

## Energy and lifetime of the $\sigma$ resonance of oriented $O_2$ physisorbed on Ag(110)

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We report an experimental and theoretical study of resonance electron scattering by physisorbed  $O_2$ /Ag(110). The cross sections for molecular vibrational excitation, obtained from high-resolution electron-energy-loss spectra, reveal changes in both the energy and the lifetime of the  $\sigma$  shape resonance of the  $O_2$  molecule as the coverage is increased from the monolayer to the multilayer regime. With the aid of a layer-Korringa-Kohn-Rostoker calculation of the resonance parameters, which embodies a proper treatment of the unoccupied electronic band structure of the surface, we find that the shift in resonance energy can be attributed to the image potential of the surface, whereas the observed reduction in resonance lifetime in the monolayer is primarily due to the interaction between the molecular resonance state and the unoccupied electronic states of the surface.

### I. INTRODUCTION

The adsorption of oxygen on Ag(110) has been the subject of considerable interest in recent years. The importance of the system lies in the fact that oxygen adsorbs on the (110) surface of silver in three forms: physisorbed, molecularly chemisorbed, and dissociatively chemisorbed, depending on the surface temperature.<sup>1</sup> The system is also of industrial relevance, as the Ag(110) surface provides a useful kinetic model of commercial silver catalysts for the ethene epoxidation reaction.<sup>2</sup>

The two chemisorbed states have been studied extensively with a variety of experimental techniques; however, the physisorbed  $O_2$ /Ag(110) system has received much less attention. Studies worth noting include a photoemission study by Prince, Paolucci, and Bradshaw<sup>1</sup> and a near-edge x-ray-absorption fine-structure (NEXAFS) study by Guest *et al.*<sup>3</sup> The NEXAFS results suggest that the second layer of  $O_2$  exhibits a substantially increased molecular tilt away from the surface, as compared to the "lying down" monolayer. This is also consistent with high-resolution electron-energy-loss spectroscopy (HREELS) angular distribution measurements, which will be reported elsewhere.<sup>4</sup> Both the physisorbed and molecular chemisorbed  $O_2$  states lie parallel to the surface,<sup>3</sup> however, there is a difference in the in-plane orientation of the molecular axes, with respect to the corrugated Ag(110) surface. For the molecularly chemisorbed species, the molecular axes are oriented in the  $[1\bar{1}0]$  direction, parallel to the "grooves" between rows of silver atoms in the surface. Intriguingly, the physisorbed  $O_2$  molecules have been found to align themselves along the

$[001]$  direction, perpendicular to the rows—possible evidence for an orientational barrier to chemisorption.<sup>5</sup> Further studies of both the geometric and electronic structure of the physisorbed species are, therefore, of particular importance.

In this paper, we present an experimental and theoretical investigation of one type of electronic state that plays an important role in surface dynamical processes,<sup>6</sup> the negative-ion resonance. In particular, we focus on the resonance energy and resonance lifetime of the (oriented) physisorbed  $O_2$  molecule on Ag(110), as a function of the structure of the adsorbed layer. Previous studies of the resonance lifetime in physisorbed monolayers appear to indicate significant changes with respect to the gas phase resonance lifetime.<sup>7,8</sup> Resonance energy shifts in physisorbed molecules,<sup>8</sup> e.g.,  $O_2$  physisorbed on graphite,<sup>9</sup> a semimetallic substrate, have also been reported. The aim of the present work is to bring together experimental and theoretical investigations of both the resonance energy and the resonance lifetime in a single well-defined system, and to explore the precise mechanisms by which these fundamental parameters of the resonance state are perturbed on the surface.

Our experimental investigation utilizes the resonance scattering mechanism in HREELS. HREELS has now been employed successfully to identify the intermediate negative-ion states responsible for the vibrational and electronic excitations of a variety of adsorbed molecules.<sup>8</sup> A displaced harmonic-oscillator model<sup>7</sup> is used to extract the resonance lifetime. Our theoretical calculations employ the layer-Korringa-Kohn-Rostoker (KKR) (LKKR) model,<sup>10</sup> which is able to predict the resonance

energy and lifetime as a function of adsorption height on the basis of a full treatment of the unoccupied electronic band structure of the surface.

## II. EXPERIMENT

The experiments were conducted at the Cavendish Laboratory, Cambridge, in an ultrahigh-vacuum chamber housing an HREELS spectrometer, a four-grid reverse-view low-energy electron-diffraction (LEED)/Auger electron spectroscopy (AES) instrument and a sputter ion gun. The typical working base pressure was  $1 \times 10^{-10}$  mbar, falling to  $4 \times 10^{-11}$  mbar at cryogenic temperatures. The sample holder was mounted on the end of a rotatable liquid-helium cold finger. The Ag(110) crystal was oriented with the [001] direction (i.e., the rows of surface atoms) at  $30^\circ$  from the experimental scattering plane, and was cleaned *in situ* by repeated cycles of argon-ion sputtering (1.5 keV for 30 mins at  $1.5 \mu\text{A}$ ) and annealing by electron bombardment (700 K for 10 min), until AES and HREELS measurements showed no contamination and sharp LEED spots were obtained. Once cleaned, the sample was cooled to  $\approx 20$  K with a continuous flow of liquid helium, and  $\text{O}_2$  layers dosed on to the cold sample. The HREELS spectrometer was operated with an instrumental energy resolution of 20–25 meV full width at half maximum and a typical sample current of 1 nA. The analyzer could be rotated from the “straight through” position to an angle of  $60^\circ$ , with respect to the incident beam from the monochromator.

## III. RESULTS AND DISCUSSION

Typical HREELS spectra of physisorbed  $\text{O}_2/\text{Ag}(110)$  are illustrated in Fig. 1, for both monolayer and multilayer coverages at 20 K. The  $\nu=0-1$  vibrational excitation of the physisorbed  $\text{O}_2$  molecule is manifest as a peak in the HREELS spectra at an energy loss of  $190 \pm 5$  meV. This value is approximately the same as that observed in the gas phase<sup>11</sup> and on both Pt(111) (Ref. 12) and graphite.<sup>9</sup> The intense vibrational overtone excitations are characteristic of the resonance excitation mechanism, arising from the relatively long lifetime of the electron-molecule interaction. Note the change in the overtone intensities (compared with the elastic peak) as a function of exposure, and, more subtly, the change in the rate of decay of the overtone intensities, which reflects the different lifetime of the  $\text{O}_2$  molecule vibrations. This issue will be discussed in detail later.

Figure 2 shows HREELS spectra as a function of temperature. When the sample is warmed up by about 40 K, the 190-meV loss peak gradually disappears as a loss peak at 80 meV emerges, which is assigned to the O-O vibrational frequency of molecularly chemisorbed oxygen on Ag(110).<sup>13</sup> By monitoring the loss intensity (both peak area and peak height, after background subtraction) of the  $\nu=0-1$  feature as a function of exposure, a change in gradient at 2 L was observed and is taken to mark the completion of monolayer adsorption.

To obtain the resonance energy profile of the  $\nu=0-1$  vibrational excitation of physisorbed  $\text{O}_2/\text{Ag}(110)$ , the in-

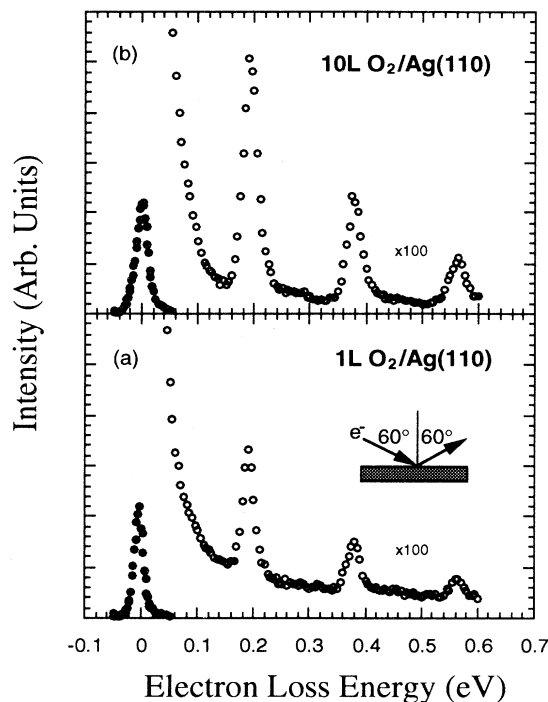


FIG. 1. Typical electron-energy-loss spectra from physisorbed  $\text{O}_2/\text{Ag}(110)$  at 20 K. (a) 1-L dose (0.5 ML), incident energy 7 eV; (b) 10-L ( $\approx 3-4$  ML) dose, incident energy 9 eV. The HREELS spectra were obtained in the specular geometry with an incident angle of  $60^\circ$ . The intense overtone excitation is a characteristic of resonance electron scattering, while the difference in overtone intensities between the two different coverages is an illustration of the change in resonance lifetime. Graph (a) has been normalized to the same elastic peak height as (b) to facilitate comparison. The raw difference is only 10%.

tensity of the loss peak was monitored as a function of the incident electron energy and normalized to the diffuse elastic intensity.<sup>8</sup> The resulting energy dependence, for both monolayer and multilayer coverages of  $\text{O}_2$ , is shown in Fig. 3. As the  $\text{O}_2$  dose is increased, the well-defined resonance centered at  $\approx 7$  eV in Fig. 3(a) is shifted to higher energy, with a peak at  $\approx 9$  eV in Fig. 3(b).

To discuss which negative ion state is producing this resonance profile, one has to take into account image potential effects.<sup>1,8</sup> In the gas phase, the  $4\Sigma_u^-$  resonance is observed at an energy of about 9.5 eV.<sup>11</sup> When  $\text{O}_2$  is physisorbed on graphite, the electron energy at which this resonance is observed is lowered by about 1 eV to 8.5 eV, an effect attributed to the image potential.<sup>9</sup> Since graphite is only semimetallic, one would expect the image charge effect to be stronger when  $\text{O}_2$  is physisorbed on a metallic substrate. Indeed, Siller *et al.*<sup>12</sup> found the  $4\Sigma_u^-$  resonance at 7.25 eV in the case of physisorbed  $\text{O}_2/\text{Pt}(111)$ . Hence, by comparison with these results, we conclude that the resonance that we observe at  $\approx 7$  eV for monolayer  $\text{O}_2/\text{Ag}(110)$ , Fig. 3(a), is also due to the  $4\Sigma_u^-$  state. The alternative  $2\Pi_u$  state is observed at 6.8 eV in

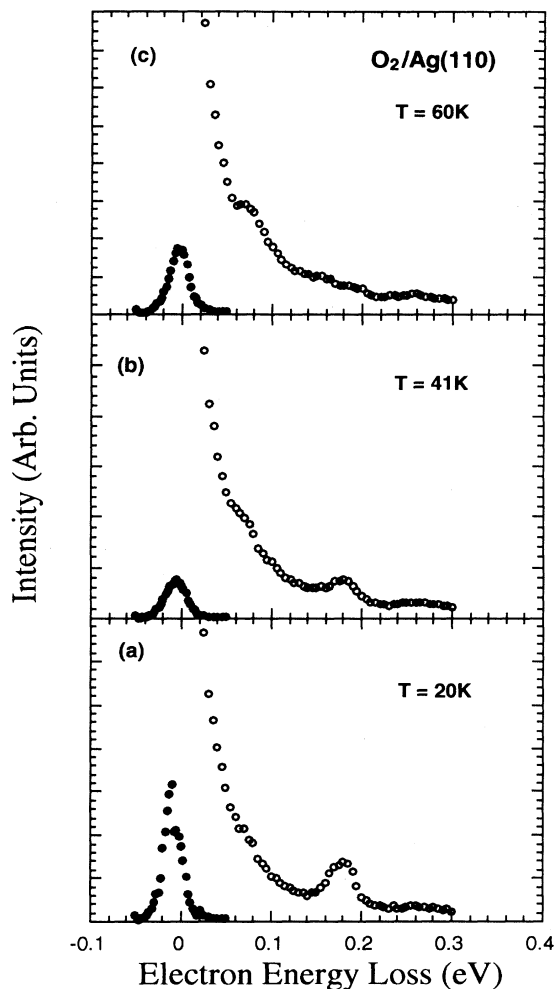


FIG. 2. Electron-energy-loss spectra from physisorbed  $\text{O}_2/\text{Ag}(110)$  (a) at  $\approx 20$  K, (b) after warming to 41 K, and (c) after warming to 60 K. Incident-beam energy, 7 eV, specular scattering geometry. The initial coverage was 2 L.

the case of  $\text{O}_2/\text{graphite}$ <sup>14</sup> and would, therefore, be expected to appear at a lower energy ( $\approx 5.5$  eV) for  $\text{O}_2$  physisorbed on a metal, such as silver.

When the  $\text{O}_2$  dose is increased to produce a multilayer, Fig. 3(b), we expect to observe a buffering effect due to the molecular layers between the substrate and the outermost  $\text{O}_2$  layer, i.e., the image potential experienced by the topmost  $\text{O}_2$  layer will be reduced. The shift in resonance energy from  $\approx 7$  eV in the monolayer to  $\approx 9$  eV in the multilayer, much nearer to the gas phase value of 9.5 eV, seems to evidence this effect.

Figure 4 displays the calculated energy of the  ${}^4\Sigma_u^-$  resonance as a function of the molecule-surface distance when the  $\text{O}_2$  molecule is adsorbed above the four high-coordination adsorption sites of  $\text{Ag}(110)$ . The resonance energy was computed from a recently developed LKKR method.<sup>10,15-17</sup> Briefly stated, the LKKR method employs a multiple scattering calculation to determine the

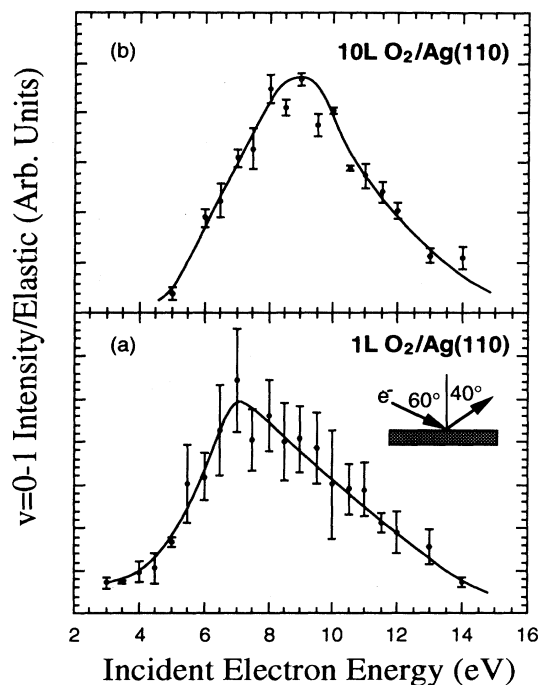


FIG. 3. Resonance energy profiles obtained from physisorbed  $\text{O}_2$  on  $\text{Ag}(110)$  at  $\approx 20$  K. The experimentally observed intensity of the 190-meV  $v=0-1$  vibrational excitation of the  $\text{O}_2$  molecule, normalized to the diffuse elastic intensity, is plotted as a function of the incident electron energy. The incident angle is  $60^\circ$  and the detection angle is  $40^\circ$  in both cases. Resonances are observed (a) at 7 eV for an  $\text{O}_2$  dose of 1 L, and (b) at 9 eV for an  $\text{O}_2$  dose of 10 L. The solid curves are drawn as a guide to the eye.

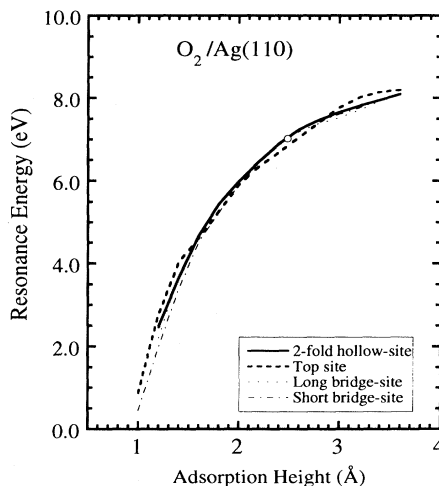


FIG. 4. The resonance energy of the  ${}^4\Sigma_u^-$  shape resonance of  $\text{O}_2$ , evaluated by a layer-KKR calculation, plotted as a function of adsorption height of the molecule. The adsorption height is defined as the distance between the molecule center of mass and the center of the first atomic plane of the substrate. The resonance energy in free  $\text{O}_2$  is set at 9.5 eV. The observed resonance energy of the physisorbed molecule ( $\approx 7$  eV) is marked by a filled circle and corresponds to an adsorption height of  $\approx 2.5$  Å.

resonance energy and lifetime of an adsorbed molecule, starting from a muffin-tin description of the atomic potentials of the substrate. The calculation employs a parametrized surface barrier potential<sup>18</sup> fitted to the energy of the image states.<sup>19</sup> The adsorption height is defined in the conventional manner, i.e., the distance between the molecular center-of-mass and the center of the first atomic plane of the substrate. The molecule is oriented parallel to the surface, and the resonance energy of the free molecule is set to 9.5 eV.

For each of the adsorption sites, the energy of the negative-ion resonance decreases monotonically as the molecule approaches the surface. The calculated variation of the resonance energy as a function of the adsorption height closely tracks the surface barrier (image) potential. From Fig. 4, it is apparent that the reduction of the energy of the negative ion upon physisorption is primarily a consequence of the electrostatic screening of the negative ion, in agreement with all prior theoretical studies of resonance scattering from adsorbates. The observed resonance energy,  $7 \pm 0.5$  eV, is obtained for an adsorption height of approximately  $2.5 \pm 0.3$  Å. This represents a reasonable physisorption height and is in agreement with a classified molecular-dynamics simulation<sup>6</sup> of this system, which predicts an adsorption height for Ag(110)-O<sub>2</sub> of  $\approx 2.8$  Å.

The reduction in resonance energy of the  $4\Sigma_u^-$  shape resonance from 9.5 eV in the free O<sub>2</sub> molecule to 7 eV when physisorbed on the Ag(110) surface is also very reasonable when compared with core-level studies of O<sub>2</sub> employing x-ray photoelectron spectroscopy (XPS). The binding energy of the free O<sub>2</sub> molecule is found to be 543.7 eV,<sup>20</sup> while for O<sub>2</sub> condensed on polycrystalline Ag, the binding energy is 536.7 eV, with respect to the Fermi level.<sup>21</sup> Taking the work function of silver as 4.7 eV gives a shift in binding energy of 2.3 eV from the gas phase to the surface. Since a chemical shift due to charge transfer to/from the substrate cannot be expected to play a major role in a physisorption system, image charge stabilization of the positive XPS final state is the natural cause of the observed shift in binding energy on the surface.

It is interesting to point out that, according to Palmer and Rous,<sup>8</sup> one should be able to selectively populate the two different resonant states,  $4\Sigma_u^-$  and  $2\Pi_u$ , of physisorbed O<sub>2</sub> by a judicious choice of symmetry, since the  $4\Sigma_u^-$  is of  $p\sigma$  symmetry, while the  $2\Pi_u$  is of  $p\pi$  symmetry. This was indeed proven by Barnard and Palmer<sup>22</sup> for the lying down  $\delta$  phase of O<sub>2</sub> physisorbed on graphite. With a common incident angle of 60°, with respect to the normal, the  $4\Sigma_u^-$  resonance dominated the resonance profile for a detection angle of 30°, while the  $2\Pi_u$  state showed up with the detector normal to the surface. However, using the latter experimental geometry, we were still able to detect only the  $4\Sigma_u^-$  state from the monolayer of O<sub>2</sub> physisorbed on Ag(110). Pursuing this issue, we performed angular measurements of the  $4\Sigma_u^-$  resonance, whose polar distribution was found to exhibit a maximum at 50°, with respect to the surface normal.<sup>5</sup> Symmetry arguments<sup>8</sup> indicate that the partial waves responsible for the capture and the emission cross sections are the same for this reso-

nance, which, therefore, implies that an incident angle of 60° would efficiently populate the  $4\Sigma_u^-$  level, inevitably drowning the (weaker)  $2\Pi_u$  resonance. Indeed, it is possible that both the excitation of and emission from the  $2\Pi_u$  negative-ion state are appreciable (with respect to the  $4\Sigma_u^-$  state) only very close to the normal direction. Unfortunately, it is not feasible with our instrumentation to make HREELS measurements with an inclusion angle of less than 60°.

We have also performed an analysis of the decay of the vibrational overtone intensities to extract the lifetime of O<sub>2</sub> physisorbed on Ag(110). This analysis follows closely the displaced harmonic oscillator model proposed by Gadzuk,<sup>7</sup> and, therefore, will not be described in detail here. This scheme has been employed previously to estimate the lifetime of the  $2\Pi_g$  resonance (2.3 eV) of N<sub>2</sub> physisorbed on polycrystalline Ag.<sup>7</sup> The basic concept of this model is that the probability of exciting higher-order vibrational overtones, via the formation of a negative ion, is a function of the resonance lifetime,  $\tau_R$ . Thus, if the resonance lifetime of a molecule is altered by adsorption, then this change in  $\tau_R$  will be manifest in the rate of decay of the intensity of the loss features as a function of the overtone number. Specifically, a decrease in the resonance lifetime will cause the vibrational overtones to decay more rapidly than for the free molecule, while an increase of the resonance lifetime will tend to have the opposite effect.

Briefly stated, we employ the usual Franck-Condon picture of resonance formation, in which the adsorbed molecule makes a pair of vertical transitions between two potential-energy surfaces corresponding to the intramolecular potentials of the neutral molecule and the negative-ion state. In the short-lifetime limit, where the resonance lifetime is much shorter than the vibrational period of the molecule, it is reasonable to assume that the nuclear wave packet explores only a very limited region of the excited-state's potential-energy surface (PES). In this case, it is reasonable to employ a harmonic potential to model those parts of the intramolecular PES's that are explored by the nuclear wave packet. In this case, the probability of excitation of a particular vibrational state of the neutral molecule, as a function of the lifetime of the negative ion, can be readily computed from the overlap integrals of the eigenstates of the harmonic potentials. A detailed description of the theory and fitting procedure may be found in Gadzuk's original paper.<sup>7</sup>

For the case of O<sub>2</sub> physisorbed on Ag(110), the harmonic potential of the free neutral molecule was chosen to reproduce the fundamental vibrational frequency,  $h\nu = 192$  meV, and the equilibrium bond length of 1.21 Å.<sup>23</sup> For the  $4\Sigma_u^-$  state of O<sub>2</sub><sup>-</sup>, a calculated value of  $h\nu = 72$  meV was used.<sup>24</sup> The resonance width in the free molecule was fitted to experimental data,<sup>11</sup>  $\Gamma \approx 5.7$  eV, corresponding to a lifetime of  $\approx 0.1$  fs. The decay of the negative ion was assumed to follow the usual exponential decay law.<sup>7</sup> The equilibrium bond length of O<sub>2</sub><sup>-</sup>, a free parameter in the calculation which defines the displacement between the harmonic potentials of the neutral and excited molecules, was fitted to the measured overtone

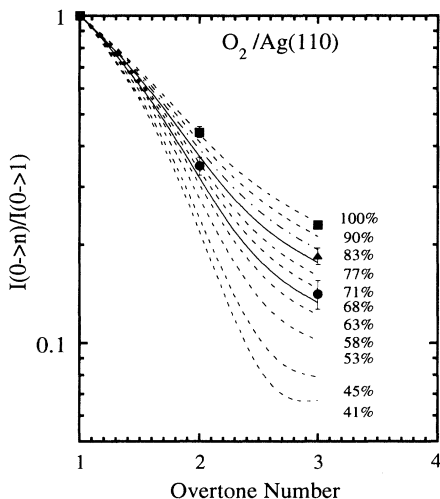


FIG. 5. Overtone intensities in resonance electron scattering by  $O_2$  (via the  ${}^4\Sigma_u^-$  resonance), plotted as a function of the overtone number and normalized to the  $\nu=0-1$  loss. Filled squares: the overtone intensities for the free molecule, measured by Wong, Boness, and Schultz.<sup>11</sup> Filled circles: the overtone intensities for 1 L of  $O_2$  physisorbed on Ag(110) (this work). Filled triangles: the overtone intensities for 10 L of  $O_2$  physisorbed on Ag(110) (this work). The dashed curves are the calculated overtone intensities obtained from the displaced harmonic-oscillator model, where the resonance lifetime (labeled as a percentage of the lifetime of free  $O_2$ ) is treated parametrically. The solid curves indicate the upper and lower bounds on the resonance lifetime that are consistent with the experimental data for physisorbed  $O_2$  at 1-L coverage.

decay of the free molecule<sup>12</sup> (see Fig. 5). The value obtained from this procedure was  $R_e^- = 1.89 \text{ \AA}$ , a value that is in reasonable agreement with the bond length obtained from an *ab initio* MCSCF calculation for the  ${}^4\Sigma_u^-$  state,  $R_e^- = 1.83 \text{ \AA}$ .<sup>24</sup> We note that the resonance lifetime in the free molecule,  $\tau_R \approx 0.1 \text{ fs}$ , is much shorter than the vibrational period of the excited molecule,  $T \approx 60 \text{ fs}$ , thus justifying the fundamental assumption of the model.

In Fig. 5, we display the loss intensities (after background subtraction) of the  $\nu=0-2$  and  $0-3$  overtones, normalized to the  $\nu=0-1$  transition, measured for both monolayer and multilayer coverages of  $O_2$  on Ag(110). Also shown are the overtone intensities computed using the displaced harmonic oscillator model described above, plotted as a function of the resonance lifetime (expressed as a percentage of the lifetime of the free molecule = 100%). The calculation assumed that the neutral and excited-state intramolecular PES's were unaltered by physisorption of the molecule. The experimental evidence suggests that this is a reasonable approximation, because the measured fundamental frequency of the physisorbed molecule,  $h\nu = 190 \pm 5 \text{ meV}$ , is not significantly different from that of the free molecule,  $h\nu = 194 \text{ meV}$ .

As can be seen from Fig. 5, the measured decay of the overtones for the free molecule, from the published gas phase data of Wong, Boness, and Schultz<sup>11</sup> is in good agreement with the predictions of the displaced

harmonic-oscillator model. For both the 1-L and the 10-L coverages of  $O_2$  physisorbed on Ag(110), we observe that the measured overtone intensities decay more rapidly than those for the molecule in the gas phase. This feature, which has also been observed in the energy-loss spectrum for resonance scattering by  $N_2$  on polycrystalline Ag,<sup>7</sup> indicates that the resonance lifetime is reduced upon adsorption and also that the resonance lifetime is shorter for the 1-L coverage (the monolayer) than for 10-L coverage (the multilayer). From Fig. 5, we observe that the calculated rate of decay of the overtone intensities from the physisorbed molecule at 1-L coverage is in excellent agreement with the measured intensities, if the resonance lifetime of the adsorbed molecule is reduced to  $70 \pm 10 \%$  of the lifetime of the free molecule. The lifetime reduction for 10-L coverage is significantly smaller; in this case, the lifetime of the adsorbed molecule is  $90 \pm 10 \%$  of the lifetime of the free molecule. These results suggest that the negative-ion state in adsorbed  $O_2$  is more strongly "quenched" in the monolayer than in the multilayer.

In Fig. 6 we show the calculated lifetime of the resonance plotted as a function of the adsorption height of an isolated molecule above the twofold hollow site. The resonance lifetime was computed by the LKKR method described earlier<sup>10,15-17</sup> for the  $O_2$  molecule adsorbed parallel to the surface. This calculation considers only the interaction between the negative ion of an isolated molecule and the substrate. Any perturbation of the resonance lifetime, due to interactions between neighboring molecules in the overlayer, is neglected. For the monolayer

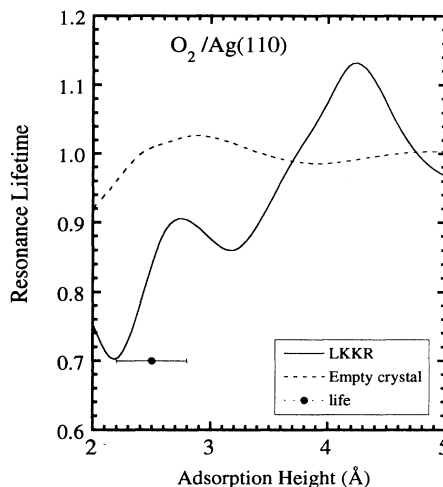


FIG. 6. The relative resonance lifetime (1.0 = gas phase lifetime) of the  ${}^4\Sigma_u^-$  shape resonance of  $O_2$ , evaluated by a layer-KKR calculation, plotted as a function of the adsorption height of the molecule. Solid curve: full LKKR calculation, including full multiple scattering of the trapped electron by the substrate. Dashed curve: the empty crystal approximation, where only the image interaction between the negative ion and the metallic substrate is included. Solid circle: the resonance lifetime determined for 1-L coverage of the physisorbed molecule corresponding to an adsorption height of  $2.5 \pm 0.3 \text{ \AA}$ .

phase, the LKKR calculation of the resonance energy as a function of the molecular adsorption height (Fig. 4) suggests that the molecule is adsorbed  $2.5 \pm 0.3$  Å about the first atomic plane of Ag(110). From Fig. 6, we see that an O<sub>2</sub> molecule adsorbed at this height has a calculated lifetime of  $80 \pm 10$  % compared with the lifetime of the negative ion in the free molecule. This reduction of the lifetime is in reasonable agreement with the resonance lifetime extracted from the measured decay of the overtone intensities;  $70 \pm 10$  %.

Also shown in Fig. 6 is the lifetime computed for an empty crystal, in which the electron scattering among the substrate atoms is neglected and only the image interaction between the negative ion and the metallic substrate is considered. In this calculation, any interaction between the negative ion and the unoccupied electronic states of the substrate is neglected. We see that the empty crystal calculation substantially underestimates the reduction of the resonance lifetime over a range of realistic adsorption heights. At an adsorption height of  $2.5 \pm 0.3$  Å, the resonance lifetime computed within the empty crystal approximation is not significantly different from that of the free molecule. We conclude that while the image interaction is primarily responsible for the shift in the energy of the resonance, the *lifetime* of the adsorbed molecule is very strongly influenced by the unoccupied electronic structure of the substrate. This conclusion is in agreement with prior theoretical studies of resonance scattering from adsorbed molecules with negative-ion states in this energy range.<sup>15-17</sup>

Finally, we note that, recently, Djamo, Teillet-Billy, and Gauyacq<sup>25,26</sup> have shown that there is a strong energy dependence in the vibrational excitation probability when the trapped electron detaches close to the threshold. In the case of the <sup>2</sup>Π<sub>g</sub> resonance of N<sub>2</sub> on Ag, it was found that a component of the observed decay of the overtone intensities could be attributed to electron scattering by the image potential, quite independently of any intrinsic reduction of the intrinsic resonance lifetime. In the case of Ag-N<sub>2</sub>, this effect is especially pronounced because the resonance energy of the adsorbed molecule (1.2 eV above the vacuum level) is almost equal to the value of the image potential at the molecule ( $\approx 1.1$  eV). In this case, excitation of even the lower-order overtones ( $h\nu \approx 0.28$  eV) leads to electron detachment close to the

vacuum level, where the electron trajectories are very strongly distorted by the image potential.

For the O<sub>2</sub>-Ag(110) system considered here, the resonance energy of the adsorbed molecule is sufficiently high (7 eV) compared with the vibrational level spacing ( $h\nu = 0.19$  eV), where scattering by the image potential has no significant effect upon the observed intensities of the vibrational losses. For example, an LKKR calculation of electron scattering by the image potential shows that this effect reduces the intensity of the  $\nu = 0-3$  loss by less than 4%. Thus, this phenomenon has no significant effect upon the extracted lifetime of  $70 \pm 10$  %, within the error bars of the analysis.

#### IV. SUMMARY

We have studied the resonance characteristics of molecular O<sub>2</sub> physisorbed on Ag(110) with HREELS experiments and a layer-KKR calculation of the resonance energy and lifetime. The coverage dependence of both the resonance energy and the lifetime of the <sup>4</sup>Σ<sub>u</sub><sup>-</sup> negative-ion state has been determined from experiment. The resonance energy is found to be 9 eV in the multilayer regime and approximately 7 eV in the monolayer. The image potential is responsible for the observed shift in resonance energy. Similarly, the resonance lifetime of the O<sub>2</sub> molecule in the monolayer is found to be reduced when compared to the multilayer. However, a different mechanism, namely, interaction of the resonance state with the unoccupied electronic states of the substrate, is primarily responsible for this quenching of the lifetime.

#### ACKNOWLEDGMENTS

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