Photodesorption of Na atoms from rough Na surfaces

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We investigate the desorption of Na atoms from large Na clusters deposited on dielectric surfaces. High-resolution translational energy distributions of the desorbing atoms are determined by three independent methods, two-photon laser-induced fluorescence, as well as single-photon and resonance-enhanced two-photon ionization techniques. Upon variation of surface temperature and for different substrates (mica vs lithium fluoride) clear non-Maxwellian time-of-flight distributions are observed with a $\cos^2 \theta$ angular dependence and most probable kinetic energies below that expected of atoms desorbing from a surface at thermal equilibrium. The half-width of the time-of-flight distributions is presented in terms of a model which assumes that following the initial surface plasmon excitation neutral atoms are scattered by surface vibrations. Recent experiments providing time constants for the decay of the optical excitations in the clusters support this model. The excellent agreement between experiment and theory indicates the importance of both absorption of the laser photons via direct excitation of surface plasmons as well as energy transfer with the substrate during the desorption process. (© 1997 American Institute of *Physics.* [S0021-9606(97)01119-7]

I. INTRODUCTION

Optical excitation of sodium (Na) globules (clusters) adsorbed on inert dielectric surfaces results in a collective electronic vibration (surface plasmon excitation), which resembles in terms of wavelength and cluster size dependence many features of the *giant resonance* known from neutron physics.¹ Since the transition from single to collective electron excitation occurs at fairly small cluster sizes of less than 10 Å (as deduced from experiments on gas phase clusters, cf. Ref. 2), the surface plasmon frequency of the clusters reaches the bulk value at radii of less than 100 Å.³ A quantitative comparison with predictions from a jellium model gave good agreement, showing that the spectra were dominated by the dipole plasmon resonance. Gas phase experiments showed the evolution of shell structures with increasing size.⁴

The excitation of surface plasmons in the clusters leads to a variety of linear and nonlinear local field enhancement effects such as strongly enhanced second harmonic generation⁵ or four-wave mixing.⁶ It also facilitates nonthermal laser-induced desorption of Na atoms and Na polymers. In the limit of very large clusters (a few hundred Angstroms in diameter) a roughened metallic surface is formed. Hence the mechanisms of laser-induced ablation from rough metallic surfaces may be understood on a very fundamental basis using these model systems.

Given these motivations it is not surprising that a wealth of experimental studies have been performed in the past. Bonch–Bruevich and co-workers have investigated laserinduced desorption of Na atoms from Na clusters and Na films adsorbed on multicrystalline sapphire and quartz surfaces in high vacuum (10^{-6} mbar) .⁷⁻¹⁰ They found the desorption yield to depend linearly on the intensity of the desorbing laser at least up to irradiances of 10^5 W/cm^2 . The yield also was strongly influenced by the wavelength of the laser, thus suggesting that the absorption of the laser light is due to excitation of surface plasmons in the clusters.

More systematic studies of the absorption of laser light in Na clusters adsorbed in ultrahigh vacuum (UHV; 10^{-10} mbar) on lithium fluoride surfaces (100) have been performed by Träger and co-workers.¹¹ This group prepared the surface by cleaving in air and subsequent annealing in vacuum and characterized the initial cluster size distribution on the surface via extinction, inelastic scattering of Na atoms and thermal desorption measurements. They found that laser ablation changes the cluster size distribution in a systematic and predictable way since the absorption cross section is a function of cluster size.

From a theoretical point of view Monreal and Apell were the first to note the obvious importance of electromagnetic field enhancement on the surface of the clusters for the desorption process.¹² Their calculations assumed spherical particles on the substrate surface and were performed on the basis of classical Mie theory.¹³ Measurements of desorption of neutrals^{14,15} and ions¹⁶ from adsorbed metallic films using excitation via evanescent waves demonstrated the efficiency of plasmon-enhanced desorption processes. The field enhancement idea was subsequently included into a qualitative model of the overall desorption process¹¹ which, however, did not allow quantitative predictions on any of the experimental observations. A quantitative approach to an understanding of the surface-plasmon-ion interaction in terms of an inverse bremsstrahlung-type plasmon excitation by the ion and subsequent collision with the surface has been given recently.17

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Both the groups of Bonch–Bruevich and the group of Träger also measured time-of-flight (TOF) distributions of the desorbing atoms. They were not able to fit the measured distributions by realistic theoretical curves but from the maxima of the distributions they determined most probable kinetic energies that varied between $450\pm50 \text{ meV}$ [at $\lambda = 530 \text{ nm}$ (Ref. 7) and for a metallic film], $600\pm50 \text{ meV}$ [at $\lambda = 353 \text{ nm}$ (Ref. 8), also for a metallic film], 200 meV [at $\lambda = 351 \text{ nm}$ (Ref. 11) and for clusters], $400\pm50 \text{ meV}$ [at $\lambda = 532 \text{ nm}$ (Ref. 11) for clusters], and 160 meV [at $\lambda = 532 \text{ nm}$ (Ref. 18) for clusters] for otherwise similar desorption conditions. As seen from this compilation, there is a considerable spread of values.

In the work of Bonch–Bruevich and co-workers⁷ a pulsed laser (second harmonic of Nd:YAG) was used to desorb the atoms. The TOF distribution of the desorbing atoms was measured via one-photon laser-induced fluorescence in a vessel filled with Na. This approach results in a strong background signal from resonant laser light and from Na vapor filling the vessel. In addition, upon laser desorption there was also a high probability for detecting Na that had been reflected from the walls of the vessel. Since Na atoms were detected along the whole length of the laser beam with nearly equal probability the distance between desorption and detection spot is not very well defined. In view of the short distances between surface and detection lasers (of the order of a few mm) this gave rise to serious uncertainties in the values of the measured translational energies.

Träger and co-workers have applied light pulses from Ar^+ or Kr^+ lasers with lengths between 2 and 5 μ s and have detected the atoms mass spectrometrically. It is well known that the ill-defined spatial point of ionization and the drift region in the mass spectrometer can lead to large errors in the measured TOF-distributions,¹⁹ especially if the flight path is only of the order of a few centimeters, as in case of the experiments of Träger *et al.*¹¹ The maximum of the observed distribution appeared at a time-of-flight between 40 and 60 μ s,¹¹ while the cited correction for the drift time inside the ionizer of the mass spectrometer amounted to 22 μ s. Given an additional uncertainty due to the length of the excitation pulse of up to 5 μ s one ends up with values of kinetic energy that could be lower than 100 meV.

An accurate determination of the product translational energy distributions is certainly of key importance for an understanding of the desorption process. Having the above discussed uncertainties in mind we therefore have recently applied a two-photon laser-induced fluorescence (TPLIF) technique^{20,21} to this problem.²²⁻²⁴ This method involves a pulsed laser desorption and cw laser detection within a spatially well defined detection spot as well as additional spectral information about the desorbing atoms and thus allows us to determine TOF distributions with well defined initial parameters and superior signal to noise ratio. First results for desorption from Na clusters on mica have been published,^{24,25} showing that the kinetic energies of the desorbing atoms are surprisingly small and also that they cannot be fitted by a Maxwellian distribution at the surface temperature. Instead they showed an additional broadening and shift of the peak to lower energies. A similar phenomenon has been reported for electron-induced time-delayed desorption from lithium fluoride^{26,27} and ion-induced desorption of neutral Na atoms from room temperature NaCl(100) surfaces,²⁸ where the loss was due to a diffusion of *F*-centers through the substrate. Such a kind of loss mechanism is highly unlikely in a metal.

Taken together, our experimental observations suggest a fairly complex desorption mechanism that shows characteristics of direct as well as substrate-mediated desorption. It is apparent from recent measurements^{29,30} that the existence of the supporting substrate, in addition to providing an easy control of the cluster temperature, changes the elementary excitation and de-excitation mechanisms compared to that of gas phase clusters, resulting, e.g., in a stronger damping of the surface plasmons. In addition, the shape of the clusters even for small radii of less than 10 nm is ellipsoidal, having a ratio of semiaxes of two, a factor which influences directly the magnitude of the local field enhancement in the clusters. In the present paper we demonstrate that the substrate surface also influences the desorption process. Clearly, the substrate is affected by the exciting laser light only via coupling between cluster and substrate as long as the absorptivity of the surface is so small that heating of the dielectric is a process of insignificant probability. Also, since the photon energy is below the band gap of the dielectric, substrate hot carrier mediated desorption³¹ can be excluded.

Discussing the experimental observations with respect to the nature of the desorption process, we would list two signatures consistent with direct desorption: (1) A linear dependence of desorption yield on incident laser irradiance over a range of four orders of magnitude, indicating an absence of surface heating effects. (2) A strong dependence of yield on laser wavelength, due to the excitation of surface plasmons.

The characteristics indicating substrate mediation are: (1) The TOF distributions are independent of laser irradiance. (2) They are also independent of laser wavelength. (3) As a function of surface temperature, T_S the full widths at half maximum (FWHM) of the TOF distributions decrease. (4) The total yield depends exponentially on T_S with Arrhenius activation energies that are different for different substrates.

In addition, there are characteristics that cannot be easily explained either by direct desorption nor by mediation via the substrate that supports the clusters. Those include: (1) The kinetic energy distributions of the desorbed particles are clearly non-Maxwellian, the characteristic velocities being significantly *slower* and the energy width being *larger* than what is predicted by a Maxwell–Boltzmann (MB) function at the substrate temperature. (2) The dependence on scattering angle θ_f is also non-Maxwellian, being fitted very well to a $\cos^2 \theta_f$ dependence, while the peak energy of the desorbing atoms is independent of θ_f . (3) There is a very long tail in the energy distribution at slow velocities as opposed to a short range tail predicted by a MB function.

The results of recent femtosecond time-resolved pumpprobe measurements³⁰ allow us to estimate characteristic values for the decay of optical excitations in large Na clusters²⁹



FIG. 1. Characteristic decay time constants for surface bound Na clusters as determined from recent experiments; see the text.

(see Fig. 1). The lifetime of the plasmon excitation, τ_{SP} , is found to vary between a few femtoseconds (fs) and ten fs, depending on cluster size and substrate stiffness.³⁰ Linear extinction spectra indicate a value of $\tau_{\rm SP} \ll 10$ fs. However, much of the observed linewidth is given by inhomogeneous broadening due to the cluster size distribution and due to chemical interface damping. The observed values of plasmon lifetime are in qualitative agreement with measurements on Ag islands.³² The subsequent inelastic electron-electron scattering is expected to result in a time constant of at least $\tau_{ee} \ge 10$ fs if one applies Fermi-liquid theory³³ and uses the bulk plasmon frequency of Na. It is noted that this time constant might approach the picosecond regime due to hot electron cascades.^{34,35} The generation of photoelectrons and ions then is highly probable³⁶ which might influence the desorption characteristics, e.g., via image charge attraction.

The hot electron gas cools via collisions with the lattice, giving rise to an electron-phonon coupling constant of the order of two picoseconds.³⁰ Since the clusters are bound to a substrate there exists an additional decay time channel via phonon coupling of the Na atoms to the dielectric. From measured phonon energies of Na adsorbate modes on adsorbed Na clusters ($\approx 2 \text{ meV}$)³⁷ we expect the corresponding time constant to be of the order of several picoseconds.

Quantitative values of the overall desorption time constant have been determined recently by use of near field TOF spectroscopy.³⁸ The evanescent wave above a glass prism surface has been used to excite the clusters via a pulsed laser, and the desorbing atoms were detected also in the evanescent wave via cw two-photon laser-induced fluorescence as described in the present paper. Hence one measures TOF spectra at virtually "zero" flight-time, allowing one to determine an intrinsic decay time of several tens of nanoseconds for the total desorption process.

In the present work, the process of laser-induced desorption of Na atoms from Na clusters is studied in great detail. In addition to total desorption yields and kinetic energy measurements as a function of laser wavelength, irradiance, angle of desorption, and substrate temperature, we have also performed time-of-flight measurements up to very long flight times and as a function of surface temperature. Although the primary detection method was TPLIF, we have also utilized two alternative detection methods for determination of the kinetic energy distribution of the desorbing particles. The first alternative being cw resonance enhanced two photon ionization. The second alternative is a fully pulsed excitation–detection method (pulsed dye laser desorption



FIG. 2. Term schemes for the two-photon laser-induced fluorescence [TPLIF, (a)] and resonance-enhanced two-photon ionization [RETPI, (b)] detection methods for Na atoms. The lasers $h\nu_1$ and $h\nu_2$ usually are counterpropagating, thus allowing doppler-free detection of the desorbing atoms.

and excimer laser ionization of the products) and provides the same values of most probable kinetic energies, although with a signal to noise ratio which is less satisfactory.

We are able to interpret the features of this complex desorption process in terms of a scattering theory model. In this context we present a detailed comparison of measured and calculated TOF distributions and discuss the physical meaning of a possible single fitting parameter. It is believed that this photoinduced, substrate mediated desorption processs is prototypical for laser induced desorption processes from rough metallic surfaces using visible laser light.

II. EXPERIMENTAL METHODS

A. Two-photon laser-induced fluorescence, TPLIF

A sensitive detection method for Na atoms is to excite them with two photons first from the $3S_{1/2}$ to the $3P_{3/2}$ state and then from the $3P_{3/2}$ to the $5S_{1/2}$ state within the overlapping focal points of two counterpropagating lasers. We detect the resulting $4P \rightarrow 3S$ UV photons with a photomultiplier behind an interference filter (Fig. 2). This detection method provides high sensitivity since it involves the Na $3S_{1/2} \rightarrow 3P_{3/2}$ transition with transition rate A = 59.1 $\times 10^6 \text{ s}^{-139}$ (oscillator strength near unity). In addition high spatial resolution is obtained since the atoms are detected solely inside the Gaussian spatial beam waists of the lasers which are 0.5 mm diameter.

The rate for the $3P_{3/2}$ to $5S_{1/2}$ transition is $4.58 \times 10^6 \text{ s}^{-1}$, ³⁹ and thus even a two-photon excitation step provides a very sensitive means of measuring densities of Na atoms as small as 10^{10} cm^{-3} . If the laser beams are counterpropagating the method has been shown to be especially useful for the Doppler-free detection of Na in the gas phase in experiments of Grynberg, Bloembergen, and co-workers^{40,41} that have been performed more than 20 years ago. The application of this method to surface-based experiments²¹ not only allows one to perform high resolution, Doppler-free spectroscopy with high sensitivity (less than 10^{-5} of a



FIG. 3. Blow-up of the excitation/detection region for TPLIF. The thickness of the substrate, *L*, in case of mica is of the order of 400 μ m, the average thickness of the cluster film, *d*, is between 60 and 240 nm and the distance Δx between surface and foci of the detection lasers is varied. The pulsed desorption laser $h\nu_D$ (λ = 500 nm) has an angle α = 30 ° with respect to the surface plane and is mainly transmitted through the transparent substrate. The Na atoms desorb with a cos² Θ distribution centered around the surface normal (Θ = 0°).

monolayer) in the neighborhood of reflecting surfaces, but in addition the atoms can be detected at nearly all positions inside the vacuum chamber without the usual large spatial restrictions that come with a mass spectrometer or an ion detector. Note that since the UV photon is emitted at 330 nm no special optics, photomultipliers, or windows are needed for its detection. Finally, since the two-photon spectroscopy of Na is very well known both for the resonant as well as the nonresonant case, at low and at high laser intensities, a spectroscopic detection method offers additional analytical tools to the desorbing atoms such as the evaluation of perpendicular velocity distributions from the measured spectral line shapes of the desorbed atoms.^{42,43}

We aim to use TPLIF mainly to measure the TOF distributions of Na atoms desorbed from the cluster surface per unit time with an optical geometry as depicted in Fig. 3. A pulsed dye laser ($h\nu_D$, $\tau=20$ ns) serves to desorb the atoms from the clusters and provides the zero point for the TOF measurements. The desorbed atoms are detected via TPLIF. Note that the resolution of this method depends on the focal diameter of the detection lasers, which is 0.5 mm. For a mean velocity of the desorbing atoms of about 500 m/s, this results in a resolution of better than 1 μ s. This value is valid even for distances Δx between surface and detection lasers of a few mm, small enough to allow a precise determination of the shape of the TOF curve; see, e.g., Figs. 6 and 8. Since we saturate the 3S-3P transition but not the 3P-5S transition with the cw detection lasers the TPLIF detector acts as a density detector and the signal intensity I(t) is proportional to the change of particle density with time, n(t). A measured



FIG. 4. Setup for pulsed ionization of desorption products. Characteristic voltages and distances are denoted. For RETPI a cw dye laser $(h\nu_1)$ and an Ar⁺ laser $(h\nu_2)$ in a counterpropagating configuration (not shown) are used to ionize the desorbing atoms. Alternatively an ArF excimer laser ($\lambda = 193$ nm) directly ionizes the atoms and TOF distributions are obtained for different masses by varying the time delay between desorption and ionization pulses.

Maxwellian TOF distribution is then given by¹⁹

$$n(t) = \operatorname{const} \times t^{-4} \exp(-m\Delta x^2/2t^2 k_B T), \qquad (1)$$

which, for a transformation of n(v) into a TOF distribution n(t), takes into account the Jacobian and the fact that the measurement depends on the velocity of the particles since we are measuring a density rather than a flux.

In order to obtain optimum detection sensitivity for the TOF measurements we use the lasers at frequencies of 16 973.35 cm⁻¹ $(3S_{1/2}-3P_{3/2})$ and 16 227.31 cm⁻¹ $(3P_{3/2}-5S_{1/2})$, which correspond to resonant transitions between the electronic states of Na.

B. Ionization techniques

Two detection methods have been applied, based on cw and pulsed laser ionization of the desorbing particles. The first method, called RETPI (resonance enhanced two photon ionization) is similar to TPLIF in that we use cw lasers to detect the atoms [Fig. 2(b)]. However, instead of exciting the atoms from $3P_{3/2}$ to $5S_{1/2}$ we ionize them within the extraction region of a time-of-flight mass spectrometer with an UV Ar⁺ laser ($\lambda = 351$ nm; $P_L = 300$ mW; focus diameter 0.5 mm) which is counterpropagating to the 3S-3P dye laser [Fig. 4(a)]. Since we are exciting into the ionization continuum the spectral restrictions for detectability of atoms as given for the TPLIF method are not relevant here. Thus the method is similar to resonant one-photon fluorescence detection but provides much better signal to noise ratio and the advantage of having a well defined crossing point of the laser foci.

The parameters of the TOF mass spectrometer, which were optimized by use of ion ray-tracing calculations, are given in Fig. 4. The flight time of the atomic ions inside the mass spectrometer is $3.15\pm0.1 \ \mu$ s. Since the detection employs cw lasers we do not obtain mass selection. Mass selection becomes possible if one uses direct ionization of the desorption products with a pulsed, slightly focused ArF excimer laser (193 nm). Upon ionization with the laser light (P_L =50 mJ/cm²) within the ionization region of the mass

spectrometer we obtain the mass of the ionized particles simply from their time-of-flight through the mass spectrometer. Since the desorption laser is also pulsed, the excimer laser pulse has to be delayed by an amount of the order of 100 μ s to count for the flight time of the neutrals between surface and ionization region. On the other hand, by changing the delay between desorption and detection lasers, TOF distributions of the desorbing particles can be obtained.

The use of the excimer laser allows us to obtain the total fraction of desorbing products which consist of dimers. However, laser-induced fragmentation processes seriously disturb the measured values. State selected data would become available by use of a dye laser, tuned to the $X \rightarrow A$ electronic transition of the dimers, and ionization of the excited dimers with a counterpropagating cw UV Ar⁺ laser.^{44,45} This method also would avoid laser-induced fragmentation processes. The disadvantage is that the expected signal intensity is small due to (i) the small transition dipole moments of the molecules compared to the atoms and (ii) the rovibrational state distribution of the desorbing molecules.

C. Preparation of supporting surfaces and clusters

The growth mechanism of Na clusters or films on dielectric surfaces depends strongly on preparation (i.e., defect density) and temperature of the dielectric. Preliminary helium atom diffraction (HAS) measurements at surface temperatures of 150 K have shown that Na indeed seems to stick first on the defect sites of vacuum cleaved mica,³⁷ where it starts forming clusters. At lower surface temperatures (50 K) there are strong hints for statistical layer-by-layer growth, probably due to the reduced mobility of the atoms on the surface. Both the HAS and additional low energy electron diffraction (LEED) measurements have shown that the long term structural quality of the mica surface depends on whether it has been cleaved in air or in vacuum. However, on a short time scale of the order of a few hours we could not detect significant differences with respect to surface quality and thus we used in most cases air-cleaved mica samples. The typical thickness of the mica is 400 μ m. The deposition of Na atoms is performed in the second, ultrahigh vacuum stage of a two-chamber apparatus, which has been described previously.46,47

At low surface temperatures (150 K and below) the sticking coefficient is of the order of unity. At room temperature it can be as low as 10^{-3} , but depends strongly on the prehistory of the substrate. Most notable is the observation obtained via LEED measurements that it is not possible to recover the initial surface quality by simply heating the mica. HAS measurements on lithium fluoride surfaces suggest a similar behavior.³⁷ In case of mica a possible explanation is the appearance of calcination processes in the course of the heating cycles. Recent more extended LEED studies, however, demonstrate the possibility of using a KrF excimer laser to microscopically clean the surface and improve the epitaxial growth of thin films while avoiding calcination.^{48,49}

Taking all the above listed facts together we conclude that at surface temperatures of the order of 150 K or lower,

the average size of the clusters on the surface can be estimated roughly from the defect density of the dielectric substrate (determining the number density of the clusters) and the flux of Na atoms reaching the surface. In order to do so one has to realize that the clusters possess a size distribution on the surface, which is determined by the Vollmer–Weber growth mode,⁵⁰ and that they are flat spheroids with the ratio of semiaxes depending on their size; e.g., for Na clusters bound to mica the axial ratio is 2:1 for small clusters, but increases to 5:1 for average radius $r_0=40$ nm.²² The size distribution of the large semiaxes, parallel to the surface, is usually⁵¹ parametered in terms of two Gaussian functions:

$$f_{\pm}(r,r_0) = C \, \exp\left[-\frac{(r-r_0)^2}{2\beta_{\pm}^2}\right],\tag{2}$$

where the normalization constant C is selected such that

$$\int_{0}^{r_{0}} f_{-}(r,r_{0})dr + \int_{r_{0}}^{\infty} f_{+}(r,r_{0})dr = 1,$$
(3)

and the two widths, β_- and β_+ , are related by

$$\boldsymbol{\beta}_{-} = \sqrt{2}\boldsymbol{\beta}_{+} \,, \tag{4}$$

thereby yielding an asymmetric distribution which, in the present case, is characterized by a FWHM of 50% of the mean cluster radius r_0 . The subscripts "+" and "-", respectively, denote cluster semiaxes, r, satisfying the inequalities $r > r_0$ and $r \le r_0$. The dependence of the ratio of semiaxes on the cluster size is much less well known and depends on the temperature of the substrate and the initial defects of the surface, and therefore, causes the main uncertainty to this kind of characterization.

The defect density in case of mica varies between $5 \times 10^8 \text{ cm}^{-2}$ (Ref. 52) and 10^{11} cm^{-2} (Ref. 53) and has to be determined for each sample surface individually via, e.g., HAS measurements. The absolute flux of impinging Na atoms can be determined by use of a Rhenium hot-wire detector ("Langmuir–Taylor-detector"), which relies on the generation of positive Na ions since the ionization energy of Na is smaller than the work function of Rhenium. This detector has a sensitivity close to unity.⁵⁴

An alternative way of determining the average cluster size on the surface, which proves especially attractive in the course of room temperature measurements, where the sticking coefficient is not unity, is the measurement of extinction spectra and the comparison of the resulting spectra with calculated values using Mie theory.^{13,24,55} Choosing the appropriate polarization of the incoming light (s or p polarized), the mean size and the ratio of semiaxes can be determined. Of course, the functional form of the distribution of sizes has to be assumed again. This method has some drawbacks in that the supporting dielectric substrate (usually taken into account via an effective dielectric constant) and the mutual electrodynamic interactions of the clusters shift the Mieresonances in a complicated way. However, since the distribution has a half width of 50%, the possible error made is small. We note in passing that optical second harmonic generation also recently has been shown to provide a useful tool for *in situ* determination of cluster size distributions.⁵

For lithium fluoride as the substrate the surface is prepared by cleaving and subsequent baking for several hours at temperatures higher than 600 K. The defect density is similar to that of mica and is of the order of 5×10^8 cm⁻².⁵⁶ Again, actual values of the average cluster radii are determined by measuring extinction spectra.

D. Heating of substrate and adsorbate by laser irradiation

Absorption of pulsed or cw visible laser light on a dielectric can lead to significant heating of the substrate,⁵⁷ the amount of which is strongly dependent on laser and surface conditions. We have treated this problem previously by solving the two-dimensional heat equation for laser irradiation of mica surfaces via extensive two-dimensional numerical simulations using a method of finite differences.^{53,58} After inclusion of radiation and finite size effects the numerical results showed quantitative agreement with measurements using a new laser-based technique for the determination of surface temperatures.⁵⁸

Here, we use the same theoretical method to obtain values of surface temperature for mica and lithium fluoride substrates after irradiation with pulsed and cw visible lasers of different irradiances. The thermal response of the substrates is determined by the thermal conductivity K and the diffusivity κ . We have for mica: $K_{\text{mica}} = 3.1 \text{ W/mK}$ and $\kappa_{\text{mica}} = 1.6 \times 10^{-6} \text{ m}^2/\text{s}^{58}$ and for lithium fluoride: $K_{\text{LiF}} = 150 \text{ W/mK}$ at $T_s = 77 \text{ K}$ and $\kappa_{\text{LiF}} = 6.61 \times 10^{-4} \text{ m}^2/\text{s}^{.59,60}$. Obviously the thermal conductivity of LiF is significantly larger compared to mica and the thermal diffusion length, $L = \sqrt{\kappa t_c}$, is correspondingly larger. Hence, for given substrate radius (5 mm) the time t_c until the laser-induced heat reaches the border of the substrate is only 40 ms in case of LiF, but amounts to 16 s in case of mica. For pulsed laser experiments or long term cw experiments this time t_c determines the maximum laser-induced temperature the substrate can reach since it is mounted such that the inner part (radius 5 mm) is free whereas the outer part is clamped to a cooled manipulator, which acts as an efficient heat sink. Hence the inner part of the substrate can loose its heat only via radiation, which is inefficient at low temperatures, or via conduction to the outer part with the above calculated time constant.

We have to take into account essentially three different experimental configurations: Irradiation with a cw laser and irradiances up to 15 W/cm²; irradiation with a pulsed dye laser (20 ns pulse length), fluences up to 30 mJ/cm² and a repetition rate of 20 Hz; and irradiation with a pulsed Ar⁺ laser (5 μ s pulse length), irradiances up to 200 W/cm² and a repetition rate of 1800 Hz.¹¹ In the latter case only LiF has been used as a substrate and we calculate for the corresponding value of t_c a rise of surface temperature of less than 1 K. The same insignificant temperature rise is calculated for the cases of irradiation with pulsed dye and cw lasers if LiF is used as a substrate. For mica we find for irradiation with a pulsed dye laser an increase in temperature of less than 5 K.



FIG. 5. Total desorption yield of Na atoms as a function of various parameters. (a) Dependence on desorption angle Θ with respect to the surface normal, following irradiation with a pulsed laser. Surface temperature T_s = 300 K, laser fluence $P_L = 10 \text{ mJ/cm}^2$, desorption laser wavelength λ_D = 450 nm, mean cluster radius r_0 = 120 nm. The solid line corresponds to a $\cos^2 \Theta$ dependence. (b) Dependence on irradiance by a cw laser. T_s = 300 K, $\Theta = 0^{\circ}$, $\lambda_D = 582$ nm, $r_0 = 40$ nm. The solid line denotes a linear increase. (c) Dependence on wavelength of the cw laser. $T_s = 300$ K, Θ =0°, P_L =2.25 W/cm², cw laser. The solid line is the spectral dependence of the absorption cross section, calculated for a mean cluster radius of 30 nm; see the text. (d) Dependence on surface temperature following irradiation with a pulsed laser. $\Theta = 0^{\circ}$, $\lambda_D = 500 \text{ nm}$, $P_L = 0.5 \text{ mJ/cm}^2$, r_0 = 120 nm. The circles are measured points for mica as a substrate, the triangles for lithium fluoride. The solid lines represent an exponential dependence on substrate temperature with activation energies of E_A = 69 meV for lithium fluoride and $E_A = 153$ meV for mica.

However, for 200 s cw laser irradiation with 15 W/cm^2 the temperature rise amounts to $\Delta T = 140$ K. Note that we have used in all cases an absorptivity of unity, which certainly results in an overestimation of the heating effect. More realistic values, calculated from the photospectrometrically determined absorption coefficients $\alpha = 2 \text{ cm}^{-1}$ (LiF at 1064 nm) and $\alpha = 16 \text{ cm}^{-1}$ (mica at 1064 nm), are A = 0.5 for 400 μ m thick mica and A = 0.17 for 1 mm thick LiF. Since the maximum temperature rise scales with the absorbed laser power, reduced values of A result in smaller temperature rises. From these estimates we conclude that the overall substrate heating effect under most irradiation conditions used in the present work is small except for cw irradiation. The latter condition, however, is of concern only for Fig. 5(b) (desorption yield as a function of irradiance) and Fig. 5(c) (desorption yield as a function of laser wavelength) and does not affect any of the conclusions of the present paper.

We also might calculate the maximum temperature rise per bond, ΔT , that results from absorption of a photon of energy $E_{ph}=2.41$ eV (corresponding to excitation with λ = 514 nm). The number of atoms in a cluster of radius R= 50 nm is given by $N = (R/r_S)^3 = 13 \times 10^6$. Here, we have assumed a spherical cluster with radius determined by a positive jellium background, i.e., a Wigner–Seitz radius of r_S = 2.12 Å. The resulting temperature rise is $\Delta T = E_{ph} / [(3N - 6)k_B] \approx 7 \times 10^{-4}$ eV. This value is insignificant compared to the binding energy per atom, which is of the order of 0.8 eV.

III. THEORY

In the Introduction we have briefly discussed the optical excitation process in large, surface bound Na clusters, which results in the generation of a nonequilibrium distribution of hot electrons. We note that for low power irradiation with a CO₂-laser (50 kW/cm²) of gold islands on dielectrics, experiment, and theory have indicated a high probability for the generation of hot electrons under steady-state conditions^{61,62} as opposed to ultrafast heating of the bulk metal. The reason for this longlasting (of the order of the laser pulse length), highly nonequilibrium electron gas was assumed to be (i) a strong suppression of electron-phonon energy exchange inside the small metal islands as opposed to a bulk metal, (ii) an efficient phonon heating of the substrate due to the good thermal contact of the islands to the substrate, and (iii) a high level of absorbed power in the clusters due to a strong local field enhancement. All these points certainly apply also to the Na clusters and we are presently measuring directly electron-phonon relaxation time constants in order to check this hypothesis.

However, following the end of the laser pulse the nonequilibrium electron temperature cools via interaction with lattice vibrations of the Na clusters, and finally only a small fraction of 10^{-5} Na atoms are desorbed per incident photon.¹¹ Since the rate limiting step of this desorption process is given by the excitation of surface plasmons a linear dependence of desorption yield on laser power has been observed. As indicated by the small desorption probability, most of the photon energy will be dissipated (mean energy per bond 10^{-4} eV) into intracluster and cluster-substrate vibrations and hence desorption can be expected to occur predominantly on defect sites at the surface of the clusters where the binding energy is lowest (similarly to thermal desorption from rough Na films on dielectrics⁶³). The defect sites resemble weakly bound metastable states. As a consequence, "subthermal" kinetic energy distributions of the desorbing atoms result, i.e., most probable velocities that are smaller than the velocities of particles desorbing in equilibrium with the cluster temperature,²⁴ and the desorption time constant has a large value. In the past, "subthermal" kinetic energy distributions have been observed in photolysis of chemisorbed molecules⁶⁴ and in thermal desorption of rare gas atoms from metals or in laser-induced rapid thermal desorption of NO molecules from LiF(100).65 Invoking microscopic reversibility, the kinetics of the desorption process can be explained by the analogous adsorption process of atoms impinging on the surface. For shallow potential wells of the order of a few hundred meV only the low energy part of the distribution of impinging particles will stick. Consequently in desorption only the trapped (low energy) molecules can be observed and the distribution is skewed, i.e., shows an energy loss. The relevance of such a model has been demonstrated previously by trajectory calculations.^{65,66}

As a result of the optical excitation-de-excitation process neutral atoms are created in the vicinity of the surface with very little translational energy and possibly weakly bound in high-lying bound states. Under these circumstances (high surface temperature with respect to the Debye temperature, large particle mass and equality of masses between surface and scattered atoms) the major mode of exchange of energy with the surface will be through multiquantum exchange of surface phonons.

Thus the characteristics of the desorbing Na atoms will be defined by the final event in this complex chain of processes, and this is the scattering of the neutral Na by the surface vibrational field. This can be regarded as a process in which the Na is initially in a very low translational energy state and then gains kinetic energy from the surface through exchange of many quanta of phonons. As we discuss in more detail below in connection with the Debye-Waller factor, this multiphonon scattering process can be adequately treated as classical scattering due to the large mass of Na atoms and the relatively low Debye temperature of the rough Na substrate. However, the most convenient way of developing a classical scattering theory which correctly includes the recoil of the substrate atoms is to begin with a completely quantum mechanical model and then take the correspondence principal limit to the classical regime, so this is the approach that we will take.

The interaction between the atomic projectile and the surface can be described by a Hamiltonian of the form

$$H = H^p + H^c + V, \tag{5}$$

where H^p is the Hamiltonian of the free particle, H^c is the Hamiltonian of the unperturbed crystal, and V is the interaction coupling the projectile and crystal.

We write the interaction potential as the sum of two parts

$$V = V^0 + V^1, (6)$$

where the part V^0 contains the terms which backscatter the projectile and prevent it from penetrating appreciably into the bulk. V^0 is composed of an attractive polarization part arising from the van der Waals forces in front of the surface and close to the surface V^0 becomes strongly repulsive because of the Pauli exchange exclusion forces arising from the overlap with the surface electronic density of the substrate. The remainder V^1 contains the major terms describing interactions with the lattice vibrations. If the interaction potential is expanded in a Taylor series in the lattice vibrations, then

$$V = V(\mathbf{r}, \{\mathbf{u}_{j,\kappa}\})|_{\mathbf{u}_{j,\kappa}=0} + \sum_{j,\kappa} |\mathbf{u}_{j,\kappa} \cdot \nabla_{j,\kappa} V(\mathbf{r}, \{\mathbf{u}_{j,\kappa}\})|_{\mathbf{u}_{j,\kappa}=0} + \cdots,$$
(7)

where $\nabla_{j,\kappa}$ is the gradient operator with respect to the (j,κ) displacement $\mathbf{u}_{j,\kappa}$. We use a notation for the set of indices (j,κ) , in which j is a two-dimensional variable that

counts unit cells of the surface and κ is three-dimensional and counts elements of the basis set within the unit cell including those in all the layers below the surface. Usually κ counts the crystal atoms making up the basis set of the unit cell, but we note that this does not necessarily need to be the case. The logical choice is to associate V^0 with the leading term of Eq. (7) which is now independent of the displacement, and let V^1 be the sum of all terms linear in the crystal displacement. Terms of higher order in the displacement coming from higher order in the Taylor series of Eq. (7) contribute very little to the inelastic exchange and in the classical limit can be neglected. Following the approach of Brako and Newns⁶⁷ and of Bortolani and Levi,⁶⁸ the probability density of exchanging, between particle and crystal, both an amount E of energy and an amount $\hbar \mathbf{K}$ of parallel momentum is given by

$$P(\mathbf{K}, E) = \frac{1}{\hbar^2} \left\langle \left\langle (n_i, \mathbf{k}_i | S^{\dagger} \,\delta(H^c - E_i^c - E) \right. \right. \\ \left. \times \,\delta(\hat{\mathbf{K}}^c - \mathbf{K}^c + \mathbf{K}) S | \mathbf{k}_i, n_i) \right\rangle \right\rangle,$$
(8)

where $\hbar \hat{\mathbf{K}}^c$ is the momentum operator for the crystal, E_i^c is the initial energy of the crystal and the symbol $\langle \langle \rangle \rangle$ signifies an ensemble average over the initial crystal states $|n_i\rangle$. The scattering operator *S* is taken in a generalized interaction picture according to

$$S(\mathbf{R},t) = e^{-i(\mathbf{R}\cdot\tilde{\mathbf{K}}^c - H^c t/\hbar)} Se^{i(\mathbf{R}\cdot\tilde{\mathbf{K}}^c - H^c t/\hbar)}.$$
(9)

The scattering operator $S(\mathbf{R},t)$ can be represented in several forms, but perhaps the most convenient for the later introduction of approximations is the time dependent exponential⁶⁹

$$S(\mathbf{R},t) = \mathscr{T}\lim_{t_0 \to \infty} \exp\left[\left(-i/\hbar \right) \int_{-t_0}^{+t_0} V(\mathbf{R},t;\tau) d\tau \right], \quad (10)$$

where \mathscr{T} is the time ordering operator.

The experimentally measurable quantity in a surface scattering experiment is the differential reflection coefficient, which is related to Eq. (8) by a density of states

$$\frac{dR}{d\Omega_f \, dE_f} = \hbar^2 k_f k_{fz} P(\mathbf{K}, E), \tag{11}$$

where $\hbar \mathbf{k}_f$ is the final projectile momentum and $\hbar k_{fz}$ is its component in the direction normal to the surface. The differential reflection coefficient gives the number of atoms scattered from the surface within a small solid angle $d\Omega_f$ and small increment of final energy dE_f centered about the final energy E_f .

Using the well-known Van Hove–Glauber transformation^{70–72} the δ functions in Eq. (8) are represented in integral form and after application of the classical trajectory approximation the differential reflection coefficient can be cast into the form of a time and spatial integral Fourier transform of an exponentiated correlation function. The result is⁶⁸

$$\frac{dR}{d\Omega_f dE_f} = \frac{\rho k_f m^2}{(2\pi)^3 \hbar^5 k_{iz}} \int_{-\infty}^{+\infty} dt \int d\mathbf{R} \int d\mathbf{R}'$$

$$\times e^{i[(\mathbf{K})\cdot(\mathbf{R}-\mathbf{R}')-Et/\hbar]}|\tau_{fi}|^{2}\sum_{l}e^{i\mathbf{K}\cdot\mathbf{R}_{l}}e^{-W(\mathbf{R},\mathbf{k})}$$
$$\times e^{-W(\mathbf{R}',\mathbf{k})}e^{2\mathscr{W}_{l}(\mathbf{R},\mathbf{R}',t)}.$$
(12)

where *m* is the particle mass, the scattering vector is $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i = (\mathbf{K}, k_z)$, and ρ is the density of surface unit cells. The scattering amplitude τ_{fi} is, in this approximation, the offenergy-shell transition matrix for scattering by a unit cell of the elastic potential $V^{0.73}$ The most important component of Eq. (12) is the correlation function $\mathcal{W}_l(\mathbf{R}, \mathbf{R}', t)$ which is a generalized time dependent pair correlation function in the crystal displacements. In the semiclassical and classical limits it is appropriate to evaluate this correlation function in the quick collision approximation, which assumes that the collision is rapid compared to the periods of the typical phonons which are exchanged. In this case $\mathcal{W}_l(\mathbf{R}, \mathbf{R}', t)$ becomes the displacement correlation function

$$2\mathscr{W}(\mathbf{R},\mathbf{R}',t) = \langle \langle \mathbf{k} \cdot \mathbf{u}(\mathbf{R},0)\mathbf{k} \cdot \mathbf{u}(\mathbf{R}',t) \rangle \rangle.$$
(13)

The Debye–Waller factors $e^{-W(\mathbf{R}',\mathbf{k})}$ appearing in Eq. (12) are related to the correlation function evaluated at equal times and positions

$$W(\mathbf{R},\mathbf{k}) = \mathcal{W}_l(\mathbf{R} = \mathbf{R}', t=0) = \frac{1}{2} \langle \langle |\mathbf{k} \cdot \mathbf{u}(\mathbf{R},t)|^2 \rangle \rangle.$$
(14)

The Debye-Waller factor governs the temperature dependent attenuation of quantum mechanical features in the scattering intensity such as diffraction peaks or single phonon peaks. However, it can be shown that the argument of the Debye-Waller function 2W has a meaning of its own, its value is a measure of the average number of phonons transferred in a given collision. Thus values of 2W < 1 imply purely quantum mechanical conditions in which sharp elastic peaks such as diffraction and single phonon transfers dominate the scattered intensity. Classical scattering is signaled by the condition $2W \ge 1$,⁷⁴ and this is the regime where the Debye-Waller factor is very small and there is negligible intensity in the quantum peaks. As a practical consideration, classical conditions are very well approximated when 2W >4-6⁷⁵ In the classical regime exchange of multiple quanta dominates and there is only inelastic scattering.

A reasonable evaluation of the Debye–Waller factor can be obtained by using a Debye model for the phonon spectrum. Then Eq. (14) becomes, in the high temperature limit

$$2W(k) = \frac{3\hbar^2 \mathbf{k}^2 T}{Mk_B \Theta_D^2},\tag{15}$$

where Θ_D is the Debye temperature, k_B is Boltzmann's constant, and M is the substrate mass which in this case is the same as the mass of the scattered particle.

Using expression (15) it is straightforward to estimate the expected range of values of the Debye–Waller exponent. Assuming room temperature conditions, taking the Debye temperature of Na to be approximately 150 K and using the measured value of approximately 20 meV for the most probable energy of the desorbed Na, one obtains a value of 2W>10 which is sufficiently large that the practical classical condition 2W > 6 is reasonable satisfied. This justifies the use of the classical limit for treating the differential reflection coefficient of the desorbed Na.

In the classical limit of particle scattering, characterized by high temperatures and large energies, the collision interaction is short in time and localized in space and the surface can be treated as a two-dimensional continuum barrier. In Eq. (12) the classical regime is characterized by the correlation function $2\mathcal{W}_l(\mathbf{R},\mathbf{R}',t)$ becoming rapidly oscillating in both time and space. The only important contributions to the Fourier transforms of Eq. (12) are for $t \rightarrow 0$ and $\mathbf{R} \approx \mathbf{R}'$ and the integrals can be carried out by the method of steepest descents. The result is a differential reflection coefficient of the following form:^{67,74}

$$\frac{dR}{d\Omega_f dE_f} = \frac{m^2 v_R^2 |\mathbf{p}_f|}{4 \pi^3 \hbar^2 p_{iz} S_{u.c.}} |\tau_{fi}|^2 \left(\frac{\pi}{E_0 k_B T}\right)^{3/2} \\ \times \exp\left[-\frac{(E+E_0)^2 + 2v_R^2 P^2}{4k_B T E_0}\right], \tag{16}$$

where $E = E_f - E_i$, the momentum $\mathbf{p}_a = \hbar \mathbf{k}_a$ of a particle in state q is divided into components parallel and perpendicular to the surface just as for the wave vector \mathbf{k}_a according to $\mathbf{p}_a = (\mathbf{P}_a, p_{az}), \mathbf{P}$ is the parallel momentum exchange, v_R is a characteristic velocity of sound parallel to the surface, $S_{u.c.}$ is the area of a surface unit cell, and $|\tau_{fi}|^2$ is the scattering form factor of a unit cell. Equation (16) is a Gaussian-like function of energy and parallel momentum exchange, but is highly skewed on the energy gain side because of the energy dependence of the semiclassical energy shift E_0 given by $E_0 = (\mathbf{p}_f - \mathbf{p}_i)^2/2m$. The functional form of Eq. (16) is identical for any realistic continuum distribution of vibrational modes, thus the only dependence on the phonon model is through the characteristic velocity v_R which is a weighted average of phonon velocities parallel to the surface.⁶⁷ For perfectly ordered surfaces the value of v_R is expected to be of the order or smaller than the Rayleigh velocity of sound, while for the roughened surfaces considered here the incoherence in phonon modes will produce considerably smaller values satisfying $mv_R^2 \ll E_f$ which is the condition that the second term in the exponential of Eq. (16) is negligible.

The quantity measured in these experiments is the timeof-flight differential reflection coefficient which is obtained from Eq. (16) upon multiplication by the appropriate Jacobian $m(\Delta x)^2/t^3$. As discussed above the detector is a density detector whose efficiency is inversely proportional to the particle velocity, thus in order to compare with the measured TOF intensities Eq. (16) must be further multiplied by *t*.

The form factor in Eq. (16) is the squared amplitude for scattering from the surface⁷⁶ and the appropriate semiclassical expression for these conditions is the transition matrix element

$$\tau_{fi} = 2p_{fz}p_{iz}/m \tag{17}$$

for scattering from a smooth hard wall surface.⁷⁷ Equation (17) can be obtained from the distorted wave matrix elements of a surface potential V^0 which has a repulsive part which back-reflects all incoming particles. For example, the

matrix element of the repulsive potential $v_0 \exp(-\beta z)$ where v_0 is an arbitrary constant, taken with respect to its own distorted eigenstates is the well known Jackson–Mott matrix element.⁷⁷ In the hard repulsive wall limit given by $\beta \rightarrow \infty$ the Jackson–Mott matrix elements become equal to Eq. (17). Since $p_{fz}=p_f \cos \theta_f$ it is clear from Eqs. (17) and (16) that this gives immediately the observed $\cos^2 \theta_f$ dependence of the scattered intensity on the final scattering angle.

Because of the curvature near the edges of the Na clusters, one could argue that the intrinsic angular distribution from a corresponding flat surface might be narrower than the observed $\cos^2 \theta_f$ form. If this would be the case, in order to obtain agreement between experiment and theory, the theory should also be capable of providing a narrower distribution. Note that this would be a higher order effect since (i) the clusters are larger than they are tall and thus present the majority of their surface area parallel to the substrate; and (ii) our theoretical expression for the scattering intensity is classical and describes scattering from a point on the surface, which is probably of the size of the surface unit cell. Thus, in order for the $\cos^2 \theta_f$ dependence of our theory to be valid we only need to argue that the majority of the surface unit cells are oriented flat with respect to the surface normal. This does indeed seem to be the case.

However, a narrower angular distribution can readily be obtained from the theory by using the Jackson–Mott matrix elements⁷⁷ for a soft potential with a finite range parameter β . On the other hand, since the surface scattering potential for Na atoms has never been measured at the present kinetic energies, estimating the softness β of the potential would require introduction of poorly known parameters. Also, since the velocity distribution is mainly determined by the Gaussian-like exponential factor in Eq. (16), it is hardly at all affected by the choice of the matrix element. Hence in order to keep the number of unknown parameters as low as possible, we use the hard wall matrix element.

We wish to consider the situation of very small initial energies, in which case the Gaussian-like function in the differential reflection coefficient is skewed over to an exponential in final energy.⁷⁸ In the limit $E_i \ll E_f$ we have for the energy exchange

$$E = E_f - E_i \to E_f \tag{18}$$

and for the present case in which the substrate and projectile mass are identical the energy shift becomes

$$E_0 = \frac{(\mathbf{p}_f - \mathbf{p}_i)^2}{2M} \to E_f. \tag{19}$$

An average over directions of initial momenta is readily carried out leading to an observed (after detector correction) differential reflection coefficient of the very simple form

$$\frac{dR}{d\Omega_f dE_f} \propto \left(\frac{1}{k_B T E_f}\right)^{3/2} p_f^2 \cos^2 \theta_f \exp\left(-\frac{E_f}{k_B T}\right).$$
(20)

In order to model the effects on the system of a small, nondirectional initial energy we utilize a simple analytically expressable approximation to averaging over initial energies which is to add a small term ΔE_0 to the energy shift E_0 .

$$\frac{dR}{d\Omega_f dE_f} = \frac{m^2 v_R^2 |\mathbf{p}_f|}{4 \pi^3 \hbar^2 p_{iz} S_{u.c.}} |\tau_{fi}|^2 \left(\frac{\pi}{(E_0 + \Delta E_0) k_B T}\right)^{3/2} \\ \times \exp\left[-\frac{(E + E_0 + \Delta E_0)^2 + 2 v_R^2 P^2}{4 k_B T (E_0 + \Delta E_0)}\right].$$
(21)

When used with $E_i \rightarrow 0$ Eq. (21) becomes a theory with the single free parameter ΔE_0 . In the discussions below we compare both the single parameter and the parameter free theory of Eq. (20) to the measured data.

It would certainly be possible to carry out the average Eq. (16) over a small distribution of initial velocities. However, this would require at least one adjustable parameter and at least a two-dimensional numerical integration, whereas the approximation of Eq. (21) has the distinct advantage that it is expressed in analytical terms which make it easy to use for interpretation of experiments. Furthermore, the approximation used in Eq. (21) is on quite sound physical grounds. It is straightforward to show that averaging over a distribution of small initial momenta will have two major effects in comparison to taking the limit as $E_i \rightarrow 0$: (i), it will give a small energy shift in the energy exchange E appearing in the Gaussian-like exponent of Eq. (16), and (ii) it will slightly increase ΔE_0 . A small energy shift in E has a negligible effect on the results, but a small change in the value of ΔE_0 appearing in the prefactor of Eq. (16) and in the width (denominator) of the Gaussian-like exponent results in a substantial reduction in intensity of the low energy tail of the distribution. Thus the important effects of averaging over an initial distribution of velocities are quite well approximated by adding a small correction to E_0 as we do with the parameter ΔE_0 in Eq. (21).

IV. RESULTS

In Fig. 5 measured total desorption yields of Na atoms from large Na clusters of mean radius r_0 as given in the figure caption are plotted as a function of desorption angle, Θ , with respect to the surface normal (a), laser irradiance (b), laser wavelength (c), and substrate temperature (d). Figures 5(a) to 5(c) refer to Na clusters bound to mica surfaces, whereas in Fig. 5(d) we also plot the results for clusters bound to a lithium fluoride substrate. The data have been taken partially using *cw* dye desorption lasers [Figs. 5(b) and 5(c)] and partially using pulsed desorption lasers [Figs. 5(a) and 5(d)].

We observe a $\cos^2 \Theta$ angular dependence and a linear increase of desorption yield with increasing laser irradiance. With increasing wavelength the desorption yield is decreasing [Fig. 5(c)]. If we assume that the rate limiting step of desorption is the absorption of laser light via excitation of surface plasmons in the Na cluster film, then the wavelength dependence should reflect directly the spectral dependence of the absorption cross section of the clusters. This dependence can be calculated straightforwardly for isolated spherical clusters in the framework of Mie theory,^{13,79} where we have



FIG. 6. Neutral Na atom desorption intensity vs TOF, detected via TPLIF for Na clusters on a mica substrate at 300 K and $\Delta x = 11.2 \pm 0.5$ mm. Desorption laser wavelength 500 nm and irradiance 0.26 mJ/cm², $r_0 = 50$ nm. The thick solid line is a Maxwell–Boltzmann distribution at T = 310 K, the thin solid line the same distribution at T = 210 K.

used wavelength dependent values for the index of refraction of the sodium clusters from the bulk dielectric function of sodium.⁸⁰ Since the clusters are supported on a mica substrate with index of refraction of $n_{\rm mica} \approx 1.56$, an effective index of refraction $n_{\rm eff} = 1.3$ has to be introduced so as to account for the embedding medium.^{81,82} The slope of the resulting curve depends sensitively on the mean cluster radius. For a radius of 30 nm, a value which is supported by independent extinction measurements, the agreement between wavelength dependent desorption yield and absorption cross section is satisfactory.

With decreasing surface temperature the desorption yield is strongly decreasing [Fig. 5(d)]. Note that for determining the surface temperature dependence of desorption yield a crucial factor is the *absolute* value of surface temperature. Due to the small thermal conductivities of both mica and lithium fluoride we determined values of surface temperature in a calibration experiment by glueing a Pt100 thermoresistance onto the surface. As seen from the straight line fits to the data in Fig. 5(d), both in case of mica and lithium fluoride the total desorption yield follows an exponential temperature dependence

$$Y_{\rm tot} \propto \exp\left(-\frac{E_A}{k_B T_S}\right),\tag{22}$$

with activation energies E_A of 153 ± 3 meV for mica and 69 ± 5 meV for lithium fluoride.

As a possible explanation for this finding we note that the surface Debye temperature for mica is 328 K as determined by helium atom scattering (HAS),⁸³ whereas that for lithium fluoride is considerably larger, namely 513 K, also determined via HAS.⁸⁴ Apparently the clusters are less strongly coupled to the more stiff substrate (lithium fluoride) than to the more soft substrate (mica), resulting in less loss of excitation energy and more efficient desorption.

Figure 6 shows a measured TOF distribution using pulsed laser excitation (repetition rate of the laser 20 Hz, λ



FIG. 7. Maxima of TOF distributions as a function of distance Δx for a mica substrate. $T_S = 300$ K, $P_L = 0.5$ mJ/cm², $\lambda = 500$ nm, average cluster radius 40 nm. The solid line, which traverses the zero point, gives confidence to the measured values of Δx .

=500 nm, P_L =0.26 mJ/cm², τ =20 ns) and detecting atoms via TPLIF at Δx =11.2±0.5 mm that desorb along the surface normal (Θ =0°). The integration time for this spectrum was 500 s, giving an effective irradiation time of 10 μ s. The mean cluster radius was 50 nm. The thick solid line is a corresponding Maxwellian TOF distribution [Eq. (1)] at the surface temperature of 310 K, which already includes laserheating of the substrate. Obviously, the curve peaks at values of time which are too small, meaning that the desorbing atoms are *slower* than atoms desorbing in thermal equilibrium with the surface. However, a Maxwellian distribution at a considerably reduced temperature of 210 K (thin line) which would reproduce the peak position, still does *not* fit the experimental curve in terms of half width.

A precise knowledge of the value of Δx is important for an accurate determination of kinetic energies. If one measures TOF distributions such as the one in Fig. 6 as a function of Δx and determines the most probable time of arrival, $t_{\rm mp}$, from the distribution, then a plot of Δx vs $t_{\rm mp}$ should result in a straight line, the slope of which directly provides the most probable velocity of the desorbing atoms. Figure 7 shows such data for mica at $T_S = 300$ K and the same conditions as in Fig. 6, resulting in a most probable velocity of 420 ± 20 m/s.

Figure 8 shows some examples of measured TOF distributions taken for Na atoms desorbing from Na clusters bound to lithium fluoride [Fig. 8(a)] and mica surfaces [Fig. 8(b) and 8(c)] for different distances Δx between surface and detection lasers. Also plotted as solid lines are the theoretical curves, see below. The laser fluence was 0.26 mJ/cm², the wavelength was 500 nm and the average cluster radius 50 nm. The corresponding MB TOF distributions have maxima that would peak always at too early flight times.



FIG. 8. Summary of TOF distributions, measured via TPLIF for lithium fluoride (a) and mica, (b), (c) for various distances Δx (in mm) as denoted next to the curves. $T_S = 300$ K, $P_L = 0.26$ mJ/cm², $r_0 = 50$ nm. The parameters of the theoretical curves (solid lines) are: (a): 11.2 mm, $\Delta E_0 = 2$ meV, 15.0 mm, $\Delta E_0 = 2$ meV; (b): 2.2 mm, $\Delta E_0 = 0.5$ meV; 10.6 mm, $\Delta E_0 = 2.5$ meV, (c): 5.7 mm, $\Delta E_0 = 2$ meV; 13.4 mm, $\Delta E_0 = 2$ meV.

The observed TOF distributions for Na atoms desorbing from mica surfaces are independent of desorption wavelength, laser irradiance, desorption angle, and surface temperature as is demonstrated in Fig. 9 by plotting the extracted most probable kinetic energies. The actual experimental conditions are described in the figure captions.

Since the detection lasers are set at fixed frequencies the effective volume of atoms that can be excited is limited by the overall linewidth of the lasers (3 MHz) and their divergence, i.e., the corresponding velocity distribution that is selected from the broad velocity distribution of the desorbing atoms. It would be desirable to check the validity of the transformation between TOF and velocity distributions by detecting the atoms with a detector without velocity selection, i.e., using a Doppler-broadened detection method. This can be done most effectively and without loosing spatial



FIG. 9. Measured values of the most probable kinetic energy, $E_{\rm kin}$, as a function of various parameters. (a) Dependence on desorption laser wavelength. $T_S = 300$ K, $P_L = 2 - 8$ mJ/cm², $r_0 = 50$ nm. (b) Dependence on desorption laser fluence. $T_S = 100 - 300$ K, $\lambda_D = 500$ nm, $r_0 = 30 - 80$ nm. (c) Dependence on desorption angle. $T_S = 300$ K, $P_L = 10$ mJ/cm², $\lambda_D = 450$ nm, $r_0 = 120$ nm. (d) Dependence on surface temperature. $P_L = 6$ mJ/cm², $\lambda_D = 500$ nm, $r_0 = 500$ nm. All values of the kinetic energy have been normalized to the mean value, which is represented by horizontal lines.

resolution by exchanging the 3P-5S laser with a cw UV Ar⁺ laser ($\lambda = 351$ nm), which ionizes the excited atoms in front of an extracting plate that accelerates them onto an electron multiplier. A resulting TOF distribution, taken with this RETPI (resonance enhanced two-photon ionization) method for $T_S = 300$ K, $\Delta x = 60 \pm 4$ mm is shown in Fig. 10. The large peak at small flight times is due to ions generated



FIG. 10. Same as Fig. 6, but for RETPI detection of laser-desorbed Na atoms from Na clusters on mica at $T_S = 300$ K and $\Delta x = 60 \pm 4$ mm. $P_L = 1.2$ mJ/cm². For the detection lasers: dye laser: 50 W/cm², Ar⁺ laser: 150 W/cm². The time-of-flight has been corrected for the ion flight time through the mass spectrometer of $3.15\pm0.1 \ \mu$ s. The sharp peak at 5 μ s is due to ions generated on the surface.



FIG. 11. Measured evanescent-wave TPLIF intensity for Na atoms desorbing from Na clusters that are adsorbed on the hypotenuse of a glass prism and are excited by a pulsed laser (500 nm, 20 ns, 1 mJ/cm^2) (Ref. 38). The dashed line is a reference curve, calculated from Eq. (20), and the solid line includes a time delay of 50 ns between excitation of surface plasmons and desorption of Na atoms.

by the Ar⁺ laser hitting the extraction plate. The TOF distribution has been corrected for the flight-time of the ions through the mass spectrometer, which has been determined by use of a pulsed TOF mass spectrometer to be 3.15 $\pm 0.1 \ \mu$ s (cf. Fig. 13).

The use of a nearly background free laser based detection method facilitates measurement of TOF distributions at very small distances Δx from the surface or even directly on the surface. The fulfillment of the latter condition $(\Delta x = 0)$ allows one to determine in a very direct manner the delay time between absorption of photons and desorption of Na atoms just by measuring a TOF distribution. However, a necessary condition is a detector with small spatial dimensions, especially in the direction of the surface normal. Such a detector is given by the evanescent wave, which exists in the course of total internal reflection of a light wave at a prism hypotenuse. In a recent experiment we have grown a cluster distribution on such a prism and have desorbed Na atoms as well as detected them via TPLIF inside the evanescent wave.³⁸ A resulting TOF distribution for such a detector with spatial dimensions of the order of a few hundred nanometers is shown in Fig. 11. The dashed line is the theoretical TOF distribution that would be expected if there would be no time delay between excitation of surface plasmons and desorption of atoms, using Eq. (20) of the present paper. The solid line, which shows excellent agreement with the experimental data, is the expected TOF distribution assuming 50 ns delay for the desorption process.

It is noted that we have used a glass prism surface without microscopic order, and that we have not attempted to determine the cluster size distribution on the surface. Thus, in contrast to the other measurements that are shown in the present paper, we prefer to talk about a cluster *film*, which might show somewhat different time constants compared to



FIG. 12. Double-logarithmic plot of the TOF distribution for Na desorption from a mica substrate with a TPLIF detector displacement Δx =12 ±1.5 mm showing the very long tail at large times. T_S =302 K, P_L =1.5 mJ/cm², r_0 =50 nm. The solid line is from a calculation with Δx =11 mm, ΔE_0 =0.5 meV. The long-dashed line is the corresponding Maxwell–Boltzmann distribution. The short dashed line represents a 1/*t* dependence.

a distribution of clusters of finite sizes. However, the fact that the *width* of the measured distribution agrees perfectly with the predictions of the present theory leads us to the conclusion that the desorption mechanisms are very similar.

As suggested by inspection of the data in Figs. 6, 8, and 10, there is a very long-range tail in the low energy part of the distribution which is clearly distinguishable from the background noise, the extremely low level of the latter being discernible at very small times. This persistent low energy tail has been measured for times up to 650 μ s (Fig. 12) and is well fitted at times above 100 μ s with a $1/t_f$ function (short dashed line in Fig. 12). The zero-parameter scattering theory of Eq. (20) gives a $1/t_f^2$ dependence (after detector correction, shown as a solid line in Fig. 12), somewhat shorter ranged than the experiment but much better than the $1/t_f^4$ prediction of the Maxwell distribution (long-dashed line). The long range tail might be due to delayed neutralization of negative Na ions trapped in their self-image potential, with subsequent scattering of the neutrals from the surface.

The use of a TOF mass spectrometer and an ArF excimer laser ($\lambda = 193$ nm, $P_L = 50$ mJ/cm²) that excites the desorbing particles inside the ionization region of the mass spectrometer allows one to obtain mass selected TOF spectra. For this purpose the delay between desorption and detection lasers is varied, and the arrival time of the particles on the open electron multiplier is measured, which together with a knowledge of the acceleration voltages enables one to calculate their masses.

Two scans for $T_S = 300$ K, $\lambda_{desorb} = 500$ nm, $P_L = 5 \text{ mJ/cm}^2$ and a cluster size distribution peaked around 100 nm are shown in Fig. 13. Since the excimer laser also generates ions from background gas and from the walls of the apparatus a considerable amount of integration has to be performed and the background signal has to be subtracted. This has been done already for the scans shown in Fig. 13. Whereas the Na signal is clearly appearing at $t_{ion} = 3.15$



Ion Time-of-Flight [us]

FIG. 13. Detection of desorbing Na atoms via ArF excimer laser (50 mJ/cm²) ionization at $\Delta x = 60 \pm 4$ mm. $T_S = 300$ K, $P_L = 5$ mJ/cm², $\lambda_D = 500$ nm, $r_0 = 100$ nm. Measured ion TOF for two different values of delay between desorption and ionization laser.

 $\pm 0.1 \ \mu$ s, there is no hint for Na₂. However, due to the high photon energy of the excimer laser (6.42 eV) we trace the latter observation mainly back to a high fragmentation probability of the desorbed dimers. This problem might be overcome in the future by the use of KrF excimer laser light at 248 nm. Recent experiments indeed have shown that the probability for desorption of dimers can be high, depending on the irradiation conditions.¹⁸

The intensity of the peaks as a function of time delay is plotted in Fig. 14. We already have subtracted the ion flight time in the TOF mass spectrometer of 3.15 μ s. The data from the fully pulsed experiment (solid symbols) are compared in Fig. 14 with the data obtained by use of the cw UV Ar⁺ laser (grey dots) and also with the theoretical prediction Eq. (21) for the given distance between surface and detector



FIG. 14. TOF distribution, deduced from ion TOF curves such as the ones shown in Fig. 13 as a function of delay time between desorption and ionization lasers (filled circles). The ion flight time through the mass spectrometer has been subtracted. The grey curve is the TOF curve obtained via RETPI (Fig. 10) for the same distance. The solid curve is from theory for $\Delta x = 56$ mm, $\Delta E_0 = 8$ meV.



Time-of-Flight [µs]

FIG. 15. Comparison of a measured TOF distribution for $\Delta x = 6.2 \pm 0.5$ mm with theoretical curves. $T_s = 300$ K, $\lambda_D = 500$ nm, $P_L = 1$ mJ/cm², $r_0 = 50$ nm. Dash-dotted line: Maxwell-Boltzmann distribution at T = 300 K; short-dashed line: zero parameter multiphonon theory; solid line: multiphonon theory with $\Delta E_0 = 2$ meV.

(solid line). All the three curves agree well within error bars, giving confidence both to the experimental procedure and the theoretical modeling.

V. COMPARISON WITH THEORY

In Fig. 15 a measured TOF distribution for $\Delta x = 6.2 \pm 0.5$ mm is compared with different theoretical curves. A Maxwellian distribution at the substrate temperature shown as a dash-dot curve is clearly too narrow. The zero-parameter theory shown as a short dashed line predicts the correct short time behavior, the correct maximum position and a long range tail. The scattering theory with $\Delta E_0 = 2$ meV (solid line) matches the experimental data well on both sides of the peak for the first 30 μ s, but then becomes too small. All calculations were carried out for $\Delta x = 5.7$ mm, which is within the measured experimental error bars.

A more systematic comparison of experiment and theory is provided in Fig. 8, showing TOF curves for different distances Δx and mica as well as lithium fluoride as substrates. In all investigated cases the theoretically predicted curves match the experimental data very well. Theory and experiment agree also very well both for mica [Fig. 16(a)] and lithium fluoride [Fig. 16(b)] with respect to a change in the half widths of the TOF distributions as a function of surface temperature for surface temperatures that are below 300 K. Note that the calculated half widths are absolute values and have not been fitted to the measured points. In case of lithium fluoride and for temperatures above 300 K the experimentally predicted increase in half width cannot be reproduced by the theory. However, the additional increasing FWHM seen at temperatures above 300 K may be due to a significant change of the cluster size distribution in the course of thermal desorption and melting (the bulk melting temperature for Na is 371.3 K^{85}).

Both versions of the theory, either Eq. (20) or Eq. (21) which includes a small additional energy shift ΔE_0 , give



FIG. 16. The FWHM of the TOF neutral atom desorption intensity as a function of substrate temperature for Na clusters on (a) a mica substrate with Δx =11 mm and (b) a LiF substrate with Δx =5 mm, λ_D =500 nm, P_L =2.5 mJ/cm², r_0 =50 nm. The calculated curve (solid line) has not been fitted to the measured data (filled circles). Error bars are single standard deviations.

kinetic energy distributions that are independent of final angle θ_f , in agreement with the experimental data (Fig. 9).

Figure 17 shows the *energy* distribution of desorbed Na atoms $dR/d\Omega_f dE_f$ taken from the TOF distribution with $\Delta x = 14 \pm 0.8$ mm. This was obtained by applying the conversion Jacobian from time to energy coordinates according to

$$\frac{dR}{d\Omega_f dE_f} = \frac{dR}{d\Omega_f dt} \left| \frac{dt}{dE_f} \right| = \frac{dR}{d\Omega_f dt} \frac{t^3}{m\Delta x^2},$$
(23)

and the data was corrected for the velocity dependence of the detector.

It is immediately apparent that the energy distribution in Fig. 17 does not exhibit a maximum, as expected for example for a thermal distribution, such as the MB distribution for the surface temperature of 300 K also shown in Fig. 17. This lack of a clear maximum is a manifestation of the very long range tail in the TOF distribution which appears here at



FIG. 17. The differential reflection coefficient $dR/d\Omega_f dE_f$ (energy distribution) for Na atoms desorbed from Na clusters on a mica substrate with a TPLIF detector displacement $\Delta x = 13.4$ mm. The data have been corrected for the velocity dependence of the detector and are shown as points, the dash-dot line is a Maxwell-Boltzmann distribution, the dashed line is the zero parameter theory of Eq. (20) and the solid line is the single parameter theory with an average initial energy of 2.0 meV.

small final energies. The two other theoretical curves in Fig. 17 are the parameter free theory of Eq. (20) (dashed line) and the single parameter theory with a small average initial energy of 2.0 meV (solid line), each calculated with $\Delta x = 13.4$ mm. Both of these theoretical curves agree well with the energy distribution of the data, although at energies above 5 meV the single parameter theory is somewhat better. The MB (dash-dot line) is in clear disagreement with the data, and here the disagreement is much more evident than above in the TOF example shown in Fig. 15.

With an energy distribution which does not vanish at zero energy the question arises as to whether it is normalizable, or stated alternatively in more physical terms, whether it describes a finite number of desorbed Na atoms generated per laser pulse. This is simply answered by comparing the data with the zero parameter theory of Eq. (20) in Fig. 17. The zero parameter theory, in this representation, becomes a simple exponential in final energy, a function which is normalizable. The experimental data at low energy, apart from apparent scatter due to experimental uncertainty, lies below the zero parameter theory curve, and thus would also be normalizable. Some TOF data was taken for very large times as shown in Fig. 12 which shows the Na desorption intensities for a detector distance $\Delta x = 12 \pm 1.5$ mm. This figure shows a very long tail extending out to more than 600 μ s, and the fall off of this tail is fitted well by a 1/t dependence. However, even if the TOF data has a 1/t large-time behavior it is still normalizable. When converted to an energy distribution after making the density detector correction, a 1/t behavior in the TOF distribution becomes at small E_f a $1/\sqrt{E_f}$ singularity in the energy distribution which is normalizable.

Although the TOF distributions can vary considerably in appearance because of the broadening produced by different flight path distances Δx , the energy distributions for a given surface substrate and surface temperature should always be identical. This is indeed the case as is shown in Fig. 18 which contains three energy distributions taken at three different flight path distances and with two independent measuring techniques. The grey line and the circles in Fig. 18 were measured using the TPLIF method for $\Delta x = 6.2$ ± 0.5 mm as in Fig. 15 and for $\Delta x = 14 \pm 0.8$ mm. The black line was measured with the RETPI detector with $\Delta x = 60$ ± 4 mm. Obviously all three of these energy distributions are identical, giving a clear demonstration not only of the reproducibility of a single measuring method but also demonstrating that the energy distributions are independent of the method of detection.

In summary we note that the present model describes quantitatively six of the nine characteristics for the desorbed neutral flux listed above in the Introduction. Specifically, because the intensity depends only on the interaction of the desorbing neutral Na with the surface phonon field, the desorbing TOF distribution of Eq. (20) is (1) independent of laser irradiance [Fig. 9(b)], (2) independent of laser wavelength [Fig. 9(a)], and (3) the energy distribution of the desorbing particles is in the thermal energy range but is non-Maxwellian because it is a scattering distribution. (The most



FIG. 18. The measured differential reflection coefficient $dR/d\Omega_f dE_f$, not corrected for the velocity dependence, for Na atoms desorbed from Na clusters on a mica substrate with three different detector displacements and two different detection methods showing the similarity of the energy distributions under different measurements. Grey line: TPLIF detector with $\Delta x = 6.2 \pm 0.5$ mm; circles: TPLIF detector with $\Delta x = 14 \pm 0.8$ mm; black line: RETPI detector with $\Delta x = 6.0 \pm 4$ mm.

probable energy is smaller and the energy width of the distribution is larger than those given by a MB distribution at the substrate temperature T_s .) Furthermore, (4) the FWHM of the TOF distribution decreases with T_s (Fig. 16), (5) the dependence on scattering angle θ_f is dictated by the form factor and is identical with the observed $\cos^2 \theta_f$ behavior [Fig. 5(a)], and (6) at large TOF times (small energies) there is a much longer ranged tail as opposed to that which would be expected for a MB distribution (Fig. 12). The remaining three characteristics (dependence of desorption yield on irradiance, wavelength, and surface temperature) are dictated by the absorption process and the adsorbate–substrate coupling, and are therefore outside the scope of the present multiphonon scattering model.

VI. DISCUSSION AND CONCLUSIONS

We have presented the results of detailed measurements of the desorption of Na atoms from large Na clusters, adsorbed on insulating surfaces. In order to simplify the discussion on this complex system it seems useful to break it down into two sub-systems: (i) the Na clusters themselves, which resemble rough metallic surfaces of finite size; and (ii) the coupled adsorbate-substrate system, where the substrate represents a very effective heat sink. Since the relevant decay constants of electronic excitation on an insulating surface are at least an order of magnitude larger compared to the decay on a metal surface, we neglect the adsorbate-substrate coupling for the initial decay process. However, as detailed in the present work, although the initial electronic excitation of the clusters is clearly nonthermal the overall desorption mechanism is delayed via interaction with lattice vibrations of the clusters, and thus a more complete theoretical model will eventually have to include the coupling to the substrate.

Compared to, e.g., a continuous metallic film, the coupling between the incoming transverse electromagnetic field and the longitudinal plasmon excitation is facilitated by the inherent roughness that the clusters exert on the surface (i.e., their finite sizes). The surface of the clusters probably has a large number of defect sites, i.e., sites with low coordination numbers, where the binding energies of the atoms to the clusters are small and desorption takes place. The absorption coupling is cluster size and laser wavelength dependent, resulting in a variation of desorption yield as a function of size, but not in a change of kinetic energy distribution (cf. Figs. 5 and 9). This, among other points, indicates that the initial photon absorption process is largely *decoupled* from the final desorption mechanism. Hence our measurements disagree with the suggestion of Ref. 12 that the local field enhancement in the clusters results directly in the creation of antibonding pairs at defect sites, which lead to desorption. Instead we suggest the desorption to occur via a thermalization process. However, we certainly agree with the possibility of generating charged particles in the process of plasmon excitation, which might have some (minor) effects on the desorption dynamics of the neutrals; see below.

The lifetime of the plasmon excitation in adsorbed Na clusters³⁰ and Au clusters³² has been measured to be of the order of tens of fs. This finding agrees with other indirect experimental evidence from work function measurements that desorption in the case of a rough sodium film occurs from long-lived (30 fs) excited electronic states, which are established at surface structural defects and include localization of conduction electrons.¹⁰ However, this lifetime of the electronically excited state is still short compared to the time scale of the nuclear motion, which is given by the vibrational frequency of the atoms in the clusters and is thus of the order of a picosecond. Consequently, by applying the "conventional" DIET (desorption induced by electronic transitions) picture⁸⁶ one would expect to observe a MB velocity distribution with a "temperature" $T = u \tau / k^{87}$ with u the slope of the excited state curve at the critical point (actually u $=s^2t_c/m$ with s the slope) and τ the electronic relaxation time at the critical distance. This model apparently cannot be applied to the Na cluster system since we can neither describe the velocity distributions by a MB distribution, nor does the temperature fit to reasonable values of u.

Instead we propose that the electronic excitation is lost by vibronic coupling and the desorption occurs along the lines which have been proposed in the course of, e.g., photolysis of chemisorbed trimethylaluminum.⁶⁴ There, too, a linear increase of desorption yield with increasing power and subthermal photoproduct distributions have been observed. This system shows similarities to our system also in other respects since there is a strong vibrational coupling of the desorbed species to the substrate (corresponding to the coupling of the Na atoms to the clusters). The velocity distributions could be reproduced well with a MB distribution albeit at a temperature that is below the surface temperature. This has been explained in terms of vibrational energy loss into the substrate and similarities with the observation of subthermal distributions in the thermal desorption of, e.g., Ar from Pt(111) (shallow potential well of 0.1 eV) have been invoked. By use of microscopic reversibility the desorption process may be explained by the analogous adsorption process of atoms impinging on the surface. If the potential well is deep enough, then all the incoming atoms will stick, resulting in a thermal MB distribution of the desorbing atoms. However, for shallow potential wells *only* molecules with low kinetic energies will stick. Here, "shallow" is always meant with respect to the surface temperature in the sense that the sticking probability deviates significantly from unity.⁸⁸ Hence in desorption only the trapped (low energy) molecules can be observed and the distribution will show an energy loss.

Let us discuss the coupling of the excited clusters to the insulating substrate. The influence of this coupling is demonstrated, e.g., in the Arrhenius type dependence of desorption yield on the substrate temperature. The increase in cluster temperature results in a higher statistical desorption rate and the coupling factor depends on the type of substrate (its stiffness); hence substrates with different Debye-Waller factors result in Arrhenius plots of desorption yield with different activation energies. The overall widths of the plasmon resonances of the surface bound clusters are also direct evidence for a strong coupling to the substrate. In recent experiments on size selected Ag clusters of radius 1 nm it has been shown that upon adsorption of the clusters on SiO₂ the width of the plasmon resonance was strongly increasing due to chemical interface damping.⁸⁹ Similar effects are expected for the present Na clusters. However, in spite of the strong coupling between clusters and substrate we tend to exclude the process of "resonant heating" ^{90,91} as a possible route to desorption of Na atoms. In resonant heating or "vibrational predesorption" the initial vibrational excitation of the adsorbate is transferred to the continuum states of the adsorbatesubstrate potential, resulting in a heating of the substrate with subsequent desorption of the de-excited adsorbate. Such a model certainly is able to explain photodesorption yields of physisorbed systems such as CO-NaCl,^{92,93} but in the present case would be applicable only to desorption of the Na clusters as a whole. Neither such a process nor significant heating of the substrate have been observed.

The TOF distributions measured in the present work were independent of cluster radius for radii between 70 and 100 nm. However, the size distribution had a width of 50%, which certainly smears out subtle effects. It is expected that more tightly in situ characterized and prepared size distributions especially for clusters with smaller radii will reveal the influence of cluster-specific "finite-size" factors on the desorption dynamics such as the cluster flatness and ellipticity or variations in the binding energy as a function of size and roughness. More precise in situ characterization methods of the cluster sizes will become available in the near future through new experimental methods such as helium atom scattering³⁷ or degenerate four-wave mixing.⁹⁴ A significant influence of surface structure (poly vs single crystalline) on the desorption dynamics has been observed, e.g., in ioninduced desorption of Na atoms from NaCl.²⁸

Let us finally note that upon irradiation of the clusters

generation of photoelectrons and of ions via the thermionic^{95,96} or plasmon mediated processes is highly probable. Copious emission of both neutral metal atoms and ions occurs when the surface is irradiated with a sufficiently intense beam of photons in the eV range.¹⁴⁻¹⁷ Also, very recently emission of both electrons and atoms from spherical Na_{91}^{-} clusters has been experimentally reported⁹⁷ and theoretically investigated.⁹⁸ The cloud of charges might influence the desorption characteristics in several ways, e.g., via image charge attraction and reneutralization processes. Note, however, that this process contributes especially strongly for small clusters where the electron-hole pair lifetime is long enough to allow escape before recombination of the electrons. The probability for electron (and ion) emission should be proportional to $\exp(-W/k_B T_{\text{electron}})$, where the work function of Na is W=2.31 eV.¹⁰ Hence for values of T_{electron} $\approx 10^4$ K an appreciable amount of electrons is expected. An accurate determination of the electron-phonon coupling constant, which is presently underway, should allow us in the near future to provide realistic values of the nonequilibrium temperatures of the hot electron gas. For the present case of large clusters and weak irradiation in the visible spectral region the role of charged particles is expected to be of minor significance to the overall desorption process.

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