

Adsorption of molecules on free-electron-like metals: CO on Al(100)

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The adsorption of CO on an Al(100) surface has been studied with use of infrared spectroscopy. In contradiction to earlier assumptions, the molecules do not lie flat on the surface. The initial sticking coefficient is very low, indicating physisorption via van der Waals interaction. No ordered structures are observed and the infrared absorption peak is found to be inhomogeneously broadened.

An often used theoretical approach in surface physics is to treat the metal as jellium, with the ion cores embedded in delocalized conduction electrons. A metal that would fit well into such a description is aluminum, with its $3s^3p$ electrons and the d band well above the Fermi level. The electronic picture is then simple; inside the metal a high density of s - p electrons with a tail reaching rather far out into the vacuum and with very little lateral corrugation. In spite of the importance of these types of systems very little experimental data on molecules adsorbed on Al exist. Using carbon monoxide as the usual test molecules, the only work that had been done on single crystalline surface was an UPS study on Al(111) by Chiang *et al.*,¹ which showed a weakly bonded molecule with a gas phase like electronic spectrum. It was proposed, with the same indirect arguments as for the likewise weakly interacting CO/Ag system,^{2,3} that the molecules were lying flat on the surface.

However, there have recently been published cluster calculations^{4,5} for CO/Al predicting weakly or strongly chemisorbed molecules oriented with their axis normal to the surface, and it has also been reported that such chemisorbed molecules have been observed.⁶ One of the few experimental methods that really can distinguish between standing up (more or less tilted) and flat lying molecules is infrared spectroscopy.⁷ The rigorous surface selection rule says that if the substrate is a good conductor the dynamical dipole moment (which is parallel to the C-O axis) must have a component normal to the surface to be excited by the infrared radiation. This work is an attempt to establish the orientation of the molecules and to get some insight in the nature of the metal-molecule interaction.

The Al(100) crystal ($20 \times 14 \times 2$ mm³) was oriented and cut within 0.3°, but because of problems with the crystal holder during the experiments the sample was slightly bent, so we estimate that the step density corresponds to a misalignment of about 1°. The crystal was mechanically polished down to 1- μ m diamond paste and then electropolished in 1:6 perchloric acid + ethanol mixture at -35°C. *In situ* cleaning by low-energy Ar⁺ sputtering (250 eV, 1 μ A/cm²) and short annealing at 700 K allowed the crystal to keep its mirrorlike finish. The sample could be cooled down to about 20 K by liquid He. The CO molecules were admitted both

through ordinary backfilling and via a doser ending 3 cm in front of the sample. The infrared spectrometer has been described elsewhere.⁸

The first observations made in this study were that CO is certainly weakly bonded on Al(100) but oriented with the axis out from the surface. This is seen by a rather strong infrared absorption around 2135 cm⁻¹ (the gas phase value of the stretch mode is 2143 cm⁻¹). In line with the results of Chiang *et al.*¹ the binding energy is about 0.2 eV, as the monolayer was stable below 40 K, whereas multilayers could be formed below 25 K (all depositions discussed here were made at 30 K to prevent this multilayer formation). More or less ordered multilayers with a vibration frequency at 2143 cm⁻¹ could be grown on a monolayer in a way similar to what was observed on CO/Cu(100).⁹ The peak at 2139 cm⁻¹ of a rapidly condensed solid was used as wave-number calibration.⁹ No ordered structure [just a weakening of the otherwise sharp Al(100) pattern] was seen in the LEED at any coverage indicating a weak lateral corrugation. It was not possible to reproduce the results of Paul and Hoffmann,⁶ who at liquid N₂ temperatures observed chemisorbed CO molecules by EELS (vibration frequency 2060 cm⁻¹), but with a sticking coefficient of 10⁻³-10⁻⁴. Under certain uncontrolled conditions very small amounts of chemisorbed CO (vibration frequency ~2050 cm⁻¹) could be obtained above 60 K after exposures of several thousand langmuirs.

An interesting feature of this system is exposed in Fig. 1, where the infrared absorption peak height is plotted versus backfilling exposure. It shows a very nonlinear behavior, quite different from what has previously been observed for chemisorbed CO. There is a small negative frequency shift and both quantities deviate definitely from the predictions of the dipole-dipole interaction theory.¹⁰ There could be two possible explanations for the behavior of the peak height. Either the molecules lie flat on the surface for low coverages and an intermolecular interaction forces them to rise as the coverage is increased, or there is a strongly coverage-dependent sticking coefficient. This latter alternative was investigated by exposing the sample via the doser and making thermal desorption measurements. The results in Fig. 2 indeed show a strong variation in sticking, with a curve shape similar to that of the peak height in Fig. 1. Obvi-

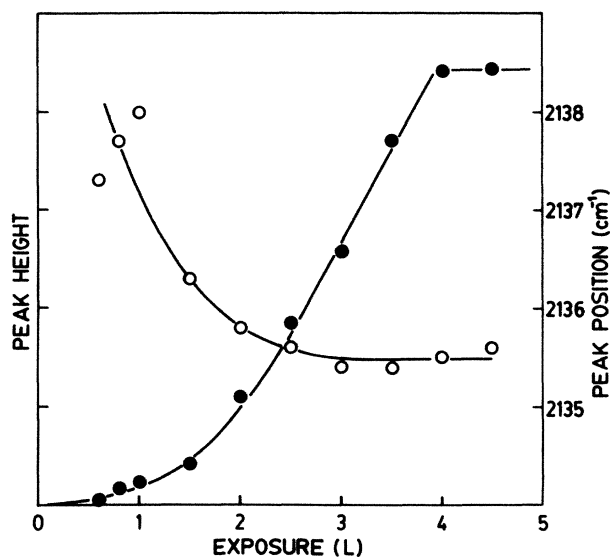


FIG. 1. The infrared absorption peak height (●) and position (○) vs backfilling doses for CO on Al(100) at 30 K.

ously, the probability for energy dissipation directly into the substrate is rather low, while collisions with other adsorbed molecules much more efficiently absorb the kinetic energy of the incoming particle. As the high-coverage sticking coefficient (the slope of the curve) by necessity has to be < 1 , the initial sticking coefficient is restricted to less than 5%. Obviously this method is too crude to give an absolute value of the sticking coefficient, but it demonstrates a significant effect. The result was not sensitive to variations in temperature and pressure, showing that the effect was not caused by two-dimensional condensation.

An important question for this system is whether the binding mechanism is weak chemisorption, physisorption via van der Waals interaction, or a mixture of both.

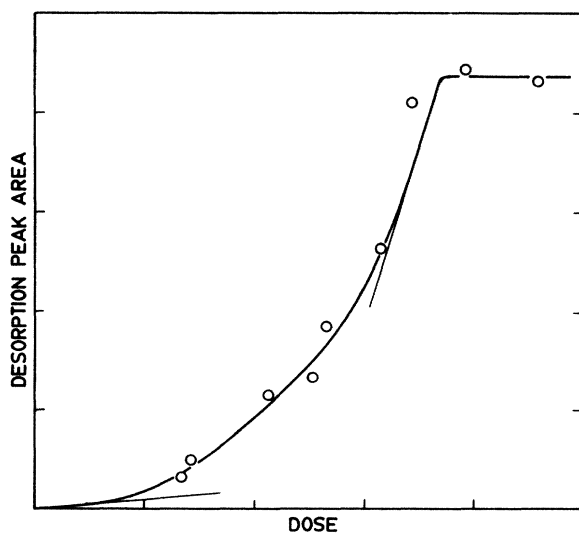


FIG. 2. Relative coverage versus dose (all in arbitrary units) as measured by mass spectrometer. Exposures made at 30 K via a doser held at room temperature.

The Hartree-Fock cluster calculation by Bagus *et al.*⁴ predicts a weak chemisorption (binding energy 0.23 eV), with the molecule in the ontop position oriented normal to the surface. The local-density calculation by Persson and Müller⁵ gives a much stronger chemisorption (1 eV) with the same configuration. There exists no calculation on the van der Waals interaction between a CO molecule and a jellium. Harris and Feibelman¹¹ pointed out that the attractive part can favor the end-on molecular orientation while the metal-molecule repulsion could give an opposite effect, the two canceling each other. As will be seen in the last paragraph there is probably a significant molecule-molecule interaction, which can play an important role for the orientation.

However, an important clue in solving this problem lies in the very low initial sticking coefficient. The situation can qualitatively be compared with a calculation by Persson and Harris¹² on the sticking of Ne on Cu(100). They consider van der Waals interaction between the substrate and the Ne atoms and excitations of phonons as the energy dissipation mechanism. For parameters comparable to the present work (room temperature molecules at 40 meV, angle of incidence 0° – 20°) they obtain for Ne/Cu a sticking coefficient of about 2%. Even if one should compensate for difference in phonon spectra, particle mass and metal-molecule interaction, the important point is that these very low sticking coefficients are something characteristic of physisorption. In fact, a similar behavior as that shown in Fig. 2 has been observed for the quite different physisorption system H_2 /Cu(100).¹³ For chemisorption on the other hand, involving rearrangements or even transfer of charge, the electronic processes are much more efficient and rapid, giving sticking coefficients close to one even for such rather weakly chemisorbed systems as CO on copper. There are also two other observations that could indicate physisorption. The vibration frequency is very close to the gas-phase value. This could indicate an unperturbed

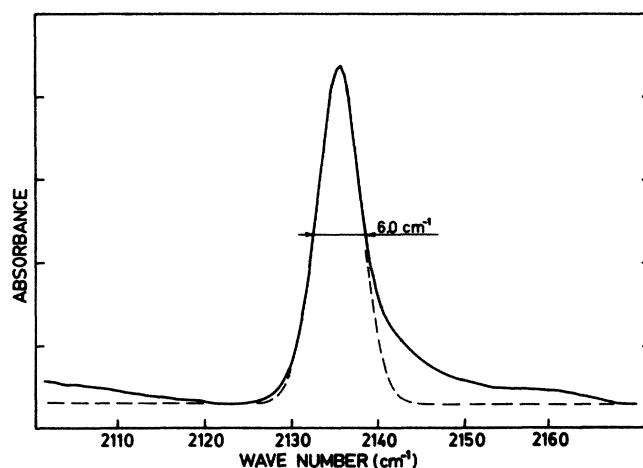


FIG. 3. The integrated infrared absorption peak of a full monolayer of CO on Al(100) at 30 K. Spectrometer slit width 1.8 cm^{-1} , modulation amplitude 0.2 cm^{-1} , compared with a Gaussian (— —) distribution.

molecule even if the vibration frequency alone is a poor measure of the electronic state of an adsorbed molecule, as compensating effects are common. Furthermore, the calculation by Bagus *et al.*⁴ predicts a two-peak UPS spectrum for chemisorbed CO, which is in contradiction with the three-peak experimental result.¹ All in all, we find that everything indicates a predominantly physisorbed molecule and hence, that much of the binding energy must come from a molecule-molecule interaction. If there exists a chemisorption state there must be an activation barrier of at least 0.5 eV, because in some extremely high-exposure experiments the doser was heated to 500 K to increase the kinetic energy of the molecules but with no measurable effect.

With the advance of infrared spectroscopy of adsorbed molecules there has been an increasing interest in studies of the shape of the infrared absorption line. We have previously argued that for the chemisorption system CO/Cu(100) the Lorentzian like peak shape probably is caused by lifetime broadening.¹⁴ In a recent calculation Crljen and Langreth¹⁵ have included the dipole-dipole interaction in addition to the asymmetry effect caused by the oscillating charge being out of phase with the exter-

nal field. The theory reproduces the experimental data very well, supporting the lifetime broadening interpretation. The width of the peak for CO/Cu(100) is 5 cm^{-1} and one should expect that for physisorbed CO/Al(100) the width should be considerably smaller. However, as stated above it is not possible to obtain an ordered structure for this system, so any intermolecular interaction will inevitably give rise to additional inhomogeneous broadening and in the first approximation produce a Gaussian shaped peak.¹⁴ Figure 3 shows the integrated absorption peak of a full monolayer, recorded with a resolution of 1.8 cm^{-1} . The intrinsic peak width is about 5 cm^{-1} and the peak has a Gaussian shape with a tail towards higher frequencies indicative of inhomogeneous broadening. It is probably a general effect, that for physisorption systems the metal-molecule interaction is not able to set up a good order in the overlayer and hence the inhomogeneous broadening will dominate, and prevent a systematic test of the peak broadening mechanism.

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