

Control of laser desorption using tunable single pulses and pulse pairs

Wayne P. Hess^{a)} and Alan G. Joly
Pacific Northwest National Laboratory, Richland, Washington 99352

Daniel P. Gerrity
Department of Chemistry, Reed College, Portland, Oregon 97202

Kenneth M. Beck
Pacific Northwest National Laboratory, Richland, Washington 99352

Peter V. Sushko and Alexander L. Shluger^{b)}
Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom

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We desorb ground state Br and spin-orbit excited Br* atoms from KBr single crystals using single pulses and sequential pulse pairs of tunable nanosecond laser radiation. Irradiation of cleaved KBr crystals near the bulk absorption threshold produces hyperthermal Br emission without a significant thermal component, and with little spin-orbit excited Br* emission. The Br kinetic energy distribution may be controlled either by choice of photon energy or by excitation of transient defect centers created within the crystal. In this latter scheme, a first laser pulse generates transient centers within the bulk crystal and in the vicinity of the surface, and a second delayed laser pulse then excites the transient centers leading to atomic desorption. The Br* to Br yield ratio is significantly enhanced using two-pulse excitation as compared to resonant single-pulse desorption. Single and multiple pulse excitation of KBr produces Br and Br* in controllable quantities, velocities, and spin state distributions. © 2002 American Institute of Physics. [DOI: 10.1063/1.1467345]

I. INTRODUCTION

Modification of the structure and properties of insulating surfaces by electronic excitation has for a long time been largely a brute force experience. Among various other phenomena, irradiation of these materials by relatively low energy electrons, γ , X, synchrotron, and ultraviolet (UV) photons can induce surface decomposition and emission of particles in different charge and electronic states, and with different velocity distributions (see, for example, Refs. 1–9). This irradiation is mostly absorbed inside the solid and only a minor part of it is manifested in desorption. A more gentle approach is used in photoinduced desorption of individual surface atoms¹⁰ specifically targeting surface chemical bonds, and in surface-aligned photochemistry^{11,12} aiming to avoid surface excitation altogether. Recently lasers and other UV photon sources^{13–16} have also been used to selectively excite particular surface features and to study the conversion of electronic excitation energy into surface decomposition, molecular dissociation, and formation of chemically active surface sites.

An issue key to all of these processes concerns the possibility of active control of the yield and properties of produced species. As discussed in a recent review,¹⁷ in application to photostimulated desorption processes, one can consider mainly incoherent control strategies where the main control parameters could be the photon energy and fluence. There have been several successful applications of incoher-

ent control¹⁷ on metal and semiconductor surfaces. Recent experiments on laser induced desorption of alkali halides^{3,14,15,18–21} have stimulated further studies of laser control of these processes on wide gap insulators. In particular, it has been shown^{15,21} that, by carefully choosing the excitation energy, it is possible to induce preferentially one mechanism of atom desorption and achieve selectivity in both kinetic energy and electronic state of desorbing bromine atoms from KBr [either the ground state Br(²P_{3/2}), henceforth Br, or the spin-orbit excited state Br(²P_{1/2}), henceforth Br*]. It was demonstrated that the velocity and the electronic state distributions of desorbing Br atoms strongly depend on photon energy. For example, excitation at 6.4 eV, just below the bulk exciton maximum at 6.6 eV at 300 K,²² led to desorption of almost exclusively hyperthermal Br atoms with a narrow velocity distribution, whereas the excitation with 7.9 eV photons produced Br and Br* atoms in both broad thermal and narrow hyperthermal components.

Another goal of reaction control research is to achieve a better understanding of the reactive mechanism. In particular, several mechanisms of photo- and electron-stimulated desorption of alkali halides have been discussed in the literature.^{4,15,23–27} Although different in detail, all of them acknowledge the primary role of excitons initially created in these materials by both types of irradiation. According to a theoretical model developed in Refs. 15, 23, and 24, hyperthermal Br desorption is caused by decomposition of an exciton created in a very thin surface layer into a desorbed Br atom and a surface F center (neutral halogen vacancy). The thermal component of desorption results from secondary

^{a)}Author to whom correspondence should be addressed; electronic mail: wayne.hess@pnl.gov

^{b)}Electronic mail: a.shluger@ucl.ac.uk

products of decomposed excitons in a thicker region near the surface.

Therefore the observed selectivity in desorption components can be due to the preferential excitation of surface excitons. However, surface excitons are very elusive species that have not been directly observed in alkali halides. Their existence has been inferred in recent studies of photoinduced desorption from KI^{14,20} and KBr,^{15,21} energy loss of low energy protons on the LiF (001) surface,²⁸ and photochemistry of ethene on NaCl crystallites¹³ (see also the discussion in Ref. 29). The results described above suggest that photoinduced surface processes uniquely manifested in the electronic state and speed distribution of desorbing Br atoms should have different scenarios depending on whether excitons are produced directly in the top surface layers or within the bulk, several layers from the surface. If this assertion is confirmed, such differences suggest methods for controlling these surface processes.

In this paper we explore the mechanisms of laser control of solid-state photoreactions in KBr using frequency selected laser pulses and sequential pulse pairs. On the basis of our recent measurements and theoretical calculations we assume that single photons of 5.5–6.5 eV energy can selectively excite surface or near-surface excitons, leading to almost exclusive desorption of the hyperthermal Br atoms.^{15,21} Another approach exploits a pump–pump scenario widely used in coherent control experiments. Generally speaking, the second pulse can be used to excite some of the relatively long-lived transient species produced near the surface by the first pulse. This idea has been used, for example, by Tanimura and Itoh to affect the yield of Frenkel defect pairs in the bulk of KBr.³⁰ Application of this approach to controlling the yield and state distributions of desorbed species requires detailed knowledge of the structure, optical properties, and lifetimes of transient species created in the crystal by pulsed excitation.

Thus the photon energy selective approach takes advantage of energetic differences between surface and bulk exciton states and directly probes the surface exciton. The two-pulse approach relies upon production and manipulation of transient species within the crystal and near the surface. Each of these approaches can be used to control the yield and properties of desorbed Br atoms. They constitute a new solid-state source of Br and Br* atoms for reaction with gas-phase species, surface reactions, or etching.³¹ The paper is organized as follows. In Sec. II we provide a detailed description our system and in Sec. III we discuss experimental technique. The results are presented in Sec. IV and discussed in Sec. V.

II. DESCRIPTION OF THE SYSTEM

Cleavage of alkali halides in air is known to produce wide flat terraces (see, for example, atomic force microscope images^{9,32}). Further sample heating to 600 °C and higher temperatures leads to exposure of screw dislocations. Cross-gap electronic excitation of alkali halide crystals produces electron–hole ($e^- - h^+$) pairs and resonant exciton absorption creates free or self-trapped excitons.^{33,34} If an $e^- - h^+$ pair recombines, a self-trapped exciton can also form. Most

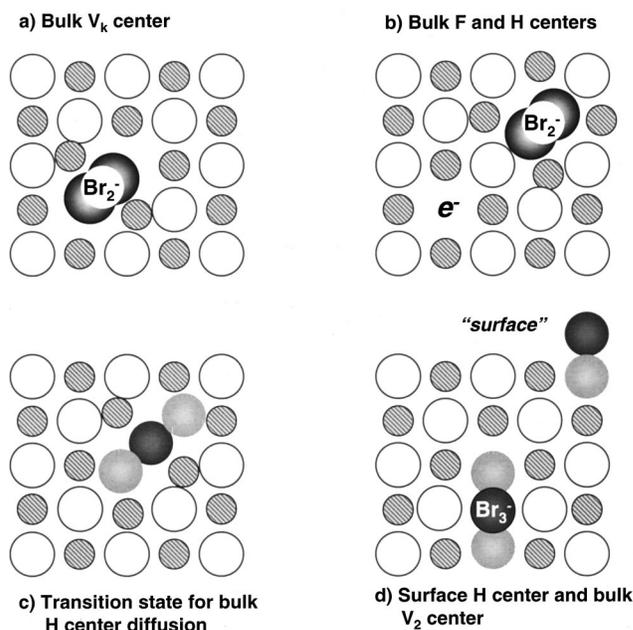


FIG. 1. Schematic diagram of bulk and surface defects involved in photoinduced desorption of KBr: (a) V_K center; (b) F and H centers; (c) transient barrier state for H center diffusion along the $\langle 110 \rangle$ crystal axis; and (d) surface H center leading to thermally activated desorption. Note that the surface H center is oriented perpendicular to the surface plane and corresponds to adsorption of a Br atom on a Br^- surface site. Also shown in (d) is a V_2 center (Br_3^- molecule occupying anion–cation–anion lattice sites along the $\langle 100 \rangle$ axis. Larger white circles represent Br^- ions). The color coding of the hole defect centers qualitatively reflects the degree of the hole localization. For example, in the transient diffusion state of the H center shown in (c) the hole is preferentially localized on the interstitial Br atom in the middle.

excitons will decay nonradiatively, but some will decompose into a pair of Frenkel defects, F and H centers [Fig. 1(b)].^{33,34} F centers are stable at room temperature and cannot lead to Br emission by a direct excitation process.^{24,35} If electrons and holes fail to recombine, then holes also self trap and form V_K centers that are stable below 160 K [Fig. 1(a)].^{33,34,36,37} We observe electron emission under photoexcitation and therefore expect some concentration of V_K centers in our samples. Both V_K and H centers can be considered as Br_2^- molecules occupying two and one Br lattice sites, respectively^{36–38} [see Figs. 1(a) and 1(b)]. Both centers are very mobile at room temperature and have broad optical absorption bands centered near 3.2 eV.^{33,34,39} Within microseconds^{40,41} they aggregate into pairs of H centers (known as V_4 centers) and V_2 centers [Br_3^- molecule occupying anion–cation–anion sites and oriented along the $\langle 100 \rangle$ axis, see Fig. 1(d)].^{37,42–45} These molecular centers are stable at temperatures higher than 300 K. According to the calculations,²³ some of the H centers can reach the surface and thermally decompose into Br^- ions in regular surface sites and desorbed Br atoms [see Fig. 1(d)].

To provide good signal to noise ratio we average over many excitation pulses. Therefore stable defect centers can accumulate inside the sample. The formation of F centers can be readily detected by a characteristic absorption band at 630 nm (1.97 eV).^{33,34,46} The V_4 and V_2 centers display an ab-

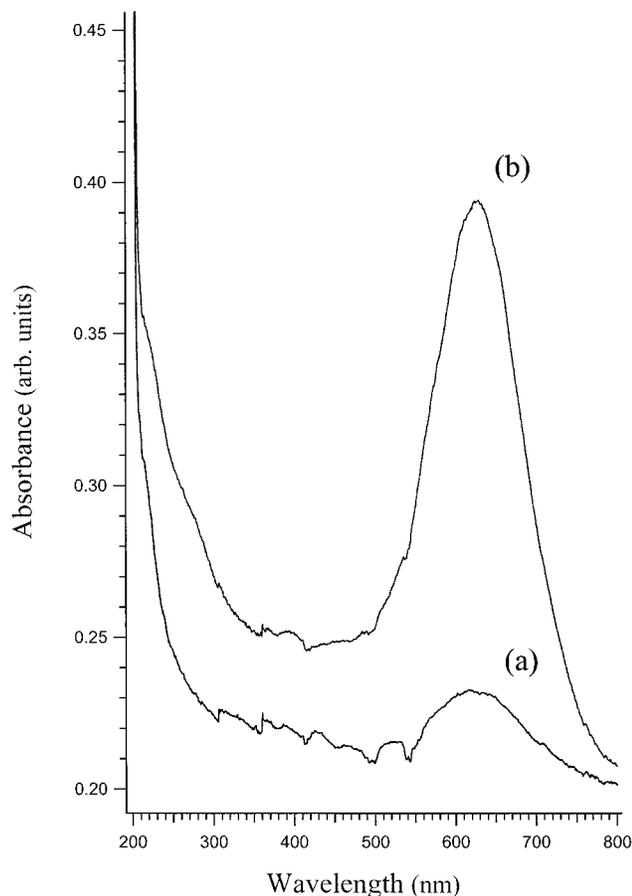


FIG. 2. Optical absorption spectrum of an (a) unirradiated and (b) irradiated alkali halide bulk crystal. The strong band centered near 630 nm is due to absorption by F centers. The shoulder observed between 220 and 300 nm is attributed to absorption by V_4 and V_2 centers.

sorption maximum at 4.4 and 4.7 eV, respectively.^{42,43,47} Other more complex centers, such as aggregates of F centers, also exist but their concentrations at our photon fluences are not significant and they are not likely to take part in Br desorption.

The surface of irradiated crystals undergoes dynamic structural changes caused both by the atom desorption^{9,27,48} and accumulation of radiation defects.⁴⁹ Surface pit formation and further degradation of the surface structure as observed in electron-stimulated desorption studies^{9,27,48} is possible under our experimental conditions. Averaging over many laser pulses means that there will be some average concentration of undercoordinated surface sites.

The optical absorption spectrum of the KBr crystal following irradiation by 40 000 pulses of 5 mJ, 4.7 eV photons is shown in Fig. 2. The strong band at 630 nm is due to F centers and the optical absorption at <320 nm is most likely due to the aggregates of H and V_K centers— V_4 and V_2 centers. Thus transient H and V_K centers, which are present in our samples for up to several microseconds^{40,41} after the irradiation pulse, accumulate into more complex and stable defect centers. Since the theory²³ predicts that the decomposition of H centers at the surface can be responsible for the thermal component of desorption, it is interesting to explore

whether optical excitation of these centers around 3.2 eV will lead to additional effects in desorption.

III. EXPERIMENTAL METHOD

The experimental techniques and data treatment have been described in detail.^{15,21,50,51} Here, we emphasize the unique aspects of these experiments. Samples of single crystal KBr are cleaved in air and mounted in the ultrahigh vacuum chamber at a base pressure of 4×10^{-10} Torr. Samples may be heated to 650 K to anneal and clean the KBr surface. We irradiate the KBr surface at room temperature using nanosecond laser pulses and pulse combinations. Irradiation of the KBr surface induces emission of fast bromine atoms and thermal potassium atoms. The desorbed atoms are detected using laser ionization combined with time-of-flight (TOF) mass spectrometry. Velocity profiles reflecting the velocity distributions of photodesorbed atoms are determined by integrating the atom yield as a function of the delay between excitation and probe lasers. The velocity profiles may be converted to kinetic energy distributions by applying the appropriate Jacobian transform.²¹

The single-pulse excitation experiments use stimulated Raman shifting of Nd:Yttrium–aluminum–garnet (YAG) laser harmonics (in hydrogen gas) to generate the necessary photon energies. The pulse pair experiments use the 266 nm Nd:YAG fourth harmonic directly to create transient defect centers at the surface and within the bulk crystal (pump pulse 1). The second excitation pulse (pump pulse 2, the Nd:YAG third harmonic at 355 nm) is delayed by 20 ns and overlapped spatially with pump pulse 1. Pump pulse 2 excites the transient defect centers leading to bromine emission. In all experiments, tunable light from a Nd:YAG pumped frequency-doubled dye laser, operating at 20 Hz, is used to ionize ground $\text{Br}(^2P_{3/2})$ and spin-orbit excited $\text{Br}(^2P_{1/2})$ atoms in a (2+1) resonance-enhanced multiphoton ionization scheme (probe pulse). The specific two-photon transitions used are $\text{Br}(^4D_{3/2}) \leftarrow \text{Br}(^2P_{3/2})$ at 260.6 nm and $\text{Br}(^2S_{1/2}) \leftarrow \text{Br}(^2P_{1/2})$ at 262.6 nm.⁵² The focused probe pulse intersects the desorbed atoms 3.8 mm above, and oriented parallel to, the sample surface.

Atomic masses are determined by a TOF mass spectrometer using chevron microchannel plates to amplify the ion signal. The output signal of the microchannel plates is input to a 500 MHz video amplifier ($\times 10$) and then sent to a digital oscilloscope. Data collection is computer controlled and the lasers can be independently delayed in time using computer interfaced digital delay generators to facilitate measurement of Br and Br^* velocity distributions. Each data point represents an average of the integrated mass selected ion signal from 200 laser pulses. Laser powers are determined using a pyroelectric detector.

IV. RESULTS

A. Kinetic energy control: Single pulse experiments

Figure 3 displays the Br atom kinetic energy distributions for photon energies of 5.56, 5.94, 6.07, and 6.46 eV. The photon energy range used overlaps the long wavelength edge of the KBr bulk absorption band (Urbach tail).²² The

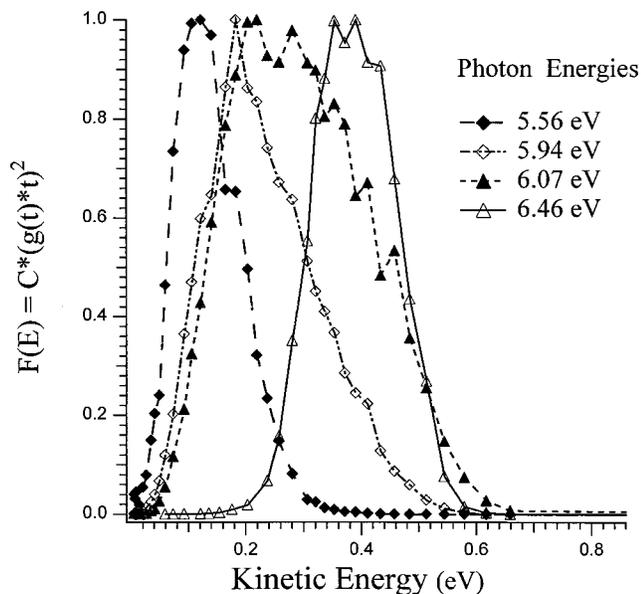


FIG. 3. Kinetic energy distributions of Br emission following tunable band edge excitation. The peak of the Br kinetic energy distribution shifts as photon energy is decreased. The solid and dashed lines serve only to guide the eye.

kinetic energy distributions change markedly with photon energy. The peak kinetic energies of desorbed Br are 0.37, 0.24, 0.18, and 0.12 eV using pump photon energies of 6.46, 6.07, 5.94, and 5.56 eV, respectively. The normalized kinetic energy distributions, at first glance, seem to show an energy width dependence upon photon excitation energy (Fig. 3). We note, however, that relatively minor variations in the

measured velocity profiles can generate significant variations in the kinetic energy distributions. We therefore do not yet place any physical significance on the differences observed in the distribution widths.

Figure 4 shows the adiabatic potential for Br desorption caused by the decomposition of the surface exciton as a function of the distance between the desorbing atom and the surface plane. It was calculated in Ref. 15 using a hybrid *ab initio*/classical polarizable lattice embedded cluster method. It predicts the excitation energy of the surface exciton at about 6.4 eV and a significant reduction of the Br kinetic energy with the decrease of the photon energy. Below 6.2 eV, the measured Br kinetic energy decreases with the photon energy in qualitative agreement with theoretical predictions.¹⁵ The absorption cross section of KBr decreases sharply between 6.46 and 5.56 eV.²² The Br emission yield also decreases sharply in this range on a per photon basis. The Br yield at 5.56 eV is less than 1% of that at 6.46 eV, for equal photon flux at the surface. The Br yield is linear with photon flux at 5.5 eV and above therefore the reduced absorption at the lower photon energies—resulting in lower Br yield—can be compensated for by increasing the photon flux. That is, the yield of Br can be controlled by laser fluence. There is a limit on this approach however. If the photon flux is increased above the multiphoton threshold then both thermal and hyperthermal velocity components will be produced and a bimodal velocity distribution observed. Within our detection limits, photon energies below 5.5 eV do not produce Br emission through a strictly linear absorption process.

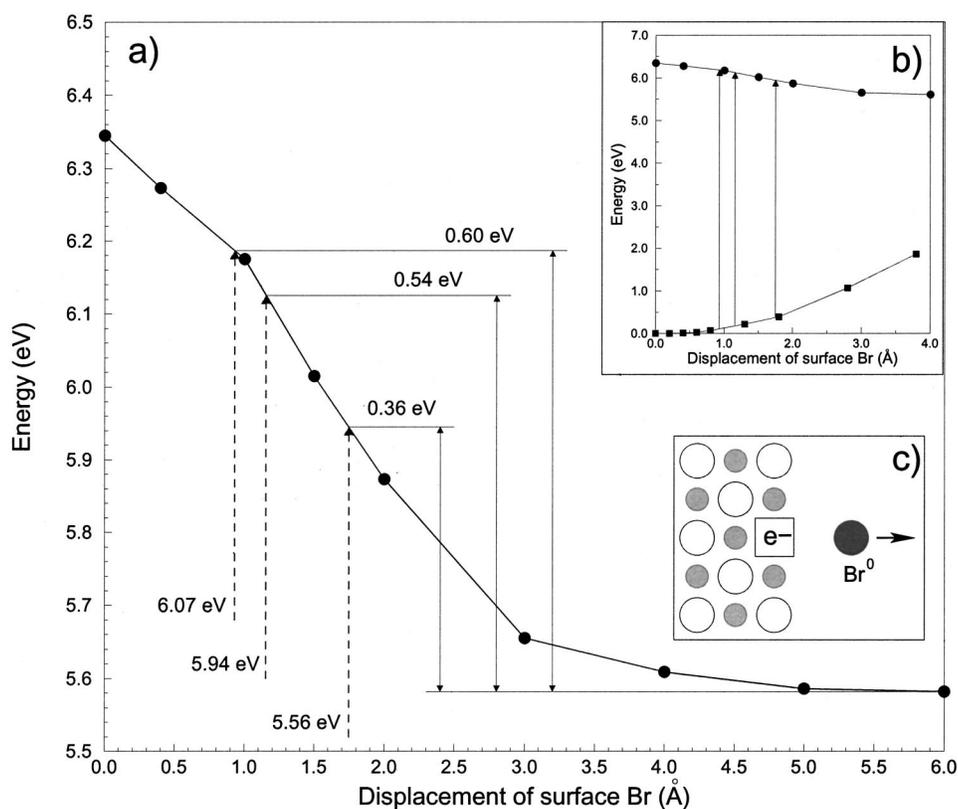


FIG. 4. Model of surface exciton decomposition and Br desorption from the KBr surface (see Ref. 15). (a) Adiabatic potential for the Br desorption due to decomposition of a surface exciton and the Br displacement perpendicular to the surface [inset (c)]. Arrows indicate vertical excitation with the experimental photon energies shown at the base of each arrow. Their positions were determined as shown in (b), where the lower curve is the adiabatic potential of the crystal ground state with respect to the same coordinate. The kinetic energies shown in (a) are calculated with respect to the surface F center and Br atom at infinity. This model predicts the Br atoms' desorption as shown schematically in (c) and the significant reduction in Br kinetic energies as the laser photon energy is decreased. The color-coding in (c) is the same as in Fig. 1.

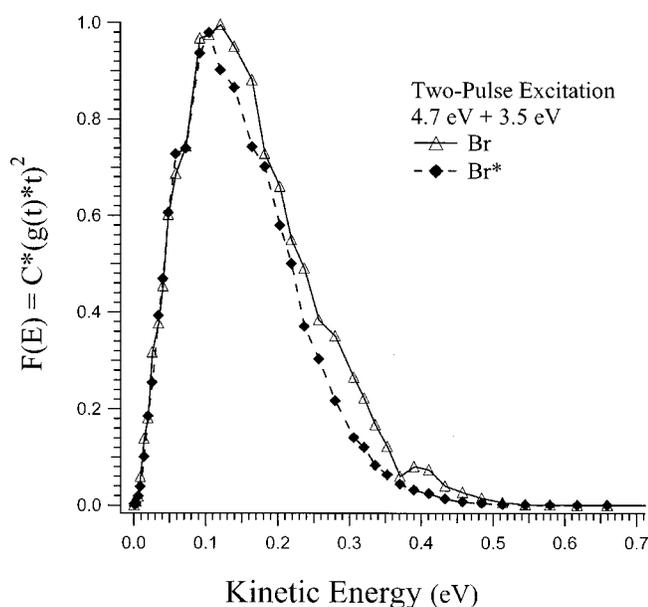


FIG. 5. Kinetic energy distributions of Br and Br* emission following 4.7 and delayed 3.5 eV excitation. The Br (triangles) and Br* (diamonds) display near identical kinetic energies. The solid and dashed lines serve only to guide the eye.

B. Spin state control: Pulse pair experiments

The goal of the pulse pair experiments is to enhance the relative Br* yield by selective excitation of transient centers near the crystal surface. As discussed in Sec. I, transient centers are generated in alkali halides using both resonant exciton excitation and cross band gap excitation that produces electron-hole pairs. We choose subresonant multiphoton excitation at 4.7 eV to create transient centers and optimize several key experimental parameters. Irradiation at 4.7 eV is below the absorption threshold and excitation occurs principally through a two-photon process. The two-photon energy of 9.4 eV lies above the 7.4 eV KBr band gap such that bulk electron-hole pairs ($e^- - h^+$) result. There is a significant yield of thermal Br atoms following 4.7 eV excitation,²¹ suggesting that H centers are produced efficiently. The Br yield versus laser power and thermal velocity distribution of desorbed Br atoms are both consistent with those reported in one-laser emission studies.²¹ No standard surface defects such as steps and kinks absorb significantly at 4.7 eV, and initial excitation at 4.7 eV is not likely to produce a surface or bulk exciton in a direct single photon process.¹⁵ Thus we expect creation of stable F centers and transient V_K and H centers, which will recombine with F centers and aggregate, producing V_4 and V_2 centers within at least several μ s.^{40,41}

V_K and H centers can be electronically excited with 3.5 eV photons. Thus the initial 4.7 eV laser pulse can generate transient absorption centers and the delayed 3.5 eV pulse can further excite these centers. The pulse energy and delay time (20 ns) of pump pulse 2 are selected to excite the newly formed transient centers at powers well below that required for forming such centers through a two-photon process.²¹

Figure 5 displays kinetic energy distributions of des-

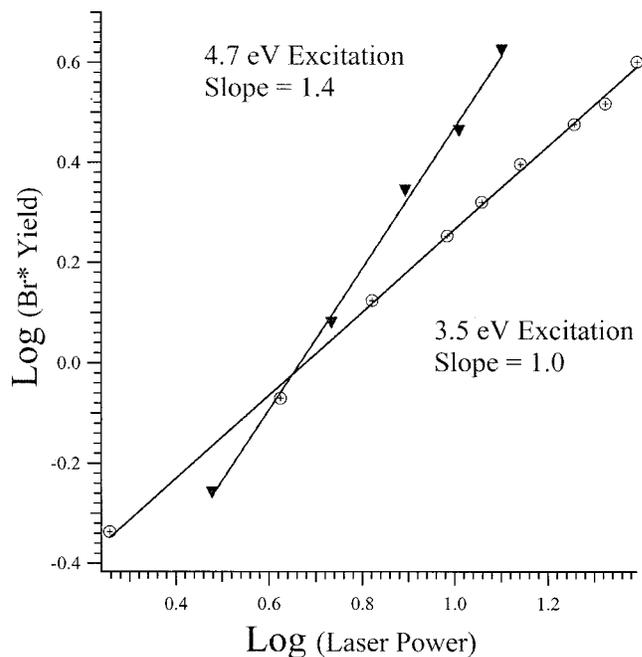


FIG. 6. Laser power dependence of Br* emission following 4.7+3.5 eV pulse-pair excitation. A linear desorption yield for Br* is observed for pump pulse 2 at 3.5 eV indicating resonant absorption by the transient center. The nonlinear slope (1.4) of pump pulse 1 at 4.7 eV was also observed in the previous single laser studies (see Ref. 21).

orbed Br and Br* atoms following sequential excitation by 4.7 (266 nm) and 3.5 eV (355 nm) nanosecond laser pulses. The energy distribution for both spin states is remarkably similar. The peak kinetic energy is roughly 0.12 eV; this is well above that expected for thermal desorption but well below that obtained following resonant one-photon excitation discussed above. The relative Br/Br* product yield ratio resulting from two-laser induced emission (4.7 and 3.5 eV) is 1.4 ± 0.6 . The relative Br* yield is approximately 500 times greater than that obtained following resonant one laser excitation although the total atom yield is much lower, approaching only 1% of the 6.4 eV yield. We have also produced Br and Br* emission using 6.4 eV excitation followed by 3.5 eV nanosecond laser pulses. The Br and Br* kinetic energy distributions produced by this latter pulse combination are identical, within error, to those displayed in Fig. 5. However, when pump laser 2 is tuned to 4.7 or 2.3 eV no significant increase in Br or Br* emission is observed.

Figure 6 displays the Br* yield versus laser fluence in log-log format. The Br* yield is linear with 3.5 eV laser fluence, indicating that the transient centers created by 4.7 eV photons absorb resonantly at 3.5 eV. The Br* yield follows a $P^{1.4}$ dependence with 4.7 eV laser fluence as found previously for 4.7 eV one-laser induced Br emission from KBr.²¹ This noninteger power suggests that, besides a two-photon cross-gap excitation, the 4.7 eV photons are absorbed in a one-photon process. This absorption is possibly due to accumulation of the V_4 and V_2 centers, as shown in Fig. 2. The fact that the one- and two-laser experiments produce the same pump laser power dependence indicates that at 4.7 eV the initial electron-hole pair creation that leads to halogen atom emission in the single laser pulse also leads to the

transient center formation. However, the Br and Br* kinetic energy distributions resulting from two-laser excitation do not conform to hyperthermal or thermal components observed in the single pulse 4.7 eV experiments, and a new kinetic energy distribution is produced.

V. DISCUSSION

Our results clearly demonstrate that one can achieve active incoherent control of the properties of photodesorbed Br atoms from the KBr (001) surface. The velocity of Br atoms photodesorbed from the surface of a cleaved KBr crystal can be controlled using tunable laser light near the UV absorption threshold. The relative yield of Br to Br* can be enhanced, over single photon resonant excitation, using a pulse-pair excitation scheme.

Changing the photon energies in the one-laser experiment we obtained the peak kinetic energies of desorbed Br atoms of 0.37, 0.24, 0.18, and 0.12 eV using pump photon energies of 6.46, 6.07, 5.94, and 5.56 eV, respectively. We regard the high-kinetic energy distribution as characteristic of the decomposition of the KBr surface exciton.^{15,21} That the kinetic energy tracks the exciting photon energy in a dynamical emission process indicates that the Br velocity distribution reflects the details of the adiabatic potential energy surface of the surface excited state. The photon energy dependent velocity profiles therefore represent an indirect measurement of the adiabatic potential along the exciton decomposition coordinate.

However, further analysis of this dependence requires a detailed account of the energy dissipation during exciton decomposition and Br desorption. The adiabatic curves presented in Fig. 4 do not take into account the energy dissipation and as such provide only the upper limit for kinetic energies of desorbed Br atoms. These energies are in satisfactory agreement with the distributions shown in Fig. 5. This agreement and the fact that the emission yield follows a single-photon power dependence provide further support to the model where the bromine emission is caused by direct photon absorption at or near the surface and decomposition of a surface exciton. Our calculations demonstrate that the surface absorption threshold is shifted to lower energies from the bulk value, due to the lower coordination of terrace, step, and corner sites.¹⁵ Laser excitation tuned selectively to such a shifted resonance below the first bulk absorption band can therefore excite these surface features preferentially. However, whether desorption happens also from step and corner sites in addition to terrace sites is still unclear. In particular, according to our calculations,¹⁵ 5.56 eV photons can resonantly excite step edges. This should lead to Br desorption at about 40° to the surface plane.^{15,53} Therefore a careful study of the angular dependence of Br desorption could elucidate more subtle features of the desorption process. The electron-stimulated desorption from step edges has been observed in Refs. 9, 27, and 48.

Under the two-pulse 4.7+3.5 eV excitation, the Br/Br* ratio was determined to be 1.4 ± 0.6 —an increase in the relative Br* yield of roughly 500 from the single laser result at 6.4 eV. The similar velocity profiles and halogen atom yield

of the two spin states, displayed in Fig. 6, suggests that both emissions result from excitation of the same transient center precursor. As discussed above, there are two types of alkali halide transient centers known to absorb 3.5 eV photons— V_K and H centers. Although V_K and H centers have similar absorption spectra, they likely behave differently under photoexcitation. In particular, it has been suggested³⁸ that a ${}^2\Sigma_u \rightarrow {}^2\Pi_u$ electronic transition of the KBr H center is at higher energy than the optically allowed ${}^2\Sigma_u \rightarrow {}^2\Sigma_g$ transition with the maximum at 3.2 eV. The ${}^2\Sigma_u \rightarrow {}^2\Pi_u$ transition is forbidden in the symmetric equilibrium position of the H center, but is allowed when it is thermally displaced from equilibrium. The ${}^2\Pi_u$ state has two components with $J = 3/2$ and $1/2$ split by about 0.25 eV.³⁶ Therefore optical excitation into this state could lead to formation of both Br and Br*. If we assume that the electronic excitation of H centers leads to dissociation or stimulates diffusion of Br and Br*, this mechanism could also explain the high Br* yield following two-laser excitation. The H center is an interstitial defect and its diffusion takes place via the displacement sequence of Br atoms^{23,35} [see Fig. 1(c)]. Near the surface this could easily bring the H center to the surface plane. As has been shown in Ref. 23, surface H centers are strongly polarized and represent a Br atom loosely adsorbed on a regular surface Br site [see Fig. 1(d)]. These Br atoms thermally desorb to produce the observed emission. On the contrary, the V_K center is not an interstitial defect and it is unclear whether photoexcited surface V_K centers can produce Br emission. Furthermore, the 3.5 eV photons can excite only the ${}^2\Sigma_u \rightarrow {}^2\Sigma_g$ transition of the V_K center and thus cannot produce Br* directly. This suggests that only H centers are responsible for both Br and Br* emission. The results of detailed theoretical simulations of this mechanism will be presented in a separate publication.

The Br and Br* emission must be derived from a thin near-surface layer since the Br kinetic energy distribution would be relaxed to a thermal distribution if Br and Br* were required to diffuse long distances through the bulk prior to emission. This conclusion is supported by the high Br* yield and the nearly identical Br and Br* velocity profiles. Thus the Br/Br* ratio could be enhanced by using smaller time delays between the first and second pulses which should allow one to excite more H centers. Since H centers are produced within a few ps of excitation,^{34,54} time-resolved experiments using femtosecond pulses could shed more light on the dynamics of defect processes near the surface and mechanisms of desorption.

We should note that the controlled desorption of Br and Br* atoms induced by UV surface excitation can be used as a source of these atoms with selected kinetic energies for reactions with gas phase species, surface reactions, and other purposes. The unique features of such a source are discussed in detail in Ref. 31. Neutral halogen emission is a generally observed phenomenon following vacuum UV and electron irradiation for a large variety of alkali halides (see, for example, Refs. 2, 3, 6, and 14). Most of the emission mechanisms outlined here for KBr should be general for alkali halides under photon and electron irradiation. Therefore active control using a one- or two-laser approach could gener-

ate different halogen atoms of selectable kinetic energy or spin state distribution. With further development, one can envision active control applied to laser desorption from oxides, and possibly other materials as well.

Finally, we would like to note that one can look at the surface processes discussed above from a different perspective and draw parallels with the extensively studied photodissociation of I_2^- molecules in gas phase clusters, liquid solutions, and in other environments (see, for example, Refs. 55 and 56). V_K and H centers in alkali halides, e.g., KI, are close analogs of these systems and have similar optical and vibrational properties. The main difference, of course, is that I_2^- or Br_2^- molecules in, e.g., $(CO_2)_n$ clusters are foreign species and their interaction with the solvent in most cases is not very strong. I_2^- or Br_2^- molecules in crystals— V_K and H centers—in contrast are surrounded by equivalent iodine or bromine ions (see Fig. 1) and therefore their diffusion mechanisms are very different. Nevertheless there are similarities in terms of relaxation mechanisms, the effect of polar environments, and indeed dissociation at the surface, which could be interesting to pursue in future time-resolved studies.

VI. CONCLUSIONS

Photoexcitation of KBr surfaces leads to Br and Br^* emission in thermal and hyperthermal kinetic energy distributions. We find that the appropriate choice of laser photon energy can control the quantum state and kinetic energy distributions of desorbed bromine atoms. Photoexcitation below the lowest bulk exciton band at 6.6 eV is used to generate nearly pure ground state Br emission. Furthermore, the kinetic energy distribution of laser desorbed ground state Br atoms from KBr surfaces may be selected through judicious choice of photon excitation energies. Kinetic energy distributions, with peak energies ranging from 0.12 to 0.38 eV, were selectively generated using photon energies ranging from 5.56 to 6.46 eV. We also find that the relative distribution between the Br and Br^* electronic state distributions can be controlled through a two-pulse excitation technique. In the two-pulse scheme, the first laser pulse is used to generate transient centers within the near surface region, and the second pulse then excites these species leading to Br and Br^* emission. We note that such control is possible because of the detailed theoretical understanding of the excited electronic process recently developed for alkali halides. Future work will focus on demonstrating that these techniques are extendable to other alkali halides and to determining what additional laser control is achievable using tailored ultrafast laser pulses.

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