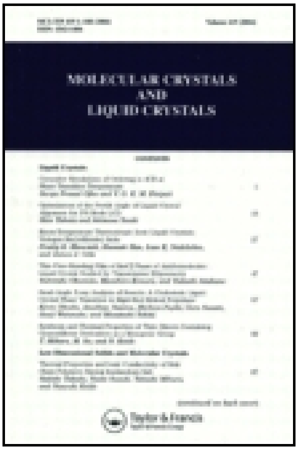

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Exclton Induced Desorption at the Surface of Rare Gas Solids

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Exciton Induced Desorption at the Surface of Rare Gas Solids

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The electronic excitation on the surface of rare gas solids can lead the desorption of a variety of species. Close investigation of the desorption phenomena will reveal the dynamical aspect of the electronic excitation and its relaxation process at the surface. In the case of rare gas solids, the desorption of an excited neutral particle is closely related to the production of an exciton.

Keywords: desorption induced by electronic transitions; photo-stimulated desorption; exciton; rare gas solid; metastable

INTRODUCTION

When the surface of a solid rare gas is irradiated with vacuum ultraviolet light, it can eject various species, such as, molecules, ions, excited neutrals, and clusters. A variety of desorption mechanisms has been proposed for each desorbed species and for the excitation energy regime. In the case of rare gas solids, the desorption of the excited neutral particle is closely related to the production of the exciton. In 1984, Colletti et al.[1] showed that the desorption of an excited neutral was initiated by the exciton creation in solid argon. Feulner et al.[2] reported the first observation of the clear correlation between the excitons and the desorption of neutral molecules from rare gas solids. Kloiber and Zimmerer[3] reported the measurement of the kinetic energies of Ne metastables desorbed by photo-excitation and that the distribution of their kinetic energy apparently depended on the photon energy. They proposed two types of desorption mechanisms; one is closely connected with an atomic type exciton and the other with a molecular one. Arakawa et al.[4] showed that there are two peaks, at 0.6 eV and 0.04 eV, in the kinetic energy distribution of metastable Ar atoms desorbed from the surface of solid Ar by electron excitation. Similar results were also obtained by Johnson and his coworkers[5]. Arakawa and Sakurai[6] showed that the second or higher order exciton leads to the desorption of the Ar metastable with the kinetic energy of 0.6 eV by PSD (photo-stimulated desorption) experiment using synchrotron radiation as a state-selective excitation source. The investigation of the desorption phenomena initiated by exciton excitation is one of the powerful tool to reveal the dynamic characteristics of the exciton. Recent topics relating to this phenomena have been reviewed by Runne and Zimmerer[7].

In the present paper, it is shown that the desorption characteristics elucidated in the experimental study can be satisfactorily explained by the proposed two basic models of desorption mechanism and thier variation. The detailed characteristics of the desorption kinetics upon the exciton creation at the surface of rare gas solids are also described.

DESORPTION MECHANISMS

Two desorption mechanisms were proposed and have been confirmed by many experimental and theoretical studies: a cavity ejection (CE) mechanism is due to the repulsive interaction between the excited atom with an inflated electron cloud and the matrix with negative electron affinity and an excimer dissociation (ED) one is the dissociation of an excimer in the vicinity of surface. The metastables desorbed through CE process have been observed for the solid which electron affinity E_A is negative, namely, solid Ne ($E_A = -1.4$ eV) and Ar (−0.4 eV), but not for solid Kr (0.3 eV) and Xe (0.5 eV)[8]. The kinetic energy E_k of the metastable desorbed through CE process is originated from the lattice distortion energy around the exciton which can roughly be estimated from the difference between the excitation energy E_x of the exciton and the corresponding excited state energy E_g of the isolated atom in gas phase[3]. After a simple mathematics on the energy conservation, the energy difference, $E_x - E_g$, is divided into the following terms: $E_x - E_g = E_k + E_{coh} + E_{lat}$, where E_{coh} is the cohesive energy of an atom on the surface and E_{lat} is the energy absorbed in the lattice after the desorption[9]. It has been shown experimentally[3] and by the molecular dynamic calculation[10] for Ne and Ar that 30 - 70 % of the lattice distortion energy is transferred into the kinetic energy of the desorbing metastable. In the case of Ne, E_k of the metastable which is desorbed by the first order surface exciton at the excitation energy of 17.17 ± 0.03 eV is 0.18 eV at the peak of the distribution, while that of the corresponding $2p^5 3s$ metastable states of Ne atom are 16.619 eV($^3P_2$) and 16.716 eV ($^3P_0$)[11].

A ground state neutral atom can be ejected by the dissociation of an excited dimer at the surface, $R_2{}^* \rightarrow R + R + E_k$; that of a highly excited dimer can result in the desorption of an excited neutral, $R_2{}^{**} \rightarrow R + R^* + E_k$. The kinetic energy E_k which is released in this ED process can be evaluated from the gas phase experiment and is 1.2 eV in the case of $Ne_2{}^*$[12].

EXPERIMENTAL

The experimental apparatus and method used in this study have been described in detail elsewhere[13] and are briefly summarized here. The solid rare gases were formed on the copper or platinum substrate which was attached to a liquid helium cryostat in an ultra-high vacuum chamber with a base pressure of 10^{-8} Pa or lower. An amount of rare gas condensed on the substrate, the layer thickness, was calculated from the exposure, the product of a pressure and a period of time of condensation, assuming the condensation coefficient to be unity. The vacuum ultraviolet light used in the experiment was obtained from the beam line BL5B of UVSOR facilities at the Institute for Molecular Science, Okazaki. The wavelength resolution, $\lambda/\Delta\lambda$, in the present experiment was about 500 ± 200. For the time-of-flight(TOF) measurement, the monochromatic light was chopped by a rotating disc with slits to the pulse beam of 16 μs duration and 2 ms interval typically. The metastables desorbed from the solid rare gas were detected by a secondary electron multiplier or a microchannel plate. The flight length, the distance between the sample and the detector, was set between 64 mm and 360 mm for the purpose of experiment. Charged particles were rejected by applying suitable potentials to a retarding grid mesh and the entrance electrode of the detector. The particles detected here are VUV photon and the metastables, Ne* and Ar*, with the internal excitation energy of about 10 eV or larger and whose life time is much longer than the flight time, namely, $^3P_2$ and $^3P_0$ states of them[11],[14].

DESORPTION AT THE SURFACE OF PURE RARE GAS SOLIDS

Dependence on Excitation Photon Energy

The time-of-flight spectra of the metastable species desorbed from the surface of solid Ne are shown in Fig. 1 (a). The sharp and strong peak at the left is due to the scattered light and the luminescence with short life time from solid Ne, the position of which is therefore an origin of the flight time measurement. The prominent peak at around 300 μs of the flight time is caused by the metastable species. If we assume that these are monomer Ne*, the kinetic energy is calculated at about 0.2 eV.

The intensity of the 300 μs peak in Fig. 1 (a) largely depends on the excitation energy as shown in Fig. 1 (b). Most of the observed peaks in the

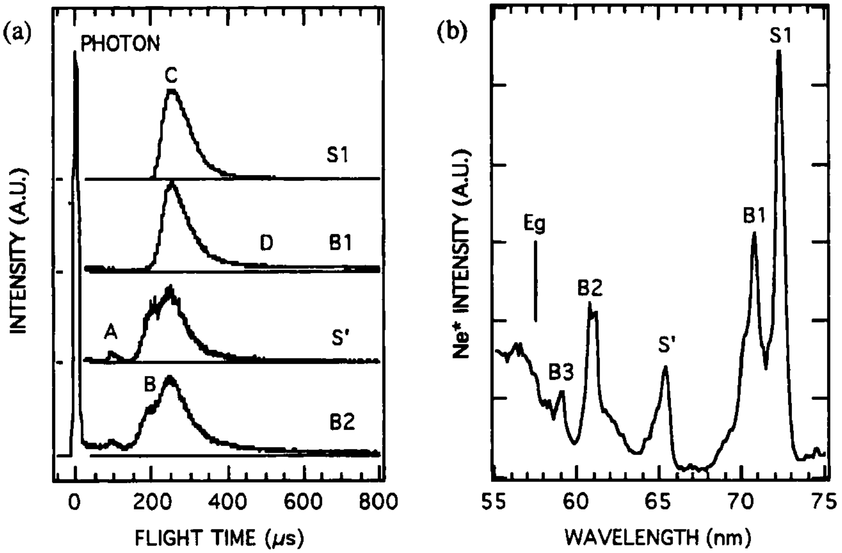

FIGURE 1 (a) Time-of-flight spectra of metastable Ne initiated by four types of excitons. The flight length is 360 mm. (b) Yield of metastable Ne desorbed through the cavity ejection process as a function of a wavelength of incdent photon. The wavelengths for the excitation of excitons, S1, B1, S', and B2 are 72.3, 70.7, 65.4, and 61.1 nm, respectively.

figure can be assigned to a series of the bulk (B) and the surface (S) excitons reported by Saile and Koch[15], where S' peak is caused by the exciton in the $2p^53p$ state which is allowed at the surface because of the reduced symmetry[16]. Additional structures, that is, the double peaks at B2, considerable yields between B2 and S', and the tail of B1 peak at the higher energy side, have always appeared, however, with poor quantitative reproducibility. It has not been clarified yet whether the origin of these peak is intrinsic to pure solid Ne or not. It is sure that these peaks are strongly affected by surface conditions, that is, surface crystal structures and impurities adsorbed on it.

The four TOF spectra of Ne* in Fig. 1 (a) were obtained by the excitations at S1, B1, S', and B2 excitons. It has been already revealed[3] that the higher kinetic energy peak A (E_k = 1.4 ± 0.1 eV)[17], which is only observed by the excitation of the higher order excitons (S' and B2), is caused by the excimer dissociation (ED) of the highly excited dimer: $Ne_2^{**} \rightarrow Ne + Ne^* + E_k$. This is also the case for Ar[6]. The lower kinetic energy peak, that is CE one, is obviously composed of two components B (E_k = 0.21 ± 0.02 eV) and C (E_k = 0.18 ± 0.02 eV)[17]. The surface excitons S' and S1 lead these peaks B and C, respectively[18]. The difference in the kinetic energy is attributed to the difference in the magnitude of the repulsive interaction because of the different size of the excitons. The low energy tail D is only observed by the bulk excitations (B1 or B2)[18] and is likely caused by the bulk exciton trapped in the underlying layer just below the surface. It may be ejected into the vacuum, loosing its kinetic energy by pushing aside the atoms in the overlayer.

Angular Distribution of Desorbed Metastables

The peaks B and C in TOF spectra of Fig. 1 (a) have a sharp angular distribution along the surface normal; however the sharpness of the distributions depends on the initial excitation energy[19]. The Ne* desorbed by S1 excitation has the sharpest distribution along the surface normal with an FWHM of 36°; n = 14 if the distribution is fitted into $\cos^n \theta$, where θ is a polar angle. This remarkable sharpness can be interpreted by the computer simulation of CE process[19]. The CE species desorbed by B1 and S' excitations have FWHM of 42° (n = 10) and 47° (n = 8), respectively. The reason for the obvious difference in the angular distribution between CE species desorbed by S1 and by S' has not been clarified yet. Tail D in Fig. 1 (a) due to B1 excitation shows FWHM of 70° - 90° (n = 2 - 4). The low kinetic energy and the broad angular distribution of tail D support that this component is desorbed through the process mentioned in the previous section.

If the dissociation of the excimer occurs at the outermost surface of solid Ne, it may be expected that the Ne metastable is ejected into the direction of [110], which is the axis of the excimer in a fcc crystal[20]. However, the recent careful experiment[18] showed that ED species, peak A in Fig. 1 (a), has an almost uniform angular distribution with FWHM of 120° or more ($0 \leq n \leq 1$ for $\cos^n \theta$) and that no azimuthal structure around the surface normal was observed. Another interpretation for this broad angular distribution is that the dissociation of the highly excited dimer, Ne_2^{**}, occurs in the vacuum after the ejection by CE mechanism. The desorption of the excimer and the luminescence from the excimer have been reported for Ne[21] and Ar[10], [22], [23]. In the case of Kr, the adsorption of hydrogen on the surface of solid Kr, which turns the electron affinity into negative, initiates this two step mechanism; CE desorption of Kr_2^{**} followed by ED process, $Kr_2^{**} \rightarrow Kr + Kr^* + E_k$, in vacuo[24].

Absolute Desorption Yield

The measurement of an absolute yield of the desorption is indispensable for making clear the excitation and the relaxation processes: branching ratio in the cascade of deexcitation process, for example. In order to calculate the absolute yields, the necessary experimental parameters, photon intensity, angular distribution of desorbed species, detection efficiency, and so on, have been either determined experimentally or estimated from the previously reported values, which details are to be published[25]. The absolute yields for the CE process have been estimated to be $(2.3 \pm 0.7) \times 10^{-3}$, $(1.4 \pm 0.4) \times 10^{-3}$, and $(7.8 \pm 2.3) \times 10^{-4}$ (atoms/photon) at the excitation of S1, B1 and S' excitons for Ne, respectively, and 1×10^{-5} (atoms/photon) at S1 excitation for Ar.

An exciton created on the surface can relax in various way such as a deexcitation of photoemission, a desorption in either optically-allowed or optically-forbidden (metastable) excited state, etc. The ratio of the number of

S1 excitons of Ne to that of incident photons with the corresponding excitation energy is roughly estimated to be 2×10^{-2} (excitons/photon) using an absorption cross section data for Ne atom in gas phase[26] and 1×10^{-1} (excitons/photon) using an absorption coefficient for solid Ne[27] assuming that the surface exciton can be created only in the first layer of the solid. From this estimation together with the desorption yield data obtained in the present work, the probability for the metastable desorption is calculated to be 10 % using a gas phase value and 2 % using a solid Ne value. It means that 2 to 10 % of S1 excitons on the solid Ne are ejected into vacuum in the metastable states of $^3P_2$ or $^3P_0$.

DESORPTION FROM THE MIXED OR ADSORBED SYSTEM

The studies on the desorption phenomena at the surface of a mixed system give useful information on the electronic state and the diffusion of excited species in a heteromatrix as well as the interaction and the excitation transfer between heteronuclei.

Shift in Excitation Energy and Kinetic Energy

Ne adsorbed on or mixed with other rare gas solids, Ar, Kr, and Xe, leads the desorption of Ne* when the excited species of Ne is produced at the surface. The desorption yields of Ne* via CE process from Ne-Kr alloy as a function of the wavelength are shown in Fig. 2 for the Kr concentrations from 2.9 % to 81.5 %. Vertical lines denote the energetic positions of the excitons for pure Ne solid. These feature is analogous to the results for Ar-Ne alloy[28]. The red shift of the excitation energy of Ne in the matrix of other rare gas relative to that for pure Ne can be explained, in terms of the well-known Wannier-Mott formula, by the increase of the dielectric constant ε as the amount of Ar or Kr around the excited Ne atom increases. The fact that the shift of peak positions for the bulk components (B1, B2) are larger than those of the surface ones (S1, S') is due to the difference in the number of surrounding molecules. The larger shift for B2 than B1 is caused by the larger radius of the expanded electron orbital of B2 and the difference in the local magnitude of ε.

The kinetic energy of the desorbed Ne* depends on the concentration of Ne and the substrate material. The kinetic energies E_k of Ne* desorbed from

Ne condensed on solid Ar, Kr, and Xe are shown in Fig. 3 as a function of the thickness σ (atomic layers) of Ne[9]. In the submonolayer region ($\sigma < 1$), E_k is

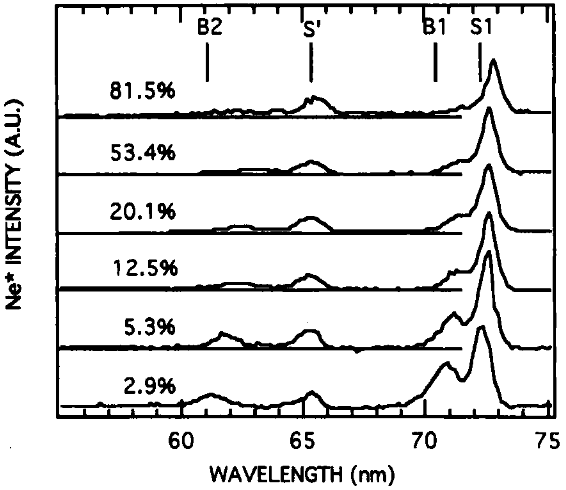

FIGURE 2 Desorption yields of metastable Ne from Ne-Kr alloys as a function of excitation wave-length for Kr concentrations from 2.9 % to 81.5 %. Vertical lines show positions of the excitons in pure solid Ne.

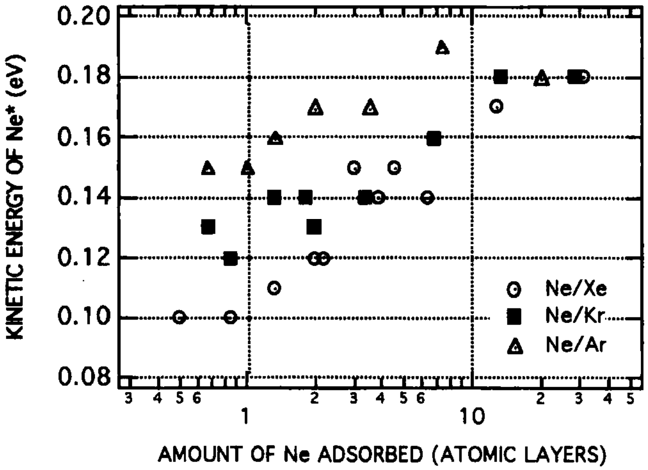

FIGURE 3 Kinetic energies of metastable Ne desorbed by S1 excitation via cavity ejection process from Ne adsorbed on solid Ar, Kr, and Xe as a function of the amount of Ne.

0.15, 0.13, and 0.10 eV for Ne/Ar, Ne/Kr, and Ne/Xe, respectively. E_k increases gradually as σ increases and reaches the value 0.18 eV, which is E_k of Ne* from pure sold Ne, at around $\sigma = 10$. The photon energy E_x that gives the maximum Ne* yield and that corresponds to S1 excitation shows a slight red shift in the adsorbed Ne: 17.00 ± 0.03 eV for Ne/Xe ($\sigma < 1$) while 17.17 ± 0.03 eV for pure Ne. The kinetic energy E_k of Ne* at the peak of distribution shifts from 0.18 ± 0.01 eV at $\sigma = 31$ to 0.10 ± 0.01 eV at $\sigma < 1$. The TOF spectrum at $\sigma = 31$ was identical with that obtained at pure Ne. The change in E_x and E_k observed in Ne/Xe is also the case with Ne/Ar and Ne/Kr though the magnitudes of the shifts are different in the three systems. The shifts ΔE_x, which are the difference of E_x between the pure Ne and the submonolayer Ne, 0.09 eV (Ne/Ar), 0.12 eV (Ne/Kr), and 0.17 eV (Ne/Xe), lead to the shifts ΔE_k of the kinetic energy of Ne*, 0.03 eV (Ne/Ar), 0.05 eV (Ne/Kr), and 0.08 eV (Ne/Xe), respectively. The ratios $\Delta E_k/\Delta E_m$ are between 30 - 50 %. It shows that the rule for the ratio between the desorption kinetic energy and the lattice distortion energy still holds in the case of the rare gas alloy.

The CE mechanism has been expected to be less efficient in solid Kr and Xe[29] which have a positive electron affinity in bulk because of their large polarizability. The above result shows that the desorption of Ne* via CE process from Ne/Kr and Ne/Xe occurs even in submonolayer region. It suggests that the electron affinity is negative at the surface of solid Kr and Xe or it turns into negative by the adsorption of Ne. It is plausible that the smaller number of the surrounding atoms at the surface is not enough to change the electron affinity from negative to positive by their polarizability.

Excitation Energy Transfer Between Ne and Other Rare Gases

In Fig. 2, the peak intensity of Ne* desorbed by bulk excitations (B1 and B2) decreases rapidly as the Kr concentration increases. This is also the case for Ne-Ar alloy. TOF spectra of the metastables desorbed from the surface of pure solid Ne, pure solid Ar and Ne-Ar alloy are compared in Fig. 4[28]. TOF spectrum (b) of the metastables desorbed by S1 excitation of Ne in the alloy resembles the spectrum (a) of Ne* desorbed from pure solid Ne. On the other hand, TOF spectrum (d) of metastables desorbed by B1 excitation of Ne from

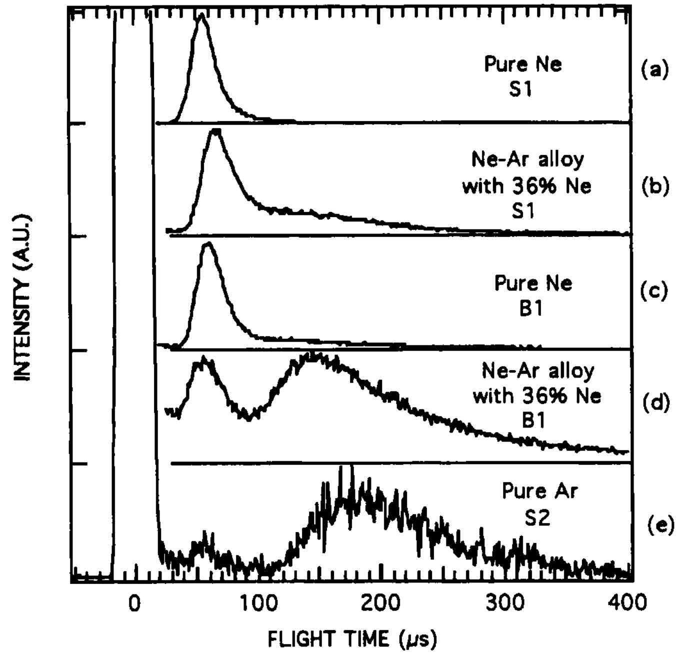

FIGURE 4 Comparison of TOF spectra of the metastables desorbed from the surface of pure solid Ne, pure solid Ar and Ne-Ar alloy. Excitation energy for each spectrum is corresponding to (a, b): S1 of Ne, (c, d): B1 of Ne, and (e): S2 of Ar.

the alloy is substantially different from the corresponding spectrum (c) for pure solid Ne but can be related to the spectrum (e) of Ar* through ED and CE mechanisms by S2 excitation of Ar. In comparison with pure solid Ar, the shift of CE peak of Ar* toward higher energy is also explained by the fact that the electron affinity is lowered by alloying with Ne.

The results of Ne-Kr and Ne-Ar alloys suggest that there are some efficient electronic energy transfer process from Ne bulk excitons to the matrix of Ar or Kr. When an exciton is created in a bulk, it must migrate towards the surface before desorption. As the Ne exciton energy is larger than the band gap energy of matrix atoms Ar (E_g = 14.2 eV) and Kr (11.6 eV), it can be transferred to a ground state matrix atom which explains the decrease of the Ne* desorption yield in the alloys. In the case of Ne-Ar alloy, this process leads to desorption of Ar* by both ED and CE processes. Though the desorption of Kr* has been observed at the excitation of the Ne bulk excitons, the details is not so clear as in the case of Ne-Ar alloy mainly because of a low detection efficiency of Kr*. There are several possible processes for energy transfer through the ionization of the heavier rare gas atom and through the formation of a heteronuclei excimer, for example[28]. A further experimental investigation is necessary to reveal which is the most efficient process in rare gas condensates.

SUMMARY

The nature of the exciton in rare gas solids have extensively been investigated by various experimental methods: photo-absorption, luminescence, electron energy loss spectroscopy, etc. The observation of the desorbed metastable is complementary one to the above approaches and is one of the most direct means to reveal the dynamic nature of the exciton, especially on a surface, because it detects the excited neutral species directly originated from the exciton. Many unclarified problems still remain in this field. As concerns the desorption from the S1 exciton, for example, the initial excitation and the deexcitation cascade leading to the desorption of the metastable have not been clarified yet. It is necessary to examine the fine structures in the relation between the exciton excitation and the desorption by using higher resolution spectroscopy. It has also been noticed that the phenomena are acutely sensitive to impurities adsorbed on a surface. As to some characteristic features observed in the present study, it should be clarified whether it is the nature intrinsic in a pure rare gas solid or is originated from impurities. Close investigation of the interaction with the impurities will provide a field of the study of the excitation transfer process between heteromolecules in a thick environment of condensate.

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