Desorption Stimulated by Laser-Induced Surface-Plasmon Excitation

W. Hoheisel, K. Jungmann, M. Vollmer, R. Weidenauer, and F. Träger
Physikalisches Institut der Universität Heidelberg, D-6900 Heidelberg 1, Federal Republic of Germany

(Received 18 December 1987)

Atoms with energies of several electronvolts are ejected if small metal particles are illuminated with low-intensity visible laser light. The desorption rate exhibits a resonant behavior with its maximum at $\lambda = 490$ nm for particles of 50 nm average radius. The novel process is explained by a mechanism of laser-induced desorption that is based on surface-plasmon excitation.

PACS numbers: 68.45.Da, 36.40.+d, 79.20.Ds, 82.65.Yh

Photodesorption stimulated by laser light has attracted much interest in recent years.[1] Such processes have been investigated in a number of experiments,[2-4] the primary goals of which were to study the underlying mechanisms and elucidate the desorption kinetics. In addition, laser-induced photodesorption phenomena are of great practical interest since such processes can play an integral part in such industrial applications as material ablation and etching. The mechanisms that promote photodesorption can be quite different and based on direct rapid heating of the surface[2] or on vibrational[3] or electronic[4] excitation. The present paper addresses a new effect, the ejection of neutral atoms from small metal particles if a surface-plasmon oscillation is excited with laser light. The underlying mechanism is *nonthermal* and the desorption yield exhibits a resonant dependence on the laser frequency. In sharp contrast to earlier work, desorption in our experiment is stimulated by electronic excitation with low-energy photons, i.e., *visible* light, and with powers of a *continuous-wave* laser beam down to as little as a few milliwatts. Specifically, we have illuminated sodium particles supported on a LiF single crystal in ultrahigh vacuum with light of an argon-ion or krypton-ion laser and have detected sodium atoms photodesorbed from the particle surface with a mass spectrometer. In order to elucidate the kinetics of the process, the velocity distribution of the desorbed particles was investigated with time-of-flight measurements.

The experimental arrangement[5] consists of an ultrahigh-vacuum system with a base pressure of 10^{-10} mbar. The LiF(100) single-crystal surface is cleaned by heat treatment, annealed, and cooled to liquid-nitrogen temperature. Its temperature is measured with a thermocouple. The UHV chamber is equipped with a number of components to generate a thermal atomic beam of sodium with a flux of typically 3×10^{12}/s. The atoms pass several liquid-nitrogen-cooled apertures and finally impinge on the LiF crystal, where they form small metal particles by surface diffusion. Alternatively, the atoms can be collected on a quartz-crystal microbalance for measurements of the Na coverage. The particle density and average size are determined by scattering experiments.[5] The density is about 10^9/cm^2 and the size ranges from 10 to 150 nm for the integral coverages studied here. An argon- or krypton-ion laser beam can be directed onto the sodium particles, then pass through the transparent LiF crystal and leave the apparatus through a window. Desorbed neutral Na atoms are detected with a quadrupole mass spectrometer operating in single-ion counting mode. The ionizer is located 3.7 cm from the LiF surface. The Na beam is turned off during the laser experiment.

In order to determine the kinetic energy of the desorbed atoms, time-of-flight measurements are performed. For this purpose the cw laser beam is chopped at a 100-Hz repetition rate by a slotted mechanical wheel mounted in the focus of two lenses. This gives light pulses of 5 μs duration and 1 μs rise and fall time. In order to determine the true velocity with which the atoms desorb from the surface, the experimental velocity distribution is deconvoluted from the response function of the detection system. For this purpose the drift time of the ions in the quadrupole filter is determined in a separate measurement by desorbed sodium atoms with the laser light pulses from the electrodes of the ionizer.

A desorption signal is shown in Fig. 1. It was obtained by our turning the laser beam on and off at 10-s intervals in order to discriminate between signal and background. Desorption decreased with time. The decay is recorded for several minutes before the remaining coverage is determined by conventional thermal desorption. A signal with pulsed excitation at $\lambda = 514$ nm and time-resolved detection is displayed in Fig. 2.

The experimental results can be summarized as follows.

(1) Desorption of sodium atoms can be readily detected when the light is incident on the sample. Even with a cw light intensity as low as 40 MW/cm^2 a signal can still be observed. The desorption rate depends linearly on the light intensity in the range from about 40 mW/cm^2 up to the highest available laser intensity of 160 W/cm^2. No threshold for the desorption signal is observed. It should be mentioned that ions possibly desorbed from the surface would be repelled by the positive potential of the en-

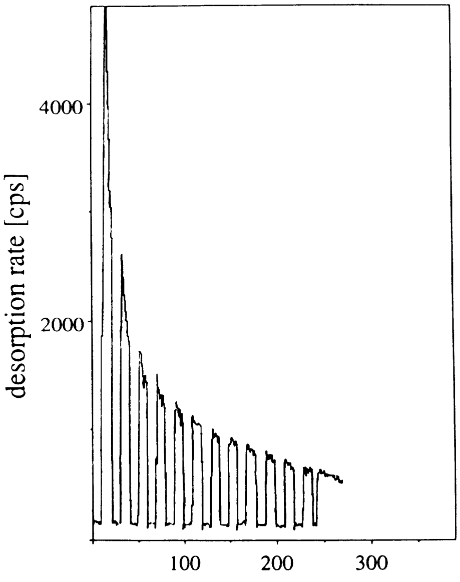

FIG. 1. Laser-induced desorption signal for Na particles of 50 nm radius. The rate of detected Na atoms is displayed as a function of time for a number of laser-on/laser-off periods. The excitation wavelength is $\lambda = 514$ nm, the intensity of the cw laser beam $I = 113$ W/cm^2.

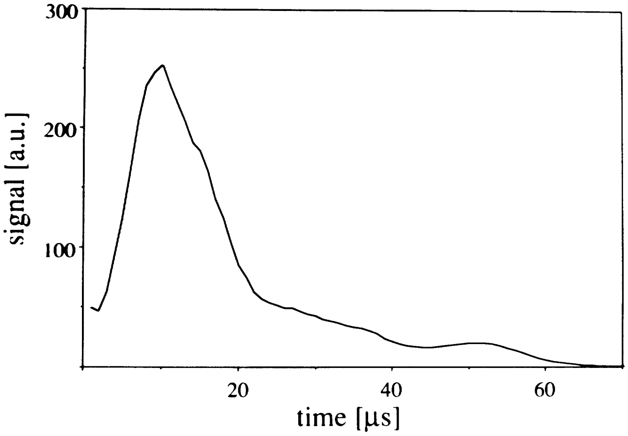

FIG. 2. Time-of-flight spectrum of Na atoms desorbed from the surface of small sodium particles. The measurement was made with laser light pulses of 5 μs duration, 514 nm wavelength, and 113 W/cm^2 intensity. The displayed spectrum has been obtained from the measured data by smoothing and deconvolution from the response function of the apparatus. The most probable atom velocity is 3.7×10^5 cm/s.

trance electrode of the ionizer. We find, however, that ion desorption is negligible. This follows since the amount of neutral atoms desorbed by the laser light and by the subsequent thermal desorption equals the coverage deposited initially on the substrate. Desorption of dimers or larger clusters is not observed.

(2) The photodesorption yield strongly depends on the laser frequency. The frequency dependence of the signal was examined by use of eight Ar$^+$-ion and Kr$^+$-ion laser lines between $\lambda = 410$ and 647 nm. The data were taken at a laser intensity of 22 W/cm^2 and with a mean particle radius of 50 nm. As can be seen from Fig. 3, major desorption occurs for the blue and green Ar-ion laser lines at $\lambda = 488$ and 514 nm. The revealed resonant structure of the spectrum has a center wavelength of $\lambda = 490 \pm 5$ nm. The full width at half maximum of the laser desorption spectrum is $\Delta\lambda = 90$ nm. This corresponds to photon energies of 2.54 and 0.46 eV, respectively.

(3) The signal depends on the particle size. If desorption is stimulated with laser light of $\lambda = 514$ nm, the detected rate is negligibly small for clusters with radii below $R = 10$ nm, reaches a maximum around $R = 40$ nm, and drops off for larger sizes.

(4) A single peak is observed in the time-of-flight spectrum at $t = 10 \pm 2$ μs (see Fig. 2). It should be pointed out emphatically that its position does not depend on the laser intensity. The position of the maximum of the spectrum gives a most probable velocity of $(3.7 \pm 0.7) \times 10^5$ cm/s which corresponds to a kinetic energy of 1.64 ± 0.7 eV for the desorbed atoms.

The decay of the signal as a function of illumination time with laser light (see Fig. 1) is quite similar to the situation in earlier experiments where the desorption was stimulated by vibrational excitation with infrared lasers[1,3] and where the signal disappears after a number of pulses, even though the coverage has only decreased by very little. Obviously, certain sites on the surface are gradually depleted so that the desorption ceases. This suggests that atoms at exposed positions, i.e., with particularly low coordination number and lower binding ener-

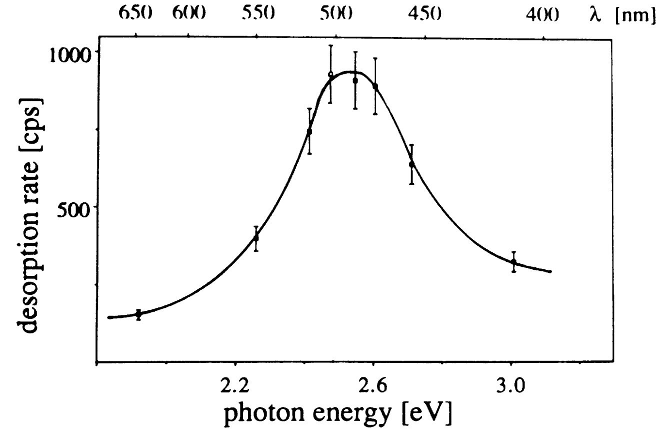

FIG. 3. Dependence of the laser-induced desorption signal at $t = 0$ (see Fig. 1) on the photon energy. The mean cluster radius was 50 nm and the data were taken at a laser intensity of $I = 22$ W/cm^2.

gy than others, desorb preferably. In our experiment a fraction of typically 20% of the total coverage can be desorbed with the laser at a given light intensity. The exact percentage depends on the particle size, on the excitation wavelength, and on the light intensity. A comparison of the optical extinction (measured with a laser power meter) with the number of photodesorbed atoms gives an absolute desorption yield of 1.4×10^5 photons per desorbed atom. This number, however, constitutes a lower limit for the efficiency of the process since a considerable fraction of the measured extinction is not due to absorption but to (elastic) light scattering. The decrease of the signal as a function of illumination time further indicates that the sodium atoms do not desorb from the LiF crystal, since the number of individual atoms on the substrate should remain constant under equilibrium conditions which are established in less than 1 s at 90 K.[5] Also, the signal does not recover, even after many minutes *without* illumination.

For a discussion of the desorption mechanism we first have to recognize that the LiF crystal is transparent to the light and that the laser is operated at low power. Therefore, thermal desorption due to direct substrate heating can be excluded. This is supported by estimates and by measurements of the temperature rise. Also, the desorption yield displays a resonant behavior on the laser frequency (see Fig. 3), which cannot be explained by absorption of light in the substrate. Therefore, the metal particles on the surface are responsible for the absorption of light. Actually, the spectrum observed here has pronounced similarities to surface-plasmon–excitation spectra for sodium particles embedded in noble-gas matrices.[6] These particles also show a broad maximum. It is centered at $\lambda=460$ nm and has a width of 60 nm for particles of 10 nm radius. We conclude that desorption in our experiment results from surface-plasmon excitation. The different peak position of our spectrum ($\lambda=490$ nm) is explained by the larger particle size, since the spectra are red shifted if the radius exceeds about 20 nm.[6] In addition, the cluster size distribution on the surface gives rise to an inhomogeneous contribution to the width of the spectrum. The interpretation of the resonance as a surface-plasmon oscillation is further supported by a comparison with measurements on free sodium particles in a beam[7] and in a sodium chloride matrix.[8] Also, the excitation of surface plasmons has been observed just recently for sodium clusters as small as the pentamer.[9]

The size effect of the desorption rate appears to be a complicated function of different parameters. First, the desorption should depend on the frequency of the surface-plasmon resonance which is red shifted with increasing particle size. Second, the number of preferred desorption sites is expected to vary with particle size and, third, the desorption signal may become weaker if other channels for deexcitation, such as transfer of energy to the substrate, play a more pronounced role. This should happen if the particles grow larger and the substrate area in contact with the particle increases.

Of interest is the question whether desorption takes place as a *direct* result of the surface-plasmon excitation, i.e., without coupling to the phonon bath, or whether the excitation energy is converted into heat so that the particle temperature rises and thermal desorption occurs. The latter possibility would correspond to the phenomenon of "resonant heating" that has been observed already for vibrationally stimulated desorption.[1,3] Evidence for the nonthermal desorption comes from a number of experimental findings. First, thermal desorption requires a certain threshold for the light intensity. In our experiment no such threshold is observed. Second, one can easily estimate that absorption of light only leads to a very moderate temperature rise of the metal particles, typically much less than the $\Delta T\approx200$ K required for thermal desorption.[5,10] The conclusion that the desorption mechanism is nonthermal in nature is further supported by the kinetic energy of the ejected atoms and its independence of the laser intensity. It is therefore concluded that the plasma oscillation is not necessarily damped by coupling to the phonon bath, but that a different deexcitation channel is important. It is worth remarking, however, that evidence for thermal desorption is also found but only if the crystal is illuminated with laser intensities above 70 W/cm^2 for more than 10 min.

The linear dependence of the desorption rate on the light intensity suggests that a single-photon process is responsible for stimulating the desorption, i.e., an atom is ejected as a result of a single surface-plasmon absorption-deexcitation cycle. Part of the excitation energy is required to break the bond of a surface atom [0.65 eV (Ref. 10)]. Within the experimental uncertainty all of the rest is converted into kinetic energy (1.64 ± 0.7 eV) of the desorbed atoms. As indicated by the large width of the resonance, such a collective electron density oscillation is damped very rapidly on a time scale of around 10^{-14} s, much faster than thermal equilibrium can be established. One deexcitation channel is the conversion of energy into a localized single-electron excitation which may subsequently decay via heat production or photon emission.[11] In the present experiment the excitation energy of 2.54 eV is not sufficient to form ions during the damping. It therefore appears that the detachment of the neutral species is not caused by ionic excitation[12] but is related to the population of an antibonding electronically excited state. The desorption efficiency of 10^{-5}, however, indicates that photodesorption has to compete with other relaxation channels, particularly with heat transfer to the substrate.

To summarize, we find that atoms are ejected if a surface-plasmon oscillation in small metal particles is excited with laser light. The effect is nonthermal and it appears that neutral atoms desorb after decay of the collective electron oscillation into a repulsive single electron state. It should be mentioned, however, that there is considerable uncertainty about the mechanisms of stimulated desorption in general and it is clear that details of the kinetics of the process described here have to be investigated further. Also, it is important to find out whether or not the excitation energy can be transferred to adsorbate species on the metal particles so that their bond is ruptured. Since the desorption depletes certain sites on the surface, the effect is not only interesting for a detailed understanding of photodesorption phenomena, but may also have implications for the generation of clusters on surfaces with a homogeneous size distribution. The desorption mechanism reported here also sheds light on how the energy is released by a small metal particle after a collective electron excitation. Very little is known about the energy dissipation after electronic or vibrational excitation in small particles and the coupling of the different degrees of freedom. This, however, is of particular importance for a detailed understanding of such aggregates that play an essential role in the size region intermediate between atoms and molecules on the one side and the condensed state on the other.[13,14] Experiments along these lines with metal clusters in the gas phase are also in preparation.

We would like to thank D. Dubbers and W. Weibler for useful advice and discussions. The help of U. Schulte with the signal deconvolution is gratefully acknowledged.

---

[1] T. J. Chuang, Surf. Sci. Rep. **3**, 1 (1983).

[2] See, e.g., J. P. Cowin, D. J. Auerbach, C. Becker, and L. Wharton, Surf. Sci. **78**, 545 (1978); G. Wedler and H. Ruhmann, Surf. Sci. **121**, 464 (1982); I. Hussla, H. Coufal, F. Träger, and T. J. Chuang, Ber. Bunsenges. Phys. Chem. **90**, 240 (1986).

[3] See, e.g., J. Heidberg, H. Stein, and E. Riehl, Phys. Rev. Lett. **49**, 666 (1982); T. J. Chuang and I. Hussla, Phys. Rev. Lett. **52**, 2045 (1984); B. Schäfer and P. Hess, Chem. Phys. Lett. **105**, 563 (1984).

[4] See, e.g., V. S. Antonov, V. S. Letokhov, and A. N. Shibanov, Appl. Phys. **25**, 71 (1981); E. B. D. Bourdon, P. Das, I. Harrison, J. C. Polanyi, J. Segner, C. D. Stanners, R. J. Williams, and P. A. Young, Faraday Discuss. Chem. Soc. **82**, 343 (1986); C. E. Bartosch, N. S. Gluck, W. Ho, and Z. Ying, Phys. Rev. Lett. **57**, 1425 (1986); T. J. Chuang and K. Domen, J. Vac. Sci. Technol. A **5**, 473 (1987); Z. Ying and W. Ho, Phys. Rev. Lett. **60**, 57 (1988).

[5] M. Vollmer and F. Träger, Z. Phys. D **3**, 291 (1986).

[6] H. Abe, K.-P. Charlé, B. Tesche, and W. Schulze, Chem. Phys. **68**, 137 (1982).

[7] D. M. Mann and H. P. Broida, J. Appl. Phys. **44**, 4950 (1973); J. Hecht, J. Appl. Phys. **50**, 7186 (1979).

[8] M. A. Smithard and M. Q. Tran, Helv. Phys. Acta **46**, 869 (1974).

[9] W. A. de Heer, K. Selby, V. Kresin, J. Masui, M. Vollmer, A. Châtelain, and W. D. Knight, Phys. Rev. Lett. **59**, 1805 (1987).

[10] M. Vollmer and F. Träger, Surf. Sci. **187**, 445 (1987).

[11] H. Raether, in *Excitation of Plasmons and Interband Transitions by Electrons,* Springer Tracts in Modern Physics Vol. 88, edited by G. Höhler (Springer-Verlag, Berlin, 1980).

[12] *Desorption Induced by Electronic Transitions, DIET II,* edited by W. Brenig and D. Menzel, Springer Series in Surface Sciences Vol. 4 (Springer-Verlag, Berlin, 1985).

[13] *Metal Clusters,* edited by F. Träger and G. zu Putlitz (Springer-Verlag, Berlin, 1986).

[14] *Physics and Chemistry of Small Clusters,* edited by P. Jena, B. K. Rao, and S. N. Khanna (Plenum, New York, 1987).