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Spectroscopic behavior of halogen photodesorption from alkali halides under UV and VUV excitation

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The photostimulated desorption yield of neutral halogen atoms from KI, KBr, and RbI at several temperatures has been measured in the photon energy range between 5 and 30 eV using synchrotron radiation and quadrupole mass spectrometry. The features observed in the desorption yield are slightly correlated with the structures of the absorption spectra of each investigated material. The behavior of the halogen desorption yield is analyzed in the frame of inelastic electron-electron scattering processes, in close analogy with data available from the total photoelectron yield and the luminescence yield. The role played in the desorption mechanism by fundamental excitations, such as valence exciton creation and band-gap electron-hole excitation, is discussed. [S0163-1829(97)01907-3]

I. INTRODUCTION

A typical process that takes place on pure alkali halides when they are irradiated with photons or hit by electrons consists of the emission of constituent particles from the clean surface. This phenomenon is known as photon-stimulated desorption or electron-stimulated desorption, according to the incident particles, and is driven by the electronic excitation of the crystal.[1] During the past decade several properties of particles emitted from alkali halide surfaces have been investigated. It is now currently believed that the phenomenon of desorption can be traced back to the formation of lattice defects in pure alkali halides irradiated by energetic particles.[2]

The decay of excited electronic states results in the formation of self-trapped excitons which act as the initial step in the formation of F-H Frenkel pairs. At the temperatures of interest here, H centers can migrate inside the crystal, arrive at the surface, and eventually decay to a halogen adatom adsorbed on the crystal surface, which evaporates out.[3,4] The formation or arrival of a F center on the crystal surface may provide the necessary electron for neutralizing an alkali ion which could be thermally emitted as a neutral alkali atom. This process is believed to be responsible for the thermal component of desorption. In the case of electron-stimulated desorption, dynamic (nonthermal) desorption also occurs when an electron-hole pair and/or free exciton localizes on a surface halogen ion.[5,6] We recently found that this nonthermal channel of desorption is not active for low-energy photon excitations.[7]

Up to now, the majority of experiments on stimulated desorption in alkali halides were performed using energetic particles, either soft x rays or electrons of kinetic energy of tens or hundreds of eV, which can excite core levels as well as valence bands.[8] Several types of excited states can be created, that go through a cascade of secondary processes before arriving at the formation of self-trapped excitons. It is not yet clear what role is played by all these intermediate steps in defect formation and, consequently, in the desorption process of neutral atoms. In addition, it has been suggested that some of these intermediate steps, or the emission of secondary electrons, could be responsible for the desorption of excited atoms or ions.

It is well known that defects can be created by irradiating the alkali halides with ultraviolet photons with an energy higher than that of the fundamental absorption threshold.[9] In order to obtain direct information about the desorption process of neutral atoms it is very important to study the behavior of the desorption yield using a selective excitation probe in the energy interval where direct exciton formation takes place and above the fundamental absorption threshold toward the first core-level excitations. The investigation of halogen atom emission provides information on the precursor state of desorption because of the close relationship between H-center production and halogen emission via the nonradiative decay of the self-trapped exciton.[10] UV and vacuum ultraviolet (VUV) photons are suitable for selective excitation, and allow us to compare desorption data with information available from other spectroscopic techniques, such as photoluminescence and total yield photoemission.

In Sec. II details are given concerning the sample preparation and measurement techniques. In Sec. III we present the yield spectra of photon stimulated desorption of neutral halogen atoms from KI, RbI, and KBr single crystals measured at several temperatures. In Sec. IV we discuss the behavior of the yield spectra, taking into account the absorption features as well as the electron-electron scattering processes characteristic of each investigated material.

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II. EXPERIMENTAL SETUP

The desorption measurements were performed at the experimental station of W3.1 beamline at Hamburger Synchrotronstrahlungslabor (HASYLAB), the synchrotron radiation laboratory at Deutshen Elektronen-Synchrotron in Hamburg. The photon energy was selected by using a 1-m normal-incidence Wadsworth-type monochromator. The photon energies available allowed us to cover excitations between 5 and 30 eV, originating both from the valence band and from the first core states. The desorption yield spectra have been measured with an average band pass of 10 Å and an average photon flux of 5×10^{11} photons s^{-1}/mA. The desorbed halogen atoms, emitted within 10^{-3} sr of solid angle, were detected by a Balzers QMG 311 quadrupole mass spectrometer (QMS) able to cover the 0–300 a.m.u. interval, which was operated in a pulse-counting mode. The signal at each halogen mass was optimized by changing the impact electron kinetic energy in the ionizing stage of the QMS. The intensity of the light reflected from the sample surface was measured, between 5 and 10 eV, together with the QMS signal in order to identify the energy position of the main absorption structures of the specimen under measurement. The sample temperature could be continuously varied between 300 and 800 K by means of a resistive heater mounted on the sample holder, and the temperature was monitored with a thermocouple.

The samples were cleaved in air along the (100) plane, and the surface was cleaned in vacuum by heating the sample up to about 650 K for several hours. This procedure is known to produce a well-ordered, single-crystal alkali halide surface.[5] In order to normalize the desorption signal, the incident radiation intensity was measured by collecting the fluorescence of a sodium salicilate coating placed on a screen behind the sample position. Data acquisition was performed using a computer automated measurement and control system connected to a μVAX computer.

III. EXPERIMENTAL RESULTS

In Figs. 1(a), 2(a), and 3(a), we report the yield curves of the desorption of halogen neutral atoms measured at different temperatures from KI, RbI, and KBr, respectively. In Figs. 1(b), 2(b), and 3(b) the absorption spectra of each material, at room temperature, are reported for comparison. The curves were obtained by digitizing the spectra published earlier by several authors.[12–14]

The KI data are an extension in the VUV of the yield of desorbed iodine presented in previous papers,[15,16] whereas the halogen desorption results from RbI and KBr are presented for the first time, to our knowledge. The insets of Figs. 1(a), 2(a), and 3(a) show the behavior of the desorption yield at the first stages of the absorption spectrum of the compound. The desorption yield spectra have been measured in three photon-energy regions using different optical filters (SiO_2, LiF, and void) in order to avoid the influence of higher-orders transmission of the monochromator. The curves shown in Figs. 1(a), 2(a), and 3(a) were obtained by joining the yield spectra from each photon energy interval. The discontinuity present at about 11–12 eV in the reported spectra is due to the lack of excitation intensity related to the drop of the grating efficiency[11] that reduces the detected signal down to zero, and consequently increases the average noise in the yield spectrum [see, for instance, Fig. 1(a)].

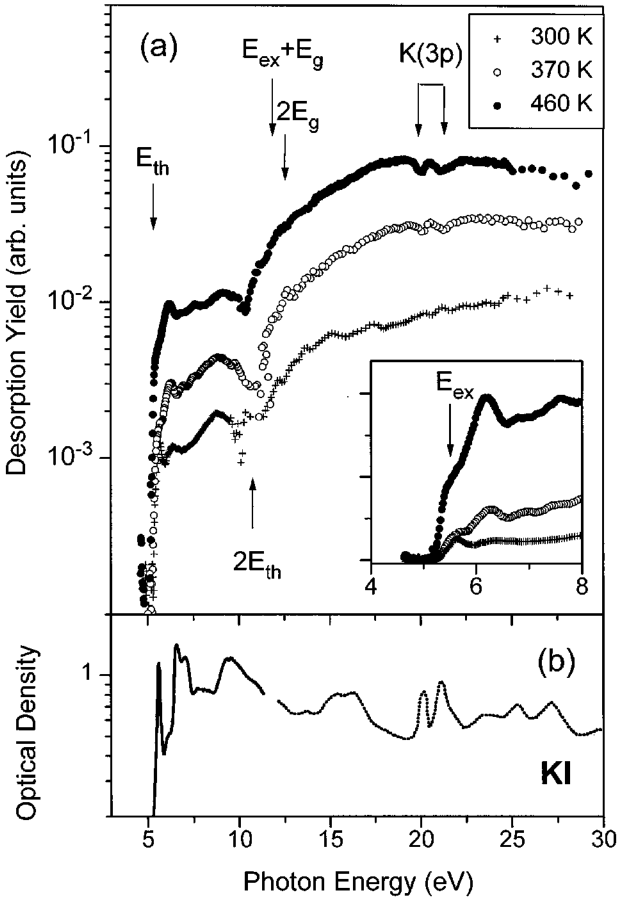

FIG. 1. (a) Desorption yield spectra as a function of photon energy of neutral iodine emission from the KI surface measured at different sample temperatures. The arrows mark the threshold energies for electron-electron scattering given in Table I, as well as the position of the K^+ $3p$ core excitons. The inset shows on a linear scale the desorption yield in the threshold region. The arrow shows the position of the first exciton. (b) Absorption spectrum of KI measured at room temperature, digitized from Refs. 12 (solid line) and 14 (dashed line).

A. KI

The spectral behavior of halogen emission from KI samples in the photon energy interval between 5 and 10 eV has been investigated in previous papers.[15,16] Present data, taken in the same photon energy interval, were measured with better resolution, reducing the excitation bandpass. Figure 1(a) reports the yield of iodine emission in the spectral range between the absorption threshold and 30 eV. The general shape of the yield curves is almost independent of the sample temperature, displaying a nearly uniform increase in intensity. The spectra show a steep desorption threshold at the onset of the optical absorption, at about 5.4 eV, followed by an almost exponential growth of the yield up to 10 eV and, after enhancement in the region between 10 and 18 eV, the yield saturates to a constant value. Superimposed on this smooth behavior there are several temperature-dependent fine structures: the first group appears in the photon-energy

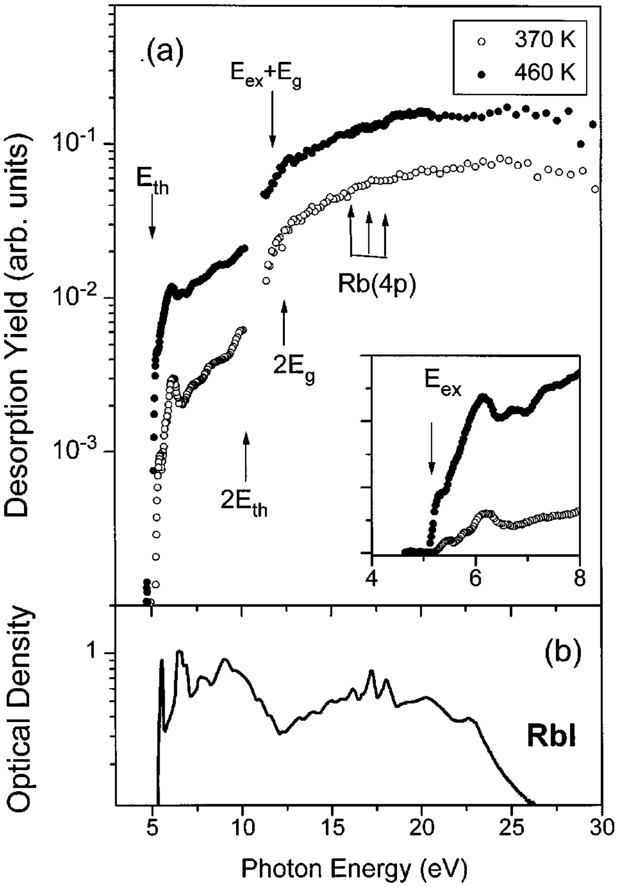

FIG. 2. (a) Desorption yield spectra as a function of photon energy of neutral iodine emission from the RbI surface measured at different sample temperatures. The arrows mark the threshold energies for electron-electron scattering given in Table I, as well as the position of the Rb^+ $4p$ core excitons. The inset shows on a linear scale the desorption yield in the threshold region. The arrow shows the position of the first exciton. (b) Absorption spectrum of RbI measured at room temperature, digitized from Ref. 13.

range of the fundamental exciton absorption peak and band-to-band transition threshold (5–7 eV). This group of features is characterized by the presence of a peak centered at 5.61 eV at 300 K, which becomes a shoulder with increasing sample temperature and shifts toward lower photon energy (about 5.5 eV at 460 K). A second structure, whose maximum is observed at about 6.2 eV at 460 K, becomes more evident with increasing temperature. The second group of features appears in the excitation region of the K^+ $3p$ core levels.[17] It consists of two dips whose minima are at 20.05 and 21.3 eV, which become better defined at higher temperature.

B. RbI

Rubidium iodide yield spectra show almost the same behavior as those of KI, with a steplike shape at the onset of the optical absorption, followed by an exponential growth up to 10 eV, where a steplike increase in the yield intensity, between 10 and 13 eV, takes place. Above 13 eV, the shape of the yield spectra goes toward a saturation value. Similar to KI, the temperature variation influences only the signal intensity, while the overall shape of the yield is unaffected. In contrast, a temperature-dependent behavior is observed for the fine structures present in the first 3 eV above threshold. The spectra at 370 and 460 K show shoulders positioned at about 5.3 and 5.5 eV, respectively, and a maximum at 6.15 eV whose intensity increases with temperature. At higher photon energies no features are observed in the RbI spectra passing through the region of the Rb^+ $4p$ core-level excitations.[18]

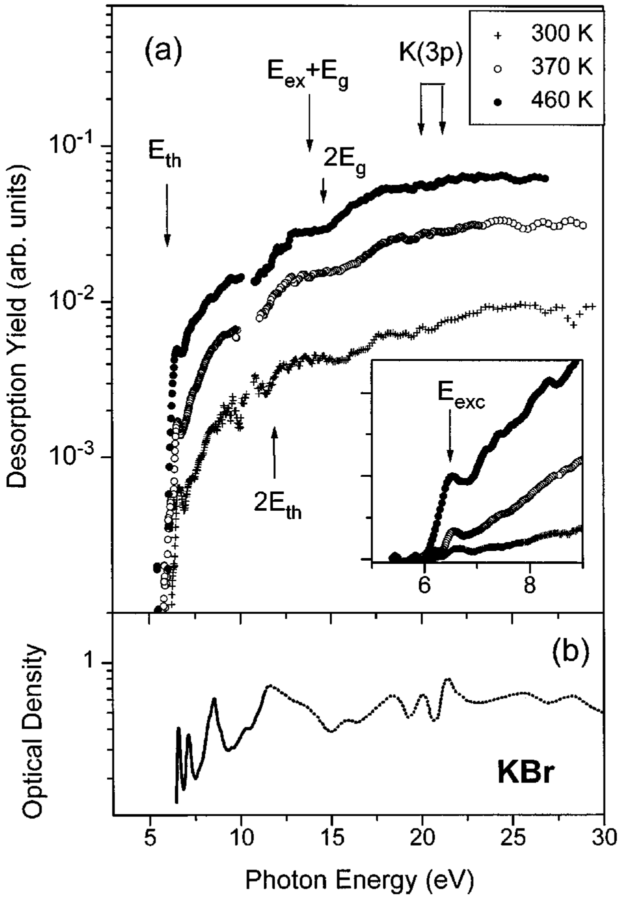

FIG. 3. (a) Desorption yield spectra as a function of photon energy of neutral bromine emission from the KBr surface measured at different sample temperatures. The arrows mark the threshold energies for electron-electron scattering given in Table I, as well as the position of the K^+ $3p$ core excitons. The inset shows on a linear scale the desorption yield in the threshold region. The arrow shows the position of the first exciton. (b) Absorption spectrum of KBr measured at room temperature, digitized from Refs. 12 (solid line) and 14 (dashed line).

C. KBr

The general trend of the bromine desorption yield from KBr follows the smooth behavior of the other alkali halide spectra. The desorption process shows its onset as soon as the optical absorption takes place at about 6.0 eV. A peak appears in the region of the first exciton absorption feature showing a maximum at 6.55 eV at 300 K, which moves toward lower photon energy (6.50 eV at 460 K), and becomes more evident as the sample temperature increases. With increasing photon energy, the yield grows almost exponentially and seems to approach a saturation value before

10 eV. A second steplike increase starts at about 12 eV, reaching a new saturation value by 15 eV, where a third growth of the desorption signal appears and, after a less marked enhancement at about 20 eV, saturates by 30 eV. The temperature dependence of the bromine yield results only in a uniform increase of the detected signal, without significant spectral dependence. At the measured sample temperatures, no evident features appear across the photon-energy region at which the absorption structures originating from the K^+ $3p$ core levels[17] take place.

IV. DISCUSSION

A. General shape of the spectra

The spectral dependence of the yield curves shows a behavior common to all three measured compounds.

(a) The energy threshold for desorption of halogen atoms is determined by the onset of the optical absorption. As previously reported for KI,[15,16] halogen desorption yield shows a direct correlation with the first exciton absorption feature as witnessed by the structure (peak or shoulder) observed for all the investigated compounds. The energy position and temperature dependence of this feature are in excellent agreement with those reported in the literature for excitonic absorption[12,19] and with the structures of the reflected light monitored during the experiment. This result clearly demonstrates that one of the origins of the desorption process in alkali halides is the decay of the fundamental exciton that is known to occur through the production of F and H centers, which are considered precursor states for alkali and halogen desorption, respectively.[10,20]

(b) At higher photon energy, corresponding to the interband transitions region and to the first core-level excitation, the yield spectra of halogen emission is almost independent of the variation of the absorption coefficient of alkali halides, as is evident by comparing the absorption and yield curves in Figs. 1–3. Let us assume a three-step model for the photon stimulated desorption process.[16]

(i) An incident photon is absorbed by the crystal. Depending on the photon energy this process will create either a bound exciton state or a free electron-free hole pair, at different depths from the surface.

(ii) The excitation is relaxed and transported to the surface. This step could follow different paths. For example, the excitation is transferred to the surface, where it decays into the precursor state for desorption, or the excited state first decays into F and H centers, which independently reach the surface.

(iii) An atom is emitted from the surface.

It is reasonable that step (iii) is not dependent on the incident photon energy. If we also assume that step (ii) does not depend on photon energy, the photon-energy dependence of the desorption yield enters through absorption coefficient involved in step (i). If the mean free path of excited states is smaller than the penetration depth of the absorbed radiation, the photon-stimulated desorption yield spectra should resemble the absorption coefficient spectrum. We do not observe any correspondence between absorption and photon-stimulated desorption yield spectra, except for the exciton structure. This lack of resemblance could be accounted for by a mean free path of the precursor state for halogen desorption greater than the penetration depth of the exciting photons.

TABLE I. Computed threshold energies for several electron-electron scattering processes in KI, RbI, and KBr. E_{th} is the energy of the desorption yield threshold measured in the present paper, E_{ex} is the energy position of the exciton absorption maximum, and E_g is the threshold energy for the band-to-band absorption. All the reported energies are given for 300-K measurements. The values of E_{ex} and E_g are taken from published optical spectra (Refs. 12 and 19).

	KI	RbI	KBr
$2E_{\mathrm{th}}$	10.8 eV	10.2 eV	12.0 eV
$(E_{\mathrm{ex}}+E_g)$	11.8 eV	11.7 eV	13.8 eV
$2E_g$	12.5 eV	12.4 eV	14.6 eV
$3E_g$	18.75 eV	18.6 eV	21.9 eV

(c) The steplike shape of the spectra suggests analogies with the results obtained in the case of the intrinsic luminescence of alkali halides excited in the UV and VUV spectral regions,[21–23] and is closely related to the total yield photoemission[24,25] measurements. The process accounting for this spectral dependence of desorption is the inelastic electron-electron scattering that, at selected thresholds for the electron kinetic energies inside the crystal, is able to enhance the number of electron-hole pairs in the sample. This process occurs only when the kinetic energy of an excited electron exceeds the value of the energy gap E_g of the crystal. In such a case the excited energetic electron may inelastically scatter with the valence electrons producing additional electron-hole pairs with a consequent multiplication of the excited quanta inside the crystal. This multiplication has been observed as an enhancement in the yield of the intrinsic luminescence,[22,23] and as a reduction of the photoemitted electrons in total yield spectra.[24,25] When increasing the photon energy, the excited electrons gain enough kinetic energy to start a series of scattering processes at values $2E_{\mathrm{th}}$ $(E_{\mathrm{ex}}+E_g)$ and $2E_g$, where E_{th} is the photon energy of the desorption yield onset and E_{ex} the photon energy at which the exciton absorption peak occurs. These threshold energies are summarized in Table I. In the yield spectra of KI and RbI the steplike increase of iodine emission takes place for photon energies $E_p>10$ eV, in agreement with the expected value for $2E_{\mathrm{th}}$, and saturates at photon energy $E_p>2E_g$ without any further increase to ascribe to the presence of additional electron-electron scattering thresholds. This is probably due to the small energy separation of the three thresholds in comparison with their widths, producing an unresolved growth in the measured spectra. This is not the case for KBr, which shows a double step in the bromine desorption yield between 12 and 20 eV. The expected threshold energies reported in Table I should be compared with the positions of the two enhancements in the yield spectra at 11.5 and 14.6 eV. The lack of an increase of the desorption signal at 13.8 eV could be attributed to spectral overlapping between the $(E_{\mathrm{ex}}+E_g)$ and $2E_g$ thresholds and/or to a relevant difference in the probability of the two scattering events. A further increase in the halogen yield of KBr is observed at about 20 eV, as shown in Fig. 4, which could be

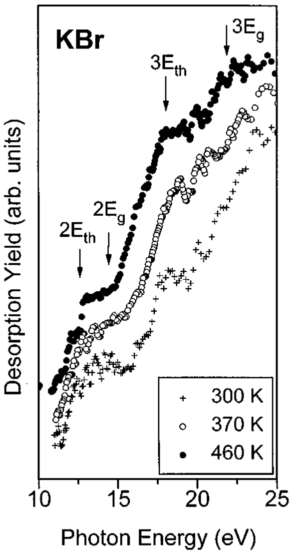

FIG. 4. Photon-stimulated desorption yield spectra of neutral bromine emission from the KBr surface measured at different sample temperatures. The data are plotted on a linear scale in the energy region of electron-electron scattering processes. The curves are normalized to each maximum intensity and shifted downward for clarity.

attributed to the contribution of multiple scattering processes leading to the production of three holes in the valence band. These multiple scattering events (i.e., $E_p = 3E_g$) are expected to be less efficient with respect to the single scattering process, because multiple scattering is only one of the possible scattering events accessible for the excited electron. The same high-energy threshold is not observed in both KI and RbI.

(d) In the lowest photon energy region, $E_{\rm ex} < E_p < 2E_{\rm th}$, no scattering events are expected. This region is characterized by an exponential increase of the desorption yield in all measured compounds. The absorption process in this photon-energy range produces holes in the valence bands with different kinetic energies. Holes at the top of the valence bands may become self-trapped in subpicosecond times[10] without moving. For $E_p > E_g$, holes can be generated deeper in the valence bands, with an extra amount of kinetic energy. This may result in an increasing mean free path for free holes and a consequent growing probability for bulk excitations to reach the surface, accounting for the measured exponential increase of the desorption yield.

(e) The temperature dependence of neutral halogen desorption from KI, KBr, and RbI results in a uniform increase of the number of emitted particles as the temperature increases. This is due to the enhancement of diffusion rates of excitations and to thermal activation of desorption at the surface. It has been shown that, at low temperature, the excitation of alkali halides produces alkali-metal enrichment of the surface[26–28] which results in island formation. The evaporation of the excess potassium and rubidium, occurring at about 360 K, may cause an additional increase in halogen-desorbed intensity due to the increase of the fraction of surface free from alkali-metal clusters. All these processes should not depend on photon energy, as observed.

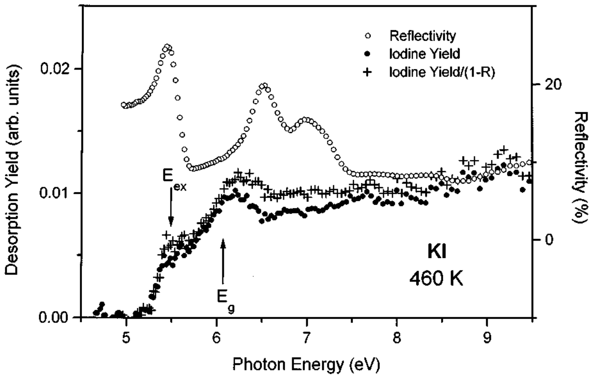

FIG. 5. Comparison between the desorption yield spectrum of iodine and the reflectivity spectrum measured simultaneously from KI at 460 K in the region of excitonic absorption. The picture reports the yield spectra obtained after normalizing the measured spectrum to the incident photon intensity (full dots) and to the estimated absorbed photon intensity (crosses). The arrows mark the position of the first exciton and the band-gap energy.

B. Fine structure of the yield spectra

Although the general behavior of the halogen desorption yield is poorly correlated with the absorption structures, some small features in the desorption yield curves of the investigated compounds show a correspondence with the optical spectra. This evidence has been found by comparing the halogen desorption yield with the simultaneously measured optical reflectivity, in the spectral region below 10 eV, as reported in Fig. 5 for KI at 460 K. Figure 5 also shows the yield spectrum corrected by the factor $(1-R)$, where R is the reflectivity coefficient, for normalizing the yield to the absorbed intensity instead of the incident intensity. This correction does not modify the shape of the spectrum substantially.

After the first structure, correlated with the first exciton absorption peak, only the yield spectra of KI and RbI show some features in the region where interband transitions and higher exciton excitations occur. The observed structures are temperature dependent, and appear as maxima, positioned at 6.2 and 6.15 eV for KI and RbI, respectively, followed by a double dip positioned in correspondence of the higher exciton excitations. The dips become more evident as the temperature increases. In order to explain the observed behavior, the relative intensities of the desorption yield should be examined in comparison with the nature of the absorption processes in this spectral region. For KI the ratio between the desorption yield intensity measured in the band-to-band transition region, and that measured at the first excitonic peak, is more than doubled in going from 300 to 460 K. The same effect is observed in RbI for the two measured temperatures. This growth of the intensity ratio appears while the depth of the two dips in the higher exciton absorption region becomes more pronounced. Because of the close quantum-mechanical analogy among the fundamental Γ exciton, its spin-orbit partner, and the X excitons, similar desorption rates are expected from their creation. In the photon absorption process, the higher exciton excitations are degenerate with the band-to-band transitions, thus reducing the fraction of photons absorbed in the latter channel. Since at low temperature the desorption yields of the two processes are comparable with each other, the total yield spectrum should be almost structureless. Instead, as the temperature increases, the desorption yield values connected with the two processes become very different, so that the higher exciton absorption features may induce a reduction of the total emitted halogen atoms with a consequent manifestation of dips in the yield spectrum. This process seems to stand for KI and RbI excitation but not for KBr, where, instead, a strong excitonic desorption efficiency is always present for all the investigated temperatures.

The substantial equivalence of the desorption yield intensities, at 300 K, when exciting the first exciton peak and the band-to-band transitions, is unexpected when considering a diffusive mechanism for transferring excitations from the bulk to the surface before desorption. The penetration depth of the light increases from 200 Å at the exciton energy, to 1000 Å at a band-to-band transition energy close to E_g. The large variation of the excitation volume for the two spectral regions suggests that similar values of the desorption yield intensities could be accounted for by either considering different values of the mean free path for excitation transport or, for both excitations, a mean free path longer than the longest penetration depth of the radiation. The latter could be excluded by analyzing the spectroscopic behavior of the desorption yield, which suggests the existence of two different mean free paths for the excitations originating from the fundamental exciton absorption and the band-to-band transitions. In fact, the poor resemblance of the desorption yield with the absorption spectrum for the analyzed compounds could be a consequence of the excitation mean free path being longer than the penetration of light. Instead, the behavior of the desorption spectrum at the first excitonic structure, whose shape follows the shape of the absorption band, suggests an exciton mean free path shorter than the penetration of the exciting radiation. The formation of excitons implies a sudden localization of the excitation energy via exciton self-trapping, which then decays through F-H pair creation, whereas band-to-band transitions produce free holes with enough kinetic energy to travel several hundreds of angstroms before becoming self-trapped,[29] capture an electron, and decay through F-H pair creation. The second mechanism could efficiently collect self-trapped holes very close to the surface. The H center created by the decay of either the self-trapped hole or the self-trapped exciton, reaching the crystal surface, should produce the proper conditions for the desorption of a halogen atom. An upper limit of about 100 Å for the mean free path of the H center effective for desorption could be estimated for KI and RbI, considering the penetration depth of the radiation at the exciton absorption peak.

Further fine structures are strongly evident only in the KI desorption yield. Well-defined dips appear at 20.2 and 21.1 eV, energies of the absorption maxima related to the K^+3p core excitons.[17] Also, luminescence excitation spectra measured on these compounds show similar dips.[21–23] In the case of alkali-atom desorption from alkali halide surfaces measured at energies suitable for core exciton excitations, neutral alkali atoms have been detected both in their ground state,[30] and in the excited state.[31,32] In both cases the maxima of the alkali-atom desorption spectra are set in positive correlation with inner-shell absorption structures.

This observed behavior for iodine emission cannot be explained by the reduction of the absorbed intensity due to reflectivity enhancement because, in this photon-energy region, the average value for reflectivity is of the order of a few percent increasing up to 5–8 % at the core exciton absorption maxima.[17] Core exciton transitions fall in the region where $E_p > 2E_g$ and the desorption yield is mainly influenced by electron-electron scattering processes. At the photon energies suitable for core-level transitions, a competition between high-energy valence-band excitation and core-exciton absorption takes place. While valence-band excitations directly produce energetic electrons, core exciton excitations produce energetic electrons through the decay processes such as direct recombination or Auger decay.[24,25] The high efficiency of these decay processes is shown by the presence of prominent peaks in the total photoelectron yield at photon energies where core excitons occur.[24,25] Attempts to determine the nature of the decay mechanism have brought only qualitative answers, showing that the specific decay process depends on the detail of the electronic structure of the crystal.[25,33,34] If the decay of a core exciton produces electrons with not enough kinetic energy for undertaking a scattering sequence, a reduction of the desorption yield should be observed. Further investigations on the mechanisms which determine the presence of core-exciton-correlated dips in the desorption and luminescence yield are needed.

V. CONCLUSIONS

The photon-stimulated desorption study performed on KI, RbI, and KBr in the UV and VUV spectral regions showed that the onset of the desorption yield spectra of halogen atoms can be correlated with the formation of the first exciton in its lowest excited state. A close relationship between absorption spectra and desorption yield spectra has not been found for exciting photon energies above E_g, suggesting that the transport of excitation toward the surface, whose decay is responsible for halogen desorption, have a mean free path longer than the penetration depth of the light. The overall behavior of the yield is determined by inelastic electron-electron scattering processes, producing a strong enhancement of the desorption efficiency at selected thresholds. Further investigations are needed in order to explain the nature of the fine structures which appear in the desorption yield spectra, and seem to be closely related to the details of the electronic configuration of each compound.

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