Anharmonicity of the $\text{O}_2$–Ag(001) chemisorption potential

F. Buatier de Mongeot, A. Cupolillo, U. Valbusa, and M. Rocca

CFSBT-CNR and INFM, Dipartimento di Fisica dell’Università di Genova, Via Dodecaneso, 33-16146 Genova, Italy

(Received 18 June 1996; accepted 29 January 1997)

The coverage dependence of the vibrational modes of $\text{O}_2$ chemisorbed on Ag(001) was studied by electron energy loss spectroscopy. We observe the dipole active modes associated to the intramolecular stretch and to the molecule–surface vibrations. Moreover two further features are present in the EEL spectra, due to the anharmonicity of the molecular potential: the combination-band of the stretching and of the molecule–surface vibration, and the first overtone of the O–O stretching mode. From the EELS intensity of the O–O stretching mode versus coverage the dynamical charge transfer $e^+ = 0.61 \pm 0.02$ e$^-$ is determined which corresponds to a dynamical dipole moment $\mu = 0.16 \pm 0.01$ D. The $\text{O}_2$–Ag vibrational frequency is found to decrease with coverage, suggesting that a weakening of the molecule–surface bond takes place. This observation is confirmed by thermal desorption spectroscopy. The anharmonicity parameter $x_e$ of the O–O potential increases significantly upon chemisorption, in analogy to $\text{O}_2$–Ag(110) and $\text{O}_2$–Pt(111). The intensity of the overtone peak is analyzed within the Morse approximation, allowing us to discriminate the contributions arising from the mechanical anharmonicity, and from the nonlinearity of the dynamical charge flow. A correlation is observed between the magnitude of $e^+$ and the contribution of the latter term to the overtone intensity. © 1997 American Institute of Physics.

I. INTRODUCTION

The observation of overtones is important in understanding the shape of the potential of gas-phase molecules, and allows an indirect observation of symmetry-forbidden fundamentals as well as an estimate of the energy of suitably decoupled bonds. The observation of the overtones of molecules chemisorbed at surfaces is also important because it gives information on the changes in the intramolecular potential caused by molecule–surface interaction, and allows an indirect observation of symmetry-forbidden fundamentals. Recent studies have shown that in certain circumstances a significant increase of molecular anharmonicity can occur upon chemisorption. Among the main effects of anharmonicity we can recall the red shift of the vibrational frequencies, an additional damping of the modes at higher temperatures, and the appearance of a red shift between the $n$th overtone and the energy loss corresponding to the excitation of $n$ fundamental vibrational quanta on different molecules. The small number of experimental studies reporting the observation of overtones and combination bands has to do with the small cross section for dipolar excitation in electron-energy-loss spectroscopy (EELS) or infrared-reflection-absorption spectroscopy (IRAS), which is nonvanishing for an anharmonic oscillator because of the mechanical anharmonicity and of the nonlinearity of the molecule–surface dynamical charge flow. The importance of the latter contribution can be comparable or greater than the former. A significant enhancement of the cross section for overtone excitation can be observed under impact and resonance scattering conditions, via the excitation of temporary negative-ion states. Under such conditions it was possible to observe transitions to high vibrational levels for several chemisorbed and physisorbed systems.

II. EXPERIMENT

Here we will report on the $\text{O}_2$–Ag(001) system. This is a good candidate for studying such anharmonic effects because (i) the O–O bond is strongly weakened upon chemisorption on Ag (the stretching frequency of the chemisorbed molecule–$\nu_2 \approx 80$ meV—is downshifted with respect to the gas-phase value $\nu_2 = 196$ meV) thus leading to an increase in mechanical anharmonicity. (ii) The $\text{O}_2$ molecule, which has no permanent dipole moment, is known to chemisorb with its axis parallel to the Ag surface; under these conditions the dynamical dipole moment is entirely determined by the surface–molecule charge flow. The contribution to the overtone cross section arising from the nonlinearity of the dynamical charge transfer is therefore enhanced. This system is in a way ideal because of the high electron reflectivity, compared for example to Ag(110), so that a good signal to noise ratio is obtained which enables the detection of the weak anharmonic modes.
dosing O$_2$ with the supersonic beam is that for sufficiently high impact energies, the activation barrier for molecular chemisorption ($E \approx 370$ meV) can be easily overcome\(^\text{16}\) (the initial sticking coefficient reads 0.6 at $E_i = 0.8$ eV while at thermal energies it reads $10^{-5}$). In this way high coverages can be obtained with low exposures, thus minimizing the impurity level compared to background dosing experiments. The O$_2$ coverage, which in the following will be expressed in monolayers (1 ML = 1.2 × 10\(^{15}\) cm\(^{-2}\)), is determined from the TDS peak area (for Θ > 0.1 ML), and by the KW uptake (for coverages below 0.1 ML). The desorption flux is calibrated against the molecular beam flux determined with a spinning rotor gauge. The EELS spectra were recorded inelastically, for an angle of incidence $\theta_i = 63^\circ$ and at an impact energy $E_i = 3.4$ eV, corresponding to optimal elastic reflectivity conditions. The energy resolution of the electron beam was set at 5–6 meV FWHM, in order to improve the count rate of the weak overtone features (count rates up to 10\(^7\) cps were achieved in the specular beam). The crystal was cooled down to $T = 100$ K fluxing liquid N\(_2\) through a cryostat.

### III. EELS SPECTRA

At a surface temperature of 100 K oxygen adsorption is nondissociative, and saturation coverages up to 0.47 ML can be achieved when exposing the surface to an O$_2$ molecular beam of $E_i = 0.8$ eV.\(^\text{16}\) In Fig. 1 we compare the EELS spectra recorded at the same coverage ($\Theta = 0.3$ ML) of the two oxygen isotopes, $^{16}$O$_2$ and $^{18}$O$_2$. As expected, the frequency of the vibrational modes of chemisorbed $^{18}$O$_2$ [Fig. 1(a)] is reduced by the factor $(m_{16}/m_{18})^{1/2}$ with respect to the light oxygen isotope [Fig. 1(b)]. Two main losses are observable, respectively, around 30 meV and 80 meV. The loss around 30 meV is due to the molecule–surface vibration ($v_0^{01}$), while the main loss around 80 meV corresponds to the fundamental of the O–O stretching mode ($v_1^{01}$). EELS spectra recorded at higher resolution\(^\text{21}\) show that two modes contribute to this peak; one centered around 79 meV and one around 84 meV. This observation is in agreement with the theoretical calculations of Mehandru and Anderson\(^\text{14}\) which suggest that more than one adsorption site can be populated by O$_2$ on Ag(001); fourfold hollow, short-bridge and long-bridge. In all cases the molecular axis is parallel to the surface. The two former sites have nearly equivalent binding energies, but different Mulliken populations (and hence different vibrational frequencies), while the contrary is true for the latter two sites. For coverages below 0.1 ML the two sites are equally populated, while for higher coverages the 84 meV mode dominates. In the following sections we will analyze the molecular anharmonicity at a fixed coverage ($\Theta = 0.22$ ML) where the 84 meV mode is preferentially populated.

In the spectra two further weak features are observable at higher frequency. The peak centered around 160 meV has two contributions; from the excitation of double losses (2 × $v_2^{02}$) and from the overtone ($v_0^{02}$) of the O–O stretching mode. The feature around 114 meV could also originate from a double loss corresponding to the excitation of modes $v_1^{01}$ and $v_2^{01}$ on different molecules, or from a combination-band, in which case both modes are excited in a single scattering event on the same molecule. All the observed modes are excited by Coulomb scattering as demonstrated by the $1/E_e$ dependence of the loss intensities, where $E_e$ is the electron impact energy (Fig. 2) and by the out-of-specular intensity drop of all the loss peaks.

For a perfect harmonic oscillator, (0–2) transitions are dipole forbidden, and the normal modes corresponding to the O–O stretch and to the molecule–surface vibration would be decoupled. The observation of combination bands and over-
tones under dipole scattering conditions therefore indicates that the anharmonic terms of the molecular potential are important.

IV. ANALYSIS OF THE EELS SPECTRA

The frequency assignment of the loss peaks in Fig. 1 is obtained by fitting a Gaussian to the upper half of the peak after subtraction of an appropriate background. The tails of the peak are not considered in the fit as they are slightly asymmetric. The position of the maximum of the loss peak is then determined with an accuracy of $\pm 0.15$ meV. The intensity of the loss peaks is defined as the peak area and is normalized to the area of the specular peak. The intensity of the modes at different energy is corrected to take into account the dependence of the width of the dipole lobe on energy loss.\(^6\) The relative error on the intensity is of the order of 10%. In order to evaluate the contribution of the double losses of the O–O stretching mode $I(2 \nu_0^{01})$ to the intensity of the 160 meV peak, we calculated their intensity $\sim 10\%$. In order to evaluate the contribution of the overtone $I(\nu_2^{01})$ contribution $I(2 \nu_2^{01})$ to the measured intensity was fitted with the following expression:\(^6\)

$$I(2 \nu_2^{01}) = \frac{I(\nu_0^{01})/I_0}{[1 + (w/2)^2/2]}$$

where $w$ is the FWHM of the single loss peak. The contribution of the overtone $[I(\nu_2^{02})/I_0]$ is then obtained [see Fig. 3(b)] by subtracting the double loss contribution [Fig. 3(a)] from the experimental intensity [Fig. 3(c)]. As one can see, most of the measured intensity is due to the overtone $\nu_2^{02}$. The frequency of the overtone peak is then determined with a Gaussian fit.

V. LOSS INTENSITIES VS COVERAGE

In Fig. 4(a) the intensity of the $\nu_0^{01}$ mode (O$_2$ stretch) is reported vs oxygen coverage. We consider here the integrated intensity of the 79 meV and 84 meV modes, which are not separately resolved in the present experiment. The intensity is proportional to the coverage up to $\Theta \sim 0.25$ ML, whereafter a temporary saturation occurs. At this coverage the filling of a $(2 \times 2)$ overstructure is expected to occur, as also confirmed by an analysis of the coverage dependence of the sticking coefficient and of the TDS spectra.\(^{16}\) Unfortunately no LEED overstructures can be observed, probably because electron induced desorption and dissociation of O$_2$ are active.\(^{23}\) To directly observe the ordering of the oxygen overlayer a He diffraction experiment would therefore be needed. For $\Theta > 0.35$ ML the loss intensity recovers. As we will see, a similar behavior is common to the other vibrational modes of O$_2$–Ag(001) and was also observed for $\nu_2^{01}$ on Ag(110).\(^{24}\) It is not a typical trend of a system where depolarization due to dipole–dipole interactions occurs, as for example CO–Ru(0001) (Refs. 25, 26), where a continuous damping of the intensity occurs up to the highest coverages; it rather seems that the ordering of the adlayer increases the damping, because for coverages above 0.25 ML where adsorption occurs again in a disordered way, the intensity recovers.

To evaluate the dynamical charge transfer $e^*$ which is associated to the stretching mode of the chemisorbed oxygen molecules, and is responsible for the excitation of the dipolar losses, the measured intensity was fitted with the following expression:\(^5\)
\[
\frac{I_n}{I_0} = \frac{\pi \hbar}{2a_0 E_c \cos \theta_i} \left(1 - 2 \theta_c\right)^{1/2} F_S(\theta_c) \\
\times \frac{4 e^* \alpha^2}{M_\omega \left(1 + \alpha_c \Sigma\right)^2},
\]

where \(a_0\) is the Bohr radius, \(E_c\) the electron impact energy, \(\theta_i\) the impact angle, \(\omega_S\) the loss frequency, \(\theta_c = h \omega_c / 2E_c\) is the angular width of the lobe of dipolarly scattered electrons, \(F_S(\theta_c)\) is an instrumental function depending on the acceptance angle of the spectrometer \(\theta_{1/2}\), \(M_r\) the reduced mass of the oscillator, \(n_0\) the surface density of Ag(001), and \(\Sigma\) is the fractional adsorbate coverage. \(\Sigma\) is the dipole sum which takes into account dipole–dipole interactions among adsorbates. The dipole sum for a randomly filled layer reads \(\Sigma = C(n_0)^{1/2} \Theta\) where the constant \(C\) depends on the surface geometry and reads 9.0336 for a square lattice. The fit to our data with Eq. (1) was limited to the range \(0 < \Theta < 0.22\) ML, where the intensity depends linearly on coverage, and is plotted in Fig. 4(a) as a continuous line. The best fit parameter is \(e^* = 0.61 \pm 0.02\) e\(^-\). From the \(e^*\) value, we obtain a dynamical dipole moment \(\mu = 0.16 \pm 0.1\) D which is larger than the one found for \(O_2–Ag(110)\), \(\mu = 9.9 \times 10^{-2}\) D (Ref. 17) in spite of the similar vibrational frequency observed on the two surfaces. In the fit with Eq. (1) we assume that the chemisorbed molecules have the same value of \(\alpha_c\) as for gas-phase \(O_2\), i.e., \(1.58\) Å\(^3\).

In Fig. 4(b) the normalized intensity of the \(\nu_{101}\) mode (\(O_2–Ag\) vibration) is plotted vs coverage. Contrary to the behavior of \(I(\nu_{02}^c)\) in this case the intensity does not increase linearly in the low coverage region (in fact the increase is almost quadratic as shown by the fit with a parabolic function). Such a behavior indicates that the dynamical dipole moment associated with the molecule–surface oscillation is increasing with coverage and suggests that a change in the molecule–surface bond takes place. As we will see in the next paragraphs, similar conclusions are drawn from an analysis of the shift of the molecule–surface stretching frequency and from the coverage dependence of the thermal desorption spectra.

In Fig. 5(a) we plot the intensity vs coverage of the overtone \(I(\nu_{02}^c)\) together with the intensity of the double loss \(I(2 \times \nu_{02}^c) = I(\nu_{02}^c)^{1/2}\). As one can see, the contribution of the double-loss to the overall intensity of the 160 meV feature is largest (20%) for coverages above 0.25 ML but accounts for less than 5% in the low coverage range. Further evidence of the fact that we are observing an overtone comes from the linear increase of the measured intensity with \(\Theta\) (in the low coverage regime); for the double-loss on the contrary the intensity would be expected to be proportional to \(\Theta^2\). The same considerations are true for the combination-band of the \(\nu_1–\nu_2\) modes whose dependence on \(\Theta\) is reported in Fig. 5(b). In this case we compare it with the intensity of the double-losses given by \([I(\nu_{01}^c)]/[I(\nu_{02}^c)^{1/2}]\); also in this case the contribution of the double-loss is negligible, about 12% of the measured intensity for coverages above 0.25 ML, and about 1% for low coverages.

VI. NORMAL MODE FREQUENCY VS COVERAGE

The assignment of the high frequency modes to an overtone and a combination band is further supported by the coverage dependence of the various vibrational modes of the chemisorbed oxygen molecule. In Fig. 6(a) we plot the frequency of the O–O stretching mode \(\nu_{02}^c\). As already mentioned, two chemisorption sites are populated by the oxygen molecule, with stretching frequencies of 79 meV and 84 meV, not resolved in the present experiment. For coverages above 0.1 ML the 84 meV mode is preferentially populated, and above 0.22 ML it dominates. Notably in that coverage range there is no evidence of a dipolar shift with \(\Theta\) of the stretch frequency. This is the case also for \(O_2–Ag(110)\). The finding is indicative of the existence of a negative chemical shift counteracting the positive dipolar shift as was reported also for CO chemisorbed on Cu(001), and on the other noble metal surfaces, Ag and Au. On transition metal surfaces on the contrary CO generally shows rather large (5 meV) and positive frequency shifts, which are well described by the dipole–dipole coupling mechanism. In Fig. 6(b) the frequency of the \(O_2–Ag\) vibration, \(\nu_{01}^c\), is reported vs coverage. For this mode a negative shift is observed with increasing coverage. Such shift is opposite to the one expected for dipole–dipole coupling. It could be associated to the existence of multiple adsorption sites characterized by the
stretching modes at 84 and 79 meV, respectively. The component associated to the 84 meV mode would then correspond to the lower O2–Ag(001) frequency and dominate the spectra at large coverage. Otherwise the shift may be related to the fact that the \( n_1^{01} \) frequency is determined by the strength of the molecule–surface bond. The observed behavior would then suggest that a shallowing of the O2–Ag potential is occurring or, in other words, that the desorption energy is decreasing with coverage as a consequence of the lateral repulsions between adsorbed molecules. As we will see in Sec. VII, this conclusion is confirmed by the O2 thermal desorption measurements. A similar correlation with the TDS spectra was recently observed for the stretching mode of CO–Ru\(~0001\)^.26

In Fig. 7(a) the frequency of the overtone \( \nu_2^{02} \) is plotted vs coverage. In this case an almost linear positive shift is observed which extends up to \( \Theta_{sat} \). For a comparison we also plot the expected double-loss frequency \( 2 \times \nu_2^{01} \) which is always higher than the overtone. The disagreement between \( \nu_2^{02} \) and \( 2 \times \nu_2^{01} \) further confirms that we are observing an overtone. Finally in Fig. 7(b) the combination-band frequency is plotted vs \( \Theta \), together with the double-loss frequency \( \nu_1^{01} + \nu_2^{01} \). Due to the opposite and almost equivalent shifts of \( \nu_1^{01} \) and \( \nu_2^{01} \), no significant displacement is observed for the combination band vs \( \Theta \). We note that the frequency of the observed loss is always about 1.5 meV higher than the sum of the single modes. This is again indicative that we are dealing with a combination band and not with a multiple loss. Due to anharmonicity, \( \nu_1 \) and \( \nu_2 \) are coupled,\(^{1,7}\) and the potential describing the molecule changes whenever one of the modes is excited. The larger frequency of the combined mode can be rationalized if we consider that the average position of the molecule is shifted outwards when the first excited state of the O2–Ag potential is occupied. The larger adsorption distance is reflected in a smaller charge transfer from the surface to the antibonding molecular orbitals, and thus to a higher O–O vibrational frequency. For O2–Ag(110) on the contrary the combination band is found at the same frequency of the multiple-loss.\(^{31}\) It is well known that on this surface the O2 molecules are chemisorbed deep into the Ag troughs, with the axis parallel to the [110] azimuth.\(^{32}\) For this adsorption configuration a slight increase of the vertical position of the molecule affects therefore more weakly the charge transfer than for the case of O2–Ag(001).

VII. COMPARISON WITH TDS SPECTRA

Additional information on the strength of the molecule surface bond can be gained from a thermal desorption measurement. In Fig. 8 the TDS spectra are plotted for different initial O2 coverages. In the low coverage regime (0–0.1 ML), where the two chemisorption sites are equally populated, a narrow desorption peak is observed, indicating that the binding energy is equivalent. Therefore according to the calculations of Mehandru and Anderson\(^{14}\) the fourfold-
hollow and short-bridge sites should be populated. For 0.1 < \Theta < 0.22 ML a continuous broadening of the desorption peak towards lower temperatures is observed with \Theta. Such broadening cannot be due to desorption from a different adsorption site as no new EELS losses appear (on the contrary for coverages above 0.1 ML preferential population of the state at 84 meV occurs). For \Theta > 0.22 ML (spectra not shown here) the desorption peak grows again on the high temperature side. Such interesting behavior, discussed in a separate paper, is due to the existence of strong repulsive interactions between the ad-molecules and to the nearly exponential decay of the sticking coefficient with coverage which affects the desorption prefactor. For the purpose of the present discussion, we just remark that for 0 < \Theta < 0.22 ML the leading edge of the desorption peak continuously shifts to lower temperatures, indicating that in this coverage range due to lateral interactions the desorption energy decreases. The same conclusion is reached considering the downward shift of the \nu_{01} mode (weakening of the O_{2}–Ag bond) with increasing \Theta [Fig. 6(b)]. In contrast to this behavior, no broadening of the TDS peak was observed for O_{2}–Ag(110).33

VIII. ANHARMONICITY OF THE O–O BOND

The anharmonicity of the O–O potential can be determined once the levels of the potential are known. Within the Morse approximation, which has the advantage of giving an analytical solution for the eigenvalues of the anharmonic potential, and describes reasonably the molecule in the gas-phase, the potential reads

\[ V(u) = D_{e} [1 - \exp(-au)]^2. \]

The parameters characterizing the potential are: \( D_{e} \), the potential well depth, and \( a \) the reciprocal of the well width. They can be extrapolated from the knowledge of the first two energy levels, corresponding to the transition from the ground state to the first (fundamental) and to the second excited state (overton). The bound states read

\[ \hbar \omega_n = \hbar \omega_e (n + 1/2)[1 - x_e (n + 1/2)], \]

where \( x_e = \hbar \omega_e / 4D_{e} \) is a dimensionless measure of the anharmonicity of the potential (mechanical anharmonicity). For small values of the displacement, \( u \), the potential can be approximated, in the harmonic limit, as \( V(u) \approx a^2 D_{e} u^2 \) and the vibrational frequency reads \( \omega_e = a(2D_{e}/M_e)^{1/2} \).

Thus from the measured transition frequencies we derive

\[ \omega_e = 3 \nu_{01} - \nu_{02}^2, \quad (4) \]

\[ x_e = \frac{\nu_{01} - 1/2 \nu_{02}}{3 \nu_{01} - \nu_{02}^2}. \quad (5) \]

We chose to determine the anharmonicity parameter at a coverage of 0.22 ML where the population of the 84 meV mode dominates over the 79 meV mode. From the spectra at \( \Theta = 0.22 \) ML we get \( \nu_{01} = 83.8 \) meV and \( \nu_{02} = 163.8 \) meV and the anharmonicity parameter results, \( x_e = 2.2 \times 10^{-2} \). The potential well depth \( D_{e} \) (dissociation energy) can then be obtained in terms of the parameters \( x_e \) and \( \omega_e \) and reads

\[ D_{e} = \frac{\omega_e^2}{4x_e \omega_e} \left( \frac{1}{2} \omega_e + \frac{1}{4} \omega_e x_e \right). \quad (6) \]

The evaluation of the dissociation energy, as inferred from Eq. (6) (Birge–Spooner analysis34), is known to give an approximate result, as it relies on a linear extrapolation based only on the knowledge of the two lowest energy levels of the true potential. \( D_{e} \) generally comes out with an overestimation from 10% to 50%, due to the deviations of the potential from the Morse-type shape.35 For O_{2}–Ag(001) at \( \Theta = 0.22 \) ML we find \( D_{e} = 0.95 \) eV.

The results of similar analyses for gas-phase O_{2}, for physisorbed oxygen and for O_{2} chemisorbed on different surfaces are listed in Table I.

It turns out that upon chemisorption on Ag(001) the anharmonicity of the oxygen potential increases by approximately a factor, 2.7 with respect to gas-phase O_{2} and by a
factor 2.7 with respect to O₂ physisorbed on polycrystalline silver. For O₂–Ag(110) and O₂–Pt(111) the increase in anharmonicity upon chemisorption is even higher. The extrapolation of the dissociation energy for O₂–Ag(001) gives a value which is larger than the one measured for O₂–Ag(110). As just discussed, the so determined absolute values of D₀ might be overestimated. The trend of D₀ on the two Ag faces is nevertheless in agreement with the measured dissociation probability [P_{diss}(110) = 0.63–P_{diss}(001) = 4.4 × 10^{-3}]. Thermochemical data for O₂ dissociation on Ag(111) and Ag(110) give D₀ = 0.35 eV (Ref. 37) (it must be however remembered that thermochemical data indicate the lowest possible energy path leading to dissociation, while the Birge–Spooner analysis is an extrapolation from the bottom of the chemisorption well). In agreement with literature we find therefore also for Ag(001) that upon chemisorption the O–O bond is strongly relaxed. The phenomenon is due to charge donation from the metal surface to the antibonding 2π* molecular orbitals,¹⁴ following which a strong weakening of the molecular bond occurs (this is evidenced by the reduction of the fundamental frequency ν₂⁰¹ to about 80 meV upon chemisorption).

IX. ANALYSIS OF THE OVERTONE INTENSITY

As the O₂ stretching mode and its overtone are excited through a dipolar mechanism, it is possible to calculate theoretically the loss probability within a perturbative approach, assuming an anharmonic potential with a Morse shape.⁶,¹⁷ The matrix element which determines the transition probability from the ground state to the first vibrational level is expressed in terms of the dynamical dipole moment of the molecule,

\[ p(u) = \varepsilon^* u (1 - \gamma au + \cdots), \]

where \( \gamma \) takes into account the nonlinearity of the dynamical molecule–surface charge flow during the vibrational stretch of the molecule.⁶,⁷ This parameter may have either sign and is independent of the mechanical anharmonicity \( x_e \). Within this framework, the ratio \( P_2/P_1 \) of the probabilities of exciting the overtone \( \nu_2^{02} \) and the fundamental \( \nu_2^{01} \) reads

\[ \frac{P_2}{P_1} = \frac{x_e}{2} (1 - 2 \gamma)^2, \]

where \( P_2 = I(\nu_2^{02})/I_0 \) and \( P_1 = I(\nu_2^{01})/I_0 \). It is thus possible to distinguish the contributions to the overtone intensity arising from the mechanical anharmonicity \( x_e \) and from the charge flow anharmonicity \( \gamma \). If \( \gamma \) were equal to 0 (no charge flow anharmonicity), the whole observed overtone intensity would be caused by the anharmonicity of the potential \( x_e \).

In Table II we list for a comparison the results of the analysis described above for O₂ chemisorbed on Ag(001), Ag(110), and Pt(111). For O₂–Pt(111) we extrapolated \( P_2/P_1, (1 - 2 \gamma)^2 \), and \( \varepsilon^* \) from the spectra shown in Ref. 36.

It is clear that according to the present model, the observed overtone intensity for O₂–Ag(001) cannot be explained in terms of \( x_e \) alone as this term accounts for 20% of the observed intensity. A significant role of the charge flow anharmonicity \( \gamma \) has therefore to be invoked. This is true also for O₂–Ag(110) but in this case the mechanical anharmonicity alone describes almost half of the observed overtone intensity. That the charge flow anharmonicity contribution to the overtone intensity is more important for (Ag)(001) than for Ag(110) can be understood if we consider that the dynamical charge transfer \( \varepsilon^* \) is, respectively, 0.65 e⁻ and 0.40 e⁻. For O₂–Pt(111) the measured overtone intensity is even smaller than predicted by mechanical anharmonicity alone. This would mean that the charge flow anharmonicity \( \gamma \) counteracts the mechanical anharmonicity contribution. Interestingly for this last system we estimate from the spectra in Ref. 36 a dynamical charge transfer \( \varepsilon^* \) smaller than that observed for O₂–Ag. We find further evidence that under dipolar scattering conditions the overtone intensity scales with \( \varepsilon^* \) if we look at the vibrational spectra of CO molecules chemisorbed end-on at on-top sites of Pt(111).³ In this case the dipolar activity is connected to the modulation of the permanent dipole moment of CO, while the dynamical molecule–surface charge transfer plays a minor role; as a matter of fact no overtones of the CO stretching mode can be detected, but just the double losses. A similar situation is met for CO–Ru(0001).²⁵,²⁶ If potassium is preadsorbed on the Ru surface, the CO molecule is found to chemisorb side-on and a higher overlapping between the molecular orbitals and the surface can take place which promotes charge transfer to the 2 π* antibonding orbitals. In this case a significant decrease of the CO stretching frequency occurs and the overtone becomes observable.⁵

X. CONCLUSIONS

We studied the vibrational spectra of O₂ chemisorbed on Ag(001) by performing EELS measurements in dipolar scattering conditions. Apart from the two main losses due to the O₂–Ag and the O–O stretching modes, two further features can be observed at higher frequency; a combination mode of the O–O and O₂–Ag vibration and the overtone of the O–O stretch corresponding to the (0–2) transition. The assignment is based on the linear coverage dependence of the loss intensity and on the shift from the multiple-loss frequency. From the measured frequency of the first two vibrational transitions of the stretching mode, the anharmonicity parameters for the chemisorbed O₂ molecule are derived. We find that, in analogy to O₂–Ag(110), upon chemisorption a consider-

<table>
<thead>
<tr>
<th></th>
<th>( P_2/P_1 ) (exp)</th>
<th>( x_e/2 )</th>
<th>( (1 - 2 \gamma)^2 )</th>
<th>( \varepsilon^*(e^-) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂–Ag(001)</td>
<td>6.1 × 10⁻²</td>
<td>1.1 × 10⁻²</td>
<td>5.5</td>
<td>0.65</td>
</tr>
<tr>
<td>O₂–Ag(110)*</td>
<td>4.6 × 10⁻²</td>
<td>2.0 × 10⁻²</td>
<td>2.3</td>
<td>0.40</td>
</tr>
<tr>
<td>O₂–Pt(111)*</td>
<td>8.1 × 10⁻³</td>
<td>2.6 × 10⁻²</td>
<td>0.3</td>
<td>0.29</td>
</tr>
</tbody>
</table>

*Reference 2.
•Reference 36.
able increase of anharmonicity occurs compared to physisorbed and to gas-phase O$_2$. Under these conditions the observation of the weak anharmonic losses becomes possible under dipolar scattering conditions. If we analyze the intensity of the overtone feature within the Morse approximation, we find that most of the overtone intensity is due to the nonlinearity of the dynamical charge transfer between molecule and surface. Comparing our results with previous studies on Ag(110) and Pt(111), we find that the charge flow anharmonicity contribution to the observed overtone intensity scales as the dynamical charge transfer $e^*$, which is particularly relevant for O$_2$–Ag(001). This is confirmed by the observation that for CO–Pt(111) and CO–Ru(0001), where adsorption occurs end-on, no overtones are observed. In these last instances, the transition matrix element for dipolar scattering is determined by the modulation of the permanent dipole moment and not by the dynamical molecule–surface charge transfer. All the considerations made until now are obviously valid only for chemisorption systems for which a dipolar loss mechanism dominates.

ACKNOWLEDGMENTS

The authors wish to acknowledge the financial support of the EEC-HCM contracts ERBCHRXT930104 and ERBCHRXT930326.