Classification of Light-Induced Desorption of Alkali Atoms in Glass Cells Used in Atomic Physics Experiments

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We attempt to provide physical interpretations of light-induced desorption phenomena that have recently been observed for alkali atoms on glass surfaces of alkali vapor cells used in atomic physics experiments. We find that the observed desorption phenomena are closely related to recent studies in surface science, and can probably be understood in the context of these results. If classified in terms of the photon-energy dependence, the coverage and the bonding state of the alkali adsorbates, the phenomena fall into two categories: It appears very likely that the neutralization of isolated ionic adsorbates by photo-excited electron transfer from the substrate is the origin of the desorption induced by ultraviolet light in ultrahigh vacuum cells. The desorption observed in low temperature cells, on the other hand, which is resonantly dependent on photon energy in the visible light range, is quite similar to light-induced desorption stimulated by localized electronic excitation on metallic aggregates. More detailed studies of light-induced desorption events from surfaces well characterized with respect to alkali coverage-dependent ionicity and aggregate morphology appear highly desirable for the development of more efficient alkali atom sources suitable to improve a variety of atomic physics experiments. [DOI: 10.1380/ejssnt.2006.63]

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I. INTRODUCTION

Alkali-atom desorption stimulated by photon irradiation is an interesting subject in atomic physics experiments, and often called “light-induced atom desorption” (LIAD). Alkali atoms are widely used in atomic physics experiments because of their simple structure and the availability of handy laser sources such as laser diodes for exciting these atoms. Because alkali metals, in particular heavier alkalis like K, Rb and Cs, have relatively high vapor pressures, evacuated and sealed glass cells containing bulk alkali metal are convenient samples that provide sufficient atomic densities in the gas phase at room temperature and above for laser spectroscopic experiments. Therefore the sealed vapor cells have long been basic tools in atomic physics laboratories, and are currently being utilized as well in many advancing experiments. Only a few of them are listed here, with the employed alkali atoms mentioned in parentheses: Ultrasonic magnetometer (K) [1]; frozen light pulse (Rb) [2]; chip-scale atomic clock (Cs) [3].

In the conventional vapor cell, the atomic density in the gas phase can be increased by heating the cell, which raises the vapor pressure. However this method is not desirable or not applicable at all for some recent experiments, in which LIAD from the glass surfaces of cells is exploited to increase the atomic densities quickly on demand. One of such cells is an ultrahigh vacuum (UHV) cell used in laser cooling and trapping experiments. These UHV cells are continuously evacuated with vacuum pumps to prolong the trap lifetime by reducing collisions with background gases. The typical cell pressure is $10^{-8}$ Pa, which is much lower than alkali vapor pressures at room temperature ($10^{-5}$ Pa ($10^9$ atoms/cm$^3$) for Rb). LIAD of K and Rb from borosilicate glass (Pyrex and Vycor) surfaces has been observed in these cells by irradiation of ultraviolet (UV) photons [4–8]. This phenomenon is useful especially for experiments generating Bose-Einstein condensations (BECs), which require seemingly contradicting conditions of both large numbers of trapped atoms (i.e. a high density of sample atoms) and long trapping times (i.e. low untrapped gas pressures). The recent achievement of a compact BEC system using a microelectronic chip [4] owes its success partly to this LIAD.

The other type of cells in which LIAD is observed are low temperature (LT) cells, sealed alkali (Rb, K) vapor cells (containing He buffer gas) cooled down to liquid helium temperatures (~2 K) [9–11]. The observed LIAD, which exhibits a resonant dependence on the photon energy in the visible light range, is used to disperse alkali atoms effectively into a cryogenic helium gas. It was then demonstrated that the cryogenic helium gas environment preserves quite long the spin polarization of the ground state of alkali atoms. This demonstration has attracted much attention [12] because the slow spin relaxation of the alkali ground state is always a key in many experiments that exploit the ground state polarization and coherence, including the above mentioned that so far use conventional vapor cells.

In spite of the important contributions of these LIAD phenomena to atomic physics, however, the understanding of their mechanisms is quite limited, and the LIAD conditions have been optimized only empirically. Recently, in surface science, two studies have been reported which seem quite helpful to understand desorption mechanisms in the vapor cells. One study was motivated by the search for the origin of atomic Na and K in the planet Mercury and the Moon [13]. These celestial bodies have
tenuous atmospheres containing atomic Na and K, which must be continuously supplied for the steady content of the alkalis. Photon-stimulated desorption was proposed as the origin of the alkali atoms, and laboratory experiments [14–16] demonstrated effective desorption induced by UV photons from model mineral surfaces (amorphous SiO$_2$ surfaces). It is supposed that the desorption is caused by charge transfer excitation from SiO$_2$ to the unoccupied orbital of the almost completely cationic alkali atoms bound to certain surface defects [17]. The other study investigated desorption from alkali (Na and K) nanoparticles (an effective mean size of 10 nm) formed on a quartz substrate held at liquid nitrogen temperature [18]. This desorption was found to be resonantly dependent on the photon energy in the visible light region. It is claimed that the localized electronic excitation of certain binding sites is responsible for the resonant desorption, and that surface plasmon resonances of the nanoparticles may enhance the desorption rate. This mechanism may be used to manipulate metal surfaces on the atomic scale.

The purpose of this paper is to reexamine the LIAD phenomena observed in atomic physics experiments on the basis of the accumulation of desorption models developed in the field of surface science. We find that the observed desorption phenomena seem to be closely related to the two surface science studies mentioned above, and can probably be understood in the following context: it appears very likely that desorption in the UHV cells originates from the neutralization of ionic isolated adsorbates by photo-excited electron transfer from the substrate; while desorption from the LT cells seems consistent with LIAD stimulated by local resonant excitation on metallic aggregates. However we have also noticed that the comprehensive study of desorption for various forms of adsorbates (from isolated atoms to aggregates) on well characterized surfaces under illumination of photons in a wide energy range (from infrared to UV) is still missing. Such a study would provide new insight for the development of a new type of efficient atomic source that can be useful in a variety of atomic physics experiments.

It is noted that LIAD in vapor cells was first observed for silane coatings (in particular, polydimethylsiloxane) on cell walls in the early 90s [19], and since then there have been many investigations [20–23] including desorption from a paraffin coating [24]. In this paper we do not discuss LIAD from polymer coatings, because its mechanism is probably different from the desorption from bare glass surfaces. A recent study on this subject is reported in Ref. [25].

II. REVIEW OF LIAD IN ALKALI VAPOR CELLS

A. Ultrahigh vacuum cells

Several groups have reported LIAD in UHV cells [5–8]. Although each group performed the experiment in a slightly different way, we summarize here the general properties of LIAD in UHV cells. The UHV cell is kept evacuated by vacuum pumps, usually ion pumps, at $10^{-7}$ - $10^{-8}$ Pa. It is usually baked at about 150°C at the cell preparation stage. Alkali atoms are supplied into the cell by heating an alkali metal dispenser [26] or reservoir when necessary. A typical procedure of filling the cell with Rb atoms is as follows [27]: A dispenser is heated for 15 minutes, while the pressure indicated by the ion pump current remains below $10^{-7}$ Pa. After termination of the heating, the cell is left overnight, during which the pressure of the cell returns to the stationary value ($10^{-8}$ Pa) due to the pumping of the alkali atoms and other gases by the cell surface and the ion pump. Laser trapping experiments are performed on the following day using LIAD from the alkali-impregnated (but transparent) cell surfaces to increase the number of Rb atoms in the gas phase. It should be noted that the desorption efficiency is not dramatically reduced even if the cell is left for one month after heating the dispenser. A similar but longer-cycle heat-and-wait procedure is reported in Ref. [8].

The irradiation of the cell walls with relatively high energy photons from, e.g., halogen bulbs or blue LEDs (photon energy: $\sim 3$ eV) rapidly induces desorption, which is monitored by the increase of the number of laser-trapped atoms. Although the absolute number of trapped atoms depends on the configuration of the laser-trapping system, this number is raised by two orders of magnitude to $10^9$ atoms with the LIAD light (blue LEDs of 140 mW, 3.1 eV) on [6], indicating that the atomic density in the gas phase increases by a similar order. The number of trapped atoms increases with increasing photon energy in the range of 1.6 eV to 4.9 eV [8]. After a sufficient number of atoms are trapped, the cell pressure is reduced quickly by turning off the LIAD light. Then the trapped atoms are processed further for, e.g., generating BEC.

Rb is the most popular sample in BEC experiments, and its desorption has been reported by many groups from Pyrex glass [5–7], one of the most commonly used material for glass cells (typical composition: SiO$_2$ 81%; B$_2$O$_3$ 13%; Na$_2$O 4%; Al$_2$O$_3$ 2%), and Vycor glass (SiO$_2$ 96%; B$_2$O$_3$ 3%; Al$_2$O$_3$ 1%) [8]. K desorption is also reported for Pyrex [6] and Vycor [8]. It is reported that quartz is much less suitable for LIAD than Pyrex [5].

It is noted that in UHV cells desorption from metal surfaces was also observed for Rb on stainless steel [8, 28] and Cs on aluminum [28].

B. Low temperature cells

LIAD has been observed by one of the present authors in LT cells, sealed Rb vapor cells cooled to liquid helium temperatures. These glass (Pyrex) cells are filled at room temperature in a manner similar to conventional sealed glass cells (see, for example, Ref. [29]). The cells are prepared under high vacuum conditions ($\sim 10^{-4}$ Pa), baked at a few hundreds degrees of Celsius for a day. Rb metal is transported into the cell from a Rb reservoir through a glass stem connected to the main body of the cell by heating the metal with a hand torch. The empirically best way to maximize the desorption efficiency is to cover the cell surface once with a visible Rb film and then remove it by heating the cell just until the film becomes invisible with the naked eye. Desorption is not observed from visible Rb films on the surfaces. The cell is filled with high-pressure helium gas (typically 3.6 atm at room
temperature), which works as a buffer gas to prevent frequent collisions of Rb atoms with the surface, and then sealed by melting off the glass stem. No visible Rb metal is left in the main body of the cell, while a small amount of solid Rb exists in the remaining part of the stem. The vapor pressures of Rb in the cells vary from cell to cell and usually amount to several ten percent of the saturated vapor pressure. This is probably because bulk Rb metal is almost confined to the stem, and the surface of the main body itself is not covered by metallic Rb [30]. This kind of undersaturation is often observed in sealed vapor cells that do not contain a large reservoir of uncontaminated bulk metal. Cells prepared in a similar fashion in a different laboratory also show LIAD [31]. Thus we believe the observed LIAD in the LT cells is generally reproducible by preparing cells in this way.

The cell is gradually cooled from room temperature. The number of gaseous Rb atoms, which is monitored by observing fluorescence of atoms excited by a probe laser, decreases with decreasing temperature because the saturated pressure of Rb decreases and the gaseous Rb atoms are observed LIAD in the LT cells is generally reproducible by preparing cells in this way.

The loading of atoms by desorption is barely observable in the cell up to about 250 K, at which residual Rb vapor hinders the detection of desorption. There seems to be no strong temperature dependence of the number of loaded atoms.

III. DISCUSSION

The desorption observed in the UHV cells is quite similar, in terms of the photon energy dependence, to the desorption studied using electron impact as well as photon irradiation in the context of the search for the origin of atomic alkalis in tenuous planetary atmospheres [14–16].

In these studies alkali desorption from model mineral surfaces (amorphous SiO$_2$) exhibits a threshold at ~3 eV for K and ~4 eV for Na, a local maximum at 9-11 eV for both K and Na, and a general trend of increasing desorption rate with increasing photon or electron energy. According to a theoretical modeling [17], the threshold can be explained by desorption of alkali adsorbates at non-bridging oxygen (NBO) defects due to the local charge transfer from the O(2p) nonbonding orbitals to cationic adsorbates, while the resonant-like peak at 9-11 eV can be related to a direct or indirect excitation from the O(2p) valence band to the cations. Considering the photon energies used for the desorption in the UHV cells, this desorption would be attributable to the former process. The cross section of the Na desorption at 5 eV is reported to be about $3 \times 10^{-20}$ cm$^2$ [14]. If we take this value for desorption observed in the UHV cells and assume the surface density of the desorbable atoms to be $10^{11}$ cm$^{-2}$, the desorption rate is estimated to be about $10^9$ cm$^{-2}$ s$^{-1}$ for desorption light of 1 mW/cm$^2$. This estimation appears to be quite reasonable [8].

For the desorption observed in the LT cells, the idea that it originates from alkali clusters is not inconsistent with regard to the resonance-like photon energy dependence in the visible light range [18], which strongly resembles the desorption from alkali clusters. This resonant behavior has long been supposed to be related to the surface plasmon resonances of alkali clusters [32]. However, a recent study points out that this kind of resonant desorption may also result from the localized resonant excitation of certain bonding sites of alkali atoms on the alkali cluster surface and the desorption described in Ref. [18] was attributed to such a mechanism [33]. Note that this desorption scenario has its origin in the excitation to the lowest $p_{\frac{3}{2}}$ states of atomic alkali in vacuum (1.62 eV for K and 1.59 eV for Rb). The photon energy dependence (see Fig. 1) observed in the LT cells for K is strikingly similar to that observed in Ref. [18] for K clusters. Thus the mechanism of resonant desorption in the LT cells can either be of this site-selective resonant type, or plasmon-assisted desorption as discussed in Ref. [10].
In order to further examine the validity of the above two explanations, it is essential to characterize the adsorbate morphology of the vapor cells as already pointed out by one of the present authors [34]. Although the two classes of desorption phenomena mentioned above are observed for K and Rb atoms adsorbed on bare glass surfaces [35], their characteristic photon energy dependencies are distinctly different, which points towards differences in the desorption mechanism operative in each case. One important factor affecting the desorption process is probably the difference in the surface condition of the alkali adsorbates as present in the two types of cells. However, the surfaces of the vapor cells used in the above experiments are not carefully prepared and characterized with respect to the alkali coverage and its aggregate condition, as possible e.g. by standard surface characterization techniques such as X-ray photoelectron spectroscopy (XPS) and work-function measurements. Therefore we here try to estimate the surface conditions in the UHV cells and the LT cells on the basis of a comparison to surface studies performed under similar experimental conditions.

There are many reports of alkali atom adsorption on oxide surfaces including SiO$_2$, the main component of common glass. From these studies, it is known that defect sites of the SiO$_2$ surface such as NBO centers strongly adsorb alkali atoms, while the bonding to regular sites is weak [36, 37]. The binding energies to such defect sites are calculated to range from 1 to 3 eV for Cs [37]. Similar binding energies are suggested experimentally for Na [38]. It is worth mentioning that adsorption with such a high adsorption energy is often considered as “reaction” or “loss” of alkali atoms on the surface in atomic physics experiments using conventional vapor cells [39] because once adsorbed the atoms do not return to the vapor phase by moderate elevation of temperature [38]. Note that penetration of alkali atoms into glass may occur [38].

Alkali adsorbs to defects are present as almost completely ionized cations by transferring their valence electron to the surface [17, 36–38]. The adsorbed ionic atoms are repulsive to each other. The surface density of this kind of adsorbate depends on that of the defect sites, which is affected by the processing history of the glass surface as well as by the type of the glass. Although most defect sites would be occupied by various species such as carbonates and hydroxides [40] before cell preparation due to, for example, exposure to air, it is reasonable to assume that some of these defect sites would become unoccupied and reactive to alkali atoms during the evacuation and baking processes.

The surface continuously exposed to alkali atoms as in vapor cells will finally become “non-reactive” ("cured") [39], with all high binding energy sites saturated by adsorbed alkali atoms. On such a cured surface, the adsorption energy for additional adsorbates is lowered, measured using conventional vapor cells to amount to 0.53 eV for Cs on Pyrex [39] and 0.66 eV on fused silica [41]. These adsorption energies are close to the heat of vaporization of bulk Cs (0.67 eV), and therefore the adsorbed alkali may become metallic under these conditions. This transition of the alkali morphology from ionic to metallic with increasing coverage is reported in many surface science studies [36, 38]. The surfaces of the UHV cells are probably quite similar to such cured vapor cell surfaces. It should be remarked, however, that we do not consider that metallic aggregates are present on the surface because the partial pressure of alkali is much lower than the saturation vapor pressure in the UHV cells at room temperature and thus metallic particles are unstable [36].

The density of atoms weakly adsorbed to the cured surface is estimated using the following relation [42] about the residence time on the surface $\tau$:

$$\tau = \tau_0 \exp(E_a/kT),$$

where $\tau_0$ is on the order of $10^{-12} - 10^{-14}$ s, $E_a$ the adsorption energy, $k$ Boltzman’s constant, and $T$ the surface temperature. By balancing the numbers of atoms impinging on and leaving the surface, one can calculate the surface density. Even for a relatively large adsorption energy of 0.7 eV and a long $\tau_0$ of $10^{-12}$ s, the surface density of weakly adsorbed atoms is still estimated to be low (compared to the monolayer coverage density of $10^{14}$ cm$^{-2}$), i.e. $10^{10}$ cm$^{-2}$ in a UHV cell with an alkali vapor pressure of $10^{-8}$ Pa. This estimation also supports the picture that the adsorbed atoms on the UHV cell surfaces are mainly isolated. Most of them are strongly bound to defects, while others are weakly trapped and eventually return into the gas phase. These conditions are similar to the ionic adsorbate conditions of low coverage surfaces in the studies of Na and K desorption from amorphous SiO$_2$.

The situation of the LT cells is different. Their surfaces are usually once covered with alkali films at the filling stage (although the films are removed afterwards by heating just until they become invisible with the naked eye), and are kept exposed to alkali vapors at pressures nearly equal to the saturated vapor pressures. These are favored conditions for the presence of alkali aggregates on the surface. The cooling of the cells is also favorable for aggregate formation, because the surface density of adsorbates increases. It is known that at low temperatures additional exposure to vapors can lead to formation of metallic aggregates [34, 38, 43]. Therefore it is rather likely that in the LT cells there exist some alkali aggregates or clusters on the surface, similarly to the study of desorption from alkali nanoparticles formed on the quartz surface. However, it should be pointed out that a solid conclusion must wait for the experimental characterization of the cell surfaces especially because we do not precisely know the amount of deposited alkali metal.

As seen above, the estimation of the surface conditions also supports close relations between the following desorption phenomena: desorption observed in the UHV cells and desorption of ionic adsorbates from amorphous SiO$_2$ on one hand, and desorption observed in the LT cells and desorption from alkali nanoparticles formed on quartz on the other. Thus, it appears reasonable to conclude that the desorption observed in the UHV cells originates from the neutralization of ionic alkali atoms adsorbed on defects by photo-excited electron transfer from the substrate, whereas the desorption observed in the LT cell may occur from alkali metal aggregates.
IV. FUTURE PERSPECTIVES AND CONCLUSION

Light-induced desorption of alkali atoms deposited on glass surfaces may occur via various mechanisms in a wide photon energy range from different forms of adsorbates, and the desorption phenomena observed in the UHV cells and the LT cells are only two prominent examples. If their mechanisms could be clarified, there should exist many possibilities to increase the desorption efficiency by optimizing the experimental conditions. For this purpose, it is very desirable to study the desorption process of ionic (isolated) and metallic (aggregated) adsorbates under well-characterized adsorption conditions using various photon energies from infrared to ultraviolet. The surface characterization with respect to the initial state of the desorption event in terms of the alkali coverage and bonding conditions is quite critical to derive a solid conclusion. Not only the photon energy dependence but also the analysis of the kinetic energy distribution of the desorbing atoms should be very helpful to elucidate the desorption mechanisms.

Experiments that nearly fulfill these requirements have been reported for K on Cr$_2$O$_3$ surfaces [34] as well as for Na and K on SiO$_2$ surfaces [14–16]. Desorption from both ionic and metallic adsorbates is studied, although only high energy photons (≥3 eV) were used. The result shows that the desorption cross section is higher for ionic adsorbates than for aggregates at this photon energy. However, because of many possible desorption sites in metallic aggregates at larger alkali coverages, the total desorption rate is not necessarily smaller than in the case of ionic atoms at much lower coverage. It is further interesting to point out that for large-scale metallic adsorbates the desorption rate may even increase under prolonged light irradiation, which indicates that the desorption cross section may be strongly sensitive to the metal particle morphology and/or the total alkali coverage.

From these as well as the other results described in this paper, the following can be anticipated. For desorption of isolated ionic atoms, which are supposed to be present as majority species on low-coverage surfaces in the UHV cells, it seems promising to use as substrates glass surfaces that have many active defect sites. Mechanically activated surfaces like the surfaces of cleaved or fractured glasses under UHV conditions are hopeful candidates [44]. Higher photon energy appears preferable, regarding the general trend of increasing desorption efficiency towards large excitation energies. Aggregates prepared on a high-coverage surface cooled in UHV chambers could be an effective LIAD source. It would be helpful to see which photon energy is the most efficient for aggregates of a given size, or whether in turn the aggregate size could be controlled to yield particularly efficient desorption at a certain excitation energy.

In the case of the LT cells, where the surface condition is less well understood than that of the UHV cells, it is important to identify first the morphology of adsorbates from which desorption occurs. This would be the first step to understand the desorption mechanism and develop a better atom loading method. It is noted that desorption using UV light has not been attempted yet and is therefore worth trying.

In conclusion, on the basis of models that have been developed in the surface science field, we reexamined LIAD phenomena recently observed in atomic physics experiments. Empirically, the reviewed results may be classified into two categories of LIAD phenomena, i.e. as desorption stimulated by UV light in UHV cells on one hand, and resonant desorption in the visible light range in LT cells, on the other. It is very likely that desorption in the UHV cells is induced by the neutralization of the ionic isolated adsorbates by photo-excited electron transfer from the substrate. The mechanism of this type of desorption has been studied in a series of studies motivated by the search for the origin of atomic alkalis in planetary atmospheres. The desorption in the LT cells appears to be closely related to LIAD from metallic aggregates by localized resonant excitation. These conclusions were supported by estimation of the surface conditions of these two types of cells: Isolated and ionic adsorption of alkali atoms is expected on the low-coverage surfaces of the UHV cells, while the LT cell surfaces with their higher alkali coverage favor the formation of metallic aggregates. However, because the surface conditions of these vapor cells are not well understood, and comprehensive data of desorption from various types of adsorbates using a wide range of photon energies is still missing, future detailed studies are very desirable. Such studies of the surfaces of vapor cells would contribute substantially to various atomic physics experiments in which the cell surface plays an important role in terms of not only LIAD but also, e.g., loss of rare radioactive atoms on the surface [39], surface electrical conductivity [41], and spin relaxation of gases on the surface [24, 29].

[27] M. Horkoski (private communication).
[35] Strictly speaking, the cell surface is coated with a helium film in the case of the LT cells. However, we do not consider that the helium film affects the desorption process as also claimed in Ref. [10].