

## Excited-Atom Production by Electron Bombardment of Alkali Halides

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We present experimental results which suggest a new mechanism for the production of excited atoms by electron bombardment of alkali halides. Doppler-shift measurements show that the electronically excited atoms have a thermal velocity distribution in equilibrium with the surface temperature. Measurements of the yield of excited atoms, the distribution of population among the excited states, and the dependence on incident-electron current support a model in which the excited atoms are produced by gas-phase collisions between desorbed ground-state atoms and secondary electrons.

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Bombardment of solids by energetic beams of electrons or photons is generally accompanied by the ejection of particles from the surface. An understanding of the basic mechanisms responsible for this electron- or photon-stimulated desorption (ESD or PSD) is of substantial current interest.<sup>1</sup> Many recent studies have focused on alkali-halide substrates because these materials have relatively simple geometric and electronic structures, and because they exhibit a rich variety of desorption phenomena. It has been established that the desorbed particles are principally ground-state halogen atoms and molecules and ground-state alkali-metal atoms,<sup>2-6</sup> with a small yield of electronically excited alkali-metal atoms,<sup>7-13</sup> and a smaller yield of ions.<sup>14-16</sup> Mechanisms for the desorption of ground-state neutrals are qualitatively understood,<sup>2-6,17-19</sup> and plausible mechanisms for ion desorption have been proposed.<sup>20,21</sup> However, the ion-desorption mechanisms have not been firmly established, and the mechanism for excited alkali-metal-atom desorption has remained an open question.

In this Letter we present experimental results which suggest a new mechanism for the production of excited atoms by electron bombardment of alkali halides. With the exception of measurements of desorbed metastables, our experiments provide the first quantitative measurements of velocity distributions of electronically excited neutrals produced by electron impact on solids. These measurements play a crucial role in our identifying the excited-state production mechanism. In addition, our results have important implications for the interpretation of ion-desorption experiments.

The experimental apparatus is briefly outlined here. A 200–2000-eV electron beam with current densities of 0.1–10  $\mu\text{A mm}^{-2}$  was used to bombard NaCl crystals in ultrahigh vacuum ( $\approx 5 \times 10^{-10}$  Torr). The NaCl crystals were cleaved in air, then cleaned by heating to 570 K in vacuum overnight. The electron beam was incident at 45° from the normal to the (100) surface. The bombarded region had dimensions of

$\approx 1 \times 2 \text{ mm}^2$ . A range of sample temperatures from 290 to 570 K was studied. The sample was electrically isolated from the grounded chamber so that small (< 50 V) voltages could be applied. In all respects, the experimental conditions for our measurements were similar to those used in previous studies.<sup>7-13</sup>

Laser-induced fluorescence (LIF) was used to measure velocity distributions of Na atoms in the  $3p$  excited state produced by electron bombardment of NaCl. A single-mode cw dye laser was tuned to excite atoms from the  $3P_{1/2}$  excited state to the  $4D_{3/2}$  state. This is a specific fine-structure component of the  $3p \rightarrow 4d$  electronic transition. The cascade  $4p \rightarrow 3s$  UV emission at 3303 Å was collected with  $f/3$  optics and detected with a monochromator and a photomultiplier (PMT). This detection scheme provides high sensitivity and excellent rejection of scattered laser light. The PMT output was monitored with an electrometer, and digitized with a 12-bit analog-to-digital converter. The incident laser beam was parallel to the NaCl surface, and it overlapped the electron-bombarded region. The LIF signal is proportional to the number of excited atoms produced per unit time that have the Doppler-selected velocity component  $v_x/c = (\omega_L - \omega_0)/\omega_0$ , where  $c$  is the speed of light,  $\omega_L$  is the laser frequency, and  $\omega_0$  is the resonance frequency in the atom's rest frame.

An experimental LIF profile of the sodium  $3P_{1/2} \rightarrow 4D_{3/2}$  transition is shown in Fig. 1. The dashed curve is the best fit for a Maxwell-Boltzmann velocity distribution. The temperature determined from the fit is  $565 \pm 10 \text{ K}$ , where the error bars indicate 95% confidence limits. This value agrees with the substrate temperature measured with a thermocouple,  $T_s = 558 \pm 1 \text{ K}$ . For the data of Fig. 1, the electron beam current was  $\approx 20 \mu\text{A}$ , the beam area was  $\approx 2 \text{ mm}^2$ , the electron energy was 1000 eV, and the laser power was  $\approx 10 \text{ mW}$  in a  $\approx 1\text{-mm-diam}$  beam. For all of the experimental conditions investigated, the excited-state signal versus laser frequency was found to be a

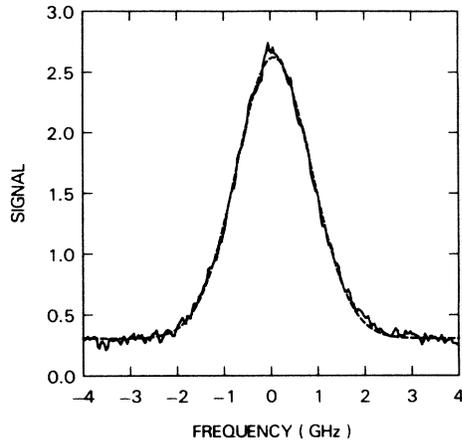


FIG. 1. Experimental Doppler-broadened profile of the sodium  $3P_{1/2} \rightarrow 4D_{3/2}$  transition measured by LIF (solid curve). The best-fit Maxwell-Boltzmann distribution (dashed curve) has  $T = 565 \pm 10$  K, in agreement with the surface temperature  $T_s = 558 \pm 1$  K.

Doppler-broadened profile which could be accurately characterized by a Maxwell-Boltzmann velocity distribution at the substrate temperature to within experimental error. If the excited atoms were directly desorbed from the surface by excitation to some repulsive electronic state, kinetic energies of order 0.1–10 eV would be expected, in sharp contrast to the thermal distributions observed. However, previous workers have shown that the *ground-state* atoms evaporate from the surface with a thermal velocity distribution in equilibrium with the surface temperature.<sup>4,11,13,22</sup> These results suggest a strong correlation between the ground-state and excited-state formation mechanisms.

Additional qualitative evidence for the excited-state formation mechanism was obtained from the observation that the  $\text{Na}^*$  emission intensity varies significantly with sample bias, as shown in Fig. 2 (solid curve). Although the applied bias voltage changes the beam energy, this has almost no effect on the  $\text{Na}^*$  emission intensity, as shown by the dashed curve of Fig. 2. The strong dependence on sample bias suggests that *low-energy* charged particles may be involved in the excited-state formation process. This effect was observed for  $T = 290\text{--}570$  K, beam currents of  $0.1\text{--}10 \mu\text{A mm}^{-2}$ , and beam energies of  $200\text{--}2000$  eV. These data suggest that the excited alkali-metal atoms may be formed by gas-phase collisions between ground-state atoms and secondary electrons. For  $\sim 1\text{-keV}$  incident electrons, secondary electrons should be much more effective at excitation than the primary beam because secondary yields<sup>23</sup> are large ( $\sim 10$ ) and the cross sections for excitation<sup>24</sup> peak at the low energies typical of secondary electrons.<sup>25,26</sup> Excitation by the primary beam should become impor-

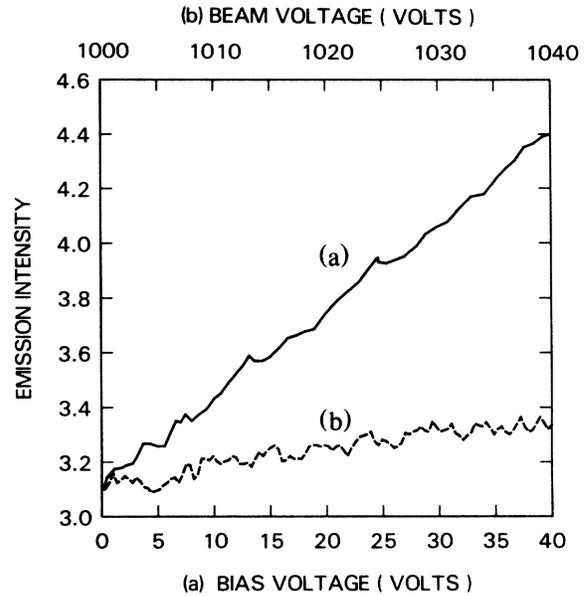


FIG. 2. Solid curve, the  $\text{Na } 3p \rightarrow 3s$  emission intensity vs sample bias; dashed curve, the emission intensity vs incident-electron energy.

tant at relatively low incident energies, where the secondary yields are small.

We now demonstrate that excitation of desorbed ground-state atoms by secondary electrons can account for (1) the absolute yield of excited alkali-metal atoms, (2) the distribution of population among the excited states, and (3) the dependence of excited-state emission intensity on incident-electron current. This mechanism also clearly explains the velocity distribution of the excited atoms and the qualitative dependence of emission intensity on sample bias.

An estimate of the excited-state signal follows. The number of excited Na atoms produced per second should equal the number of secondary electrons produced per second times the probability that a given secondary electron will excite some ground-state Na atom. This probability is  $\approx n_{\text{Na}} \sigma_{\text{ex}} L$ , where  $n_{\text{Na}}$  is the ground-state Na density,  $\sigma_{\text{ex}}$  is the excitation cross section, and  $L$  is an appropriate path length. The excitation probability depends on the energy and angular distributions of the secondary electrons, and these quantities depend on experimental conditions such as surface charging. Nevertheless, a rough estimate can be made to determine whether the gas-phase mechanism can explain the order of magnitude of the signal. From data on secondary-electron energy distributions,<sup>25,26</sup>  $\sim \frac{1}{2}$  of the secondary electrons are expected to have energies sufficient to excite Na to the  $3p$  state. The excitation cross section<sup>24</sup> is  $\approx 40 \text{ \AA}^2$  for energies above threshold. We measured the ground-state Na density directly by tuning the cw dye laser

across the  $3S_{1/2} \rightarrow 3P_{3/2}$  resonance line and monitoring absorption. For the conditions of Figs. 1 and 2, the Na density was  $\approx 1.1 \times 10^{12} \text{ cm}^{-3}$  at the sample surface. This implies a ground-state Na yield of  $\approx 4.5$  atoms per incident electron, in good agreement with Szymonski *et al.*<sup>13</sup> If we assume that  $L \approx 1$  mean beam radius ( $\approx 0.75 \text{ mm}$ ), the excitation probability is  $\approx 3.3 \times 10^{-4}$ . Using a secondary-electron yield of  $\approx 14$  per incident electron,<sup>23</sup> we predict a  $\text{Na}^*(3p)$  yield of  $\approx 3 \times 10^{11} \text{ s}^{-1}$  for our  $20\text{-}\mu\text{A}$  electron beam. For comparison, the signal at the PMT was  $\approx 15 \mu\text{A}$ . When we take into account the PMT gain  $\approx 2 \times 10^6$ , quantum efficiency  $\approx 15\%$ , monochromator transmission  $\approx 15\%$ , window and lens transmission  $\approx 72\%$ , and fractional collection solid angle  $\approx 6.9 \times 10^{-3}$ , the experimental  $\text{Na}^*(3p)$  yield is  $\approx 4 \times 10^{11} \text{ s}^{-1}$ . This agrees with the above prediction within the factor-of-2 uncertainties in the estimates, and provides very strong support for the gas-phase excitation mechanism.

In Table I we compare our measured relative emission intensities for a number of  $\text{Na}^*$  emission lines (corrected for wavelength-dependent sensitivity) and those of Szymonski *et al.*<sup>13</sup> with the gas-phase excitation cross sections at  $5 \text{ eV}$ .<sup>24</sup> To within experimental error ( $\sim 30\%$ ), the measured intensities are proportional to the gas-phase excitation cross sections. This correlation provides strong additional support for the gas-phase excitation mechanism.

Further evidence for gas-phase excitation was obtained from studies of the excited-state emission intensity as a function of incident electron current. Sample temperature and electron dose are important parameters in these studies. Our experiments, like previous studies,<sup>7-13</sup> were done with an electron dose sufficient to remove more than a monolayer of ground-state halogen atoms during the experiment. At high temperatures ( $T > 470 \text{ K}$ ), ground-state alkali-metal evaporation keeps up with halogen loss, and the surface remains stoichiometric.<sup>13</sup> For these conditions, the ground-state alkali-metal-atom yield is

TABLE I. Comparison of the gas-phase electron-impact excitation cross sections for sodium at  $5 \text{ eV}$  (Ref. 24) and the experimental emission intensity ratios (Ref. 13 and this work). The cross sections and emission intensities are scaled to 1.00 for the  $3p \rightarrow 3s$  transition.

Transition	Ref. 24	Ref. 13	This work
$3p \rightarrow 3s$	1.000	1.000	1.000
$4p \rightarrow 3s$	0.0095	0.011	0.008
$3d \rightarrow 3p$	0.103	. . .	0.090
$4d \rightarrow 3p$	0.0090	0.005	0.008
$5d \rightarrow 3p$	0.0048	0.004	0.004
$6s \rightarrow 3p$	0.0022	0.002	. . .

proportional to the incident electron flux  $I_e$  and the secondary-electron yield is  $\propto I_e$ ; thus the yield of excited alkali-metal atoms should be  $\propto I_e^2$ . In Fig. 3 we show that a quadratic dependence of emission intensity on incident current is observed. Concurrent measurements of the ground-state Na density showed a linear dependence on incident current. In contrast, at low temperatures ( $T < 370 \text{ K}$ ) the surface becomes alkali-metal enriched because ground-state alkali-metal evaporation becomes rate limited. The ground-state alkali-metal yield then becomes nearly independent of electron current (and principally dependent on temperature), and the excited alkali-metal-atom yield takes on an approximately linear dependence on incident electron flux, as observed by previous workers.<sup>7</sup> This effect is dose dependent and occurs only when the sample has received sufficient dose to modify the surface stoichiometry.

A substantial body of experimental data on excited-state production has been obtained by previous workers.<sup>7-13</sup> Here we indicate how gas-phase excitation can explain two key observations which were considered to be indicative of a specific electronic desorption mechanism. We expect gas-phase processes to be dominant in PSD as well as ESD since in both cases the ground-state atom<sup>13,22</sup> and secondary electron<sup>23,26</sup> yields are large. First, the excited-state yields have been observed to be correlated with core-level ionization processes.<sup>9,10</sup> For gas-phase excitation by secondary electrons, such a correlation is expected because the secondary-electron yield is strongly correlated with core-level ionization.<sup>16</sup> Second, in the earliest studies, only the lowest excited state,  $\text{Na}^*(3p)$ , was observed,

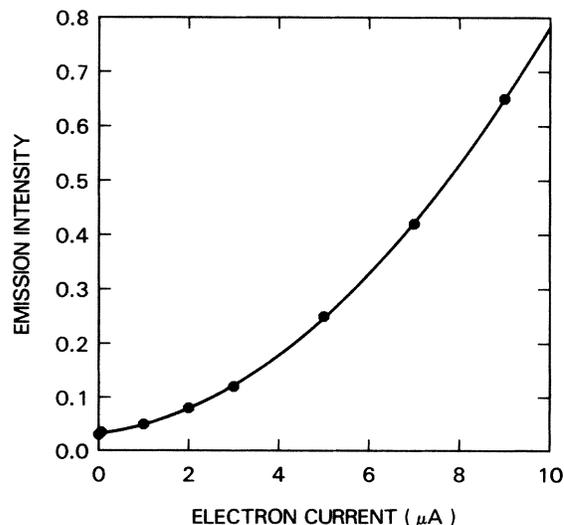


FIG. 3. The Na  $3p \rightarrow 3s$  emission intensity as a function of incident-electron current. The sample temperature was  $555 \text{ K}$ , and the electron energy was  $1000 \text{ eV}$ .

suggesting either a selective excitation process or non-radiative deexcitation of the more highly excited states at the surface.<sup>7-10</sup> In these experiments the more highly excited states could not be detected because the weak emission lines from these states were masked by continuum emission from the bulk. At higher substrate temperatures, the bulk luminescence is quenched and the higher states can then be observed.<sup>13</sup> We have shown that the population distribution among these states is as expected for a gas-phase excitation process.

Gas-phase collisions may also account for a significant fraction of the ion yield observed in ion-desorption experiments.<sup>14-16</sup> We have made an estimate of the ion "yield" using the known ionization cross section<sup>27</sup> and the experimental conditions of Pian *et al.*,<sup>15</sup> and shown that the gas-phase ionization mechanism can explain the order of magnitude of the experimental signal observed. Gas-phase processes can explain why the excited-state yields are larger than the ion yields—the excitation cross sections are larger than the ionization cross sections. In addition, this mechanism explains the similarity between ion-desorption yields and secondary-electron yields versus beam energy.<sup>16</sup> Gas-phase ionization of desorbed neutrals clearly deserves strong consideration for the interpretation of ion-desorption experiments on alkali halides.

In conclusion, we have presented experimental data which indicate that the excited sodium atoms produced by electron bombardment of NaCl are formed by gas-phase collisions between secondary electrons and ground-state atoms. Similar processes are expected to be important for other alkali halides. In addition, gas-phase ionization may account for a significant fraction of the ions observed in ion-desorption experiments on these materials. More generally, gas-phase excitation and ionization processes can be important when the yields of ground-state neutrals and secondary electrons are both large. The alkali halides provide outstanding examples of materials where these conditions are satisfied.

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<sup>1</sup>A good collection of recent work appears in *Desorption Induced by Electronic Transitions, DIET 1*, edited by N. H. Tolk, M. M. Traum, J. C. Tully, and T. E. Madey (Springer-Verlag, Berlin, 1983); *Desorption Induced by Electronic Transitions, DIET 2*, edited by W. Brenig and D. Menzel

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