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Chemical Reactions on the Surface of Metal Nanoparticles Studied by Optical Spectroscopy

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The influence of molecular adsorbate layers on surface plasmon excitation in small supported metal particles has been investigated and exploited to study adsorption reactions on their surfaces. For this purpose sodium nanoclusters on quartz and LiF substrates served as model systems. Their optical transmission spectra are dominated by two maxima which are due to the excitation of surface plasmon resonances in the direction of the long and short axes of the oblate particles. By recording the spectra under ultra-high-vacuum conditions and, subsequently, after exposure to gases such as O_2, N_2O, CO_2, H_2 and N_2, changes in the optical spectra can be identified if the clusters are covered by as little as half a molecular monolayer. Depending on the adsorbed molecules, different modifications of the maximum position, the width and the amplitude of the surface plasmon resonances are observed. The results of a series of measurements together with calculations using the quasi-static approximation indicate that the variations in the spectra allow one to distinguish between physisorption and chemisorption, i.e. to characterize the strength of the chemical bond. In addition, diffusion of the molecules into the bulk of the particles can be detected. Particularly interesting is the observation that the clusters can experience a change in their shape if gases such as O_2 or CO_2 react with their surface.

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1 INTRODUCTION

Engineering and assembly of materials at the nanometer scale is of great promise for the production of smaller technological devices than are currently available.[1–3] In particular, research on metal nanoparticles with size-dependent optical, chemical and electronic properties is motivated by such potential applications, which include for example novel optical components or catalytic converters with enhanced performance. For a variety of scientific and practical reasons characterization of reactions between metal particles and adsorbate molecules is of great value and interest. For example, if metal clusters with tailormade absorbance are embedded in devices such as optical filters or components for ultrafast switching of light, uncontrolled modifications of their electronic and optical properties due to reaction with the chemical surroundings must be excluded. In addition, the particles are often protected by organic ligands to prevent coagulation and interaction between them or with other materials.[4,5] Depending on the nature of the adsorption reaction, the electronic and optical properties of the particles can be strongly influenced due to the interaction with ligand molecules.

In this paper we report studies with the objective of clarifying whether and how the optical spectra of small metal particles are changed by adsorption reactions on their surface. The goal of this work is to distinguish between the different physical processes contributing to adsorbate-induced modifications. Understanding of these effects would open the door to exploiting the optical spectra in order to study chemical interface reactions on the surface of supported metal particles and, furthermore, to predict possible variations of their electronic and optical properties caused by adsorption.

In general the optical spectra of nanoparticles are dominated by pronounced resonant features which are commonly attributed to excitation of plasmon

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polaritons, i.e. collective oscillations of the electron gas driven by the electromagnetic field.[2,3] The energetic position, the width and the amplitude of these resonances vary strongly as a function of the size and shape of the nanostructures and thus reflect the influence of these parameters on their optical properties. Measurements on clusters embedded in different matrices have shown that the chemical environment also influences the optical properties drastically (see e.g. Refs [2, 6–9]). For example, the spectra of silver clusters exhibit an increase in the width accompanied by shifts in the position of the plasmon resonance to lower energy compared with the gas phase if the particles are embedded in different materials.[6–8] It could be shown that the major part of the peak shifts is brought about by modifications of the Maxwell boundary conditions. However, the observed shifts exceed this classical electrodynamic effect for most materials investigated, and modifications resulting from permanent charge transfer from the metal cluster to the molecules of the surrounding medium must also be taken into account.[2,6,8] The increase in the width of the plasmon resonance was interpreted by a dynamic charge transfer of conduction electrons from the metal cluster to partially unoccupied levels of the adsorbed atoms or molecules, and treated theoretically by Persson.[10]

In our experiments sodium (Na) particles were generated with variable, predetermined sizes under ultrahigh-vacuum (UHV) conditions by deposition of atoms, subsequent surface diffusion and nucleation. As a second step, the optical transmission spectra were recorded in order to determine the average cluster size and — by using *s*- or *p*-polarized light — to determine their axial ratio, i.e. the particle shape.[11,12] Subsequently, the clusters were exposed to gases such as O_2, N_2O, CO_2, H_2 or N_2. The dosage being well defined, different coverages of molecules on the cluster surface could be chosen. After completion of the exposure, the optical transmission spectra were recorded again. The main advantage of the investigations is threefold: first, changes in the optical spectra induced by a single (contaminant-free) molecular species can be studied, the experiments being performed in UHV at a base pressure of $P = 2 \times 10^{-10}$ mbar. This opens up the possibility of distinguishing between different processes which are responsible for changes in the optical spectra. Secondly, the dosage of the gases can be controlled in a sensitive and reproducible manner, making possible a gradual variation of the dielectric surrounding of the clusters and thus a systematic study of the changes in the optical spectra as a function of coverage. Third, modifications of the shape of the clusters brought about by chemical reactions with adsorbates can be studied using *s*- and *p*-polarized incident light.

2 EXPERIMENTAL SET-UP AND PROCEDURE

The experimental set-up is described in detail elsewhere.[11] In short, it consists of an ultrahigh-vacuum system with a base pressure of 2×10^{-10} mbar, the sample, a xenon-arc lamp combined with a monochromator for measuring the transmission spectra, a Knudsen cell for evaporating Na atoms and a gas-inlet system. Either quartz(100) or LiF(100) single crystals were used as substrates for the Na clusters, the transmission spectra of which were measured. Being mounted on a manipulator, the substrate could be cooled to $T = 80$ K and heated to about $T = 750$ K. A thermal atomic beam of Na atoms with well-defined flux was generated by the Knudsen cell and directed onto the substrate in order to deposit a predetermined coverage of atoms on the surface held at $T = 80$ K. The flux of the atomic beam was about 10^{12} atoms per second. It was measured with a quartz microbalance. The deposited atoms assembled into small particles by surface diffusion and nucleation. The experiments reported here were carried out under conditions in which the generated clusters are well separated from each other and far from growing together. As the defects of the quartz or LiF surface were 'decorated' during nucleation, the number density of the clusters remained essentially constant during their growth. Consequently the coverage, i.e. the number density of deposited atoms, and the average particle size are unequivocally related to each other. The deposition time was chosen such that the mean radius of the particles was about $R = 30$ nm. Because of different diffusion constants of the deposited metal atoms on the substrate and on the surface of the growing particles, the clusters were not spherical but could be described roughly as oblate rotational ellipsoids with the short axis pointing in the direction of the surface normal.

As mentioned above, the transmission spectra of the Na clusters were measured with the light of a xenon-arc lamp and a grating monochromator.[11] The light was polarized by a rotable Glan polarizer before it was focused to a 5 mm spot on the sample.

Photon energies ranged from 1.0 to 4.5 eV and the spectral resolution of the monochromator was usually chosen to be $\Delta E = 10$ meV. The light transmitted through the transparent substrate crystal was collected by a lens and finally registered with a photodiode. The measured spectra were corrected for the spectral emission profile of the xenon-arc lamp as well as the wavelength-dependent transmission of the optical components and the spectral response of the photodiode.

Subsequently, the clusters were exposed to either O_2, N_2O, CO_2, H_2 or N_2. The gas entered the vacuum system through a leak valve which allowed well-controlled and reproducible dosages. They were measured in Langmuir (L), i.e. the product of the chosen pressure rise in 10^{-6} Torr (μTorr) and the exposure time in seconds. If a sticking coefficient of unity is assumed, a dosage of 1 L implies formation of one monolayer. After the dosage was completed, recording of the optical spectra was repeated. As the last step of each experimental run the substrate was cleaned by heating to 700 K.

3 EXPERIMENTAL RESULTS

As an example, Fig. 1 presents extinction spectra measured with *p*-polarized light of bare Na particles and particles after different O_2 and CO_2 exposures. For clean particles two peaks are measured. They are located at $E = 1.83$ and $E = 4.30$ eV. These resonances are well-known, dipolar, surface plasmon excitations, i.e. collective oscillations of the free electron gas driven by the electromagnetic field.[2,11,12] The amplitudes of the two resonances depend on the polarization direction of the incident light: *p*-polarized light can excite the (1,1) mode at $E = 1.83$ eV and the (1,0) mode at $E = 4.30$ eV, i.e. oscillations of the electron gas in the direction parallel to the long and short axes of the oblate particles, respectively. The energetic separation being a fingerprint of the particle shape, the average axial ratio of the Na clusters can be determined from the resonance positions to be $a/b = 0.24$. For this purpose the experimental results have been compared with calculations performed by the Mie theory and the quasi-static approximation. Furthermore, shifts in the resonances due to influences of the substrate and the surrounding medium have been taken into account.[11] Upon exposure to oxygen of 5 L the (1,1) mode shifts from $E = 1.83$ eV for the bare

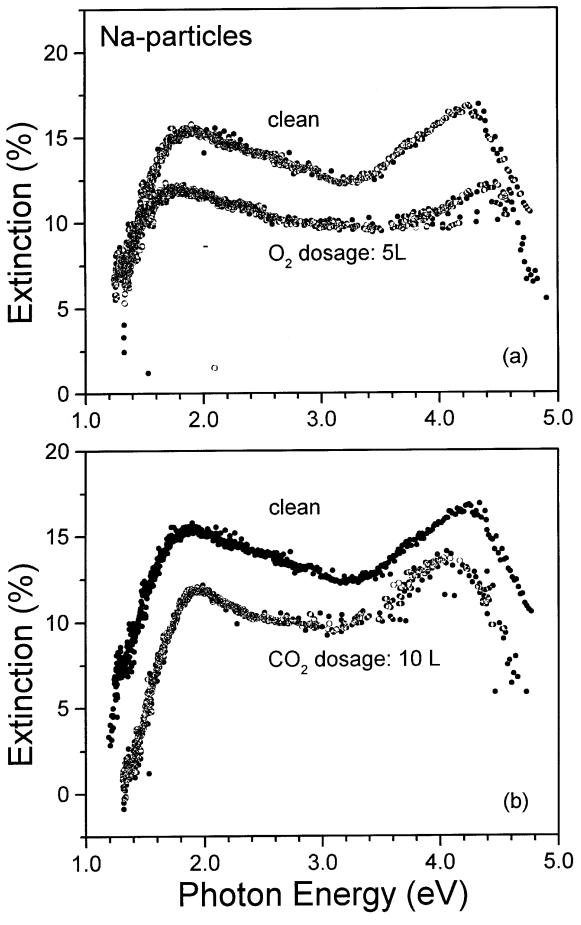

Figure 1 Optical spectra of Na clusters. The upper panel (a) shows experimental spectra of the bare clusters and after different O_2 dosages. The lower panel illustrates the change in the spectrum that occurs if the clusters are covered with CO_2. The spectrum measured for 10 L CO_2 exposure is shifted by 3% to lower extinction values in order to illustrate the modification of the peak position of both modes.

clusters to $E = 1.74$ eV. In contrast, the (1,0) mode shifts to higher energy for similar exposures. Furthermore, the width of both resonances increases and the amplitude shrinks. In contrast to oxygen, CO_2 shifts the (1,1) mode to higher and the (1,0) mode to lower energy. The width and amplitude remain unchanged (the spectrum measured for 10 L CO_2 exposure is shifted by 3% to lower extinction values in order to illustrate the modification of the peak position of both modes). Figures 2 and 3 summarize the results obtained for all the gases. Figure 2 displays (a) the peak shift of the (1,1) mode, (b) the shift of the (1,0) mode and (c) their energetic separation as a function of gas

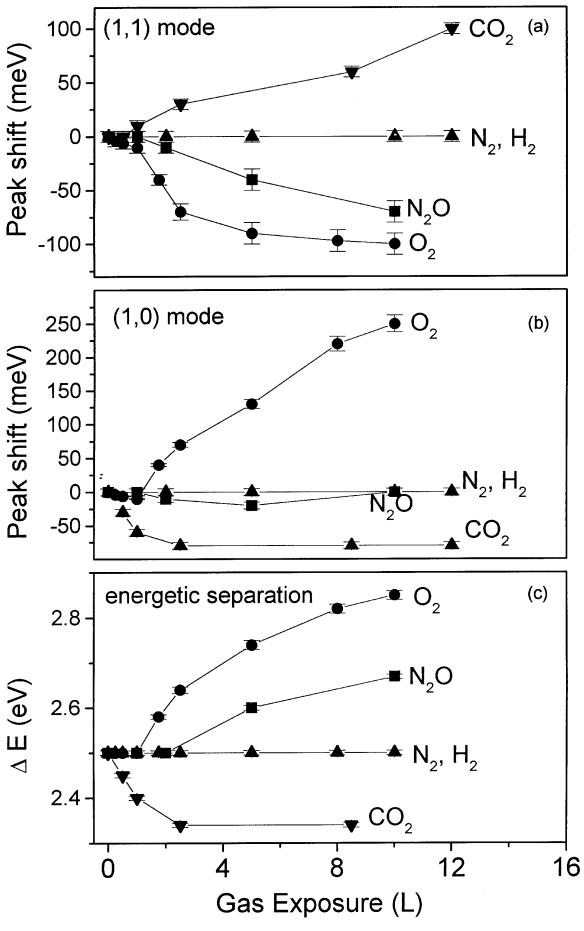

Figure 2 Shift of the center frequency of (a) the (1,1) and (b) the (1,0) mode and their energetic separation (c) as a function of exposure to O_2, CO_2, N_2O, H_2 and N_2.

exposure. An oxygen dosage lower than 1.0 L gives rise to a peak shift of both modes to lower energy by 20 meV whereby the energetic separation remains unchanged. For exposures above 1.5 L the energetic shift of the (1,1) mode continues, but with a growing gradient. In contrast, the center frequency of the (1,0) mode is now displaced to higher energy. Consequently, the energetic separation starts to increase. Figure 3 illustrates how (a) the width and (b) the amplitude of the (1,1) mode change with increasing gas dosage. Oxygen exposure lower than 2 L leads to a decrease in the amplitude. The width of the plasmon peak remains unchanged in this exposure range. For dosages exceeding 2 L the amplitude decreases further and the width starts to increase. Finally, for an oxygen exposure of 15 L the plasmon peaks have vanished. Similar changes of the width and amplitude can be observed for the (1,0) mode.

N_2O induces very similar modifications of the optical spectra. The amplitude of both modes decreases and the widths grow for exposures exceeding 2.5 L. In addition, the center frequency of both modes is displaced to lower energy until, for dosages larger than 5 L, the (1,0) mode is displaced to higher energy and the energetic separation has increased slightly.

In sharp contrast to the dosage of O_2 and N_2O, adsorption of CO_2 gives rise to a shift of the (1,1) mode to higher and of the (1,0) mode to lower energies, whereby the width and the amplitude of the plasmon peaks remain unchanged. Exposure of the particles to N_2 and H_2 does not modify the optical spectra at all.

4 DISCUSSION

We first note that measurement of the optical spectra clearly provides a sensitive technique for detecting molecules on the surface of small particles. As can be seen from Figs 2 and 3, even coverages below a single molecular layer can induce measurable shifts in the peak position and noticeably attenuate the amplitude of the plasmons.

As mentioned above, the optical spectra depend on the cluster material, the size and shape of the particles and the dielectric constant of their environment. As a consequence, a variety of effects can induce the observed changes in the energetic position, width and amplitude of the surface plasmon resonances upon adsorption of molecules. First, adsorbate layers can modify the dielectric constant of the cluster environment, i.e. change the Maxwell boundary conditions. Secondly, chemisorption of molecules influences the electronic structure of the cluster surface[2,8] and thus gives rise to coverage-dependent spectra. Third, reaction of molecules with the cluster surface can induce variations of the shape of the oblate particles due to changes of surface tension. Fourth, formation of a compound layer by chemisorption of molecules is accompanied by shrinking of the remaining metallic core and a decrease in the axial ratio. This effect is particularly pronounced if the adsorbate molecules penetrate into the interior of the clusters by diffusion and react chemically with the core, thus gradually reducing its size until, finally, the particles generated originally have been transformed into clusters of the compound material. In

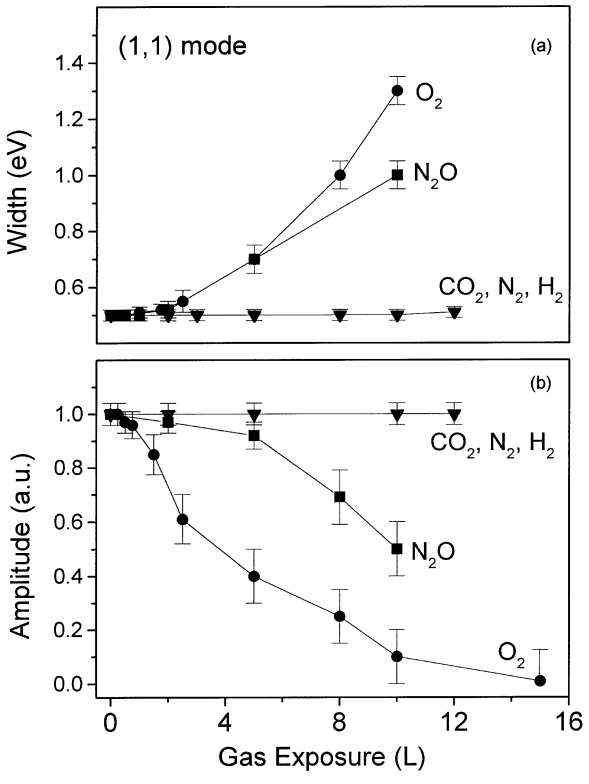

Figure 3 Full width at half maximum (FWHM) (a) and amplitude (b) of the (1,1) mode as a function of exposure to O_2, CO_2, N_2O, H_2 and N_2.

order to distinguish unambiguously between all of these effects, theoretical spectra have been calculated for different particle sizes, axial ratios, molecular adsorbates and overlayer coverages. For this purpose the quasi-static approximation[2,12] has been used. Figure 4 illustrates how the particles and their adsorbate layer were treated theoretically. The dielectric surrounding of the bare clusters, i.e. the quartz substrate on one side and vacuum on the other, is modeled by a weighted average function $_m = 1.37$ that falls between the vacuum value and the value of the support material.[2,11] Upon exposure to molecules, a shell grows consisting of the adsorbed species bound to the sodium atoms of the surface (Figure 4b). In the calculations this shell has been taken into account by a dielectric constant $_{shell}$ different from ε_m. For clusters without an adsorbate layer the plasmon resonances are located at about $E = 1.8$ and 4.3 eV, in good agreement with the experimental spectrum of Fig. 1. If the clusters have an adsorbate shell, the resonances shift to higher photon energy for $\varepsilon_{shell} < \varepsilon_m$. Conversely, the plasmon peaks experience a red shift if $_{shell} > \varepsilon_m$ is assumed (Fig. 4f). For constant shell thickness the direction and magnitude of the peak shift depend on the difference between ε_{shell} and the dielectric function ε_m of the surrounding medium without adsorbate. The energetic separation of both modes remains almost unchanged. In addition, Figs 4(c,g) and 4(d,h) present theoretical spectra obtained for increasing shell thickness, i.e. decreasing axial ratio *a/b* of the metal core. In these calculations the known dielectric function of Na_2O was used.[13] Now, the plasmon resonances are displaced so that the separation of the modes increases if the thickness of the Na_2O shell grows, Figs 4(g,h). Details of the calculations will be published elsewhere.[14]

It is essential to mention that the quasi-static approximation applied here is based on a step-like change in the dielectric function $\varepsilon(\omega)$ at the particle surface.[2,12] This assumption, however, is not justified on a microscopic scale (see e.g. Ref. 15). In particular, charge transfer from the clusters to chemisorbed molecules (see above) may induce changes in the position and width of the plasma resonance which are not contained in the theoretical approach. Depending on the occupation and overlap of the adsorbate states with the Fermi level in the metal clusters, electrons can tunnel to or from the adsorbate, resulting in permanent charge transfer and thus changing the density of the conduction electrons in the metal.[2,6,10] Charge transfer from the cluster to the adsorbate causes a red shift, since the energy of the plasmon resonance is proportional to $N^{1/2}$, N being the diminished number of conduction electrons.

The spectra of the particles recorded for different experimental conditions together with the results of the theoretical calculations allow us to suggest the following interpretation of the variations in the amplitude, position and width of the surface plasmon resonances upon adsorption of molecules.

From measurements with electron energy loss spectroscopy, X-ray photoelectron spectroscopy, low-energy electron diffraction and second-harmonic excitation,[16–18] O_2 is known to react very effectively with sodium surfaces. Oxygen is chemisorbed dissociatively on Na(110) surfaces and thin Na films with a considerable charge transfer to the adsorbed oxygen atoms. Therefore, it is not surprising that even an oxygen coverage lower than one monolayer induces pronounced changes of the optical spectra of the Na clusters. Following an oxygen exposure of 0.25 L the amplitude of the plasmon peak starts to decrease.

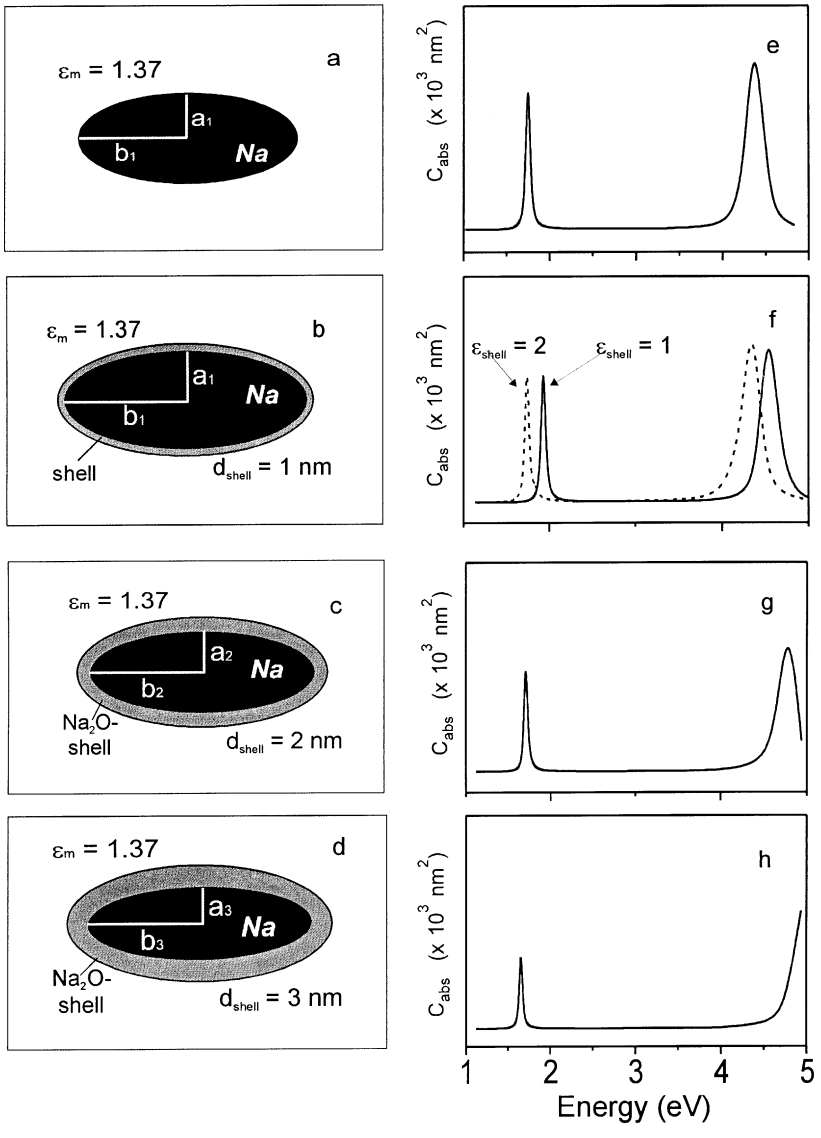

Figure 4 Schematic representation of supported oblate spheroidal Na clusters (left-hand side) together with their calculated absorption cross-section of surface plasmon excitation (right-hand side). The computation was made for Na clusters embedded in a medium with dielectric constant ε_m (a,e) and with a shell of dielectric constant (b,f) $\varepsilon_{shell} = 1$ and $\varepsilon_{shell} = 2$. In (c,g) and (d,h) the influence of increasing shell thickness of an Na_2O layer is shown.

The oscillator strength of the surface plasmon shrinks, indicating that the number of conduction electrons in the Na cluster is reduced because of charge transfer to the adsorbed oxygen molecules. Most probably Na_2O is formed by chemisorption of oxygen on the cluster surface.[17,18] Furthermore, even in the lowest exposure regime a peak shift to lower energy is observed. As already mentioned above, this can be caused by the modified chemical environment, changes in the shape of the Na clusters and charge transfer to the oxygen atoms. Since the energetic separation between the (1,1) and (1,0) modes remains unchanged below 1 L, changes in the shape of the particles do not play a role in this exposure range, i.e. for an oxygen coverage lower than one monolayer. Furthermore, comparison between the calculated spectra of the bare Na clusters (Fig. 4) and the clusters with an

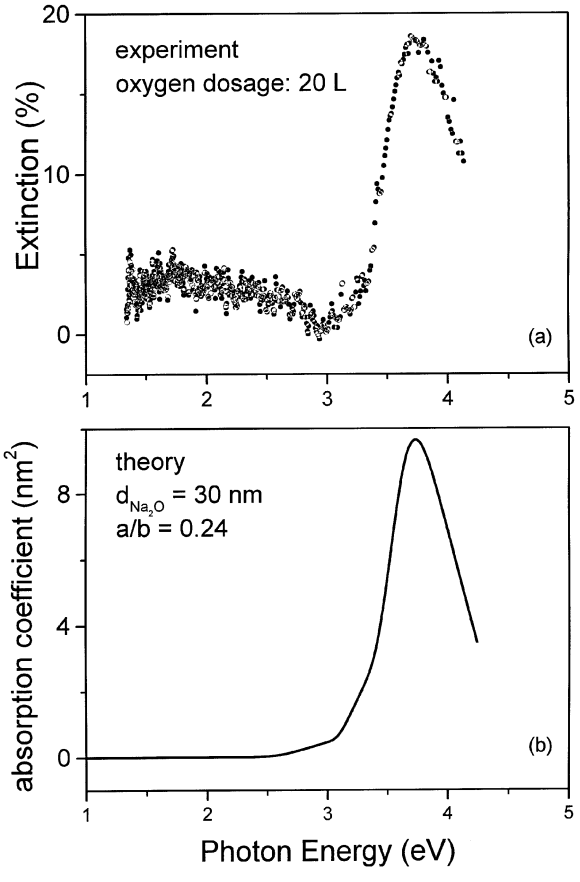

Figure 5 Experimental (a) and theoretical (b) optical spectra of Na_2O. The optical constants of Na_2O used in the calculations were taken from Ref. 13.

Na_2O shell of 1 nm thickness (not shown in Fig. 4) indicates that the modified chemical environment is also of minor importance. In fact, the calculations give a plasmon peak shift of the modes to higher energy. This is the result of the difference between the dielectric function of the Na_2O shell and the surrounding medium ε_m without adsorbate. This displacement is in contrast to the experimentally observed red shift and we therefore interpret the measured peak shift as charge transfer from the sodium clusters to the adsorbed oxygen atoms. It overcompensates an eventually existing blue shift brought about by the modified environment.

Exposures between 1.5 and 4 L give rise to an even larger diplacement of the (1,1) mode as a function of oxygen exposure. In addition to charge transfer, a second effect clearly contributes to the measured red shift. In this exposure regime the energetic difference between the (1,0) and (1,1) modes also starts to increase. Our calculations of the peak position as a function of increasing Na_2O shell thickness reproduce the growing energetic separation between the plasmon modes, (see Fig. 4). Therefore, we interpret the additional red shift of the (1,1) mode accomplished by the increasing energetic difference between both modes as being due to a decrease in the axial ratio of the (metallic) Na cluster brought about by the growing Na_2O overlayer thickness.

For exposures above 4 L the amplitude of the plasmon resonance drops off and the width increases drastically. This can be understood as follows. As already mentioned above, the adsorbed oxygen does not simply form an overlayer on the metal particles. Rather, it penetrates into the cluster, thus gradually transforming the metal into Na_2O. This interpretation is corroborated by two arguments. First, the disappearance of the Na plasma resonances goes hand in hand with the growth of a new distinct resonance which is located at 3.8 eV and is characteristic of particles consisting of the compound formed, Na_2O. Secondly, the dielectric constant of Na_2O being known, theoretical spectra of Na_2O clusters can be computed and also show a peak at 3.8 eV (Fig. 5).

In summary, the following model for the reaction of oxygen with Na clusters is proposed. In the low-exposure regime up to 1–2 L, chemisorption occurs whereby the oxidation reaction is limited to the very surface of the cluster. As a consequence, a slight decrease in the amplitude and a small shift in the energetic position of the plasmon peak, but a constant width of the resonance, are observed. In the regime between 2 and 4 L, oxygen starts to diffuse into the cluster. The thickness of the Na_2O shell gradually increases. A transformation of the Na cluster into Na_2O begins. In the high-exposure regime this reaction continues; the sodium is gradually oxidized. As a result, the plasmon resonance originating from Na disappears. At the same time, a resonance characteristic of Na_2O emerges.

As already mentioned above, N_2O induces similar changes in the optical spectra, the main difference being that the observed modifications occur at higher gas exposure compared with oxygen. Molecular beam experiments have shown that N_2O dissociates into nitrogen and oxygen if the molecules are adsorbed on Na clusters,[13] a reaction also observed, for example, on single-crystal surfaces of transition metals. We interpret the modifications of the optical spectra studied here also by dissociation of N_2O into N_2 and O, the

oxygen atoms being chemisorbed on the Na cluster surface. As a consequence, the spectra exhibit similar modifications to those already discussed for oxygen. The higher exposures needed to induce comparable changes result from the smaller dissociation cross-section of N_2O compared with O_2.[13] On the other hand, the nitrogen molecules split off from the N_2O do not remain on the cluster surface. This is confirmed by experiments in which the Na clusters were exposed to N_2 and in which no changes of the optical spectra were found (Figs 2 and 3).

A very interesting observation is the decrease of the energetic separation upon exposure of the Na particles to CO_2; see Figs 1 and 2. As mentioned above, this clearly indicates a change in the shape of the Na clusters, i.e. the particles more and more resemble spheres. Since the amplitude and width of the plasmon resonances remain unchanged, noticeable charge transfer and formation of a compound layer do not seem to occur. Therefore, the observed shape change is probably brought about by a variation in the surface tension of the metal particles. It is known that adsorption of molecules can induce considerable strain and tension in thin metal films and therefore modify their morphology.[19,20] In the case of metal particles this obviously leads to a change in the axial ratio of the oblate clusters.

Molecular hydrogen does not induce any measurable changes in the optical spectra. It is very likely that these molecules are not adsorbed on the particle surface.

5 CONCLUSIONS

In conclusion, the present results show that optical spectroscopy can be effectively used for the detection and characterization of adsorption reactions on supported metal clusters. Upon exposure to molecules the optical spectra change in a variety of ways depending on the nature of the reaction. The measurements do not only provide submonolayer sensitivity but also allow one to distinguish between physical condensation and chemisorption, i.e. the strength of the chemical bond can be determined. Even diffusion of atoms into the interior of the clusters and subsequent transformation of the clusters into Na_2O can be detected. Finally, to the best of our knowledge shape changes brought about either by the formation of a compound layer with increasing thickness or by change in surface tension have been observed for the first time.

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