

Evidence for a surface exciton in KBr via laser desorption

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We demonstrate that direct photoexcitation of the single crystal KBr surface leads to desorption of hyperthermal neutral bromine atoms. We have produced *separately* the hyperthermal and the near-thermal components of neutral halogen emission from an alkali halide. The source of hyperthermal bromine emission is attributed to decay of a surface exciton excited at photon energies below that of the bulk exciton. We argue that the frequently observed near-thermal component is derived from excitation within the bulk crystal. Our experimental data provide strong support to a theoretical excitonic emission model previously described in the literature.

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INTRODUCTION

Emission of atoms induced by irradiation of alkali halides has been an ongoing topic of general interest. For decades, rigorous studies of halogen emission have been carried out using electron, synchrotron, ion, and laser sources.¹⁻⁶ The observed energy distribution of emitted halogen atoms has two components: a fast “hyperthermal” component for which the most probable kinetic energy is 0.3 eV and a “near-thermal” component characterized by a Maxwellian distribution of energies of emitted atoms.^{7,8} To date, these two components of halogen emission have only been observed together. The linear dependence of the number of emitted atoms on the number of excitations indicates that a single excitation, namely, formation of an exciton or an electron-hole pair leads to emission. The emission mechanism following single excitation, however, remains controversial. In all the cases, it has been claimed that the threshold of desorption is at the absorption threshold and not below it.⁹

It is well established that excitons or electron-hole pairs in bulk alkali halides are localized by interaction with phonons or recombine to form self-trapped excitons (STE's).¹⁰ According to the currently accepted model, the STE consists of an electron and an off-centered X_2^- molecular ion (where X denotes a halogen atom) occupying two lattice sites. Further displacement of the X_2^- molecular ion along the molecular axis transforms the self-trapped exciton into an F -center and H -center pair (the H center is the X_2^- molecular ion centered at a halogen lattice point). Recent calculations of the unrelaxed bulk exciton and STE in KBr reaffirm this picture.¹¹

An early model published by Pooley predicted halogen emission along the $\langle 110 \rangle$ axis caused by the phonon-mediated migration of excited STE's through halogen lattice sites.¹² Subsequent angle-resolved electron-stimulated desorption (ESD) experiments conducted by Szymonski *et al.* showed emission occurring strongly along the $\langle 100 \rangle$ axis, not the $\langle 110 \rangle$ direction and the authors proposed “hot” hole migration to the surface as the source of neutral halogen emission.¹³ However, the inability of the hot-hole model to explain satisfactorily the mechanism for hyperthermal emission led to additional ESD experiments.¹⁴ A different scheme was put forward in which the near-thermal component of

halogen emission was attributed to the H -center migration/displacement sequence while the source of the hyperthermal component was proposed to be hot, unrelaxed exciton migration to the surface.¹⁴ This has become an accepted mechanism.

In this hot-carrier model, excited electron-hole pairs are created within the bulk penetration depth of the ESD electrons followed by rapid hot-carrier diffusion to the surface where hyperthermal emission occurs. In an apparent confirmation of this mechanism and the bulk nature of the hyperthermal component, subsequent low fluence photostimulated desorption experiments failed to produce hyperthermal emission.¹⁵ This result was explained by stating that at photon energies corresponding to fundamental exciton absorption, the resulting primary excitons would be static and that moreover, even if the excitons are created directly at the surface they would not contribute to desorption since only singlet excitons are created directly by light.

While this previous groundbreaking work was unable to detect photoemission, we observe hyperthermal neutral Br photoemission using low-fluence sub-band-gap photoexcitation combined with a highly sensitive resonant-enhanced multiphoton ionization (REMPI) time-flight mass spectrometry (TOF-MS) technique. Sub-band-gap excitation can produce surface excitons directly. Excitons or electron-hole pairs formed near the surface can lead directly to neutral halogen emission. Calculations of the first excited states (unrelaxed excitons) of NaCl show the surface excitation energy significantly below the bulk threshold due to lower coordination of the halogen and exciton localization on the surface ion.¹⁶ The relaxation process of a surface exciton can be different from that in the bulk as the surface exciton may self-trap and decompose into an F center and a neutral halogen, a scenario not predicted in the hot carrier model. In this “excitonic” model for NaCl, excitons at or within three layers of the surface trap and produce hyperthermal halogen emission.^{16,17}

Few experiments showing evidence for a unique surface exciton, or even direct surface excitation, in alkali halides have been reported; the recent experiments on KI being notable.¹⁸ However, ESD threshold experiments on alkali ha-

lides, while demonstrating the efficiency of above band-gap bulk excitations in halogen desorption, lack the resolution and sensitivity to probe excitation of the surface at energies below the absorption band threshold.

Spin-orbit interaction in KBr leads to a distinct doublet at 6.63 and 7.17 eV in the absorption spectrum of the bulk single crystal that has been assigned to the $p^5\gamma_1$ single exciton transition (p^5 hole; $\Gamma'_4-\Gamma_1$).¹⁹ We probe below and above the first bulk exciton absorption band of KBr using very low fluence laser irradiation. We show that by selecting the appropriate photon energy we may produce *separately* the hyperthermal or near-thermal components of neutral bromine emission. We have resolved the bromine velocity distributions and power dependences at photon energies of 3.5, 4.7, 6.4, and 7.9 eV and have avoided macroscopic crystal edge effects (common in ESD experiments) by maintaining high spatial resolution of our laser light on the sample surface. Our results indicate direct surface excitation—the unrelaxed surface exciton—as the source of the hyperthermal emission.

EXPERIMENT

The ultrahigh vacuum apparatus (UHV) and data treatment utilized in these experiments are described in detail previously.²⁰ Briefly, freshly cleaved single crystals of KBr are mounted in the UHV sample holder. Laser pulses of 3- or 5-ns duration are generated using excimer or Nd:YAG (yttrium aluminum garnet) laser sources, respectively. Laser light is directed at the KBr sample at 60° angle of incidence to the surface normal. The laser pulses induce desorption of neutral bromine and potassium atoms. A focussed probe laser pulse intersects the desorbed atoms 3.8 mm above and parallel to the sample surface. Tunable light of 5-ns pulse duration from a frequency-doubled dye laser at 250.98 nm is used to ionize ground state ($^2P_{3/2}$) bromine atoms in a (2 + 1) REMPI scheme. The probe laser also nonresonantly ionizes neutral ground state ($^2S_{1/2}$) potassium atoms. Ions are detected by dual microchannel plates located at the end of the TOF-MS tube. The lasers can be independently delayed in time allowing the measurement of photoproduct velocity distributions.

We irradiate the KBr surface at fluences that will maintain a desorption regime; that is, each laser pulse desorbs only a small fraction of the surface layer. For example, a laser fluence of 10 $\mu\text{J}/\text{cm}^2$ at 6.4 eV (193 nm) represents a flux of 10^{13} photons over $\sim 10^{15}$ surface sites or approximately 1% coverage. Absorption will occur at far fewer surface sites because even a strong resonant transition will absorb less than 1% of incident light per layer. From these estimates the greatest possible fraction of the surface desorbed per laser pulse is 10^{-4} . The fraction desorbed per pulse is further reduced when a realistic surface absorption cross section and desorption quantum yield are included in the estimate. Therefore, each laser pulse produces a low-density emission. The laser fluence required to obtain a detectable signal depends strongly upon the photon energy. The fluence ranges used in this study are 0.1–10 $\mu\text{J}/\text{cm}^2$ at 6.4 eV, approxi-

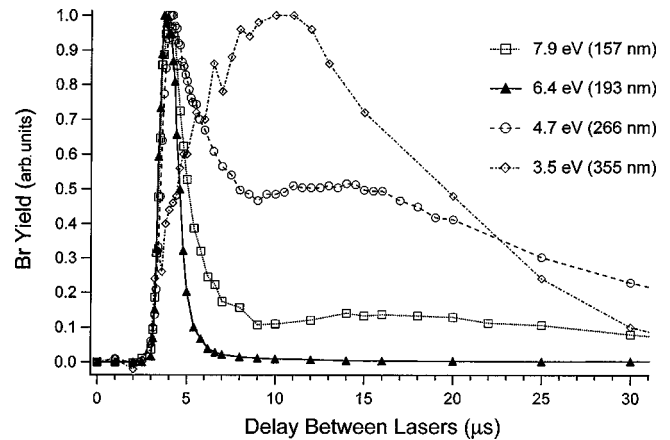


FIG. 1. Velocity distributions of Br atom emission. The integrated Br ion signal is plotted as a function of the delay time between the excitation and probe laser pulses. Legend: \square , 7.9 eV; \blacktriangle , 6.4 eV; \circ , 4.7 eV; \diamond , 3.5 eV. Excitation at 6.4 eV produces only the hyperthermal velocity distribution. Excitation at 3.5 eV is dominated by the near-thermal velocity distribution. At 4.7 and 7.9 eV, both hyperthermal and near-thermal components are distinguishable.

mately 100 $\mu\text{J}/\text{cm}^2$ at 7.9 eV, 1.8–36 mJ/cm^2 at 4.7 eV, and 7–49 mJ/cm^2 at 3.5 eV.

We observe no change in KBr surface stoichiometry following considerable laser irradiation. We determined the relative surface concentration of potassium and bromine ions before and after 266-nm irradiation using x-ray photoelectron spectroscopy (XPS). To enhance surface selectivity, x-ray photoelectrons were collected at low emission angle. The integrated relative intensity of all bromine and potassium photoemission bands (binding energies less than 400 eV) remained constant throughout total irradiation fluxes up to ten times that used in laser desorption experiments. The XPS experiments revealed only very minor surface contamination. The only contaminant observed was due to carbon at levels slightly above the detection threshold corresponding to a 1% surface coverage. Although ultraviolet irradiation of insulating materials can lead to moderate surface charging due to photoemission, such charging is unlikely to affect measurements of neutral atom velocities and we observe no evidence of space or surface charging effects in our experiments.

RESULTS

Figure 1 displays the normalized, velocity distributions of Br ($^2P_{3/2}$) following excitation at 6.4, 7.9, 4.7, and 3.5 eV. Excitation at 6.4 eV, below the bulk exciton absorption band, produces a single well-defined hyperthermal velocity component. Above both the bulk exciton band and the material bandgap, at 7.9 eV, two distinct velocity components are observed; a near-thermal velocity component and the hyperthermal component. Well below the absorption threshold, at 4.7 eV, both hyperthermal and near-thermal components are again observed. Finally, far below the absorption threshold, at 3.5 eV, the near-thermal component dominates.

To obtain kinetic-energy distributions from the raw data,

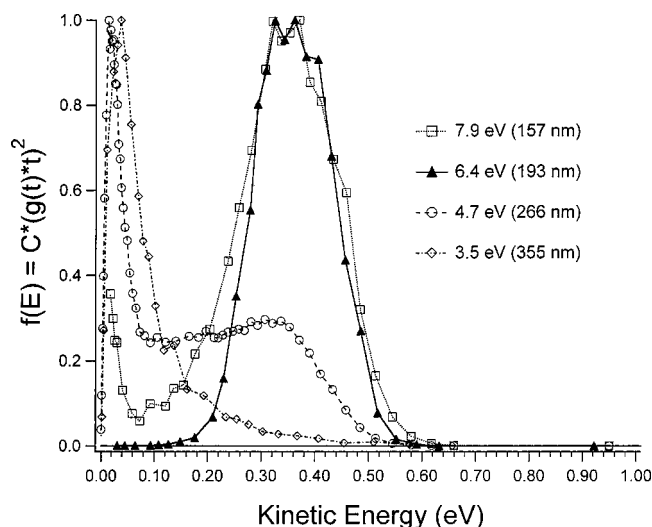


FIG. 2. Energy distributions of Br atom emission. The time-of-flight signal response function $g(t)$, represented in Fig. 1 as the peak area, is transformed from time to energy space and normalized. This function $f(E)$ is plotted against the measured kinetic energy of Br photoproducts. Legend: \square , 7.9 eV; \blacktriangle , 6.4 eV; \circ , 4.7 eV; \diamond , 3.5 eV. For all excitation energies excepting 6.4 eV, a near-thermal energy distribution centered at 0.03 eV is identifiable. A hyperthermal energy distribution centered at 0.35 eV is observed at all excitation energies except 3.5 eV.

the time-of-flight signal response function $g(t)$, represented in Fig. 1, is transformed from time to velocity space through the Jacobian for density-sensitive detection ($1/t$). Conversion gives the energy distribution $f(E) = C*[g(t)*t]^2$, where C is the normalization constant.²¹ This function is plotted versus Br atom kinetic energy in Fig. 2. From the data it is clear that there are two distinct distributions, a hyperthermal energy distribution centered at 0.35 eV and a near-thermal-energy distribution centered at 0.03 eV.

Excimer laser excitation of KBr at 6.4 eV leads to hyperthermal Br atom emission exclusively. Figure 3 displays a log-log plot of the integrated Br atom yield as a function of laser fluence at 6.4 eV. The power dependence is linear and indicates a single-photon process for Br emission. The

single-photon fluence dependence and the detection of Br atom emission at extremely low laser fluence (~ 100 nJ/cm²) indicates resonant absorption. Bulk absorption of 6.4 eV photons is weak. Therefore, Br emission must result from either excitation of surface states or defect states within the near surface region of the bulk. It is unlikely that the density of defect states is large enough to produce the large observed Br yields, therefore, the emission most likely results from direct absorption at the surface. Therefore we argue that the hyperthermal component originates from surface excitation.

Excitation above the bulk band gap at 7.9 eV produces both hyperthermal and near-thermal velocity components. At this energy, both bulk and surface excitations may occur. A cursory power dependence performed at 7.9 eV is linear and indicates that the excitation is single photon although the difficulties associated with laser power measurement in the vacuum ultraviolet makes a rigorous power-dependence determination problematic. Strong Br atom emission is again obtained using extremely low laser fluences. However, laser fluences an order of magnitude greater are required at 7.9 eV than at 6.4 eV to obtain an equivalent Br atom yield. This indicates that 7.9 eV photons must have a lower surface absorption cross section than 6.4 eV photons.

Photons at 7.9 eV can directly lead to both surface and bulk excitations. We have identified the hyperthermal component with surface excitation. It is likely that bulk excitation would lead to a much more thermalized distribution as the excitation may travel many atomic layers before reaching the surface and desorbing. Therefore, we argue that the near-thermal Br velocity component originates from bulk excitation.

Surprisingly, excitation at 4.7 eV, well below the absorption threshold, leads to strong Br emission but only at a much higher laser fluence. To obtain similar Br atom yields, laser fluences approximately 1000 times greater than that at 6.4 eV and 100 times greater than that at 7.9 eV are required. At 4.7 eV, no direct excitation of the perfect bulk or surface is expected although it is possible that multiphoton excitation or direct excitation of defect states can occur. The integrated Br atom yield as a function of laser fluence displays a non-linear power dependence that is always greater than single

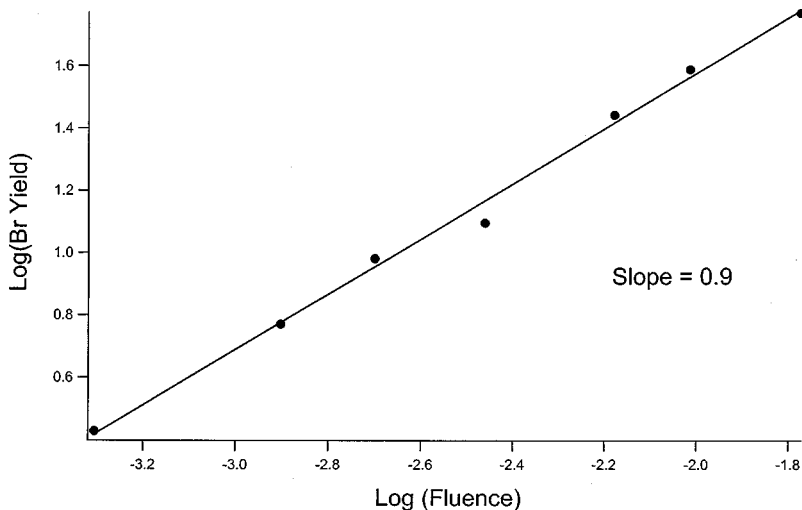


FIG. 3. Power dependence of Br atom emission at 6.4 eV. Log-Log plots of the integrated Br ion signal as a function of laser fluence indicate a single photon power dependence for Br-atom emission at 6.4 eV.

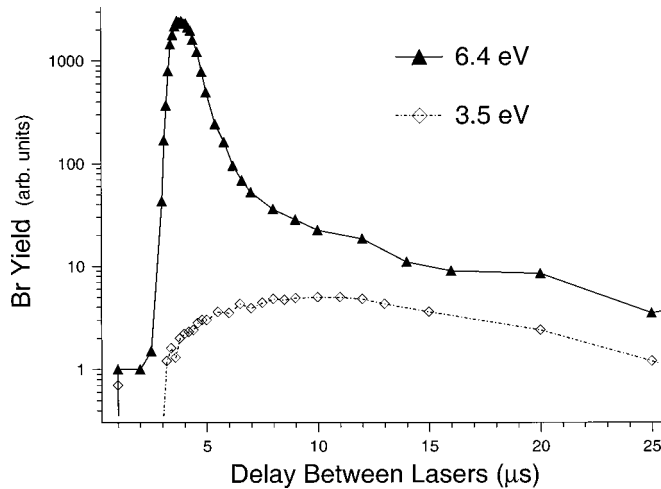


FIG. 4. Comparison of neutral Br atom yield at 6.4 and 3.5 eV. A logarithmic plot of neutral Br yield as a function of delay time between excitation and probe laser pulses for 6.4 and 3.5 eV is shown. For these data sets, the fluence at 6.4 eV was 100 nJ/cm^2 and at 3.5 eV the fluence was 10 mJ/cm^2 . The neutral bromine-atom yield is nearly three orders of magnitude greater at 6.4 eV than at 3.5 eV despite using a laser fluence five orders of magnitude smaller.

photon. Both hyperthermal and near-thermal velocity components are observed. The hyperthermal component shows a $P^{1.3}$ power dependence while the near-thermal component displays a $P^{1.7}$ dependence. Noninteger values for power dependences may arise from a number of sources. For example, at 4.7 eV, multiple absorption processes with different absorption cross sections may lead to Br emission and account for the noninteger power dependence. Alternatively, at the moderate fluences used in the 4.7 eV experiments, laser saturation effects can also lead to noninteger values.

Excitation at 3.5 eV, approximately 3 eV below the ab-

sorption threshold, produces measurable Br emission provided sufficiently high laser fluence is used. At this energy no significant direct excitation should occur in the bulk, at the surface, or at defect sites and only multiphoton excitation is expected. Only the thermal Br velocity component is significant at 3.5 eV indicating absorption occurs by a multiphoton process largely within the bulk. The power dependence measurement yields a highly nonlinear result of $P^{2.5}$. To emphasize the differences between resonant and nonresonant excitation regimes, the bromine atom yield following 6.4 and 3.5 eV excitation is displayed in Fig. 4. The neutral Br yield is nearly three orders of magnitude greater at 6.4 eV than at 3.5 eV despite a laser fluence five orders of magnitude smaller. This indicates a surface resonance at or near 6.4 eV.

In addition, we also observe thermalized neutral potassium emission following laser excitation. Potassium emission is required to maintain surface stoichiometry as observed in the XPS studies. In Fig. 5, we directly compare K and Br photoemission velocity distributions. The normalized areas of the simultaneously recorded K and Br ion signals are plotted as a function of the delay time between the excitation and probe laser pulses. The inset displays time-of-flight mass spectra of neutral potassium and bromine atoms following laser ionization. The spectra are recorded at three different laser delays to illustrate the unique K and Br velocity distributions. The natural isotopic abundances expected for potassium and bromine are also evident.

DISCUSSION

A directly excited surface exciton can lead to desorption of a hyperthermal neutral halogen atom.¹⁶ The theoretical calculations of the lowest energy unrelaxed exciton in NaCl derived in the ‘excitonic’ model suggest a configurational difference between the bulk exciton ($\text{Cl}_2^- + e^-$) and the sur-

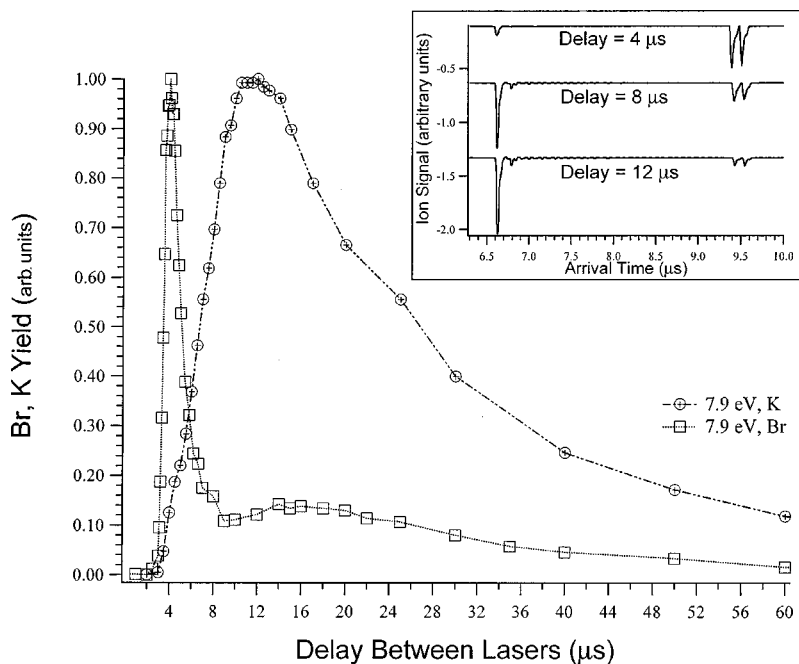


FIG. 5. Comparison of K and Br emission velocities. The normalized areas of the simultaneously recorded K (\circ) and Br (\square) ion signals are plotted as a function of the delay time between the excitation and probe laser pulses. At 7.9 eV, the near-thermal velocity distribution of potassium appears to initiate coincidentally with the bromine emission. The inset displays mass spectra recorded at three laser delays. The time-of-flight spectra illustrate both the differences in emission velocities and the natural isotopic abundances expected of potassium and bromine.

face exciton ($F+Cl^0$).¹⁶ The calculations predict the excitation energy is 0.98 eV lower at the surface compared to the bulk. Preliminary calculations of the surface electronic structure in KBr indicate that 6.4 eV photons may be resonant with such a surface exciton.²²

Sub-band-gap single-photon excitation at 6.4 eV should be sufficient for excitation of the predicted surface exciton ($F+Br^0$). As we only observe a hyperthermal component at 6.4 eV with single-photon power dependence, the source for this bromine emission likely must originate through direct absorption at or very near the surface. We postulate that this is evidence for creation of a unique surface exciton as proposed by Shluger and co-workers.^{16,17}

We observe a dominant hyperthermal velocity component accompanied by a significant near-thermal component following the above gap excitation at 7.9 eV. Both velocity components arise from a linear (single-photon) absorption process. The hyperthermal component displays a kinetic-energy distribution identical (within error) to that produced by 6.4-eV excitation (Fig. 2). Therefore, the hyperthermal emissions at 7.9 and 6.4 eV seem to arise from the same surface excitonic state. Calculations on NaCl indicate that an exciton located in the second layer is also unstable and decomposes into an F center and a Cl atom desorbed into the vacuum.¹⁶ If the analogous mechanism exists for KBr then near-surface (within the top few layers) bulk absorption could contribute to hyperthermal Br emission following migration of the initially formed exciton to the surface.

The near-thermal Br velocity component generated by 7.9 eV excitation results from absorption within the bulk. Several authors have postulated that above band-gap irradiation generates bulk $F-H$ centers, which through phonon-mediated migration or coagulation near the surface lead to thermal halogen emission.¹⁰⁻¹⁵ Such initially excited bulk defect centers are largely relaxed during migration to the surface thus accounting for the near-thermal velocity distribution. That the near-thermal kinetic-energy distributions vary somewhat (Fig. 2) indicates that relaxation is not always complete at time of desorption. The desorbed atoms likely arise from a distribution of nearly relaxed H centers or aggregates leading to a distribution of emitted Br velocities.

Excitation well below the absorption threshold is not likely to produce a surface or bulk exciton in a direct single photon process. Significant linear absorption by defect species is highly unlikely at 3.5 eV. The nonlinear power dependences measured at 4.7 and 3.5 eV indicate that a multiple photon process is required for Br atom desorption. A 3.5 eV photon is almost exactly two-photon resonant with the spin-orbit split bulk exciton band. It is possible that two-photon bulk absorption is a key step in the Br emission process at 3.5 eV. The Br velocity distribution is dominated by a near-thermal component such that the 3.5 eV excitation must occur nearly entirely in the material bulk. This is consistent with the measured power dependence of $P^{2.5}$.

At 4.7 eV it is possible that near-surface defects absorb weakly leading directly to the hyperthermal Br velocity component. Specific minor crystal defects may absorb directly at 4.7 eV (e.g., a V center composed of a Br_3^- molecule), but it is unknown whether standard surface defects such as a step,

kink, or corner absorb significantly at 4.7 eV. However, one would expect a direct linear absorption and subsequent emission process to display a linear-yield power dependence. The measured power dependences are always observed to be greater than linear. In addition, far greater laser fluence is required to obtain an equivalent Br atom yield at 4.7 eV than at resonant photon energies. Together these results suggest that Br atom emission at 4.7 eV requires a multiple-photon process. The near-thermal Br velocity component displays a power dependence close to 2, again consistent with bulk two-photon excitation. Yet, the mechanism for multiple-photon halogen emission may not be a simple mechanistic modification but depend both on the degeneracies of the excitonic transition and the rates of phonon dissipation and relaxation in STE's (e.g., our near-thermal component is not identical for every wavelength).

At 7.9 eV, the near-thermal velocity distribution of potassium appears to initiate coincidentally with bromine and not as a "delayed" emission. Neutral alkali-atom emission was predicted by Puchin *et al.*,^{17,23} in a theoretical study of excited NaCl surfaces. It may be possible to extend this model to explain the observed photostimulated desorption of neutral potassium atoms from KBr.

CONCLUSION

We have excited *separately* the hyperthermal and the near-thermal velocity components of neutral halogen emission from an alkali halide. We associate the hyperthermal velocity component with the decay of a surface exciton and picture a hyperthermal emission model corresponding closely to the excitonic emission model developed for surface excited NaCl.¹⁶ The near-thermal Br atom velocity component, on the other hand, results from either single or multiphoton excitation of the bulk (depending upon photon energy). Results indicate that, well below the bulk absorption threshold at 4.7 and 3.5 eV, multiple photon processes near the surface or within the bulk lead to Br atom emission. The observation of an initial potassium emission coincident with bromine emission does not contradict the hypothesis that a primary pathway may be active for alkali metal desorption. Since such a process may occur on a picosecond timescale, future studies including femtosecond time-resolved photoemission experiments are planned to elucidate the dynamics of STE creation and decay in KBr.

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