

## Photoinduced charge-transfer reaction at surfaces. II. $\text{HBr} \cdot \cdot \text{Na}_n / \text{LiF}(001) + h\nu(610 \text{ nm}) \rightarrow \text{Br}^- \text{Na}_n^+ / \text{LiF}(001) + \text{H}(g)$

Sergey Dobrin, Hong He,<sup>a)</sup> Fedor Y. Naumkin, John C. Polanyi,<sup>b)</sup> and Sergei A. Raspopov<sup>c)</sup>

*Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6*

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A sub-monolayer of atomic sodium was deposited on LiF(001) at 40–90 K. The adsorbed sodium atoms and clusters were dosed with HBr, to form  $\text{HBr} \cdot \cdot \text{Na}_n / \text{LiF}(001)$  ( $n=1,2,\dots$ ) complexes which were then irradiated by 610 nm laser-light to induce charge-transfer reactions. The reaction-product atomic H(g) was observed leaving the surface, by two-color Rydberg-atom TOF spectroscopy. The H-atom translational energy in its “fast” (0.9 eV) component exhibited structure ( $40 \pm 10$  meV spacing) attributed to vibration of the NaBr residue at the surface following photoinduced reaction in  $\text{Na} \dots \text{HBr}$ . The cross-section of the harpooning event was obtained as  $7.5 \times 10^{-19} \text{ cm}^2$  for the “fast” H-atom reaction-product. Investigation of the coverage and temperature dependencies of the H-atom signal and of temperature programmed desorption (TPD) and x-ray photoelectron spectra gave an activation barrier for surface diffusion of Na-atoms  $E_{diff} < 170$  meV. High-level *ab initio* calculations were employed to interpret the TOF and TPD spectra. The reaction precursors and products, Na-HBr,  $\text{Na}^+ \text{-HBr}$ ,  $\text{Na}_2\text{-HBr}$ ,  $\text{Na}_2\text{Br}$ , NaBr, and NaBr-HBr, were investigated in terms of potential energy surfaces, equilibrium structures, binding energies, and vibrational frequencies. © 2003 American Institute of Physics. [DOI: 10.1063/1.1615756]

### I. INTRODUCTION

The photoinduced charge transfer reactions between sodium atoms and HF molecules in van der Waals complexes in the gas phase have been studied both theoretically and experimentally by this laboratory.<sup>1–5</sup> It has been found that photoinduced electron transfer from a Na-atom to another reactant, HF, can trigger bond cleavage in the HF molecule followed by formation of NaF molecule and H-atom photo-products. Recently, such a reaction has been observed for adsorbed  $\text{Na}_n \dots (\text{HX})_m$  complexes ( $m=1,2$ ), and  $\text{X}=\text{Cl}, \text{F}$ .<sup>6,7</sup> No experiments on photoinduced charge transfer in  $\text{Na} \dots \text{HBr}$  complexes have been reported until now in either the gas phase or the adsorbed state. This is the subject of the present work.

Several studies of HBr alone or Na adsorption alone on the LiF surface have been reported in the literature as follows. The configuration of adsorbed HBr, and its direct photolysis on the LiF surface have been studied in earlier work from this laboratory.<sup>8–15</sup> The experiments were performed using FT-IR spectroscopy of adsorbed HBr and also TOF mass spectrometry of H-atoms leaving the surface under UV laser irradiation. The findings were consistent with the Br-atom of the intact HBr molecule adsorbed on top of the  $\text{Li}^+$

of the substrate, with the H-atoms located adjacent to the  $\text{F}^-$  anion.

Adsorption of Na on the LiF surface has been extensively studied by Träger and co-workers.<sup>16–18</sup> They studied Na-clusters formed at 90 K on the LiF surface using laser-induced desorption, optical spectroscopy, and second harmonic generation. To interpret the experimental data, they postulated that Na-atoms were mobile at 90 K forming clusters on the LiF surface. These clusters had a large absorption cross-section in the visible region and could be studied by the techniques referred above.

Formation of  $\text{Na}_n$  clusters on the NaCl surface has been studied theoretically by Hakkinen and Manninen.<sup>19</sup> They found that Na-atoms would preferably adsorb on top of substrate  $\text{Cl}^-$  anions, 2.80 Å above the surface plane. The adsorption energy was calculated as 400 meV and the diffusion barrier as 80 meV. Sodium clusters ( $n=8$  and 20) on NaCl surfaces have also been studied by Kohl *et al.*<sup>20</sup> Theoretical studies conclude that small Na-clusters in ground state are planar, i.e., one monolayer thick.

Barriers for the surface diffusion of Na adsorbed on several metals have been measured by Toennies and co-workers using scattering of He atoms. They found an activation barrier of 75 meV for Na diffusion on  $\text{Cu}(001)$ <sup>21</sup> and less than 50 meV for Na diffusion on  $\text{Pt}(111)$ .<sup>22</sup> These experiments were performed at surface temperatures ranging from 100 to 400 K.

### II. EXPERIMENT

The experimental procedure used in the present work has been described previously.<sup>6</sup> Briefly, the experiments were

<sup>a)</sup>Present address: Department of Atmospheric Chemistry and Air Pollution Control Technology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences and National Environmental Protection Agency, Beijing, 100085, China.

<sup>b)</sup>Corresponding author. Electronic mail: jpolanyi@chem.utoronto.ca

<sup>c)</sup>Present address: Department of Chemistry, Univ. of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

carried out in ultra-high-vacuum (UHV), with a base pressure better than  $2 \times 10^{-10}$  Torr. The LiF(001) surface was cleaved in air from a LiF single crystal (Harshaw Chemical Co.) and then annealed in UHV for 1 h at 700 K. During experiments, the crystal was cooled to 40–100 K by a closed-cycle He refrigerator (CSW-204SLB-6.5, APD Cryogenics Inc.). Sodium was dosed from a commercial SAES-getter mounted on a holder, with a small defining aperture between it and the LiF(001) crystal. The Na-getter was degassed by passing 4.50 A through it for 5 min prior to each dose. Thereafter the Na itself was dosed by passing 6.50 A through the getter for 50 s to obtain a 25% monolayer coverage as described previously.<sup>6</sup> This dosage was repeated several times if a higher Na coverage was necessary. The HBr gas was obtained from Matheson with stated purity of 99.0%, and was further purified by freeze–pump–thaw cycles.

Photoreaction was studied by H-atom Rydberg TOF spectroscopy in UHV.<sup>6</sup> Upon excitation of the  $\text{Na}_n \dots \text{HBr}(ad)$  complex at 610 nm, the outgoing H-atom reaction-product was tagged by a two-color excitation, using 121.6 and approximately 365 nm, to a high- $n$  Rydberg state,  $\text{H}^{**}$ . The translationally-hot H-atoms traveled as neutral  $\text{H}^{**}$  in UHV to a microchannel plate (MCP) detector where they were field-ionized and counted. This H-atom TOF spectrometer was calibrated using direct photolysis of HBr at 193 nm, studied in earlier work.<sup>15</sup> Typically, 600 laser pulses (610 nm, 1.0 mJ per pulse) were used for each spectrum, prior to depositing fresh Na and HBr on the surface. The average number of H-atom counts per laser pulse was typically 4–5. To improve the signal-to-noise ratio in the evaluation of the observed vibrational spectra, this procedure was repeated ten times and the ten spectra were averaged for a total of 6000 laser pulses. This corresponded to approximately 25 000 counted H-atoms.

In the TPD experiments, HBr desorbing from the surface was detected at an angle normal to the crystal by a doubly-differentially-pumped quadrupole mass spectrometer (QMS). Crystal temperature was increased linearly at 2 K/s; using feedback from thermocouple fixed inside the crystal to control heating current. The HBr was dosed onto the cold LiF crystal at 45–55 K TPD. Spectra were analyzed using the Habenschanden-Kuppers method, and what has been termed “complete analysis”<sup>23,24</sup> so as to obtain desorption energies. The order of the desorption process was usually slightly below unity, in the range 0.8–1.1.

The XPS spectra of the surface for increasing amounts of Na were obtained using Mg-K $\alpha$  (1253.6 eV) radiation, with the electron analyzer at 8° off-normal.

### III. THEORETICAL METHODS

High-level *ab initio* calculations were carried out for the gas-phase systems Na-HBr,  $\text{Na}^+ \text{-HBr}$ ,  $\text{Na}_2\text{HBr}$ , NaBr, and NaBr-HBr at the all-electron level. The extensive basis sets,<sup>25,26</sup> cc-pVTZ and cc-pVQZ for the Na-atom, and aug-cc-pVTZ and aug-cc-pVQZ for the H and Br atoms were used. The internally-contracted configuration-interaction (CI) and the 2nd-order Møller-Plesset perturbation-theory (MP2) procedures were employed, as implemented in the MOLPRO

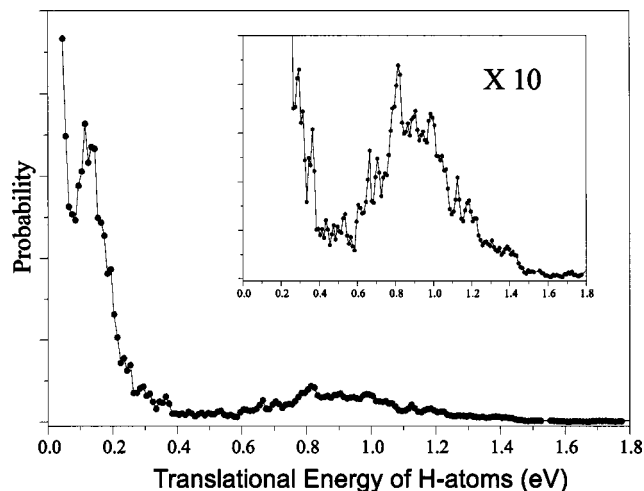


FIG. 1. TOF spectrum of H-atoms ejected to the gas-phase after 610 nm photolysis of HBr/Na/LiF(001) system at 0.25 ML Na coverage.

2000 package.<sup>27</sup> Only the ground electronic states were explicitly involved in the reference space for the systems containing HBr molecules, plus a few lowest-energy excited states for NaBr and  $\text{Na}_2\text{Br}$ .

## IV. EXPERIMENTAL RESULTS AND DISCUSSION

### A. Photoinduced charge transfer reaction

H-atom TOF spectra were obtained at 0.25 ML Na coverage under 610 nm irradiation (Fig. 1). In this experiment Na and HBr were sequentially deposited on the LiF(001) surface at 40 K immediately before starting laser photolysis. The H-atom TOF spectrum obtained during laser irradiation of the surface contained two peaks: one at 0.9 eV (“fast”) and another one at 0.1 eV (“slow”). The “fast” peak at 0.9 eV has a vibrational structure with spacing of  $40 \pm 10$  meV ( $320 \pm 80$   $\text{cm}^{-1}$ ) that is close to the NaBr vibrational frequency in the gas phase ( $302$   $\text{cm}^{-1}$ ), known from previous IR experiments.<sup>28</sup> This coincidence suggests that a single Na-atom reacts with a single HBr molecule, and forms a NaBr photoproduct that is left behind in various vibrational states at the surface. The fact that sharp features ( $\pm 10$  meV) are observable in the TOF spectrum indicates that the H-atom has escaped the surface directly, without subsequent collisions with the surface or adsorbate.

Assignment of vibrational peaks can be done, based on the energy balance of the reaction. The bond dissociation energy of HBr is 3.78 eV,<sup>29</sup> and the binding energy between Na and HBr in the van der Waals precursor complex have been calculated as 0.016 eV (see the theoretical section of the present paper). The total energy of reactants relative to the constituent atoms is therefore 3.80 eV, that is very close to the total binding energy of reaction products NaBr+H, which is just the bond dissociation energy of NaBr molecule (3.8 eV).<sup>29</sup> Thus, the reaction is thermoneutral. After reaction, the photon energy (610 nm, 2.03 eV) is shared mainly between translational energy of the desorbed H-atom and vibrational excitation of the NaBr molecule that remained on the surface. We neglect the small energy-loss from recoil of the NaBr and energy transfer to the surface during the time

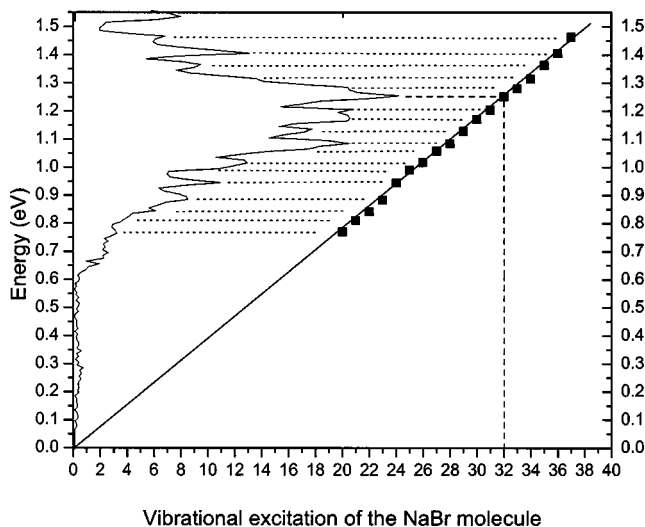


FIG. 2. Assignment of vibrational peaks in the TOF spectrum of H-atoms resulted from 610 nm photolysis of HBr/Na/LiF(001).

(less than one vibrational period) that H moves out of range of NaBr, and also neglect the small amount of energy deposited in NaBr as rotation.

The origin of the vibrational progression corresponds therefore to an H-atom translational energy equal to the photon energy, and is located at 2.03 eV on the TOF spectrum. No H-atoms were observed at this energy. The most probable H-atom energy is 0.8 eV, which corresponds to 1.25 eV energy of vibration in the newly-formed NaBr molecule. This would involve excitation of the NaBr molecule to its 32nd vibrational level. The quantum number was arrived at assuming the vibrational spacing to be 40 meV, and zero anharmonicity. The assignment of vibrational peaks to quantum numbers is shown in Fig. 2. The Y-axis shows energy accumulated in the NaBr molecule, and the X-axis the number for the corresponding vibrational level.

The amplitude of the “fast” peak decreased to one half after irradiation of the surface with approximately 300 laser shots of 1 mJ each. This decay of this “fast” peak originated in Na-HBr allows us to estimate the photoreaction cross-section for photoreaction of a single Na-atom with an HBr molecule. A laser pulse with energy of 1 mJ at 610 nm (photon energy equal to 2.03 eV) contains  $n = 3.07 \times 10^{15}$  photons. The size of the irradiated surface is approximately  $1 \text{ cm} \times 1 \text{ cm} = 1 \text{ cm}^2$ . After 300 pulses, that is  $9.2 \times 10^{17}$  photons, half of the Na...BrH complexes have reacted. Assuming the exponential decay of the reagent (as in first-order reaction), one obtains reaction cross-section;  $\ln(2)/9.2 \times 10^{17} = 7.5 \times 10^{-19} \text{ cm}^2$ .

The “slow” peak at 0.1 eV has a much less pronounced vibrational structure than the “fast” peak. The spacing is 25 meV ( $200 \text{ cm}^{-1}$ ). This frequency could be due to internal excitation in a  $\text{Na}_n\text{Br}$  cluster ( $n = 2, 3, \dots$ ). The “slow” peak is depleted less rapidly than the “fast” peak under laser irradiation; it takes about 900 laser shots to decrease the intensity of this peak by a factor of 2.

As we know from our TPD spectra (Fig. 5), adsorbed Na...HBr does not undergo spontaneous reaction to form alkali halide, via  $\text{Na} + \text{HBr} \rightarrow \text{NaBr} + \text{H}$  reaction, if the surface

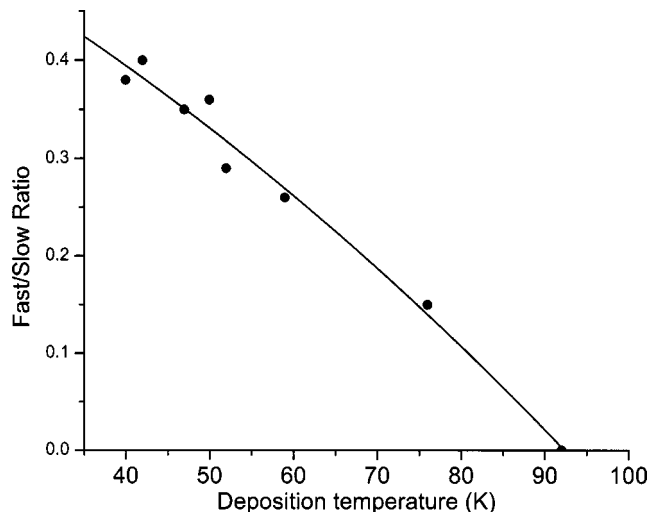


FIG. 3. Ratio between intensities of fast and slow peaks at various temperatures.

temperature is below 110 K. The HBr desorbs as an intact molecule at  $T < 110 \text{ K}$ . The activation barrier for  $\text{Na} + \text{HBr} \rightarrow \text{NaBr} + \text{H}$  reaction is therefore higher than that for HBr desorption from Na at 110 K, which is  $E_a = 0.28 \text{ eV}$ . This is consistent with the value of  $E_a = 0.70 \text{ eV}$  (16 kcal/mol) predicted by a semiempirical calculation performed by Shapiro and Zeiri,<sup>30</sup> and also with the value of  $E_a = 0.75 \text{ eV}$  obtained in our *ab initio* calculations (to be discussed below in Sec. V A).

### B. Na adsorption on the LiF(001), analysis of the TOF data

From the vibrational structure in the H-atom TOF spectrum the “fast” peak was attributed to photolysis of HBr adsorbed on single Na-atoms on the LiF surface, and the “slow” peak to photolysis on Na-clusters. To verify this assignment the Na coverage and the surface temperature at the time of Na deposition have been varied. In one experiment we deposited a 1.0 ML coverage of Na to exclude single sodium atoms and found that the “fast” peak disappeared.

In another experiment we varied the temperature of the LiF surface at which sodium was deposited. The ratio of the integrated areas of the “fast” to “slow” peaks measured at various deposition temperatures is shown in Fig. 3. This ratio is zero at 90 K (i.e., no “fast” peak), increasing up to 0.4 at 40 K. This, once again, is consistent with the presence of single Na-atoms and Na-clusters on the surface. If sodium is deposited at 90 K, fast diffusion of Na-atoms leads to efficient formation of Na-clusters with few single Na-atoms. This is, in turn, in agreement with results obtained at 90 K by Träger and co-workers.<sup>16–18</sup> If, however, sodium is deposited at 40 K the surface diffusion of Na-atoms is much slower than at 90 K, and some single Na-atoms are likely to remain on the surface. These Na-atoms are, we believe, responsible for the smaller “fast” peak in the TOF spectrum at 0.9 eV.

The fraction of Na-atoms present as clusters at various temperatures can be estimated from the ratio between intensities of “fast” and “slow” peaks. A ratio between amounts of HBr molecules reacted with Na-clusters and HBr mol-

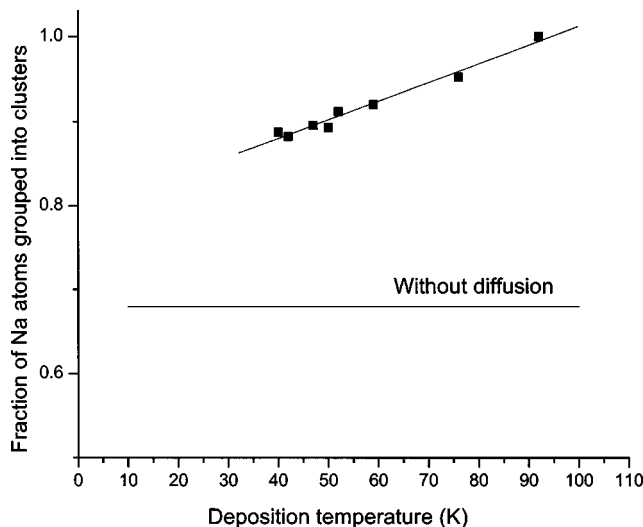


FIG. 4. Fraction of Na-atoms involved in clusters formed at various deposition temperatures at 0.25 monolayer of Na.

ecules reacted with single Na-atoms can be found as  $Q = 3A(\text{slow})/A(\text{fast})$ . Here,  $A(\text{slow})$  and  $A(\text{fast})$  represent intensities of “slow” and “fast” peaks, respectively. The TOF spectrum was accumulated during first 600 laser shots after Na deposition. As discussed above, the “fast” peak decreases to small intensity after this irradiation, but “slow” peak still is present in the spectrum and depletes approximately 0.3 as fast. To take this into account, and to estimate a total number of HBr molecules reacted with sodium clusters, the value of the  $A(\text{slow})$  was multiplied by a factor of 3 in the above equation. We assume that sodium clusters are planar, as previous theoretical studies of small Na-clusters on the NaCl surface suggested<sup>19,20</sup> and therefore the  $Q$  value can be used as a good approximation for the ratio between amounts of single sodium atoms and atoms grouped into clusters. The ratio between Na-atoms collected into clusters and total amount of sodium atoms, including both single atoms and those from clusters, can be then found as  $F_{\text{exp}} = Q/(1+Q)$ . Results obtained for Na deposition made at various temperatures are shown in Fig. 4. It can be seen that if sodium was deposited at 40 K, about 88% of the Na-atoms are in clusters.

This number should be compared with a theoretical estimate of the statistical fraction of Na-atoms grouped into clusters in the absence of the surface diffusion. This fraction can be found as follows. The probability of finding a Na-atom at a particular adsorption site is  $p=0.25$  at 0.25 ML coverage. This probability counts all types of Na-atoms: single and those in clusters. For further analysis a Na-atom will be defined as a single atom if sodium atoms do not occupy the four nearest adsorption sites. The probability of finding nearest adsorption sites not occupied is:  $(1-p)^4$ , and the total probability of finding a single Na-atom on a particular adsorption site is  $P(s) = p(1-p)^4 = 0.08$ . The probability of finding a Na-atom with one or more neighbors, i.e., a Na-atom that belongs to a sodium cluster, is  $P(c) = p - p(1-p)^4 = 0.17$ . The corresponding single/cluster fractional ratio is  $R = 0.47$  and the fraction of Na-atoms grouped into the cluster is  $F_{\text{calc}} = P(c)/(P(c) + P(s))$

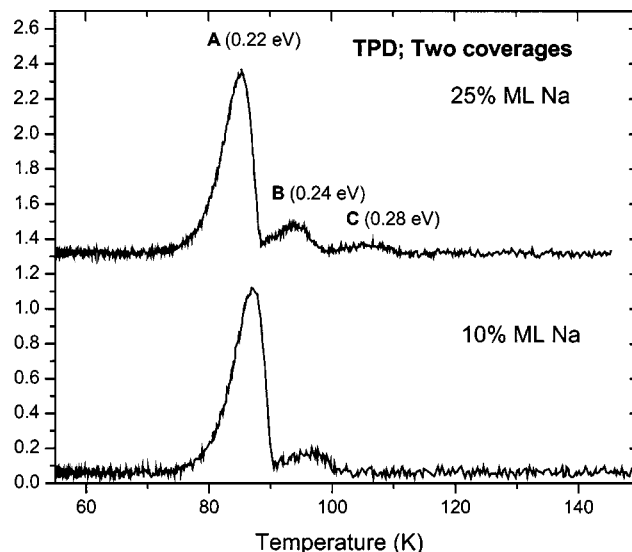


FIG. 5. Temperature programmed desorption spectra for HBr desorption from the HBr/Na/LiF(001) at 0.25 and 0.1 monolayer of Na.

$=0.68$ . This is less than the value of  $F_{\text{exp}}=0.88$  determined from the experiment at 40 K. The value of  $F_{\text{calc}}$  is shown in Fig. 4 as a horizontal line. Comparison of experimental and calculated values shows that the surface diffusion is still important at 40 K.

It should be noted that the  $A(\text{slow})/A(\text{fast})$  ratio changed with time. After two weeks of experiment the “slow” to “fast” ratio increased approximately by a factor of 1.5. This effect can be explained by formation of new defects on the LiF(001) surface after multiple photolysis and flashing to 700 K. The presence of larger amounts of defects accelerates formation of Na-clusters.<sup>16–18</sup> Dependencies of the H-atom signal upon temperature of deposition and sodium coverage were obtained in one day, so they were unaffected by these long-term changes.

### C. Na adsorption and diffusion on the LiF(001), from TPD data

Further information on Na adsorption comes from the TPD spectra of HBr adsorbed on the LiF(001) surface pre-covered by a sub-monolayer of sodium. TPD spectra obtained at various Na coverages are shown in Fig. 5. The TPD spectrum of 0.3 ML of HBr adsorbed on a clean LiF surface exhibited only one peak at 85 K (labeled “A”). This TPD peak is close to that at 87 K reported by Giorgi *et al.*<sup>15</sup> (The difference of 2 K can be due to inaccuracy of the temperature measurements.) The amount of deposited HBr was determined by taking 1 ML=3 L as was found by Giorgi *et al.*<sup>15</sup> If 0.1 ML of sodium is adsorbed on the LiF surface prior to HBr deposition, a small additional peak “B” appears in TPD spectrum at 95 K (Fig. 5). The corresponding adsorption energies are 0.22 eV (TPD peak A) and 0.24 eV (TPD peak B). If 0.25 ML of sodium is deposited, a new weak peak appears at 110 K (0.28 eV binding energy) in the TPD spectrum. This demonstrates that sodium can adsorb in various forms; one form, which is responsible for the TPD peak “B,” is more

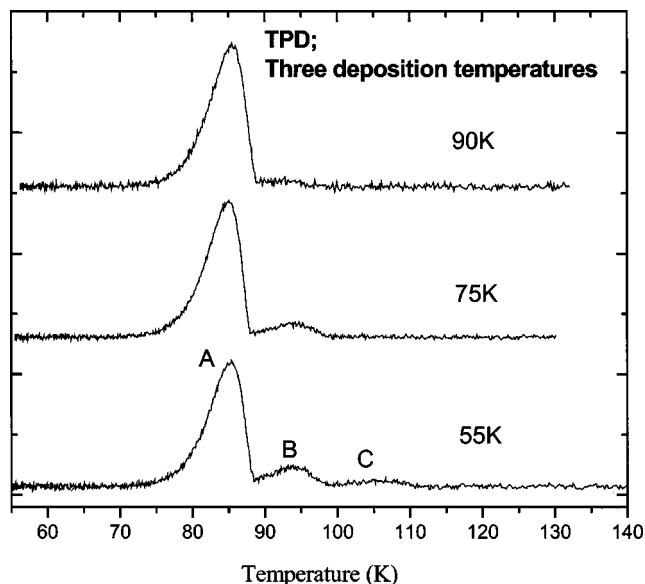


FIG. 6. Temperature programmed desorption spectra for HBr desorption from the HBr/Na/LiF(001) after 0.25 monolayer Na deposition at 55, 75, and 90 K.

important at low coverages. This peak is likely to be that for adsorption of HBr on single Na-atoms, for the following reasons.

The temperature behavior of this peak "B" is similar to that of the "fast" peak in the TOF spectrum (Fig. 6). The TPD peak "B" decreases with increasing surface temperature at the time of sodium deposition, and disappears almost completely if sodium is deposited at 90 K. The fact that TPD peak "B" disappears at the higher temperature is consistent with the Na-atoms forming clusters, which give this broad peak of small amplitude. We know that Na-atoms remain on the surface at 90 K, from TOF and XPS.

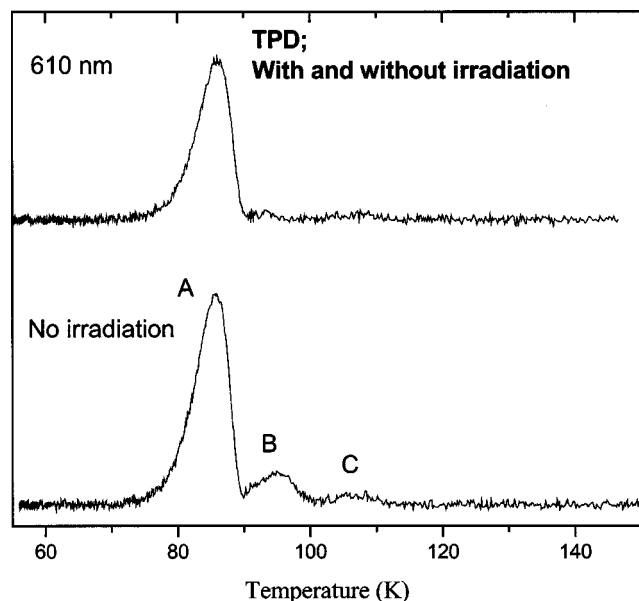


FIG. 7. Temperature programmed desorption spectra for HBr desorption from the HBr/Na/LiF(001), 0.25 ML NA, without laser irradiation and after 6000 laser pulses, 1 MJ, 610 nm, fired at surface at 50 K.

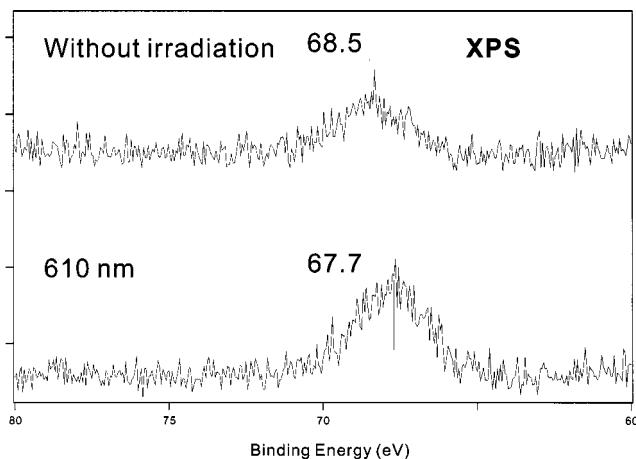


FIG. 8. XPS spectra of Br(3d) from species adsorbed on Na/LiF(001) taken at 50 K, before and after 6000 laser 610 nm pulses, 1 mJ each.

Additionally, the TPD peak "B" can be eliminated by laser irradiation at 610 nm, as can the "fast" single-Na-atom peak in the TOF spectrum; 6000 laser pulses of 1 mJ eliminate the TPD peak "B" completely (Fig. 7). The same amount of laser radiation eliminated the "fast" peak from the TOF spectrum. From XPS measurements we know that Br atoms remain on the surface after the irradiation, but shows a 0.8 eV shift to smaller electron binding energy of the 3d line (Fig. 8). This shift is due to the strong electron transfer to Br from the Na-atom. From XPS data we know, therefore, that the HBr is converted into NaBr during irradiation.

These observations combine to suggest that the peak "B" in the TPD spectra and the "fast" peak in the TOF spectrum have the same origin, which is single HBr molecules undergoing photolysis while complexed to single Na-atoms. By the same reasoning, the "slow" peak in the TOF spectrum and the peak "C" in the TPD data are thought to be due to the alternative initial state, HBr adsorbed on sodium clusters.

#### D. Surface diffusion of Na-atoms

We can use our results to estimate an activation barrier for surface diffusion of Na-atoms on the LiF(001) surface. The LiF(001) surface with 0.25 ML Na coverage is shown schematically in Fig. 9. For the sake of simplicity, the so-

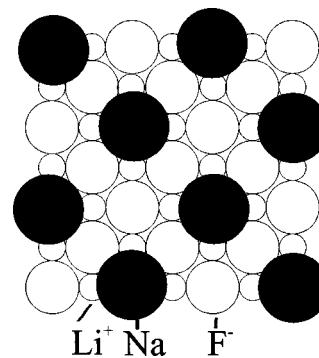


FIG. 9. Pattern of Na-atoms adsorbed on LiF(001) at 0.25 ML coverage.

dium atoms are placed on the surface in a regular pattern. In this case, each Na-atom has four empty adsorption sites next to it. Our data do not allow us to determine on which site ( $\text{Li}^+$  or  $\text{F}^-$ ) the Na-atom is adsorbed. Following the theoretical study of Hakkinen and Manninen<sup>19</sup> for Na adsorption on the NaCl(001) surface, we place Na-atoms on top of the  $\text{F}^-$  anions. The lattice constant of the LiF crystal has been taken to be 4.01 Å at 80 K as in the previous studies of HBr photolysis on the LiF surface.<sup>15</sup> With this lattice constant the distance between two nearest adsorption sites is 2.84 Å. If an Na-atom jumps from its original site to any nearest one, it arrives at a distance of 2.84 Å from another Na-atom. For comparison, the Na-Na distance in the  $\text{Na}_2$  molecule is 3.08 Å.<sup>32</sup> Therefore, two Na-atoms on the two nearest adsorption sites will form an adsorbed sodium dimer.

From the temperature behavior of the “fast” and “slow” peaks in the TOF spectrum and from vibrational structure observed in the TOF fast component we conclude that the “fast” peak is due to single sodium atoms. The “fast” peak is prominent if Na is deposited at 50 K. The typical TOF spectrum accumulation-time is 10 min (600 s). We can estimate the *lower* limit for the activation barrier of Na surface diffusion, assuming that the lifetime of the Na-atom at one adsorption site is longer than 600 s at 50 K. The lifetime can be then calculated as  $10^{-13} \times \exp(E/kT)$ , and from this a value of the activation energy,  $E_{diff} > 150$  meV. The *upper* limit for the diffusion barrier can be found from the experiments at 90 K. Na was deposited at 90 K for 50 s and the heater of the crystal was immediately switched off. After the crystal was cooled down to 50 K, the TOF spectrum was measured. No H-atom signal from reaction on single Na-atoms was found for 90 K sodium deposition. The residence time of the Na-atom on a particular adsorption site at 90 K can therefore be estimated to be less than 100 s. For the lifetime to be so short, the activation barrier for the diffusion must be  $E_{diff} < 170$  meV. We conclude that  $E_{diff} = 150\text{--}170$  meV. This estimate could be high, since in reality Na-atoms do not form an ideal structure as shown in Fig. 9, and a single sodium atom may need to make more than one jump to reach another Na-atom and form a cluster. As has been mentioned in the Introduction, the activation energies for the diffusion of Na-atoms on metal surfaces Cu(001) and Pt(111) have been found to be less than 100 and 50 meV, respectively.<sup>21,31</sup> It appears that the diffusion of Na on a LiF surface is not as fast as on the surfaces of metals.

## V. THEORETICAL RESULTS AND DISCUSSION

In this section we report calculations for neutral, Na...HBr, ionic,  $\text{Na}^+ \dots \text{HBr}$ , and cluster reactant complexes,  $\text{Na}_2 \dots \text{HBr}$ , and for two reaction products,  $\text{Na}_2\text{Br}$  and  $\text{NaBr}\cdot\text{HBr}$ . We shall show that our experimental data are consistent with presence of neutral adsorbed complexes Na...HBr and  $\text{Na}_2 \dots \text{HBr}$  at the surface, and with formation of NaBr and  $\text{Na}_2\text{Br}$  photoproducts. Reactions of larger sodium complexes are also possible but are beyond the scope of present work. The presence of ionic  $\text{Na}^+ \dots \text{HBr}$  and formation of NaBr·HBr photoproducts are found to be unlikely.

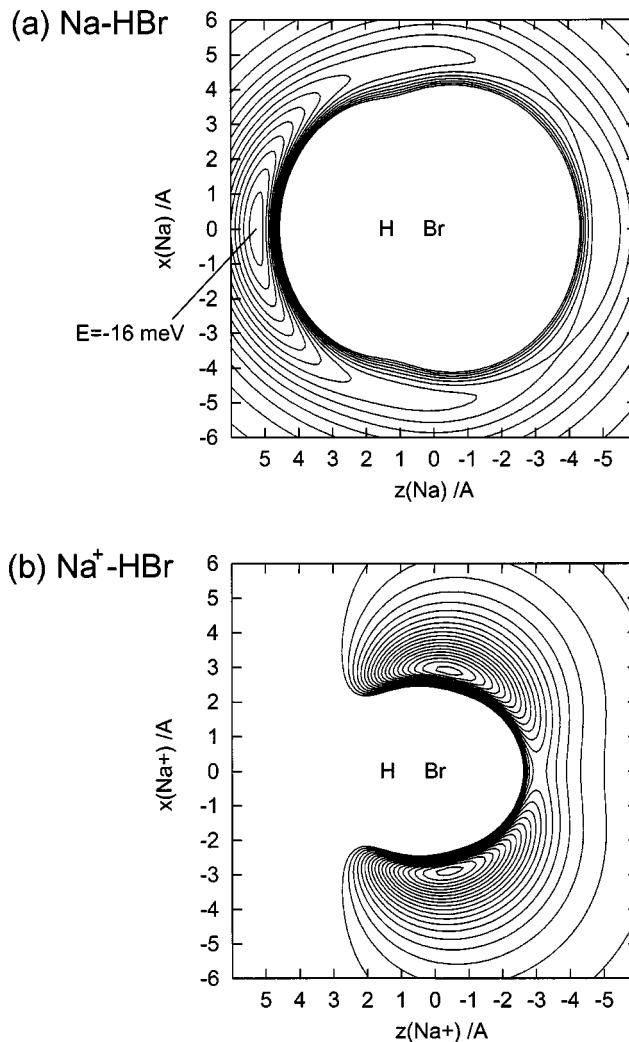


FIG. 10. Contour plots of the ground-state PES of the (a)  $\text{Na}\cdot\text{HBr}$  and (b)  $\text{Na}^+\cdot\text{HBr}$  complexes. The HBr is fixed at its equilibrium internuclear separation of 1.41 Å. The  $x$  and  $z$  coordinates specify the position of Na or  $\text{Na}^+$  relative to the Br-atom. Contours are given from zero potential-energy with Na-atom at infinity in steps of 1 and 20 meV, respectively, for (a) and (b).

### A. Na...HBr neutral complex

The ground state  $^2A'$  potential energy surface (PES) for the  $\text{Na}\cdot\text{HBr}$  complex has been evaluated at the CI level of theory for a number of positions of the Na-atom around the HBr molecule fixed at its equilibrium (gas-phase) internuclear separation. The restriction on the HBr bond-length is based on the assumption of a weak Na–HBr interaction expected from previous data<sup>3,6</sup> for  $\text{Na}\cdot\text{HF}$  and  $\text{Na}\cdot\text{HCl}$ . The contour map of the interpolated PES is shown in Fig. 10(a). It exhibits a single major well for the linear geometry with Na near the H-end of the molecule. This is similar to the topology of the  $\text{Na}\cdot\text{HCl}$  PES and is different from that for  $\text{Na}\cdot\text{HF}$ , which has a bent equilibrium configuration with Na neighboring the F atom.<sup>3</sup> The difference can be associated with an increased size of the halogen atom (Cl,Br) and hence weaker electrostatic interaction of Na with the halogen atom compared to that with H.

The Na-HBr dissociation energy is found to be  $D_e \approx 16$  meV, and the equilibrium Na-Br and Na-H distances

$R_e \approx 5.23$  and  $3.81$  Å, respectively, for both basis sets. These values should be compared with  $D_e \approx 13$  meV, and  $R_e(\text{Na-Cl}) \approx 5.22$  and  $R_e(\text{Na-H}) \approx 3.95$  Å, calculated for the  $\text{Na} \cdots \text{HCl}$  complex at the same level of theory, and with  $D_e \approx 76$  meV, and  $R_e(\text{Na-F}) \approx 2.47$  and  $R_e(\text{Na-H}) \approx 3.01$  Å, calculated previously for  $\text{Na} \cdots \text{HF}$ .<sup>3</sup> The results for Na-HF are very closely reproduced at the present level of theory. There is a shallower second well in the Na-HBr PES,  $\approx 7$  meV deep, for the other linear geometry with Na next to Br, separated from the major well by a low ( $\approx 1$  meV) potential barrier.

The value of  $D_e \approx 16$  meV calculated for Na-HBr agrees with the gap between the “A” and “B” peaks in the TPD spectrum,  $\approx 20$  meV, supporting its interpretation as due to HBr desorbing from single adsorbed Na-atoms. The small energy difference ( $\approx 10$  meV) between the two linear configurations, Na-H-Br and Na-Br-H, suggests an almost free rotation of HBr relative to Na at room temperature or, for lower temperatures high-amplitude bending vibrations of the complex, allowing it to readily access configurations favorable for the charge-transfer reaction.

Figure 11 shows the potential energy of the neutral system for the linear Na-Br-H geometry, as function of the Na-Br and H-Br distances, from the CI calculations. This PES exhibits a typical shape with two valleys corresponding to reactants and products separated by a potential barrier. The barrier height was found to be  $\approx 0.75$  eV from the side of reactants, only 0.05 eV larger than the value predicted semiempirically.<sup>30</sup> A similar PES calculated for the L-shaped geometry with the Na-Br-H angle equal to  $90^\circ$  exhibited a slightly higher barrier.

### B. $\text{Na}^+ \cdots \text{HBr}$ ionic complex

In order to investigate the effect of possible charge-transfer between Na and the surface, the  $\text{Na}^+ \cdots \text{HBr}$  ionic system has also been considered, at the same level of theory. Assuming only a small contribution from this ionic component to the real system, the H-Br separation has been kept at the value for the neutral complex. This is consistent with the H-Br distance increasing by only  $\approx 0.01$  Å at the fully optimized equilibrium configuration of the ionic complex. The ground state  $^1A'$  PES of the system, mapped in Fig. 10(b), exhibits a single well for the L-shaped geometry. In this geometry the  $\text{Na}^+$  ion is closer to the Br end of the molecule and the equilibrium configuration corresponding to the  $\text{Na}^+ \cdots \text{Br}/\text{Na}^+ \cdots \text{H}$  distances of 2.92/3.42 Å ( $\text{Na}^+ \cdots \text{Br-H}$  angle of  $\approx 98^\circ$ ). Both linear configurations correspond to saddle points, with a substantial repulsion for  $\text{Na}^+$  near the positively charged H-end of the molecule. The structure of this ionic complex is different from that for its neutral counterpart. This can be shown to result from a simple sum of  $\text{Na}^+ \cdots \text{H}$  and  $\text{Na}^+ \cdots \text{Br}$  interactions.

The  $\text{Na}^+ \cdots \text{HBr}$  interaction is much stronger than that for Na-HBr, as could be expected for an ion-molecule pair compared to the neutral atom-molecule one, and produces deeper wells at shorter distances. The calculated  $\text{Na}^+ \cdots \text{HBr}$  binding energy  $D_e \approx 0.41$  eV, more than an order of magnitude larger than the value we infer for  $\text{Na} \cdots \text{HBr}$ . Therefore, if to con-

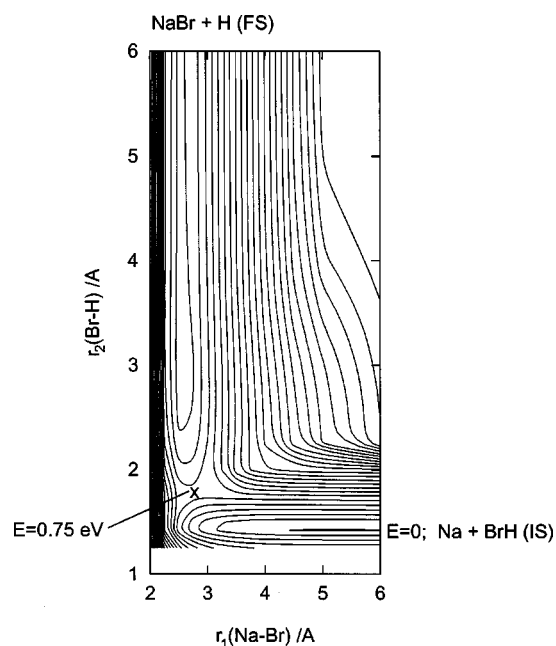


FIG. 11. Contour plot of the Na-Br-H PES for the linear geometry. Contours are at steps of 130 meV. The cross marks the saddle point at the top of the barrier; 0.75 eV above the initial state, IS. The final state is FS.

sider the adsorbed system state as a mixture of the pure neutral and ionic components, even a small charge on adsorbed Na would significantly increase the Na-HBr binding as well as affect the equilibrium configuration of the system on the surface. However, the good match between the predicted  $D_e$  value for the neutral complex and the gap between the “A” and “B” peaks in the TPD spectrum appears to imply a very small charge, if any, on adsorbed Na. This is in accord with the DFT studies of Na/NaCl(001), which indicate no charge transfer from the surface to the sodium atoms.<sup>19</sup> On these grounds, only neutral systems are considered from now on.

### C. $\text{Na}_2 \cdots \text{HBr}$ complex

In order to evaluate possible contributions of the HBr interaction with Na-clusters to the experimental data, the  $\text{Na}_2 \cdots \text{HBr}$  potentials have been calculated at the same (CI) level of theory. We compared several geometries, with the  $\text{Na}_2$  dimer fixed at its equilibrium (gas-phase) internuclear separation of 3.08 Å and HBr approaching collinearly and perpendicularly to the Na-Na axis, and pointing to the dimer with H- and Br-ends. The interaction is more attractive for the perpendicular (T-shaped) geometry for either orientation of HBr. The molecule prefers to approach with the H-end pointing to the dimer, similar to the Na-HBr case. The binding energy is calculated to be  $D_e \approx 86$  meV at  $R_e \approx 3.10$  Å (between H and the dimer center), similar to our results for  $\text{Na}_2 \cdots \text{HCl}$ ,  $\approx 85$  meV at  $\approx 3.17$  Å. The collinear approach leads to a rather flat or even repulsive potential. These findings can readily be interpreted in terms of a simple electrostatic model for the interaction of the HBr dipole and  $\text{Na}_2$  quadrupole. In the fully optimized equilibrium configuration, HBr tilts slightly from the symmetric T-shaped configuration, by  $\approx 8^\circ$  in the system plane.

The calculated  $\text{Na}_2\text{-HBr}$  binding energy of 86 meV should be compared with the  $\approx 60$  meV gap between the peaks “A” and “C” in the TPD spectrum. The binding energy difference of  $\approx 64$  meV between the two T-shaped configurations of the complex hinders rotation of HBr near the dimer but still allows for bending vibrations facilitating the charge-transfer reaction. Due to a significant difference between the corresponding  $R_e$  values, these vibrations couple with those for stretching modes.

In above analysis (Secs. V A–V D) we considered the species as being in the gas-phase. It is recognized that the interaction between Na and HBr, or  $\text{Na}_2$  and HBr, will be modified in the adsorbed state from their gas-phase values. Nonetheless these calculated binding energies of 16 and 86 meV are in adequate agreement with the 20 and 60 meV measured differences between the peak “A” and peaks “B,” and “C,” respectively, in the TPD spectrum. This accords with our interpretation of these two peaks as due to  $\text{Na}\dots\text{HBr}$  and  $\text{Na}_n\dots\text{HBr}$ , on the basis of our other evidence.

As discussed above, the presence of the  $\text{Na}\dots\text{HBr}$  and  $\text{Na}_n\dots\text{HBr}$  complexes in their ground states is consistent with our TPD data. Interpretation of the TOF spectrum requires consideration of an electronically excited state. The mechanism of photoreaction is, as previously described,<sup>2</sup> charge-transfer reaction to yield H via an excited electronic state. The electronically excited complex,  $(\text{NaHBr})^*$ , is thought to exist for sufficient time for its geometry to change. In the ground state NaHBr is most stable if H points toward Na. Following charge-transfer in the excited state,  $(\text{NaHBr})^*$ , the ionic product,  $\text{Na}^+\text{Br}^-\cdot\text{H}$ , gives evidence of separating with H moving freely away from NaBr, given the well-defined fine-structure in the H-atom translational energy. This ionic intermediate may be linear or bent, so long as H is not trapped in the region between  $\text{Na}^+$  and  $\text{Br}^-$ . Calculations for the excited states are beyond the scope of the present work.

#### D. $\text{Na}_2\text{Br}$ photoproduct

The charge-transfer reaction in the  $\text{Na}_2\dots\text{HBr}$  system produces an  $\text{Na}_2\text{Br}$  ionic species, that could be reflected in the TOF spectrum of ejected H-atoms. The  $\text{Na}_2\text{-Br}$  potentials calculated at the multireference-CI level of theory indicate the symmetric isosceles-triangular configuration as equilibrium one for the system in the ground state. The associated binding energy is found to be only  $\approx 0.3$  eV larger than for NaBr calculated at the same level of theory. This, together with  $D_e(\text{Na}_2)\approx 0.7$  eV, results in  $\approx 1$  eV energy for the  $\text{Na}_2\text{Br}$  dissociation into  $\text{NaBr}+\text{Na}$ . The peak in the TOF spectrum, associated with the (thermoneutral)  $\text{Na}+\text{HBr}$  reaction, lies at  $\approx 0.9\pm 0.3$  eV, which implies  $1.1\pm 0.3$  eV energy loss by the 2.03 eV photon to the vibrational excitation of the NaBr product. Similar excitation of  $\text{Na}_2\text{Br}$  can lead to its dissociation into (vibrationally cool) NaBr and Na. The reaction leading to a higher vibrational or electronic excitation of  $\text{Na}_2\text{Br}$ , on the other hand, would produce H-atoms with low kinetic energies. This could explain the origin of the low-energy peak (near 0.1 eV) in the TOF spectrum (Fig. 1).

#### E. NaBr-HBr photoproduct

In the case of the  $\text{Na}+\text{HCl}$  reactive system studied previously,<sup>6</sup> the TOF spectrum was interpreted in terms of the  $\text{NaCl-HCl}$  species formed via a charge-transfer reaction  $\text{Na}(\text{HCl})_2\rightarrow\text{NaCl-HCl}+\text{H}$ . Since the  $\text{Na}\dots\text{HCl}$  and  $\text{Na}\dots\text{HBr}$  systems are found to have comparable binding energies (13 and 16 meV, respectively), formation of similar di-hydrogen-halide  $\text{Na}(\text{HBr})_2$  complexes and their transformation into NaBr-HBr can be expected as well. If the reaction  $\text{Na}(\text{HBr})_2\rightarrow\text{NaBr-HBr}+\text{H}$  takes place, the NaBr-HBr product complex should exhibit itself in the TOF spectrum. To test this possibility we studied the NaBr-HBr complex.

For the fully optimized NaBr-HBr complex, our *ab initio* (MP2) calculations predict a binding energy of  $\approx 0.3$  eV, which is less than  $\approx 0.5$  eV for the  $\text{NaCl-HCl}$  counterpart.<sup>6</sup> The equilibrium configuration of NaBr-HBr is intermediate between those for L-shaped  $(\text{HBr})_2$  and rhombic  $(\text{NaBr})_2$ , similar to the Cl-based systems. Both diatomic components in the complex are perturbed weakly. The H-Br and Na-Br distances are longer than in the free molecules by, respectively,  $\approx 0.02$  and  $\approx 0.05$  Å only. These differences are about half as large as for the  $\text{NaCl-HCl}$  case.<sup>6</sup> Such a weakly bound NaBr-HBr complex cannot explain the vibrational progression observed in the experiment. This progression covers 0.6 eV energy interval (from 0.8 to 1.4 eV, Fig. 2) and does not show a significant anharmonicity which would be expected for the weakly bound NaBr-HBr complex. Formation of this complex appears therefore to be unlikely.

#### VI. CONCLUSIONS

In the present paper we report results of H-atom Rydberg TOF spectroscopy, TPD, XPS, and *ab initio* studies of a photoinduced (610 nm) charge-transfer reaction between single sodium atoms or small sodium clusters as charge donors and HBr as charge acceptors in  $\text{HBr}\dots\text{Na}_n$  complexes adsorbed on the LiF(001) surface at 40–90 K.

In the TOF spectrum of atomic H we were able to distinguish between peaks originating in photoreaction involving single Na-atoms and that for sodium clusters. The H-atom translational energy TOF spectrum in its “high”-energy region (0.9 eV) exhibited structure of  $40\pm 10$  meV spacing, thought to be due to vibrational excitation in the NaBr residue of  $\text{Na}\dots\text{HBr}\rightarrow\text{NaBr}+\text{H}(\text{g})$  photoinduced reaction on the surface. The cross-section of the photoreaction at 610 nm was estimated as  $7.5\times 10^{-19}$  cm<sup>2</sup> for the single sodium atoms. The TPD spectra also gave evidence of desorption peaks arising from single Na-atoms and from sodium clusters. The assignment was based on the dependence of the intensities of the peaks in the TPD spectra on the Na coverage, and on the temperature of the LiF(001) surface at which Na was deposited. These peaks in the TPD spectra can be identified with corresponding peaks for  $\text{Na}\dots\text{HBr}$  and  $\text{Na}_n\dots\text{HBr}$  in the TOF spectrum.

The *ab initio* calculations (at the CI level) support, approximately, in terms of calculated binding energies, the assignment of the TPD peaks to HBr adsorbed on the Na single atoms and clusters. The isolated  $\text{Na}\dots\text{HBr}$  complex is predicted to be bound by  $\approx 16$  meV. This value is close to the



experimentally measured energy difference of  $\approx 20$  meV between the desorption energies for HBr molecules adsorbed on the LiF(001) surface and for HBr incorporated into the Na...HBr complex adsorbed on the LiF(001) surface, i.e., the difference in energy between the peaks "A" and "B" in the TPD spectrum. For the Na<sub>2</sub>...HBr complex, the binding energy is calculated to be  $\approx 86$  meV. This is in a qualitative agreement with the energy gap of 60 meV between the peaks "A" and "C" in the TPD spectrum. The calculated Na<sup>+</sup>-HBr interaction is much stronger ( $D_e \approx 410$  meV) than that in Na-HBr. From this we conclude that there is no detectable charge-transfer between the LiF substrate and adsorbed Na atoms.

Equilibrium configurations and the PES topologies of the neutral isolated Na...HBr and Na<sub>2</sub>...HBr complexes have been examined. The preferred Na...HBr complex was found to be linear with H pointing to Na but with a low barrier ( $\approx 10$  meV) to rotation of HBr. The Na<sub>2</sub>...HBr complex was T-shaped with H pointing to the center of the dimer, with a significantly higher barrier ( $\approx 60$  meV) for the HBr rotation. The low-energy peak in the TOF spectrum can be explained in terms of HBr reaction with Na<sub>2</sub> dimers and larger clusters, as suggested by the *ab initio* calculations for Na<sub>2</sub>Br.

The experimental data showed that the activation barrier for spontaneous charge-transfer reaction in the ground state exceeded 0.28 eV, in accord with the *ab initio* value of  $\approx 0.75$  eV. The barrier for Na surface-diffusion on the LiF(001) surface was found experimentally to be less than 160 meV, in agreement with studies of comparable systems.<sup>20-22</sup>

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