The frustrated translational mode of CO on Cu(110): Azimuthal anisotropy studied by helium atom scattering—A comparison with time-of-flight electron stimulated desorption of ion angular distribution measurements

J. Braun and J. Weckesser
Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-37073 Göttingen, Germany

J. Ahner, D. Mocuta, and J. T. Yates, Jr.
Departments of Chemistry and Physics, University of Pittsburgh, Surface Science Center, Pittsburgh, Pennsylvania 15260

Ch. Wöll
Ruhr-Universität Bochum, Lehrstuhl Physikalische Chemie I, Universitätsstrasse 150, D-44801 Bochum, Germany

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The frustrated translation of isolated CO molecules parallel to the surface, or *T* mode, has been studied on a Cu(110) substrate using helium atom scattering. A small but significant anisotropy in *T*-mode vibrational frequencies was found for the on-top site species with oscillator frequencies of 3.6 and 3.2 meV along the [1̄10] and the [001] directions, respectively. These results are compared with recent results from time-of-flight electron stimulated desorption of ion angular distribution measurements [Ahner *et al.*, Phys. Rev. Lett. **79**, 1889 (1997)], where also a significant anisotropy has been observed. © *1998 American Institute of Physics.* [S0021-9606(98)03713-1]

The study of the frustrated translation mode (*T* mode) of small molecules adsorbed on metal substrates has attracted increasing interest during the past decade. The energies of the *T* modes typically lie in the thermal energy regime (<20 meV) and, as a result, the vibrations are thermally occupied even at temperatures below 100 K. This fact has consequences not only for the thermodynamical properties of the adsorbed layer but also with regard to a precise experimental determination of molecular geometries, e.g., with low energy electron diffraction (LEED)[1,2] or electron stimulated desorption of ion angular distribution (ESDIAD).[3] Most of the data available today on *T* modes were recorded for substrates with threefold or higher symmetry, where—for on-top sites—the *T*-mode is twofold degenerate. For anisotropic adsorbate sites, e.g., bridge (and also on-top) positions on a face-centered-cubic (fcc) (110) surface, an anisotropy in the thermally induced displacements is expected. Recent HAS data obtained for CO adsorbed at the on-top sites of a Ni(110) surface surprisingly did not reveal any detectable anisotropy for the *T*-mode frequency.[4] In a study on N_2 adsorbed on the same substrate a significant dependence of the *T*-mode energy on the adsorption site was seen (on-top versus bridge),[5] but again for the on-top site no anisotropy was observed. For the Ni-bridge-site species a soft (<10 meV) *T* mode could be seen only along one direction,[5] in agreement with the expected behavior for this highly anisotropic adsorbate site (see also Refs. 6 and 7).

Recently published time-of-flight (TOF)-ESDIAD measurements[8] have revealed a pronounced anisotropy in the desorption pattern for CO adsorbed on the on-top sites of Cu(110), which showed a strong dependence on the normal kinetic energy of the desorbing CO and on the surface temperature. An analysis of these data for a substrate temperature of $T_s=32$ K, based on the assumption that the momentum of the adsorbed particle parallel to the surface is preserved in the desorption process, yielded a surprisingly large anisotropy for the *T* energies, namely 3.1 and 4.9 meV along the [001] direction and the [1̄10] direction, respectively. In the present study we have used He-atom scattering to independently determine the energies of the low-energy *T* modes along the two different high-symmetry directions.

The HAS experiments are carried out in an apparatus (base pressure 1×10^{-10} mbar) described elsewhere[9] in more detail. Briefly, a helium beam with a typical velocity resolution of 1% is formed by a supersonic expansion of the gas through a 10 μm nozzle. After scattering off the surface the He atoms are passed through an electron bombardment analyzer followed by a magnetic mass spectrometer, and detected by a particle multiplier. The angle between the incident beam and the detector was fixed to 90.5°. The precise amounts of the energy loss and gain of the scattered He atoms during the collision process are determined using the TOF technique.

The Cu(110) crystal used in these experiments was oriented to better than 0.25°. The sample was mounted on a homemade crystal holder capable of cooling the sample to 95 and 40 K using liquid nitrogen and liquid helium, respectively. After several crystal cleaning cycles consisting of Ar-ion bombardment (45 min, 500 eV, 0.8 μA/cm^2) and heating up to 900 K, XP spectra did not reveal any traces of impurities on the Cu surface. The CO gas (purity better than 99.99%) was dosed by backfilling the scattering chamber through leak valves.

In order to be able to directly compare the present results to the TOF-ESDIAD measurements utmost care was taken in the preparation and coverage calibration of the CO overlay-

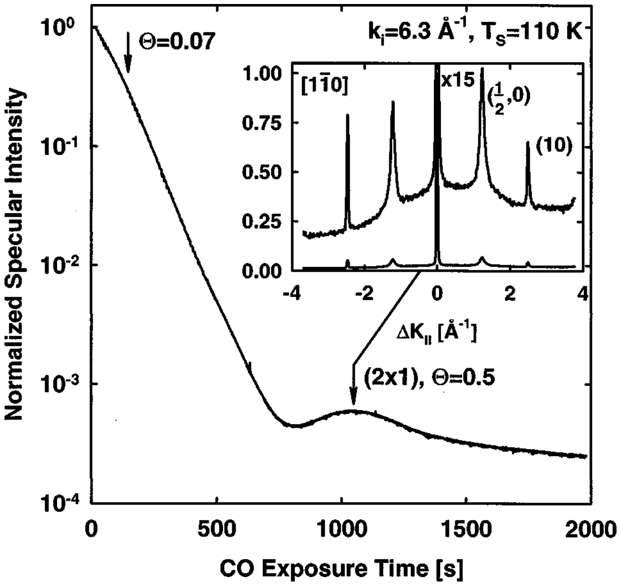

FIG. 1. Typical measurement of He beam reflectivity vs CO exposure time, recorded at $T_s = 100$ K. Inset: He atom diffraction in the [1$\bar{1}$0] azimuthal direction corresponding to the completion of a well ordered (2×1) CO layer with a nominal coverage of $\theta = 0.5$ monolayers (ML).

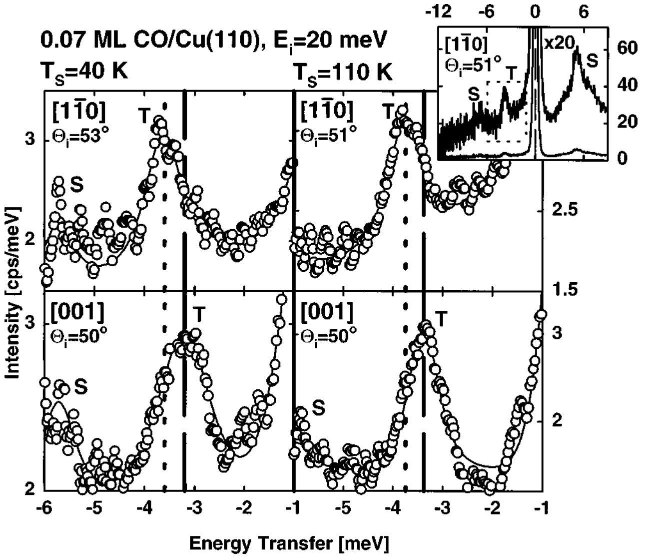

FIG. 2. HAS results along the [1$\bar{1}$0] and the [001] directions for sample temperatures of $T_s = 40$ K and of $T_s = 110$ K displayed in the upper and the lower panels, respectively. Inset: TOF spectrum converted to an energy transfer scale for the Cu(110) surface (at $T_s = 110$ K) covered with isolated CO molecules. The spectrum was recorded along the [1$\bar{1}$0] azimuthal direction. The solid lines were obtained by fitting the energy loss peaks by Voigt functions (see the text) and the peak at zero energy transfer by a Gaussian. The CO-induced and the substrate phonon peaks are labeled by *T* and *S*, respectively.

ers. Figure 1 shows a typical measurement of He beam reflectivity versus CO exposure time, recorded at $T_s = 100$ K. During the exposure the CO partial pressure was monitored by a mass spectrometer and remained at a constant value of about 1×10^{-9} mbar. Initially the He-atom specular intensity is strongly reduced due to the large scattering cross section of adsorbed CO molecules [120 Å^2 (Ref. 10)] and reaches a minimum of about 0.03% of the initial value after about 700 s. The nearly exponential decay of the intensity can be attributed to the fact that initially isolated CO molecules[11] are present on the surface, similar to the case for other metal surfaces.[12–14] Figure 1 reveals that after passing through the minimum the He-atom specular intensity increases again until after about 1100 s a maximum is reached. As confirmed by recording an angular distribution along the [1$\bar{1}$0] azimuth (see the inset in Fig. 1) this maximum in reflectivity corresponds to the completion of a well ordered (2×1) CO overlayer with a nominal coverage of $\theta = 0.5$ monolayers (ML). The full width at half-maximum (FWHM) of the extra half-integer diffraction peaks is about three times larger than that of the specular and the substrate diffraction peaks. This observation indicates the formation of ordered CO-(2×1) domains with a coherence length of about 35 Å, roughly three times smaller than that of the Cu(110) substrate.

For the experiments described here a low-density adsorbate phase was prepared by using exposure times of 140 s under the above conditions. Inspection of Fig. 1 reveals that for this exposure (denoted by a vertical arrow) the reflectivity decrease is still within the exponential regime, thus confirming the presence of isolated adsorbate species. Previous work has shown that the sticking coefficient, s_0, of CO on Cu(110) remains constant at $s_0 = 0.46$ up to a coverage of $\theta = 0.5$.[15] Since previous measurements have shown that at low coverages CO adsorbs in on-top sites on this surface[16] we can estimate that this exposure results in a coverage of CO adsorbed in on-top sites of 0.07 ML.

The HAS energy loss spectra are displayed in Fig. 2. The inset shows a TOF spectrum converted to an energy transfer scale for the Cu(110) surface (at $T_s = 110$ K) covered with isolated CO molecules. The spectrum was recorded along the [1$\bar{1}$0]-azimuthal direction and the kinematic conditions were chosen such that the inelastic gain and loss features corresponding to surface phonons (labeled by *S*) are well separated from the CO-induced inelastic peak (denoted by *T* in Fig. 2). Only a part of the spectra (marked by a dashed rectangle) in the energy range of interest between -1 and -6 meV is presented in the other panels.

Typical spectra recorded along the [1$\bar{1}$0] and the [001] directions for a sample temperature of $T_s = 40$ K are displayed in the upper and the lower left-hand panels, respectively. To determine the center of the peak precisely, in both cases the loss peaks were fitted by Voigt functions and the results are shown as solid lines in Fig. 2. This fit procedure accounts for the fact that the shape of a gain or loss peak can be described by a convolution of a Gaussian peak originating from the instrumental broadening, which can be predicted by a formula given in Ref. 17, and an additional broadening due to a coupling to substrate phonons and electron–hole pairs,[18,19] which is described by a Lorentzian peak. However, in this work we will restrict ourselves to the discussion of the position of the CO-induced peaks.

In analogy to the findings for CO adsorbed on other metal surfaces[19] we assign the CO-induced peaks in the HAS energy loss spectra to the frustrated translational (*T*) mode of the CO molecules parallel to the surface (*T* mode). The fits give energy losses of (3.60 ± 0.1) and (3.20 ± 0.1) meV

TABLE I. Comparison of HAS and TOF-ESDIAD measurements of the energy of the frustrated translation (T mode) of isolated CO molecules adsorbed in on-top sites on Cu(110).

	$E_{[1\bar{1}0]}$ (meV)	$E_{[001]}$ (meV)
TOF-ESDIAD (32 K)	4.9 $\pm$0.7	3.1 $\pm$0.5
HAS (40 K)	3.60$\pm$0.1	3.20$\pm$0.1
HAS (110 K)	3.75$\pm$0.1	3.40$\pm$0.1

along the $[1\bar{1}0]$ and the [001] directions, respectively, for the measurements at $T_s = 40$ K. A dispersion of the positions of the maxima with transferred wave vector could not be observed along either the [110] or the [001] directions, consistent with the presence of isolated CO-molecules behaving as Einstein-like oscillators.

Similar results for the T-mode energies were found for a sample temperature of $T_s = 110$ K. The TOF spectra corresponding to this temperature are presented in the right-hand panels of Fig. 2. Using the same fitting procedure as described above we find slightly larger energy losses of (3.75 $\pm$0.1) and (3.40$\pm$0.1) meV along the [110] and the [001] directions, respectively. This temperature-induced shift reveals a slight anharmonicity in the CO-substrate potential as discussed for the CO/Cu(001) system in detail in Ref. 19. Whereas the energies of the T modes in the two crystallographic directions differ only by about 10% there is a small difference in the corresponding widths of the losses which are significantly larger for the [001] direction.

The assignment to the T mode has been additionally confirmed along the [001] direction at $T_s = 110$ K by an experiment where an isolated CO structure was prepared using the heavy isotopomer $^{13}C^{18}O$. The corresponding TOF spectrum reveals now a T mode at an energy of 3.20 $\pm$0.1 meV. As has been discussed previously in more detail,[13,19] this isotope frequency ratio shift can be approximately expressed by the mass ratio factor $\sqrt{}(^{13}C^{18}O/^{12}C^{16}O) = 1.052$. This is in accordance with the measured ratio of $3.40/3.20 = 1.06$.

The HAS-TOF data for the CO T mode presented in this section are in accord with the T-mode energies of isolated CO molecules adsorbed on several flat and stepped copper surfaces compiled in Ref. 20. Whereas for the flat, close-packed Cu(111) and Cu(001) surfaces a T-mode energy of 4.0 meV was found, isolated CO molecules on the stepped Cu(211) and Cu(511) surfaces reveal T-mode energies between 3.0 and 3.1 meV. However, in these experiments a dependence of the T energy on the azimuthal direction was not observed.[20]

The comparison of the HAS measurements with the reported results of the TOF-ESDIAD pattern analysis as compiled in Table I is of interest, since the two methods are based on different physical principles. The HAS measurements directly determine the difference in energy between the vibrational ground state of the CO molecule and the lowest excited states, which are determined by the corresponding potential energy surface. In the present case the vibrations lowest in energy are two T modes, one polarized along [001] and the other along [110], see Fig. 3. Note, however, that for the present experimental geometry because of selection rules, of these two different T vibrations only the mode with the displacement vector along the respective azimuth can be seen. In the TOF-ESDIAD measurement, on the other hand, the trajectories of particles desorbing as a result of an electronic excitation are detected,[8,3] which in turn are determined by the orientation (tilt angle) and the lateral momentum of the adsorbed CO molecule. In a previous experiment[8] a pronounced elliptic shape of the ESDIAD pattern has been observed at low substrate temperatures ($T_s = 32$ K), with the longer axis along the [110] azimuth. By assuming that the lateral momentum of the CO molecule is essentially conserved in the desorption process the ESDIAD patterns were analyzed in the context of a simple model;[8] the resulting T-mode frequencies are listed in Table I.

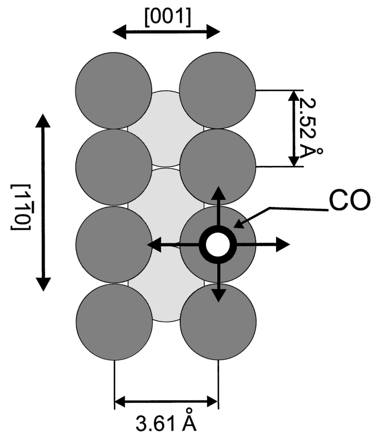

FIG. 3. Schematic diagram of the isolated CO molecule adsorbed on a Cu(110) surface. The two arrows denote the displacement vectors for the T modes polarized along the two different high-symmetry azimuths.

Both sets of data reveal an anisotropy in the T-mode energy with the T mode along [110] being higher in energy than that along [001]. Thus the HAS data provide an independent confirmation for the finding reported in Ref. 8 in that the anisotropy in the ESDIAD-desorption patterns is influenced by the momentum of the adsorbed particle and by the dynamic tilt angle of the adsorbed CO molecule. Despite the fact that along the [110] direction the value obtained from an analysis of the TOF-ESDIAD angular distributions and kinetic energies is larger than the corresponding HAS value, just outside the error bars, the present results reveal that TOF ESDIAD is a new, powerful tool in determining the two-dimensional lateral momentum distributions of adsorbed species. The remaining frequency differences (see Table I) are attributed to neglecting possible anisotropic final state effects on the measured angular distribution of the desorbing CO molecules in the analysis of the ESDIAD data (see Ref. 8 for a detailed discussion of the assumptions underlying the analysis).

The small (10%) but significant anisotropy seen for the T-mode of CO adsorbed in an on-top site appears to be the first case where a local anisotropy has been seen for a molecule chemisorbed in an on-top site. In previous work for isolated CO molecules adsorbed in on-top sites on a Ni(110) substrate no anisotropy could be seen.[4] Also in the case of N_2 adsorbed on the same surface, the difference in energy between the two different vibrations was too small to be detected.[5]

In conclusion the present data corroborate earlier findings obtained with TOF ESDIAD in that isolated CO molecules adsorbed in on-top sites of Cu(110) exhibit a significant azimuthal anisotropy of the frustrated translational (T) mode. Although the bonding between CO and a metal surface is one of the most extensively studied cases in surface chemistry, no thorough theoretical analysis for the T-mode frequencies is available. The present results indicate that the computation of an *ab initio* potential energy surface (from which the frequencies can be obtained in a straightforward fashion) would be highly desirable with regard to a detailed understanding of the different contributions to the bonding between CO and a metal surface.

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