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Electron-energy-loss studies of physisorbed O_2 and N_2 on Ag and Cu surfaces

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High-resolution electron-energy-loss spectroscopy is used to study the adsorption of O_2 and N_2 on Ag and Cu surfaces at about 20 K. We utilize resonance-electron scattering to observe vibrational overtones and low-lying electronically excited states of these adsorbed species. From the overtones we can determine the anharmonicity and dissociation energy for adsorbed O_2. Values of -1.6 ± 0.2 meV and 5.8 ± 0.5 eV, respectively, are found which are close to the free-molecule values of -1.49 meV and 6.44 eV. A similar analysis for N_2 is less certain due to possible multiple scattering. However, in both cases the data indicate weakly perturbed, i.e., physisorbed species. In the case of physisorbed N_2, we observe a more rapid decay of the overtone intensity with increasing vibrational quantum number than in the gas-phase molecule and associate this with a reduced lifetime of the temporary negative-ion state formed during the resonant-electron scattering process. The $^1\Delta_g$ and $^1\Sigma_g^+$ electronically excited states of O_2 and their vibrational progressions are also observed. The origins (O-O bands) of these excited states are red-shifted by only ~ 10 and ~ 30 meV, respectively, from their gas-phase energies.

I. INTRODUCTION

The interaction of molecules with surfaces can be generally classified according to the strength and nature of bonding into two categories: chemisorption and physisorption. Chemisorption involves chemical interactions with heats of adsorption usually greater than 5—10 kcal/mole, while physisorption generally involves dispersive interactions (i.e., van der Waals forces) and significantly weaker bonding energies.[1] While considerable knowledge exists regarding chemisorption systems, information regarding physisorption is generally limited as most spectroscopic probes are not sensitive to the small changes involved in physisorption.

It has been proposed that such weakly bound states may momentarily exist prior to molecular chemisorption and/or dissociation, in which case they are referred to as precursor states. Here, we report high-resolution electron-energy-loss spectroscopy (EELS) studies of O_2 and N_2 on Ag and Cu surfaces at low temperatures from which we obtain information about the changes in the molecular interaction potential accompanying physisorption. Previous uv photoemission studies of CO, O_2, and N_2 adsorbed at low temperatures have revealed ionization potentials uniformly (within ~ 0.1 eV) shifted from their gas-phase value and which are interpreted as indicating physical adsorption.[2] This behavior strongly contrasts with the strong relative ionization potential shifts observed in chemisorption systems. However, the photoemission levels of even physisorption systems are relatively broad (~ 1 eV) and possible final-state effects associated with the ion state may obscure level shifts needed to understand the details of physisorption. Electron-energy-loss spectroscopy, on the other hand, probes the ground-state vibrational excitations of adsorbed species and can detect with significantly higher resolution subtle changes in vibrational properties. While this technique has been widely applied to chemisorption systems, our EELS studies are the first to examine weakly bound physisorption systems. We observe small changes in the fundamental vibrations of these physisorbed species as compared with the free molecule and also probe the higher vibrational overtones to obtain information regarding the interatomic interaction potential. We find that since these are weakly perturbed systems we can utilize resonance electron scattering (i.e., scattering proceeding via the intermediate formation of temporary negative ions), to observe strong losses due to vibrational overtones and low-lying electronically excited states of the adsorbates. In this paper we analyze our results in an effort to understand how physisorption modifies the adsorbed molecule. Previous publications have dealt with our identification of resonance scattering for such systems,[3] and the observation of rotational transitions[4] of physisorbed H_2 and are not discussed here.

II. EXPERIMENTAL PROCEDURES

These experiments were performed in an ion- and sublimation-pumped UHV chamber which contained a cryogenic sample holder, an ion-sputter gun, Ag and Cu evaporation sources, and an energy-loss spectrometer. The base pressure of our chamber was 6×10^{-11} Torr. The sample holder consisted of a copper block braised onto a stainless steel tube into which an Airco cryotip was placed. The cold He gas from the cryotip directly cooled the thermally unshielded copper block. Temperatures of 20 K were measured by a carbon resistance thermometer embedded in the copper block. (However, our ability to condense and maintain multilayers of molecular hydrogen at pressure of 2×10^{-10} Torr suggests that lower temperatures were actually achieved.) The copper block was fixed and could not be rotated. High-purity ($>99.9\%$) Ag or Cu was evaporated from a Ta boat source onto the cooled copper block.

Electron-energy-loss spectroscopy was performed using a hemispherical deflection analyzer at a pass energy of ~ 0.5 eV. The monochromator and analyzer were mounted at a fixed scattering angle of 90°. The copper block was oriented $\sim 3°$ from conditions for specular scattering. Both our use of polycrystalline samples and the fixed position of the copper block prohibited achieving optimal resolution. Typical resolution used here was 10—15 meV full width at half maximum (FWHM). The loss energies were determined by directly measuring (on a chart recorder) the acceleration potential applied to the analyzer relative to the monochrometer. Here, elastic scattering corresponds to an applied potential of zero. The accuracy of such loss energy measurements is about ± 1.0 meV. Since our beam profile is symmetric we define peak positions from the center of each loss peak profile.

Nitrogen or oxygen were adsorbed by direct exposure to the films for prescribed dosages. All exposures are cited in Langmuir ($1\ \mathrm{L}=10^{-6}$ Torr sec) and are corrected by the appropriate gauge correction factors. Although we cannot calibrate surface coverages, we can delineate the monolayer regime from multilayer adsorption by either of two means, i.e., by the difference in resonance energies between monolayers and multiple layers or from changes in the observed loss features above certain exposures.[3,4] The exposure values found to produce monolayers are consistent with near-unity sticking probabilities. Surface contamination associated with residual gases was monitored by the EELS spectrum.

III. RESULTS

The EELS spectrum of 0.8-L oxygen adsorbed on an Ag film at 20 K is shown in Fig. 1. The energy of the incoming electron beam is 6.5 eV, close to the resonance maximum.[3] The loss due to excitation of the fundamental molecular vibration ($v=0\rightarrow v=1$) occurs around 192 meV and is close to the gas-phase value of 196 meV.[5] Several losses with decreasing intensities are observed at higher loss energies and by comparison with gas-phase spectra[6] are assigned to vibrational overtones of the $^3\Sigma_g^-$ ground state. In addition, the $^1\Delta_g$ and $^1\Sigma_g^+$ electronically excited states and their vibrational manifolds are also observed.

In Fig. 2 we show EELS spectra of N_2 adsorbed on polycrystalline Ag and Cu films. Spectra *A* and *B* were recorded after exposing 1.2 and 10 L of N_2 gas to the cold surface corresponding to monolayer and multilayer condensed N_2, respectively. Both spectra show energy losses due to excitation of the fundamental stretching frequency at 290 meV and several overtones of molecular nitrogen. The observation of these higher overtone states is possible, as in the case of O_2, because the incident electron energies are close to the resonance maxima found for the inelastic cross section of nitrogen in monolayer and multilayers.[3] The resonance maxima for the fundamental ($v=0\rightarrow v=1$) excitations occur at 1.5 eV for monolayers and at 2.0 eV for condensed multilayers.[3] The resonance maxima for the observable overtones do not significantly differ in the monolayer regime. Curve *C* shows a spectrum taken with higher beam energy (2.7 eV), which is off the peak

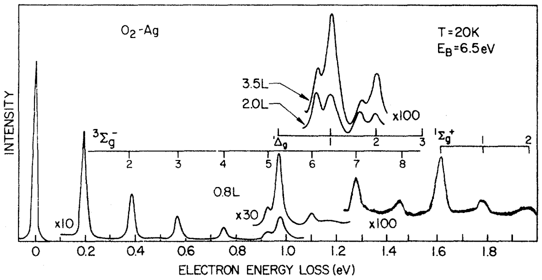

FIG. 1. EELS spectra of oxygen adsorbed on a polycrystalline Ag surface at about 20 K. The energy of the incident electron beam is 6.5 eV. Overtones of the $^3\Sigma_g^-$ ground state up to $v=8$ and the $^1\Delta_g$ and $^1\Sigma_g^+$ excited states are observed. The coverage of 0.8 L corresponds to about one monolayer. At higher coverages (2.0- and 3.5-L exposures) the relative intensities of the ground-state overtones and the $^1\Delta_g$ vibronic bands change (inset).

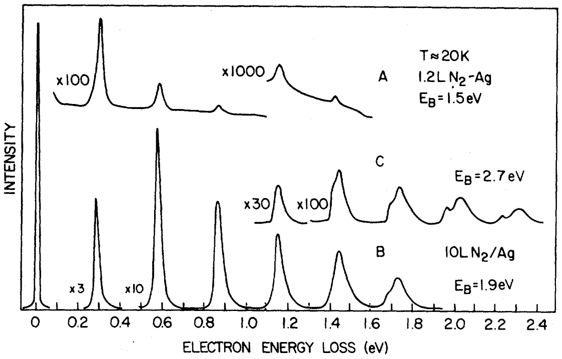

FIG. 2. EELS spectra of nitrogen adsorbed on a polycrystalline Ag surface at about 20 K. The coverage in curve *A* (1.2 L) corresponds to about one monolayer, the energy of the incident electron beam is 1.5 eV. Curves *B* and *C* are spectra of multilayer condensed nitrogen (10 L). The beam energies are 1.90 eV (*B*) and 2.70 eV (*C*).

of the resonance, enabling the observation of even higher overtones. The intensities are now lower but still high enough to observe several features. We observe that the higher overtones are split into a narrow low-energy peak and a broader loss at higher energies which are discussed later.

IV. DISCUSSION

The discussion is divided into three sections dealing with the following: (IV A), the determination of molecular vibrational constants of the adsorbed molecules, (IV B), the change induced by physisorption in the lifetime of the temporary negative ion state of N_2, and (IV C), the interaction of the electronic states of physisorbed O_2 with the metal surface.

A. Molecular vibrational constants

The vibrational overtone energies of a molecule can be expressed by the Birge-Sponer relationship[6] $\Delta E(0\rightarrow v)=Av+Bv^2$. Here, A is the vibrational frequency in the ground state, B the anharmonicity of the intramolecular potential, and v is the vibrational quantum number. Therefore, a plot of $\Delta E(0\rightarrow v)/v$ vs v gives A and B. The dissociation energy D_e of a Morse oscillator can then be obtained as $D_e=-(A-B)^2/4B$. This spectroscopic approach tends to give somewhat higher values for D_e than those measured thermochemically.[6] For diatomic molecules this difference in D_e is usually not more than 30%.[6]

A plot of $\Delta E/v$ vs v for a monolayer of oxygen on Ag films is given in Fig. 3. For comparison a corresponding plot of gaseous O_2 is also given. From these plots the following anharmonicities and dissociation energies are obtained: $B(O_2/Ag)=-1.6\pm0.2$ meV and $D_e(O_2/Ag)=5.8\pm0.5$ eV. The corresponding gas-phase data are $B=-1.49$ meV and $D_e=6.44$ eV.

Our data suggest that O_2 adsorbed on Ag at low temperatures (20 K) has a somewhat (~10%) reduced dissociation energy and higher anharmonicity than the free molecule. These observations can be explained by a charge transfer process from the metal to the antibonding $1\pi_g^*$ orbital of O_2. In neutral O_2 two electrons occupy the $1\pi_g^*$ orbital resulting in a bond order ρ of 2. Correlations between the dissociation energy and bond order have been proposed by many authors. Recently such a correlation for diatomic molecules has been given by Ibach and Mills.[7] These authors note that D_e and ρ are related by the following relation: $D_e=c\rho^{0.75}$, where c is a numerical constant. Using the D_e of adsorbed O_2 obtained from the Birge-Sponer plot (Fig. 3) and the gas-phase value of 6.44 eV we find that adsorption results in a decrease of the bond order by

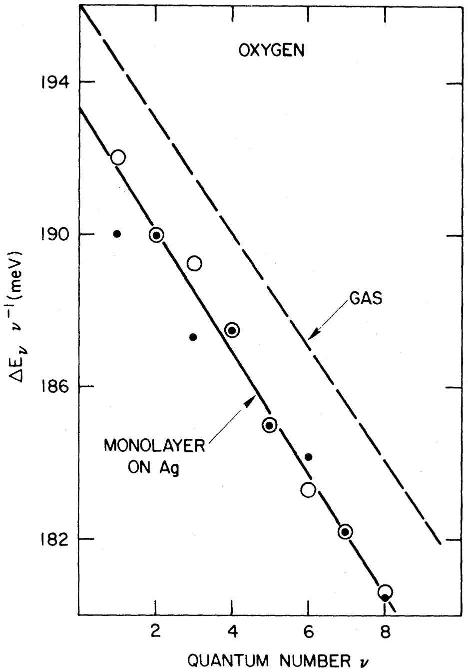

FIG. 3. Birge-Sponer plot for oxygen monolayers adsorbed on a polycrystalline Ag surface. The data are from two different runs. The gas-phase values are taken from Ref. 5.

$\Delta\rho = -0.25$ (i.e., an increased occupation of the $1\pi_g^*$ orbital). Since such a charge transfer requires the overlap between the π^* orbital of O_2 and the metal electron density, an adsorption geometry where the molecular axis is parallel to the surface is suggested. As a result of the weakening of the molecular bond by the charge transfer process a larger bond length is expected for adsorbed O_2.

A simple correlation between D_e and the bond length can be achieved using Badger's rule: $D_e = c'(R_e - d_{i,j})^{-3/2}$, where R_e is the equilibrium bond length, $d_{i,j}$ is a parameter, and c' a numerical factor. The indices i,j in $d_{i,j}$ refer to the row of the Periodic Table of the elements which form the molecular bond. For O_2, $d_{ij} = 0.68$.[7]

Using our D_e value and the $R_e = 1.2072$ Å of free O_2 (Ref. 5) we find that the O—O bond length on the Ag surface has $R_e = 1.24$ Å, i.e., it expands by ~0.03 Å. If we utilize only the change in the fundamental frequency and perform a linear interpolation between the properties of O_2 and O_2^- (Ref. 5) we arrive at a lower bond-order change $\delta\rho = -0.13$ and $\Delta R_e = 0.01$ Å. Studies of O_2 molecular adsorption on an Ag (110) surface at ~100 K have provided evidence of another form of adsorbed O_2 with an even stronger transfer. The bond-order change deduced in that experiment was $\Delta\rho = -0.85$, i.e., ~1.7 electrons are transferred from the metal to oxygen.[8] The state of molecularly adsorbed oxygen which we observe at 20 K may be considered as a precursor state to this more strongly adsorbed state. An analogous behavior, where charge transfer occurs at low temperatures followed by strong charge transfer at higher temperatures has been proposed, on the basis of photoemission studies, for O_2 on a gallium surface.[9] In contrast to O_2 monolayer results, we find that for O_2 multilayers on Ag the energies of the fundamental and overtone vibrations are essentially identical with the energies of the free O_2.

Birge-Sponer plots for nitrogen molecules adsorbed in the first monolayer on Ag and Cu films are shown in Fig. 4. For N_2 on Cu and Ag films the relative energies are close to those of gaseous molecules. However, the more limited number of observable N_2 overtones (as compared to O_2) and possible contributions from multiple scattering to the observed loss features (see discussion below) prohibits us from obtaining accurate molecular constants. Despite these uncertainties it is clear that the interaction of N_2 with the surface is weak: The N_2 is physisorbed.

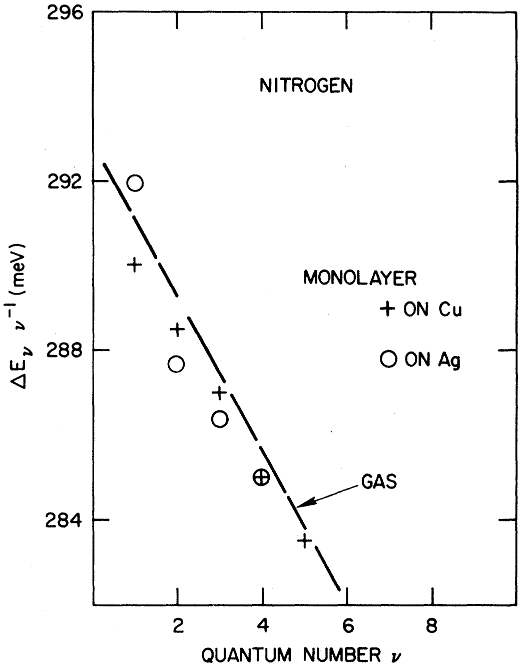

FIG. 4. Birge-Sponer plot for nitrogen monolayers adsorbed on polycrystalline Ag and Cu surfaces. The gas-phase values are taken from Ref. 5.

For condensed nitrogen [Figs. 1(b) and 1(c)] a splitting of the higher overtones can be observed. This splitting has also been reported in a recent EELS study of solid N_2.[10] In that study the broader higher energy peaks were interpreted as phonon sidebands of the narrower overtone peak at lower loss energy. However, because the intermolecular coupling among the N_2 molecules is weak, phonon sidebands may not be the cause of the broad and intense bands seen. We prefer to interpret these broad peaks as due to multiple scattering losses. This explanation is supported by the following observations. First, the broader peaks appear at approximately harmonic intervals of the fundamental frequency. Their slight shift to lower loss energies can be accounted for by the simultaneous occurrence of multiple scattering involving combinations of overtones and the fundamental loss. Further evidence for multiple scattering arises from the linewidths. After deconvoluting the sharp and broad peaks we find that the full width at half maximum of the broad peaks increases approximately linearly with the order of the multiple-scattering loss. Such broadening due to self-folding of the linewidth of the fundamental loss is expected, and is observed in other multiple-loss processes.[11]

The ability to observe multiple-scattering features in any system depends on the ratio of the elastic to the $v=0\rightarrow v=1$ inelastic scattering strength. For N_2 we observe strong inelastic scattering via the resonance scattering mechanism. For O_2 the corresponding inelastic scattering cross section is a factor of 10 smaller which explains why multiple scattering is not as readily observed as for N_2. The significant intensity of the multiple-scattering peaks relative to the intensity of the overtones has previously been used to argue against assigning these broad features to multiple scattering.[10] However, several conditions can occur which increase the relative intensity of higher multiple-scattering peaks. First, although the intensity of each multiple-scattering event n decreases geometrically as $(\sigma_{\mathrm{in}}/\sigma_{\mathrm{el}})^n$, where σ_{in} and σ_{el} are the $v=0\rightarrow v=1$ inelastic and elastic scattering cross sections, respectively, the number of possible scattering centers increases very rapidly with the number of multiple-scattering events. The details of this increased scattering depend on the differential scattering cross section, the packing orientation and density of the scatterers—factors which we cannot currently determine. Another factor which tends to increase the intensity of the multiple losses relative to the intensity of the higher overtones comes into play when we utilize higher beam energies to probe the higher overtones. Namely, for $E_B=2.7$ eV, which is above the resonance maximum at 2 eV,[3] the overtones are suppressed more than the multiple losses (Fig. 2). This arises because the multiply scattered electrons will obtain an energy closer to the resonance maximum after a few (~3) scattering events, while the direct overtone excitations are "off"-resonance. Thus, although we cannot theoretically predict the intensity of our higher-order multiple-scattering features, their high intensity is not unreasonable.

B. Lifetime of the negative ion state N_2^-

In Fig. 5 the intensities (peak heights) of the observed overtones, normalized to the intensity of the fundamental loss, are plotted as a function of quantum number v. For comparison the intensities (peak areas) of the overtones of molecules in the gas phase are given.[12] In the physisorbed state the intensities decrease faster with increasing v than in the gas phase. We find an exponential decrease of the overtone intensity for the monolayer which differs from the dependence in the gas phase.

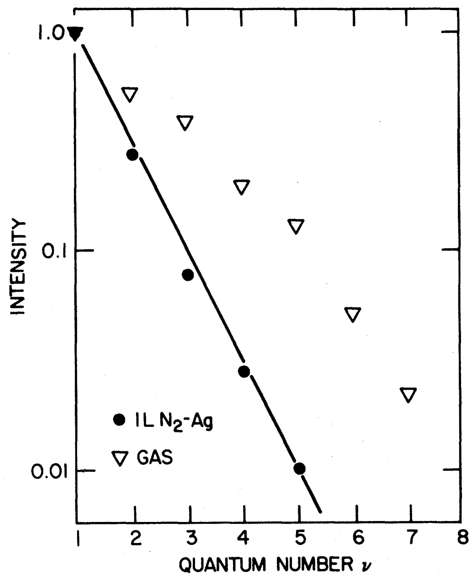

FIG. 5. Normalized intensity of the observed overtones of a monolayer N_2 on Ag compared to the corresponding intensities for gaseous N_2 (Ref. 12).

In gas-phase resonance scattering from N_2 the cross-section profile shows oscillations characteristic of the "boomerang" limit[13] (i.e., the autoionization lifetime of the temporary negative ion N_2^- is $\sim 10^{-14}$ sec). From the absence of such oscillations in the adsorbed phase and because of the large observed width of the resonance, we have concluded[3] that the autoionization lifetime of the N_2^- in the adsorbed phase is shorter than 10^{-14} sec. Such short lifetimes are characteristic of the "impulse limit"[14] scattering. In the impulse limit the nuclei do not have sufficient time to rearrange toward the equilibrium geometry of the negative ion state and this results in a reduced Franck-Condon overlap of the ion state and the high-amplitude overtones of the neutral. These changes in the Franck-Condon factors between the free and adsorbed molecule explain the faster decrease of the overtone intensity with increasing v in the adsorbed phase and provides further evidence for a reduced negative ion lifetime for physisorbed N_2.

We believe that this reduction of the autoionization lifetime is the combined result of the screening by the metal of the long-range polarization forces between the incoming electron and the N_2 and the perturbation of the corresponding centrifugal forces. As a result, the magnitude of the potential barrier trapping the electron is lower and its permeability higher in the adsorbed phase.

C. Electronic excitations

In the spectrum of oxygen on Ag we also observe electronic excitations at 970 and 1620 meV. They are assigned as the $^1\Delta_g$ and $^1\Sigma_g^+$ excited states of the oxygen molecule, respectively, by their close correspondence to the values of the free molecule (979 and 1646 meV, respectively).[4] The vibrational excitations of these states are also observed and their energies are close to those of the free molecule. The intensities of these excitations depend on the O_2 coverage. This is shown on an inset in Fig. 1 for the $v=5$ and 6 overtones of $^3\Sigma_g^-$ ground state in comparison with the closely lying $v=1$ and 2 vibronic bands of the $^1\Delta_g$ state. The intensities of the excited-state vibronic bands increase until about 4-L exposure of oxygen. Above that exposure the intensity ratios remain constant. This relative change in cross section provides, we believe, a way to delineate between mono- and multilayers of O_2.

Optical transitions from the $O_2\ \tilde{X}\ ^3\Sigma_g^-$ ground state to the $\tilde{a}\ ^1\Delta_g$ and $\tilde{b}\ ^1\Sigma_g^+$ excited states are highly forbidden in the free molecule. We can observe these transitions even for submonolayer coverages through the decay of negative ion states which lie at higher energies. At 6-eV electron beam energy the $^2\Pi_u\ O_2^-$ state is formed in the gas phase[15] which, upon autoionization, gives the $^1\Delta_g$ state. An analogous mechanism may operate in the adsorbed phase. The detailed excitation mechanism of the $\tilde{b}\ ^1\Sigma_g^+$ state is uncertain even in the gas phase.[16] It is particularly interesting that the excitation energies are about the same in both the gas and physisorbed phases. This fact implies that the ground and excited states of O_2 interact with the surface with about the same strength. We have already established from the study of the vibrational overtones that the ground-state potential surface is weakly perturbed by the surface; the same therefore should be true for the two excited states. Classical theory[17] explains shifts in molecular electronic transitions induced by a metal surface in terms of transition dipole—image dipole interactions. The expected spectral shift is proportional to the oscillator strength of the respective transition. The very small red shifts observed upon physisorption are explainable within the image-field theory description by assuming that the corresponding transition remains dipole forbidden as in the gas phase.[18]

The dependence of the relative intensity of the ground-state ($^3\Sigma_g^-$) overtones and the excited-state ($^1\Delta_g$) vibronic bands on coverage (inset Fig. 4) can be explained by at least two mechanisms. In one case both ground-state overtones and excited states are produced from a common ionic state. The $^2\Pi_u$ valence Feshbach state of O_2^- satisfies both spin and energy requirements to produce the overtones and the excited state. The variation with coverage would then represent a change in the decay branching ratio of $^2\Pi_u$. Another interpretation involves different ionic states. The $^4\Sigma^-$ shape resonance, which is also expected to be energetically accessible at the electron beam energies employed here,[19] can decay to give the overtones of the $^3\Sigma_g^-$ ground state but cannot decay into singlet, i.e., $^1\Delta_g$, products (due to spin conversation rules). In such a case the observed variation can be explained by different energy shifts of the $^2\Pi_u$ and $^4\Sigma^-$ resonances as a function of coverage.

V. SUMMARY AND CONCLUSION

We have used resonant electron scattering to evaluate the properties of physisorbed N_2 and O_2 molecules on Ag and Cu films. From our study of the vibrational constants of these physisorbed molecules, we find the influence of the surface to be weak. Anharmonicities and dissociation energies are comparable to the gas-phase values. In the case of O_2 on Ag the data suggest a weak charge transfer from the metal to the molecule and a somewhat longer (~ 0.03 Å) bond length.

For multilayers of N_2 we find strong multiple scattering and attribute this to the large inelastic cross section at resonance scattering conditions. The inelastic cross section for O_2 is a factor of 10 less than for N_2, which makes multiple scattering less important for O_2. Possible contributions of multiple scattering, as in the case of N_2, may prohibit the determination of the molecular constants of some physisorbed molecules unless higher resolution is used. We also find that, for nitrogen, the autoionization lifetime of the intermediate negative ion state formed during the resonance scattering process is reduced by interaction with the surface to a value lower than 10^{-14} sec. For oxygen we observe low-lying optically forbidden electronic transitions and their vibrational progressions even at submonolayer coverages. These excited states are also weakly perturbed.

ACKNOWLEDGMENT

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