numerical comparison assuming the same H/D isotope effect on the corresponding IR absorption intensities. It is seen that HKrCl forms relatively more efficiently in the early stage of irradiation whereas DKrCl is relatively more abundant after long photolysis. As an additional product, KrHKr<sup>+</sup> and KrDKr<sup>+</sup> ions appear after photolysis,<sup>18</sup> but based on their ab initio infrared intensities (MP2/aug-cc-pVTZ level) their concentration is negligible.<sup>5</sup>

Upon annealing of a photolyzed sample at  $\sim 30$  K, hydrogen atoms become mobile and HKrCl and DKrCl molecules form efficiently as monitored by the H-Kr and D-Kr stretching absorption bands at 1476 and 1106 cm<sup>-1</sup>, respectively (see Fig. 1, the upper trace).<sup>19</sup> The annealing-induced formation of the products clearly depends on the annealing temperature as demonstrated in Fig. 3(a) for HKrCl obtained in the HCl/Kr (deuterium-free) samples (matrix ratio  $\sim$ 1:1000). The data points were normalized by the values measured after additional annealing at 30 K, which saturated processes caused by hydrogen mobility. In fact, the increase of the matrix temperature by 1 K accelerated the growth of the HKrCl concentration by a factor of 3-4. As shown in Fig. 3(a), the formation kinetics can be successfully fitted by the stretched-exponential function  $1 - \exp(-k_0 t^a)$  typically with  $a \sim 0.55$ . On one hand, the formation kinetics at a given temperature is quite reproducible for various samples with similar compositions. On the other hand, the formation rate



FIG. 3. (a) Formation kinetics of HKrCl at various annealing temperatures of photolyzed HCl/Kr matrixes (~1:1000). The concentration values obtained by integrating the 1476 cm<sup>-1</sup> band of HKrCl are normalized by the values obtained after additional annealing at 30 K. The lines are fits of the experimental data by  $1 - \exp(-k_0 t^a)$  with a ~0.55. (b) Characteristic formation time (at the 0.63 level) and formation efficiency of HKrCl as a function of the Kr/HCl ratio obtained upon annealing at 25 K. The formation efficiency is defined as the ratio between the integrated absorption of resulting HKrCl and the integrated absorption of photolyzed HCl. The IR absorption spectra were measured at 8 K.

obviously slows down for less concentrated samples. Figure 3(b) shows a nearly linear dependence of the characteristic time of HKrCl formation on the initial Kr/HCl ratio obtained at 25 K. The precursor concentration influences also the HKrCl formation efficiency, which is defined as the ratio between the integrated absorption of resulting HKrCl and the integrated absorption of photolyzed HCl. This parameter was quite similar for the 1:1000, 1:2000, and 1:5000 matrix ratios, and it somewhat decreased for the HCl/Kr ratio of 1:500.

Figure 4(a) compares the formation kinetics of HKrCl and DKrCl at 26 K, the data being normalized by the values measured after additional annealing at 30 K. The curves are obtained in the same experiment with an initial HCl/DCl concentration ratio of  $\sim$ 1. It is seen that the DKrCl formation during annealing is significantly slower than that of HKrCl. HKrCl is formed upon H mobility and it grows at the initial annealing stage whereas the DKrCl formation controlled by D mobility is clearly delayed. In analogy with the case of solid Xe,<sup>9</sup> this experimental data can be qualitatively explained by faster thermal motion of H atoms compared with D atoms.



FIG. 4. (a) Formation of HKrCl and DKrCl upon annealing at 26 K of a photolyzed HCl/DCl/Kr matrix (~1:1:2000). (b) Formation of HKrCl and DKrCl upon annealing at 29 K. The first data point corresponds to annealing during 1 min. Note the similar characteristic time of the DKrCl growth and the HKrCl decay upon longer annealing. The HCl/DCl/Kr matrix (~1:3:4000) was used. (c) Formation of HKrCl upon annealing at 27 K of a photolyzed HCl/Kr (~1:1000) and HCl/DCl/Kr (~1:1:2000) matrixes. Note that in the partially deuterated sample the HKrCl concentration decreases in the final stage of annealing due to its destruction by reaction with D atoms. The concentrations are obtained by integrating the 1476 and 1106 cm<sup>-1</sup> bands of HKrCl and DKrCl and then normalized by the values obtained after additional annealing at 30 K. The IR absorption spectra were measured at 8 K.

slightly decreases at the last stage of annealing while the DKrCl concentration increases. This behavior can be demonstrated more clearly using higher annealing temperatures [see Fig. 4(b)]. Importantly, the increase of the DKrCl concentration and the decrease of the HKrCl concentration occur in the same time scale. Moreover, this decrease of the HKrCl concentration occurs only when D atoms are present in the matrix. To illustrate this fact, Fig. 4(c) presents the formation kinetics of HKrCl in HCl/Kr and HCl/DCl/Kr matrixes upon

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FIG. 5. Ratio of DKrCl and HKrCl photodecomposition rates in solid Kr at 8 K as a function of the photon energy. The line is a linear fit.

annealing at 27 K. Without D atoms, the HKrCl concentration smoothly increases. If D atoms are present in the matrix (in significant amounts), the shape of the HKrCl formation kinetics changes remarkably, namely, the curve saturates much quicker and finally the concentration even decreases by  $\sim 10\%$ . In analogy with similar findings for HXeH in solid Xe,<sup>10</sup> we explain the present decrease of the HKrCl concentration in long annealing by reactions of HKrCl with D atoms.

The HKrCl photodecomposition profile is known to have maximum at ~280 nm.<sup>5</sup> In the present work, the photodissociation rates for HKrCl and DKrCl were compared. If both species are present in the same matrix, this comparison can be performed quite reliably even if the difference is rather small. Clear distinctions in the solid-state photodissociation rates for HKrCl and DKrCl were found, and the result is presented in Fig. 5. Upon irradiation at longer wavelengths (>280 nm), DKrCl is more stable than HKrCl whereas the situation becomes opposite at shorter wavelengths. The excitation range in Fig. 5 is limited by 240 nm due to possible artifacts caused by the secondary Kr<sub>2</sub>Cl emission as discussed later.

#### **IV. DISCUSSION**

# A. Photolysis-induced formation of HKrCl

The permanent photodecomposition of HCl in solid Kr requires quite many absorption events due to the low cage exit probability ( $\sim 5\%$ ).<sup>20</sup> In the case of a successful cage exit, either the HKrCl intermediate or the H+Cl pair is formed. The HKrCl intermediate can be further decomposed by light leading to the H+Cl final product. For the HKrCl concentration, this model yields:<sup>5</sup>

$$[\text{HKrCl}] \propto \frac{k_1}{k_1 - k_2 + k_3} [\exp(-k_2 t) - \exp(-k_1 t - k_3 t)],$$
(1)

where  $k_1$  is the rate constants of the HCl decomposition in the HKrCl channel,  $k_3$  is the rate constants of the HCl decomposition in the H+Cl channel, and  $k_2$  describes the HKrCl decomposition. It was measured by us earlier that  $k_1/k_3 \sim 1.4$  for the 193 nm photolysis of HCl in solid Kr,<sup>5</sup> i.e., formation of the photolabile HKrCl intermediate is the major channel for permanent solid-state dissociation of HCl with excess energy of 1.8 eV. In particular, this model suggests essentially short-range travel of the H atoms from the parent cage in the primary photolysis event without essential long-distance contribution. This conclusion on the locality of the solid state photodissociation was verified by experiments with very diluted matrixes ( $\sim$ 1:5000 and 1:15000), and the formation of the intermediate was at least as efficient as in the more concentrated matrixes.<sup>5</sup> As a relevant example discussed by Buck,<sup>21</sup> photolabile HXeI intermediates were supposed to be formed in Xe clusters via local photodissociation of HI molecules irradiated at 243 nm.

The three-component model of local photolysis explains the observed differences between the evolution of the HKrCl and DKrCl isotopologues. The faster increase of HKrCl compared with DKrCl seen in the beginning is a direct consequence of the faster decomposition of HCl as compared with DCl. The larger relative concentration of DKrCl after long irradiation can be explained by its higher photostability and the larger residual concentration of DCl. Based on the initial stage of photolysis kinetics, the production of the HKrCl and DKrCl intermediates is quite proportional (with accuracy of 10%) to the decomposition of the HCl and DCl precursors. Following Eq. (1) and taking into account that  $k_2 > k_1 + k_3$ , we see that our present data does not indicate any large difference in solid-state photodissociation dynamics of HKrCl and DKrCl, which is characterized by the  $k_1/k_3$  ratios. The strongest isotope-induced distinctions in photolysis kinetics occur at the HCl and DCl photodissociation step (cage exit controlled by  $k_1 + k_3$ ), and the branching ratio between the short range and long range stabilization of hydrogen atom seems to be rather similar for the H and D forms. Thus, it can be tentatively concluded here that no large isotope effect on the light-induced dynamics of H and D atoms takes place for 193 nm photolysis of HCl and DCl in solid Kr. A more precise numerical analysis is complicated due to a number of parasitic processes. For instance, the secondary Kr<sub>2</sub>Cl emission excited at 193 nm is capable of contributing to decomposition of the unstable intermediates, and this decomposition is somewhat different for HKrCl and DKrCl (see Fig. 5). Furthermore, in the present experiments, the photolysis kinetics is self-limited due to the rather high concentrations of the absorbing Cl product and the rather thick samples.<sup>17</sup> More accurate data obtained with very diluted and thin matrixes is needed to detect a small isotope effect on the  $k_1/k_3$  ratio and theoretical analysis seems to be valuable.

The observed difference in the HCl and DCl photodissociation rates should be commented. First, this effect can be explained by isotope effect on photoabsorption crosssections. Cheng *et al.* measured HCl and DCl photoabsorption cross-sections for gas-phase HCl and DCl in the 120– 220 nm spectral region.<sup>22</sup> The values of  $8.37 \times 10^{-20}$  and  $2.53 \times 10^{-20}$  cm<sup>2</sup> were obtained at 193 nm for HCl and DCl, respectively, i.e., they differ by a factor of 3.3. Our



FIG. 6. Natural logarithm of the characteristic formation time (in seconds) of HKrCl and DKrCl in solid Kr as a function of the reciprocal annealing temperature. The data for HKrCl are obtained in experiments with HCl/Kr samples and the data for DKrCl are from experiments with dominating DCl precursor. As defined, the characteristic formation time corresponds to the 0.63 level of the saturation HKrCl (DKrCl) concentration. The lines are linear fits yielding activation energies of  $(64\pm4)$  and  $(68\pm6)$  meV for the H and D forms, respectively. The same difference value of  $\sim 4$  meV can be obtained if we *a priori* assume the same pre-exponential factors ( $\sim e^{23}$  1/s) in the Arrhenius plots for H and D.

solid-phase measurements give a smaller ratio for the corresponding photodecomposition rates (2.0). The distinction between the gas-phase and matrix ratios can be in principle due to a matrix shift of the absorption cross-section contours. Indeed, the gas-phase photoabsorption cross-sections of HCl and DCl differ by a factor of 2 already at 185 nm.<sup>22</sup> As the second factor for the observed difference in the HCl and DCl photodissociation rates, the exit probabilities for H and D atoms might be different, however, we have neither experimental nor theoretical basis to estimate its contribution.

### B. Thermal mobility of H and D atoms

It is known that both annealing-induced decrease of the H concentration and the formation of rare-gas molecules in solid Xe slow down in time demonstrating a stretchedexponential shape of the corresponding curves.<sup>9</sup> In addition to the direct kinetic reasons for the deviation from a singleexponential shape, the physical reasons contributing to this behavior can be distribution of activation energies due to structural inhomogeneity and change in the matrix lattice properties during annealing.<sup>7</sup> In order to avoid problems with finding the proper fitting function, the annealing-induced formation of Xe-containing species was numerically described using the characteristic time  $\tau_0$  that corresponds to the 0.63 level of the saturation concentrations.<sup>9</sup> In the present work, we follow this approach.

Figure 6 presents the characteristic time (in seconds) for the formation of HKrCl and DKrCl as a function of the annealing temperature. The data for HKrCl are obtained in experiments with HCl/Kr matrixes, and the data for DKrCl are from experiments with the dominating DCl precursor, the



FIG. 7. Concentrations of H atoms and  $H_2$  and HKrCl molecules as a function of the annealing time calculated using models (2)–(6). Initial conditions:  $[H]_0 = [Cl]_0 = 1$ . Note that the H concentration is divided by 3.

concentration of the precursors being similar in all experiments. The two dependencies exhibit Arrhenius behavior with activation energies of  $(64\pm4)$  and  $(68\pm6)$  meV for the H and D forms, respectively, as obtained by their linear fits. The extracted difference between the activation energies for the HKrCl and DKrCl formation (4 meV) is somewhat smaller than the possible error. However, the same value of  $\sim$ 4 meV can be extracted if we *a priori* assume the same pre-exponential factors ( $\sim e^{23}$  1/s) in the Arrhenius plots for H and D, which makes this estimate quite confident.

The annealing induced formation of rare-gas molecules allow thermal mobility of hydrogen atoms to be studied.<sup>9</sup> This approach implies that the formation of the product occurs at a similar time scale as the decrease of the H concentration, and the characteristic times are proportional to the jump time of H atoms in the lattice. This conclusion can be illustrated using a kinetic scheme with the following solidstate reactions:

$$H+H \rightarrow H_2, \tag{2}$$

$$H + Kr + Cl \rightarrow HKrCl, \tag{3}$$

$$H + HKrCl \rightarrow H_2 + Kr + Cl, \tag{4}$$

$$H + HKrCl \rightarrow HCl + Kr + H, \tag{5}$$

$$H + HCl \rightarrow H_2 + Cl. \tag{6}$$

These reactions are considered as fully controlled by diffusion of H atoms and possessing the same reaction radius,  $k_H$  being the corresponding rate constant. The branching ratio between reactions (4) and (5) is taken 1:1. A representative computational result is given in Fig. 7. The simulations show that the ratio of the characteristic formation time of HKrCl molecules and the characteristic decay time of H atoms is 1.18, and it is independent of the initial HCl concentration and of the annealing temperature. The curves for H and HKrCl can be fitted by stretched exponents with a = 0.78 and 0.83, respectively, and these values are also concentration

independent. It should be emphasized that the stretching effect is introduced in this model purely by kinetic factors without including any time dependence of the rate constant. Taking into account the smaller experimental stretching parameter obtained for HKrCl formation ( $\sim 0.55$ ), we suggest some annealing-induced modification of matrix morphology in the present experiments. According to models (2)–(6), the characteristic time of the product formation is inversely proportional to the initial H and Cl concentration, which is in accord with the experimental data [see Fig. 3(b)]. Of course, this simple kinetic model yields no concentration dependence of the formation efficiency. The experimentally observed decrease on the HKrCl formation efficiency for more concentrated samples should be explained by experimental factor, such as a relative increase of various traps for H atoms due to improper lattice structure, HCl multimers, etc. Some losses of H atoms during photolysis might become important for the concentrated samples.

The present results show the kinetic difference between reactions promoted by mobility of H and D atoms (see Fig. 4). It should be emphasized once more that we connect this difference in formation of HKrCl and DKrCl with slower thermal motion of D atoms compared with H atoms, i.e., with a smaller rate of the elementary jumps for deuterium. In this consideration, we essentially assume that the reaction barriers for the formation of HRgY molecules can be neglected at  $\sim 30$  K. This assumption is experimentally verified. Indeed, HKrCl and HKrF show identical formation kinetics upon the long-range H atom mobility,<sup>3</sup> which would not be the case if the reaction activation energy were important. The formation of HKrCN occurs at similar temperatures even though the detailed data is not available.<sup>23</sup> The formation of HArF molecules takes place in solid Ar at temperatures below 20,<sup>2</sup> which is known to promote H mobility in solid Ar.8 A part of the HRgY products always form at temperatures that do not allow global motion of H atoms. Following Ref. 24, we call this phenomenon local (short-range) atomic mobility, and it was studied in details for formation of HXeI.<sup>25</sup> The presence of low-temperature local formation of these molecules does not allow essential H+Rg+Y reaction barriers. Moreover, the formation of HXeCl and HXeBr in solid Ne at 12 K supports the very low intrinsic formation barriers of the HRgY molecules.<sup>26</sup> Thus, we conclude that these reactions are mainly diffusion-controlled.

The spatial distribution of H atoms produced by solidstate photolysis of HCl deserves brief discussion. As shown earlier, the *primary* UV photolysis of HCl in solid Kr is an essentially local event.<sup>5</sup> This locality means stabilization of escaping H atoms at small distances (comparable with the lattice parameter) from the parent cage. After the successful escape, the H atom can react with some probability with the parent Cl–Kr center resulting in the HKrCl molecule. The formed rare-gas molecules can be photodecomposed efficiently, making the distribution of H atoms more homogeneous taking into account the large excess energy upon 193 nm photodissociation of HKrCl (~5 eV). Additionally, lightinduced motion of H atoms can be promoted by neutralization of (KrHKr)<sup>+</sup> ions.<sup>23</sup> As a result of this homogenization, H atoms lose memory of the parent cage and globally diffuse in the matrix upon annealing. A strong experimental evidence for this image is a nearly linear dependence of the HKrCl formation time on the initial Kr/HCl ratio shown in Fig. 3(b).

Thus, we claim that the formation kinetics of HKrCl and DKrCl reflects differences in thermal mobility of H and D atoms with activation energies of approximately 64 and 68 meV. When compared with the literature data on H atom mobility, our data is in perfect agreement with the activation energy of 66 meV obtained by Eberline and Creuzburg,<sup>7</sup> but it is considerably smaller than the value of 90-140 meV extracted by Vaskonen et al.8 A computational model qualitatively explained the different mobility of H and D atoms in solid Xe even though it did not provide numerically accurate results.<sup>9</sup> The model estimated energies in the relaxed interstitial and transition-state configurations of H and D atoms in solid Xe taking into account the zero-point energies. Analogous calculations would qualitatively support the H/D isotope effect on thermal mobility in solid Kr as well. However, in the present work, we do not repeat those calculations for solid Kr because we believe that a more advanced theoretical approach is needed to reach adequate description.

#### C. D+HKrCl reaction

As assumed in kinetic models (2)-(6), the formed HKrCl molecules can further react with hydrogen atoms. This process can be tested using different thermal mobility of H and D atoms. HKrCl molecules are formed quickly upon H mobility. Motion of D atoms spreads into a longer time scale, after formation of the main part of HKrCl molecules. If HKrCl molecules react with D atoms, these kinetic distinctions should lead to a decrease of the HKrCl concentration upon selective mobilization of D atoms. This qualitative picture was analyzed using kinetic models (2)–(6) with added analogous reactions for D atoms. We assumed  $k_H/k_D = 8$  and  $[D]_0/[H]_0=3$ , which corresponded to the experimental conditions. A representative result of the calculations is shown in Fig. 8. The HKrCl concentration increases quickly, reaches the maximum, and finally decreases by about 10%, which is in remarkable agreement with experiment (see Fig. 4). The simultaneous presence of H and D atoms in the matrix changes the shapes of the kinetic curves compared with the previous "D-free" consideration: The stretching parameters for the build up of the HKrCl and DKrCl concentrations become different, 1.02 and 0.81, respectively. This trend was found qualitatively for the experimental data presented in Fig. 4. The good agreement between the experimental and computational data strongly support the efficient D+HKrCl and, consequently, H+HKrCl reactions. Similarly to the experiment, the simulation shows that the HKrCl concentration increases and the DKrCl concentration decreases in similar time scales. The similarity in these time scales means that the D+HKrCl reaction barrier does not exceed much the activation energy for thermal mobility of D atoms, i.e., the reaction can be considered as diffusion-controlled. These conclusions are analogous to those done by us earlier for the H+HXeH reaction.10



FIG. 8. Concentrations of H and D atoms and HKrCl and DKrCl molecules as a function of the annealing time calculated using models (2)–(6). Initial conditions:  $[H]_0=0.25$ ,  $[D]_0=0.75$ ,  $[Cl]_0=1$ . The ratio between rate constants of H and D mobility is 8. Note that the D concentration is divided by 3.

#### D. Solid-state photodissociation

The results presented in Fig. 5 indicate a difference between photodissociation contours of HKrCl and DKrCl molecules in solid Kr. Based on the photodissociation data obtained previously for HKrCl,<sup>5</sup> we generated the corresponding contour for DKrCl, and it is shown in Fig. 9. The data points at 193 and 230 nm are omitted, and the reason for this disregard should be commented. The Kr<sub>2</sub>Cl emission is excited at wavelengths below 240 nm, and the absorption maximum is at 222 nm. The Kr–Cl chargetransfer cross-section is unknown to the best of our knowledge, however, it is probably quite large. This secondary emission locates in the 300–430 nm region, and it can produce artifacts in numerical comparison of the HKrCl and



FIG. 9. Photodecomposition contours of HKrCl and DKrCl in solid Kr at 8 K. The data for HKrCl are from Ref. 5. The data for DKrCl are obtained using the HKrCl photodecomposition contour and the fitting line in Fig. 5.

DKrCl photodissociation because in this spectral region the H form is less stable than the D form. In fact, we observed a relative decrease of the HKrCl photostability at 230 and 193 nm, however, the proportion of the artificial contribution from the secondary  $Kr_2Cl$  emission is unclear. In order to test this idea further, we compared the HKrCl photodissociation rates at 193 nm for matrixes with very different initial HCl/Kr ratios (1:1000 and 1:15 000). In agreement with our qualitative consideration, the HKrCl photodissociation was essentially slower for the less concentrated sample.

It is seen in Fig. 9 that the solid-state DKrCl photodissociation contour is blue shifted by  $\sim 0.1 \text{ eV} (\sim 800 \text{ cm}^{-1})$ with respect to the HKrCl photodissociation contour. An obvious reason for this difference is the smaller zero point energy of DKrCl compared with that of HKrCl. However, the direct gap between the zero point energies does not exceed  $300 \text{ cm}^{-1}$  suggesting that additional factors should exist. For example, anharmonicity of the potential surface should lead to the isotope effect of the same direction. Indeed, the typical asymmetry of a potential surface with a steeper repulsive wall should shift the photodissociation contour for DKrCl up in energy compared with that of HKrCl. This additional shift is an indirect consequence of the smaller zero point energy for DKrCl. It is also possible that complex dynamical processes of solid-state photodissociation can introduce some additional difference between HKrCl and DKrCl. One can speculate that the hydrogen atom (H or D) should escape the interstitial site neighboring to the Kr-Cl center for permanent decomposition of the molecule, and this process requires larger excess energy for D atoms. Furthermore, a possible H/D isotope effect on the Cl  $(^{2}P)$  spin–orbit branching ratio (in analogy with photodissociation of HCl and DCl),<sup>27</sup> might also contribute to the observed distinctions.

#### **V. CONCLUSIONS**

In this work, H/D isotope effects on formation and photodissociation of HKrCl in solid Kr have been studied. We can conclude the following:

- (i) The distinctions in the HKrCl and DKrCl formation kinetics during 193 nm photolysis can be explained by different photoabsorption cross-sections of HCl and DCl. No difference for light-induced travel of H and D atoms is claimed here.
- (ii) The kinetic difference in annealing-induced formation of HKrCl and DKrCl molecules is due to the isotope effect of global atomic hydrogen mobility in solid Kr, similarly to the recently reported effect in solid Xe (see Ref. 9). As an estimate, the activation energies for thermal mobility of H and D atoms in solid Kr are 64 and 68 meV, respectively.
- (iii) The different thermal mobility of H and D atoms allowed us to demonstrate a reaction between D atoms and HKrCl molecules. This reaction can be considered as diffusion-controlled. The experimental observations agree with the predictions of our simple kinetic model.

(iv) The solid-state photodissociation contour for DKrCl is blue shifted by  $\sim 0.1$  eV as compared with that of HKrCl. The smaller zero-point energy of the deuterated species presumably contributes to this difference.

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