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Photo-atomic effect: Temperature dependence of the photodesorption of Na and Na_2 from polymer surfaces

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Abstract. Alkali metals adsorbed to surface films of the polymer poydimethylsiloxane (PDMS) have been shown to exhibit a unique photodesorption behavior, characterized by a frequency threshold and high efficiency. In this work, the temperature dependence of the photodesorption yields of Na and Na_2 from PDMS surfaces were measured between room temperature and 183 K. Over most of the temperature range, the yields exhibited an Arrhenius behavior characterized by thermal activation energies of 0.36 eV and 0.34 eV for Na and Na_2, respectively. These values are suggestive of a surface diffusion as one of the elementary steps in the photodesorption mechanism. Moreover, the similarity of the two values indicates that the same elementary step applies to the desorption of both Na and Na_2.

PACS. 34.50.Dy Interactions of atoms, molecules, and their ions with surfaces; photon and electron emission; neutralization of ions – 79.20.La Photon- and electron-stimulated desorption

1 Introduction

Alkali metals adsorbed on films of polydimethlsiloxane (PDMS) are observed to be very easily desorbed when exposed to visible radiation [1–4]. The photon stimulated desorption (PSD) is unusual because it is easily induced by weak visible radiation in vapor cells at room temperature. For adsorbed sodium this effect is visually quite startling when first observed using laser induced fluorescence of Na atoms. A few hundred milliwatts per cm^2 of visible laser radiation applied to a glass cell with a PDMS coating can produce a sodium vapor density that is six orders of magnitude larger than the thermal value at room temperature. Besides sodium, the effect has also been observed for potassium [1], rubidium [1,4], and cesium [5] atoms as well as Na_2 molecules [1,2].

The PSD yield as a function of frequency is found to be characterized by an energy threshold and a functional dependence on photon energy that is analogous to that of electron photoemission from metals:

$$Y(h\nu) = c(h\nu - \chi)^2 \tag{1}$$

where χ is the threshold energy or work function [6,7], and c is a constant. Equation (1) holds for conditions where $h\nu > \chi$ and gives the well-known linear Fowler plot [8] when the square root of the photoyield is plotted *vs.* photon energy. The Fowler plot has long been used as a method for the determination of values of the photoemission work function, χ the theoretical treatment of Fowler [6], extended by DuBridge [7], follows from the application of Fermi-Dirac statistics to the delocalized electrons in a metal, and gives an accurate description of the frequency dependence of the photoemission yield near threshold. When $h\nu > \chi$, the expression for the yield reduces to the quadratic dependence in equation (1) which is also a characteristic of the more modern theory of photoemission in which the radiation induces direct transitions between initial and final electron states in the bulk material [9]. Because the atomic and molecular photodesorption yield from PDMS also exhibits a quadratic dependence on photon energy as well as a threshold, one is drawn to an exploration of mechanisms that incorporate electronic excitation from highly delocalized states characterized by a band structure where the Fowler treatment and its modern extensions would be applicable. For atomic and molecular desorption, this dependence on the frequency of the desorbing light appears to be quite distinct from the other well-known radiation induced desorption mechanisms which include desorption from small metal clusters arising from excitation of surface plasmon polaritons as well as desorption due to excitation of inner shell electrons [10–15].

In addition to the frequency threshold, an unusual observation is the measured difference in threshold energy between the photodesorption of sodium atoms and sodium dimers from the PDMS surface. This difference is found

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to be approximately $\chi(\mathrm{Na}_2) - \chi(\mathrm{Na}) = 2\,000\ \mathrm{cm}^{-1}$, and is accounted for by a model in which some of the adsorbed sodium forms a charge transfer complex with the PDMS surface film: $\mathrm{Na}^+\mathrm{PDMS}^-$ and $\mathrm{Na}_2^+\mathrm{PDMS}^-$. Indeed, a reasonable structure for the adsorption of Na atom on the PDMS is the formation of a Na cation, stabilized by the formation of a complex with a nest of oxygen atoms belonging to the polymer. A similar charge transfer structure holds for adsorbed sodium dimers. For Na, the atomic valence electron can be delocalized into orbitals originating from a basis of low-lying empty atomic orbitals on the Si atoms of the polymer. These charge transfer sites are the source of the PSD. The adsorption-PSD process can be schematized as follows:

$$\text{adsorption}$$

$$\mathrm{Na(gas)} + \mathrm{PDMS(solid)} \Rightarrow \mathrm{Na}^+\mathrm{PDMS}^-\mathrm{(solid)}$$

$$\mathrm{Na_2(gas)} + \mathrm{PDMS(solid)} \Rightarrow \mathrm{Na}_2^+\mathrm{PDMS}^-\mathrm{(solid)}.$$

The absorption of photons produces a reverse electron transfer, neutralizing the alkali with enough kinetic energy (KE) left over to eject it from the surface, according to:

$$\text{photodesorption}$$

$$\mathrm{Na}^+\mathrm{PDMS}^- + h\nu \Rightarrow \mathrm{Na} + \mathrm{PDMS} + \mathrm{KE}$$

$$\mathrm{Na}_2^+\mathrm{PDMS}^- + h\nu \Rightarrow \mathrm{Na}_2 + \mathrm{PDMS} + \mathrm{KE}.$$

This electron transfer model is supported by the measured difference in threshold energy between Na and Na_2 [2]. A similar electron transfer model has been shown to be the mechanism for the PSD of Na atoms from surfaces of amorphous SiO_2 thereby explaining the existence of a tenuous atmosphere of Na vapor on the Moon and the planet Mercury [16].

In order to gain further insight into the desorption mechanism, the thermal dependence of the photodesorption yield was measured for both Na and Na_2. As in previous work, laser induced fluorescence (LIF) was used to probe the Na and Na_2 vapor densities. Illumination of the Na coated PDMS surface in the vapor cell environment produces an increase in sodium vapor density which reaches a steady state value dictated by an equilibrium between several elementary kinetic processes [1]. If any one of the elementary steps are thermally activated, the temperature dependence of the steady state increased vapor density would be expected to yield an Arrhenius activation energy, the measurement of which is the objective of the present work.

2 Experimental

The vapor cell preparations were identical to those previously described [1,2] except that the cells were 1.5 cm diameter spheres, small enough to fit inside a Galileo Model KIC ST cryostat. The temperature of each cell is monitored with a thermocouple in contact with its outer surface. In every case the interior PDMS coating is prepared as previously described from commercial liquid material having 350 000 $\mathrm{mm}^{-2}\mathrm{s}^{-1}$ viscosity. After preparation of the surface coating and baking, a small amount of sodium metal is deposited under vacuum by evaporation from an adjoining reservoir of the metal. No buffer gas is added. Na vapor density was monitored by measuring the intensity of the LIF produced by a 1 mm diameter 10 mW probe beam tuned to the Na D_1 transition. With this probe beam of radiation alone, a measurable desorbed Na atomic density could be detected at temperatures as low as 183 K.

For the temperature dependence study of the Na atomic desorption a measurement was made of the increased Na density produced by an additional 200 mW beam of 514 nm radiation expanded to match the 1.5 cm cell diameter. The Na D_1 fluorescence intensity induced by the 1 mm diameter, 10 mW probe beam was measured with a photomultiplier after passing through a JY 1000 monochromator to discriminate against scattered 514 nm radiation. The increase in Na resonance fluorescence produced by the application of the 514 nm radiation was measured as a function of temperature.

Laser radiation at 488 nm was used to monitor the Na_2 density as well as desorb Na_2. A constant 60 mW, 1 mm diameter laser beam was used as the Na_2 LIF probe and, when applied to the cell, also produced desorption from the spots of entry and exit to the cell. A second beam of 488 mm radiation (88 mW expanded to 1 cm diameter) was also used to illuminate the cell, and was turned on (and off) to produce an increase (decrease) in Na_2 LIF at different temperatures. The Na_2 fluorescence from the 1 mm diameter probe laser beam was imaged on the slit of the JY 1000 monochromator which was set to pass the strongest Na_2 rovibrational transition LIF at 530 nm and to discriminate against scattered 488 mm radiation. The same experiments were repeated for both Na and Na_2 in a second cryostat using flowing N_2 which was first precooled to near liquid N_2 temperatures and then subsequently passed over a heater to obtain the desired temperature. The results of the latter measurements were identical to those obtained with the thermoelectric cryo-cooler, but with a slightly higher error of measurement. While the Na atomic desorption data reported here was obtained down to 183 K for Na atoms, the Na_2 measurements data could be obtained only down to 255 K.

3 Results and discussion

The temperature dependence measurements of the steady-state desorption yield obtained from the intensity measurements of the LIF of Na and Na_2 are displayed in Figure 1. The fractional decrease in yield is plotted as a function of inverse temperature on a semi-log plot in order to test whether the yields are adequately described by an Arrhenius rate law with the desorption yield proportional to $\exp[-(E_\mathrm{A}/kT)]$, where E_A is the activation energy. While the data do exhibit Arrhenius behavior over a substantial range of temperature, there is some deviation at the lower. For the upper temperature range, activation energies of 0.36 eV and 0.34 eV can be extracted for Na and Na_2, respectively. For the lower temperatures

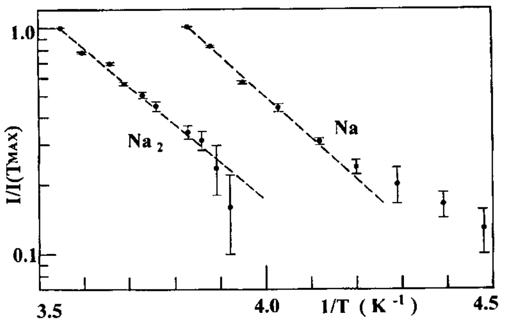

Fig. 1. The temperature dependence of the photodesorption of Na and Na_2 from PDMS surfaces. The data are displayed as the decrease in density from that at the highest temperature measured, $T_{\max}$.

the error increases because of the low signal/noise in this region.

The kinetic model for the elementary steps in the PSD process proposed in the initial announcement of the discovery of this new phenomenon [1] consists of several mechanistic steps that are ultimately responsible for the steady state desorption yield: (1) the photoejection from the charge transfer sites that are PSD active, (2) the readsorption of atoms and dimers to the walls of the cell which include not only the PSD active sites, but also regions possibly occupied by neutral clusters and films, and (3) the surface diffusion of atoms and dimers from these "reservoirs" or non-PSD active sites to those from which photoejection can again be induced. While the details of the surface morphology are unknown, it is likely that not all Na and Na_2 adsorbates occupy sites that are susceptible to photodesorption by visible light. The existence of regions where the sodium can exist as clusters on the surface or as films of neutral metal cannot be ruled out. The small magnitude of the thermal activation energies extracted from the temperature dependence data are consistent with barriers to surface diffusion of the neutral species. They are significantly smaller than the PDMS photodesorption threshold values of 1.18 eV and 1.43 eV for sodium atoms and dimers, respectively, and the value of the metal surface binding energy for a Na atom which is 0.7 eV [15]. The surface adsorption energy of Cs to a variety of gas cell wall coatings closely related to PDMS has been studied yielding values of about 0.40 eV [17]. It is also significant that the activation energy for Na atoms is nearly identical with that for Na_2 dimers. This suggests that the same elementary step exists for both, possibly being surface diffusion of Na atoms to find Na^+ to produce Na_2^+ as well as finding an unoccupied PSD active site.

It also should be pointed out that the thermal activation energy for the Na atomic yield is similar to that obtained from PSD measurements on small Na metallic particles on quartz surfaces where the desorption mechanism is due to the excitation of surface plasmons. This necessitates a re-examination of the similarities and differences between the two experiments. Desorption of atoms and molecules due to the surface plasmon mechanism has been observed for a number of metals including sodium [10–15]. One similarity between the surface plasmon and PDMS experiments is the linear dependence of the desorption yield on laser intensity and absence of a power threshold. Neither phenomenon appears to be due to thermal heating. The quantum efficiency for the surface plasmon desorption [13] is of the order of 10^{-4}. While an accurate value for that from PDMS remains to be obtained, it appears that it is at least an order of magnitude larger than for the plasmon excitation. In the case of Rb on PDMs, the PSD efficiency has be found to be 10^{-2} in experiments similar to those described here [18]. The Na photodesorption from PDMS surfaces can easily be observed by turning on the room lighting or illumination with a flashlight. On the other hand, using the identical cell preparation conditions and illuminating lasers, no detectable photodesorptin could be observed in glass cells in the absence of PDMS films. Also, the effect could not be observed for cells coated with a variety of other polymers such as saturated hydrocarbon films or films of crown ethers. Structurally, it seems that the film coating requires the presence of Si as in the siloxanes. A major difference between the two photodesorption mechanisms is the dependence of the yield on the light frequency. The plasmon mechanism in Na does not appear to display a frequency threshold, but one is definitely observed for Na on PDMS. Furthermore, the surface plasmon experiments exhibit a resonance in the frequency dependence of the yield which is a function of particle size: a resonance centered around $\lambda = 500$ nm is found for Na particles with a 50 nm mean radius, for example [11]. No such resonance is observed in the frequency dependence of the PSD yield from PDMS surfaces. For the surface plasmon mechanism, the position of the frequency resonance shifts to longer wavelength with an increase in particle size, and the yield is suppressed when the samples are annealed at room temperature. In the PDMS case the photodesorption yield increases with temperature, and there is an absence of a frequency resonance. For a frequency resonance in the yield to occur at room temperature for the PDMS case, it would have to be in the UV, a direction opposite to the shift in the resonance maximum found for surface plasmons when the temperature of the adsorbate is raised to room temperature. However, it should be noted that surface plasmons are known to enhance a variety of phenomena including photoemission of electrons [14]. It is not known whether these play a role in the photodesorption from PDMS films.

While there seem to be major differences between the photodesorption of sodium from PDMS and that for sodium from particles due to plasmon excitation, the present study does reveal a similarity in thermal activation energies. In the plasmon work it was found in one experiment that the activation energy for the photodesorption rate of Na atoms from particles having a fixed mean radius of 50 nm, residing on quartz surfaces at 100 K, is $E_A = 0.14$ eV using 7 W of 514 nm laser radiation in a 2 mm diameter beam [11]. The similarity of this value to those found in the present study for Na and Na_2 from

PDMS surfaces suggests a similar thermally activated process for both experiments. Although the substrates are different, surface diffusion of Na atoms could be that elementary step for both experiments, especially if the surface diffusion were across regions of neutral metal. However, it should also be pointed out that the thermal activation energy was obtained for the PDMS surface from data taken between 200 and 300 K while that in the surface plasmon experiments on quartz was taken from measurements near 100 K. Furthermore, a characterization of the surface morphology of Na on PDMS has yet to be carried out. Nevertheless, the temperature dependence data for the PSD of both Na and Na_2 are consistent with a kinetic scheme whereby (i) Na is photodesorbed from "active" sites, believed to be charge transfer in nature, (ii) Na vapor being adsorbed on the surface at both "active" sites and "reservoir" sites that consist of cluster or films of neutral metal, and (iii) surface diffusion from the reservoir sites to the PSD active sites.

Because of its dramatic sensitivity to light and its ease of observation, the desorption phenomenon from PDMS surfaces clearly deserves more attention aimed at understanding its mechanism. Experiments designed to determine the surface morphology of Na on PDMS are clearly indicated.

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