Photon-stimulated desorption of Na from a lunar sample: temperature-dependent effects

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Abstract

We report recent results in an investigation of source mechanisms for the origin of Na atoms in tenuous planetary atmospheres, focusing on non-thermal processes. Experiments include photon stimulated desorption (PSD), electron stimulated desorption (ESD), and ion sputtering of Na atoms from the surface of a lunar basalt sample. Bombardment of the sodium covered surface by 3 keV Ar$^+$ ions removes Na from the surface by sputtering into vacuum and by implantation into the sample bulk. Bombardment of the Na covered surface by ultraviolet photons or by low energy electrons ($E > 3$ to 4 eV) causes desorption of “hot” Na atoms. These results are consistent with our previous measurements of sodium and potassium desorption from a silica surface: electron- or photon-induced charge transfer from the substrate to the ionic adsorbate causes formation of a neutral alkali atom in a repulsive configuration, from which desorption occurs. There is a strong temperature-dependence of Na ESD and PSD signals, under conditions where the Na surface coverage is constant and thermal desorption is negligible. The yield of Na (atoms/photon) increases by $10^5$ from 100 to 470 K; an activation energy of $\sim 20$ meV is measured. This phenomenon may be attributed to thermally-induced changes in surface bonding sites, and will affect recent modeling of the sodium atmospheres of Mercury and the Moon.

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1. Introduction

Earth’s Moon and the planet Mercury have extended tenuous atmospheres containing suprathermal sodium and potassium atoms (Potter and Morgan, 1985, 1988, 1997; Potter et al., 2002), and Mercury’s atmosphere has been discovered recently to contain traces of Ca atoms (Bida et al., 2000). The lifetime of an alkali atom in the atmosphere is on the order of hours due to photoionization by solar photons, so the atmospheres must be continuously resupplied in order to maintain the observed concentrations. Various mechanisms and source processes have been proposed as origins of the Na, K atmospheres (Hunten and Sprague, 1997; Killen and Morgan, 1993; Killen and Ip, 1999), including sputtering by the solar wind, electron, and photon stimulated desorption (ESD and PSD), (McGrath et al., 1985; Madey and Yakshinskiy, 1998; Mendillo et al., 1999; Madey et al., 2002), thermal desorption (Yakshinskiy et al., 2000), micrometeorite impact (Morgan et al., 1988; Cintala, 1992; Verani et al., 1998; Wilson et al., 1999; Smyth et al., 1999, 2001), and thermal diffusion from the crust (Sprague, 1992; Killen and Morgan, 1993). There are also detailed theoretical models of the sources, sinks and transport dynamics of Na and K in the lunar and mercurian atmospheres (Smyth and Marconi, 1995, 1995b; Leblanc and Johnson, 2003; Wurz et al., 2003).

Recently we presented evidence based on laboratory experiments that photon-stimulated desorption (PSD) is likely to be the dominant source process for desorption of Na from the Moon (Yakshinskiy and Madey, 1999, 2000). Since those experiments were performed on a model substrate, SiO$_2$, it is desirable to determine whether or not PSD is an important process for a lunar sample, a much more complex oxide substrate. Preliminary measurements using a lunar basalt sample (Yakshinskiy and Madey, 2003) indicate that PSD of Na is indeed an efficient source process.

In the present paper we report new data on PSD, ESD, and ion sputtering of Na deposited onto a lunar basalt sam-
The most striking new result is the observation of a strong temperature dependence of the PSD and ESD atom desorption yields; the yield of Na (atoms/photon) increases by $\sim 10 \times$ from 100 to 470 K. Recently, surface temperature variations were shown to be critical in understanding the observed variability of Mercury’s atmosphere (Leblanc and Johnson, 2003). This new result means that not only does surface temperature play an important role over a large area of Mercury’s surface, but it is also important for understanding the lunar atmosphere.

2. Experimental procedures

Experiments are performed in a baked, stainless steel ultrahigh vacuum (UHV) chamber with a base pressure $\sim 5 \times 10^{-11}$ Torr; the apparatus and procedures have been described previously (Yakshinskiy and Madey, 2000, 2003). X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering (LEIS) are used for surface characterization. The sample is a piece of Ti-rich lunar basalt (Sample #74275) with area $\sim 1$ cm$^2$ and thickness of 1 mm (Fink et al., 1998). The sample is attached to a piece of 0.5 mm thick Mo sheet by thin Ta straps. The sample is mounted on an XYZ-rotary manipulator, and can be cooled to $\sim 100$ K using liquid nitrogen as well as heated by resistive heating of the Mo sheet to a maximum temperature of $\sim 600$ K (to maintain the integrity of the sample, we do not heat above 600 K). To reduce the concentration of surface impurities, the sample is sputtered by 1–2 KeV Ar$^+$ ions at 45$^\circ$ incidence. Sputtering depletes the surface of oxygen, which is restored by exposure to $10^{-6}$ Torr of O$_2$ in UHV. To increase the surface concentration of Na to measurable levels, Na is deposited onto the sample surface by thermal evaporation from an SAES Getters source.

The measurement procedure for PSD and ESD of Na from the lunar sample involves a pulsed low energy electron source (0 to 200 eV) and a highly sensitive detector based on surface ionization of Na on hot Ir ribbons ($\sim$ 1800 K). The neutral Na atoms incident on the hot Ir surface desorb as Na$^+$ ions and are detected using a channeltron electron multiplier. The velocity distributions of neutral atoms are measured using a time-of-flight (TOF) method. For PSD measurements, a mechanically-chopped (3.3 kHz) photon source (500 W Hg arc lamp) is used. Glass bandpass filters are used for wavelength discrimination.

3. Results

An X-ray photoelectron spectrum of the lightly Ar$^+$-sputtered lunar sample is shown in Fig. 1. In the binding energy range displayed here (0–400 eV), evidence for C and for oxide forms of Fe, Mg, Al, Si, Ca is seen; Ti and O are also present, as found by increasing the energy range. The C impurity is mainly from atmospheric exposure, and is reduced by heating and Ar$^+$ sputtering. A very small Na signal is observed, at a level $\leq 1$ atom percent (see inset). The relative elemental concentrations in the surface region mirror the bulk composition (Fink et al., 1998).

Electron bombardment of the lunar sample induces desorption of atomic Na from the Na low concentration present in the surface layer, but the signal is too small for accurate measurements of desorption threshold energies. To generate a measurable signal Na is deposited onto the surface and ESD/PSD measurements are made. The coverage (measured in monolayers, ML) is determined using XPS, and the ESD/PSD yields (atoms/electron, atoms/photon) are found to scale linearly with coverages $< 1$ ML. At coverages $< 1$ ML, the XPS data indicate that Na is adsorbed ionically.

Figure 2 shows the ESD and PSD yields as a function of excitation energy for $\sim 0.5$ ML of Na adsorbed at 100 K. The threshold energies for both ESD and PSD are in the range 3 to 4 eV, and the desorption signals rise sharply for higher energies. The horizontal bars in the PSD data represent the effective filter bandwidths at 70% peak transmission level. The electron energies are corrected for the emitter work function and estimated electron affinity of the lunar sample (Yakshinskiy and Madey, 2003). The data are qualitatively similar to measurements on pure SiO$_2$ films, but the magnitude of the Na desorption signal is about 30% of the corresponding signals for desorption of Na from SiO$_2$ (Yakshinskiy and Madey, 2000); the PSD cross-section at $h\nu \sim 5$ eV is estimated to be $\sim 10^{-20}$ cm$^2$.

Figure 3 shows the velocity distribution for ESD of Na from the lunar sample at 100 K. The peak velocity of $\sim 800$ m/s is less than that observed for desorption of Na from an SiO$_2$ film (Yakshinskiy and Madey, 2000) but the
 Photon-stimulated desorption of Na

Fig. 2. Solid line: ESD yield of neutral atomic Na from 0.5 ML of Na deposited onto surface of lunar basalt sample at 100 K, as a function of electron bombardment energy. Inset: PSD yield of Na atoms as a function of photon energy. The horizontal lines represent the effective bandwidths of optical filters.

Fig. 3. Velocity distribution ($dN/dV$ vs. velocity) for neutral Na from $\sim 0.5$ ML of Na on lunar basalt. $dN$ is the number of desorbing atoms having velocities in the range $V + dV$.

desorbing Na is suprathermal ($\sim 900$ K) with respect to the 100 K substrate. Focusing on the DIET processes, our experiments provide an average Na escape velocity $\sim 1$ km/s from an SiO$_2$ surface, with extended tail up to $\sim 2.5$ km/s; as shown in Fig. 3 for the lunar sample, the extended tail reaches $\sim 2$ km/s. Based on our results, UV solar photons and electrons with $E < 300$ eV do not contribute appreciably to the desorbing Na flux with speed $V > 2$ km/s. The higher Na ejection speeds of 2.1–2.4 km/s from the lunar surface have been associated with micrometeorite impact vaporization (Smyth and Marconi, 1995b; Wilson et al., 1999).

Figure 4 illustrates the temperature dependence of Na desorption yield. In Fig. 4a, the PSD Na intensity is plotted vs. time as the sample is heated and cooled. To maximize the signal, 1 ML of Na is irradiated with “white light,” 1–5 eV (IR is filtered out). The incident photons do not cause a detectable change in substrate temperature. The signal increases and decreases as light is turned on and off, and also as the sample is heated and cooled. The Na signal varies reversibly with temperature, and is $\sim 10\times$ more intense at 470 K than at 100 K. In this temperature range, there is negligible thermal desorption of Na as verified using XPS; the surface Na concentration is constant. The temperature dependence of Na PSD signal is displayed on a Boltzmann plot, log $I/I_{300}$ vs. $1/T$, in Fig. 4b. Here, the data are normalized to the magnitude $I_{300}$ of the signal measured at 300 K. Both PSD data and ESD data ($E_e = 200$ eV) dis-

Na PSD vs Temperature, reversibility

Fig. 4. Temperature dependence of Na PSD desorption yield from lunar basalt. Sample is irradiated with “white light” $\sim 1–5$ eV. (a) Na intensity vs. time as sample is heated and cooled; light is turned on and off. (b) Boltzmann plot of PSD intensity ($h\nu \sim 1$ to 5 eV) and ESD intensity ($E_e = 200$ eV) as function of reciprocal temperature. The activation energy is 20 ± 2 meV.
Fractional monolayers of Na deposited onto oxide surfaces (SiO$_2$ and lunar sample) also adsorb as Na$^+$, whereas multilayers (> 1 ML) contain metallic Na (Yakshinskiy et al., 2000). The ESD and PSD data of Figs. 2–4 are interpreted in terms of a model described previously to explain ESD and PSD of Na and K from a model mineral surface, SiO$_2$ (Yakshinskiy and Madey, 1999, 2000, 2003). Electron or photon bombardment of the lunar surface with energies greater than threshold values of 3 to 4 eV can induce electron transfer from an electronic state in the bulk, or from a surface state, to the unoccupied Na$^+$ 3s level. Once the 3s level is occupied, the neutral Na atom has a larger radius than the original Na$^+$ ion; the atom is in a highly repulsive configuration. For Na adsorbed on a wide bandgap insulator, the rate of charge transfer from the neutralized Na atom to the substrate is slow, and the atom in its repulsive state can survive and desorb from the surface. Sodium desorbs from the lunar sample with escape velocity peaked at ~ 800 m/s (Fig. 3) with corresponding temperature ~ 900 K, which we associate with the desorption of ground state “hot” neutrals. In independent experiments, neutral ground state K atoms have been found in studies of the ultraviolet laser-induced desorption of potassium from Cr$_2$O$_3$ (0001) (Wilde et al., 1997); the authors use a resonance excitation method to demonstrate directly that the desorbing species are translationally hot ground-state neutrals. Nonetheless, the possibility of a contribution to the high velocity tail in Fig. 3 from the desorption of Na Rydberg atoms cannot be excluded (Holmlid, 2002; Yarygin et al., 2003). Note that both ESD and PSD proceed via a similar charge transfer mechanism, especially near threshold. Of course, we have a much greater experimental energy range available for electron-induced excitations as compared to photon-induced studies. At higher energies, desorption can also be initiated by core hole excitations (e.g., O 2p at ~ 25 eV) (Madey and Yakshinskiy, 1998).

4.2. Temperature-dependent effects in ESD and PSD

Temperature dependences in desorption yields of ionic and neutral species have been reported in an number of studies involving ESD of adsorbed monolayers under ultrahigh vacuum conditions. The most common effect is an irreversible change in desorption yield as temperature increases, due to thermally-induced desorption and/or decomposition of an adsorbed layer (Madey and Yates, 1971). In many instances, a sharp decrease of desorption yield coincides with thermal desorption (Faradzhev et al., 2003). However, there are also reports of reversible changes in desorption yield as a function of temperature; measurements are made under conditions where the maximum temperature is lower than that required for thermal desorption, i.e., the surface coverage of adsorbate does not change with temperature. In two cases (Menzel, 1969; Kutsenko, 1969) the ESD positive ion yield is reported to increase with temperature, a phenomenon that the authors associate with an increased average
distance of the atom from the substrate due to population of excited vibrational states. In contrast, a small (∼10%) reversible decrease of O⁺ ESD signal for oxygen on W (110) is attributed to an increased neutralization rate of ions as substrate temperature increases (Madey and Yates, 1969). The temperature dependence of ESD yield of alkali metal ions from a siliicided iridium surface (Ageev and Yakshinsky, 1995) is associated with the transfer of thermal energy from the solid during the reverse motion of the desorbing ion, and with the increasing initial escape velocity of the ion from the surface. Somewhat larger reversible effects are seen in ESD of neutral Eu and Sm atoms from adsorbed monolayers on oxygen-covered W surfaces (Ageev et al., 2003a, 2003b). In both cases, the electron-stimulated desorption mechanism involves resonant electronic excitations of W, Sm, and Eu core levels; the temperature dependence of the ESD atom yield is associated with the lifetimes of core excitons. A reversible temperature dependence is also observed for desorption of alkali atoms from oxidized W at \( E_e > 25 \text{ eV} \) (Ageev et al., 1996), and attributed to temperature dependent charge transfer.

The reversible temperature dependences shown in Fig. 4 for PSD and ESD of Na from a lunar sample are quantitatively different from the measurements described in the previous paragraph. The excitation energy (1–5 \( \text{eV} \) for PSD) is much lower than for the above-mentioned ESD studies, and the desorption yield follows a Boltzmann plot over a wide range of low temperatures; the yield increases by ∼10× from 100 to 470 K. The effect is too large to be explained easily by changes in vibrational amplitudes or electron tunneling probability (charge transfer rates). Note also in Fig. 4b that both PSD (\( h\nu \lesssim 5 \text{ eV} \)) and ESD (\( E_e \sim 200 \text{ eV} \)) at different excitation energies exhibit the same temperature dependences. PSD proceeds via charge transfer neutralization, while the ESD signal contains contributions from core-level excitations. This suggests that the temperature-dependent desorption yields are less influenced by the details of electronic excitation mechanisms than by the initial-state bonding configuration and final state survival probability.

A possible explanation of the data of Fig. 4 is a temperature-dependent change in binding sites, where the local atomic coordination changes and, therefore, the PSD/ESD desorption rate is different. Recent calculations for binding of alkali atoms to amorphous SiO₂ surfaces indicate that the alkali is completely ionized, and that the two most energetically-favorable sites involve coordination to two and three O⁻⁻ anions, respectively (Lopez et al., 1999). In this case, the difference in adsorption energy is ∼0.5 eV, much greater than the energy of ∼0.02 eV derived from the slope of Fig. 4b. The lunar sample is a much more heterogeneous material than pure SiO₂, and it is possible that there are subtle reversible changes in local bonding configuration of Na⁺. That is, Na⁺ may diffuse locally and reversibly to O⁻⁻ sites associated with different cations (Ca⁺⁺, Si⁺⁺, Al⁺⁺, etc.). The more stable site at lower temperature could involve higher O⁻⁻ coordination number, and a correspondingly low PSD yield. As population shifts from a “PSD-inactive” site at low \( T \) to a “PSD-active” site at higher \( T \), the measured PSD signal changes.

For insights into how changes in bonding can affect desorption of alkalis, consider a phenomenological description of ESD and PSD that is based on models of Menzel and Gomer (1964) and Bass and Sanche (2003). For excitation energies near threshold, the cross-section for desorption of an alkali atom can be expressed as

\[
\sigma = \sigma_c(E)P_s, \tag{1}
\]

where \( \sigma_c \) is the cross-section for excitation and capture of an electron by a surface Na⁺ cation, i.e., the cross-section for charge transfer from the substrate to the cation resulting in formation of Na⁺ in a repulsive configuration. \( P_s \) is the survival probability of the Na⁺ atom against autodetachment of the electron via hopping back to the substrate. \( P_s \) is given by

\[
P_s = \exp\left\{-\int_{Z_c}^{Z_0} R(z)/v \, dz \right\}, \tag{2}
\]

where \( R(z) \) is the rate of electron hopping (s⁻¹) from Na⁺ to the substrate, \( v \) is the velocity of the atom away from the surface along the excited state potential curve, \( z_c \) is the equilibrium substrate-cation bond length, and \( z_0 \) is a critical distance for electron hopping (if the atom survives beyond \( z_c \), it will desorb as Na⁺).

We can simplify the integration by defining an average lifetime \( \tau_a = R(z)^{-1} \) and letting \( \tau \equiv (z_c - z_0)/v \), to give

\[
P_s \approx \exp[-\tau/\tau_a] \quad \text{and} \quad \sigma \approx \sigma_c \exp[-\tau/\tau_a]. \tag{3}
\]

Thus, the desorption cross-section has an exponential dependence on the lifetime \( \tau_a \) of the transient atom and on its velocity \( v \) away from the surface. For a given value of \( \tau \), if \( \tau_a \) is very short (fast electron hopping time from atom to substrate) the cross-section \( \sigma \) is smaller than for the case of long \( \tau_a \) (slow hopping time) where the cross-section is large.

If there are multiple adsorption sites on the surface for which \( \tau \) and \( \tau_a \) are very different, then this lifetime argument can be used to provide insights into the temperature dependent data for ESD/PSD of Na from a lunar sample.

Assume there are two adsorption sites (1 and 2) separated in energy by \( \Delta E \sim 20 \text{ meV} \) and located in close proximity to one another, so that adsorbed Na can diffuse or “hop” between them. The lower energy site (1) is preferentially populated by Na⁺ at 100 K (concentration \( N_1 \), atoms/cm²), and as temperature increases, the Na⁺ population (\( N_2 \), atoms/cm²) in the higher energy site (2) increases according to the Boltzmann factor \( N_1/N_2 \approx \exp[-\Delta E/kT] \). If during ESD or PSD, the Na desorption cross-section at site 2 is higher than at site 1, a temperature dependent desorption yield is measured. That is, if the lifetime \( \tau_a \) of the transient Na atom formed in site (1) is shorter
than the lifetime $\tau_a$ of the transient Na atom formed in site 2, the cross-section for desorption from site 1 (Eq. (3)) is correspondingly smaller than from site 2. As indicated above, subtle changes in bonding configuration and coordination number may be the cause of such lifetime effects, giving rise to “PSD-inactive” and “PSD-active” sites.

Future measurements will focus on PSD studies of Na on a binary system, SiO$_2$, for which the adsorption chemistry will be easier to characterize than that of the complex lunar sample.

These data have important implications for attempts to model the source processes for Na in tenuous planetary atmospheres. Whereas thermal desorption of Na is expected to contribute to Mercury’s atmosphere due to the high surface temperature ($\sim 700$ K at the subsolar point), the present measurements indicate that thermally-assisted PSD can also occur. That is, under conditions such that thermal desorption of Na is negligible (e.g., at the lunar surface), variations in surface temperature can have a large effect on the PSD rate.

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References


