Anomalous C-O Bond Weakening of Side-On–Bonded Carbon Monoxide on a Potassium-Promoted Ru(001) Surface

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The coadsorption of low coverages of CO and potassium ($\theta_K < 0.10$) on Ru(001) is characterized by a single adsorption state with a C-O stretching frequency of ~ 1460 cm^{-1}. Vibrational overtone spectroscopy and isotopic scrambling in thermal desorption reveal anomalously weak C-O bonds. Comparisons with metal carbonyls, molecularly adsorbed acetone, and oxygen on transition metals suggest a side-on–bonded molecule with its molecular axis parallel to or inclined towards the metal surface.

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Recent studies of the adsorption of carbon monoxide on metals precovered with small amounts of alkali metals ($\theta < 0.10$) have demonstrated that C-O stretch frequencies of the adsorbed molecule can shift with increasing alkali "promotion" from 2000 cm^{-1} to values as low as 1400 cm^{-1}.[1-3] Conventionally, C-O stretching frequencies in the range between 2000 and 1700 cm^{-1} can be understood in terms of different adsorption sites,[4] where for higher coordination (e.g., bridge) sites, increased back donation into antibonding $2\pi^*$ orbitals of carbon monoxide results in a weakening of the C-O bond and hence in lower C-O stretch frequencies. C-O stretches below 1600 cm^{-1}, however, are usually not observed for molecular CO adsorbed on metal surfaces and have but few analogs in carbonyl chemistry.[5] The object of this paper is to present data which show that the C-O bonds of these molecules are unusually weak and can be regarded as precursor states to dissociation similar to molecular oxygen adsorbed on Pt(111)[6,7] and Ag(110).[8] Furthermore, we conclude from our vibrational data and from comparisons with metal carbonyls and acetone-metal bonding that carbon monoxide is bonded side-on to the metal surface, i.e., with its molecular axis either parallel or inclined to the surface.

Experiments have been performed in a multilevel UHV system equipped for low-energy electron diffraction, Auger, multiple-mass thermal desorption, work-function measurements (Kelvin probe), and electron energy-loss spectroscopy (EELS). Potassium was evaporated from a commercial source (SAES getter) and carefully characterized for cleanliness and surface coverage with above methods.[9]

The potassium precoverage of $\theta_K = 0.10$ on Ru(001) selected here[10] is characterized by mutually repulsive and largely *ionic* potassium adatoms,[11] as evidenced by the large work-function decrease as well as by low-energy electron diffraction and thermal desorption measurements.[9] *Low exposures of CO* [0.25 L (Langmuir; 1 L = 10^{-6} Torr sec)] on this potassium-precovered surface result in thermal desorption (mass 28) in a desorption state shifted by 80 K to higher temperature compared to the same exposure on clean Ru(001) (see Fig. 1, inset). The vibrational spectrum in Fig. 1(a) shows a shift of the C-O stretching fundamental $\nu^{(1)}$ from 2000 cm^{-1} on clean Ru(001) to 1465 cm^{-1} on the potassium-promoted surface. That this frequency shift of the C-O fundamental actually implies an extremeley weak C-O bond can be convincingly demonstrated by the separation of the first overtone $\nu^{(2)}$ (2750 cm^{-1}) from the double loss $2\nu^{(1)}$ (2930 cm^{-1}) in Fig. 1(a). This results in an anharmonicity $\omega_e X_e = 90$ cm^{-1}, where $\omega_e X_e = (\nu^{(1)} - \nu^{(2)})/2$, which is discussed in more detail elsewhere.[12] The assignment of the 1465-cm^{-1} loss to a C-O stretch can be considered as unambiguous; isotopic replacement of $^{12}C^{16}O$ by $^{13}C^{18}O$ results in frequency shifts expected for C-O stretches.[9] Noticeable in the vibrational spectrum of Fig. 1(a) is the absence of any intense low-frequency modes, which can be ascribed to *M*-CO stretching or bending modes. The intense loss at 120 cm^{-1} can be assigned to a *M*-K stretch,[9] while the loss at 465 cm^{-1} is still present after annealing to 950 K [Fig. 1(b)], indicating adsorbed oxygen from a small amount of dissociated CO ($\theta_{\text{oxygen}} \sim 0.01$). The absence of an observable *M*-CO stretch is significant. Conventionally bonded CO, i.e., with its molecular axis perpendicular to the surface and carbon end down, is expected to have an intense *M*-CO stretch at 400 to 500 cm^{-1}. On the potassium-precovered surface only higher exposures of 1–2 L CO, which result in CO stretching frequencies at 1700–2000 cm^{-1}, exhibit larger intensities of the *M*-CO stretch.[9] Correspondingly, the thermal desorption states for these high CO

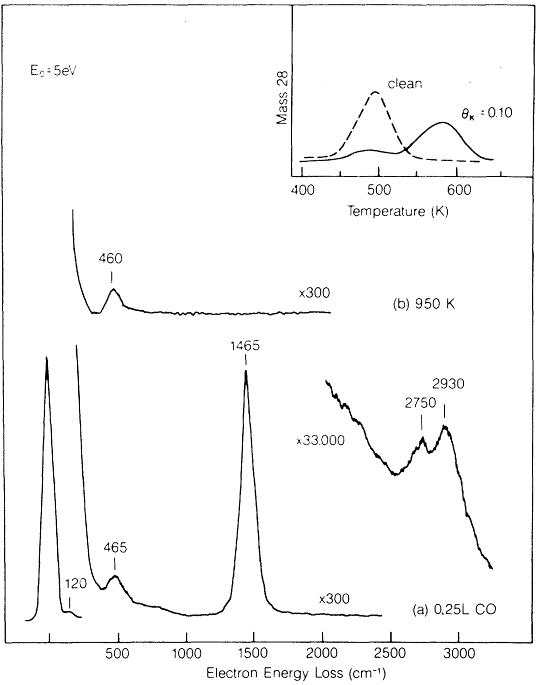

FIG. 1. Vibrational spectrum obtained with EELS for (a) 0.25 L CO adsorbed at 80 K on potassium-precovered Ru(001) ($\theta_K = 0.10$) with C-O stretch fundamental at 1465 cm^{-1} and its overtone at 2750 cm^{-1} well separated from the double loss at 2930 cm^{-1}; (b) same as in (a) after annealing to 950 K. The inset shows the CO thermal desorption spectrum obtained after exposure of 0.25 L CO to the potassium-precovered surface (solid line) and to the clean Ru(001) surface (broken line) for comparison.

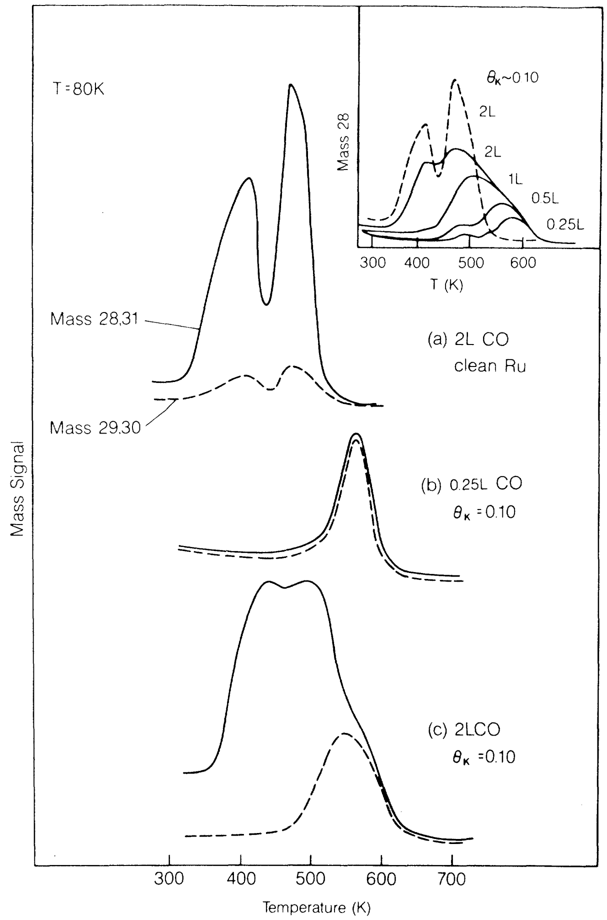

FIG. 2. Thermal desorption mass spectra of a $^{12}C^{16}O/^{13}C^{18}O$ mixture (1:1) with simultaneous monitoring of masses 28, 31 (solid line) and masses 29, 30 (broken line): (a) 2 L CO on clean Ru(001), (b) 0.25 L CO, and (c) 2 L CO on K/Ru(001), $\theta_K = 0.10$. The inset shows a sequence of increasing exposure of pure $^{12}C^{16}O$ on potassium-promoted Ru(001) (solid line) and, for comparison, 2 L CO on clean Ru(001) (broken line).

coverages are close in temperature to those obtained for the nonpromoted surface (see Fig. 2, inset). The fact that the CO adsorption states with C-O frequencies below 1700 cm^{-1} are due to a radically different adsorption state is further demonstrated by the observation of isotopic scrambling in thermal desorption shown in Fig. 2. There, the clean and potassium-promoted ruthenium surface has been exposed to a 1:1 mixture of $^{12}C^{16}O$ and $^{13}C^{18}O$. Simultaneous monitoring of masses 28 ($^{12}C^{16}O$), 29 ($^{13}C^{16}O$), 30 ($^{12}C^{18}O$), and 31 ($^{13}C^{18}O$) allows one to follow the desorption of the scrambled as well as the unscrambled molecules. As expected, an exposure of 2 L CO to *clean Ru(001) shows no scrambling* [Fig. 2(a)], whereas 0.25 L CO exposed to the *potassium-promoted surface results in complete isotopic scrambling* [Fig. 2(b)]. Significantly, a saturation exposure of 2 L CO to promoted Ru(001) exhibits only partial scrambling, indicating the presence of two chemically different CO species. A comparsion with our EELS data reveals that the *CO molecules which exhibit isotopic scrambling are characterized by C-O stretch frequencies below 1700 cm^{-1}*, thus confirming the vibrational data, which suggests highly weakened C-O bonds for this species.

It is clear that the low C-O stretch frequency, the absence (or low intensity) of *M*-CO modes, the strong anharmonicity of the CO potential well, and the isotopic scrambling cannot be explained in terms of a conventional, bridge-bonded CO oriented perpendicularly to the surface, as has been suggested earlier for potassium-promoted Pt(111) by Crowell, Garfunkel, and Somorjai.[1] We therefore postulate by comparison with metal carbonyls, as well as with molecularly adsorbed acetone and oxy-

TABLE I. Comparison of vibrational data for CO and O_2 in gas phase and adsorbed on metal surfaces with $\nu^{(1)}$ the fundamental stretching vibration; ν_{ad}/ν_{gas} the fundamental frequency shift of the adsorbed species with respect to gas phase; $\omega_e X_e$ and X_e the anharmonicity parameter as defined in the text; and D_0 the dissociation energy as determined from a Birge-Spohner plot (Ref. 7).

	$\nu^{(1)}$ (cm^{-1})	$\nu_{ad}^{(1)}/\nu_{gas}^{(1)}$	$\omega_e X_e$ (cm^{-1})	X_e	D_0 (eV)	Ref.
CO (gas phase)	2143		13	0.0060	11	5
CO/K/Ru(001)	1465	0.68	90	0.055	0.8	This work
O_2 (gas phase)	1556		12	0.0076	6.4	5
O_2/Pt(111)	875	0.56	52.5	0.053	0.56	7

gen on transition metals, a CO adsorption state in which the molecule is side on, presumably π bonded with its molecular axis either parallel to or strongly inclined towards the metal surface.

In *metal carbonyl* chemistry, only few complexes are reported where carbonyl ligands have C-O stretches below 1700 cm^{-1}. For example, carbonyl frequencies at 1620 cm^{-1} are found for cyclopentadienyl complexes $[(\pi\text{-}C_5H_5)M(CO)]_4$ of iron[13] and ruthenium.[14] These have been interpreted in terms of *conventional bridge bonding* of the carbonyl ligands, although no structural analysis was given to confirm this interpretation. The most relevant example of a side-on–bonded carbonyl group is that of the carbonylniobum cluster $(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_7$ where a C-O stretching frequency of 1330 cm^{-1} is observed.[15] From a detailed structural analysis, the corresponding carbonyl ligand was found to be for both carbon and oxygen atom within bonding distance of three niobium atoms such that carbon is threefold coordinated to all three metal atoms and oxygen twofold to two of them. This bonding mode, interpreted as evidence for the engagement of the carbonyl π system in the bonding, consequently leads to the low C-O stretching frequency of 1330 cm^{-1} and a dramatic lengthening of the C-O distance (1.30 Å) as compared to well-behaved terminal carbonyl groups (1.08–1.17 Å). An example of side-on–bonded CO on *metal surfaces* has been shown by Avery *et al.* [16] to exist for acetone molecularly adsorbed on Ru(001). There, side-on–bonded acetone produces a carbonyl stretching frequency at 1280 cm^{-1} compared to 1660 cm^{-1} of the end-on bonding mode.

The most significant analogy perhaps can be drawn to *molecular oxygen* adsorbed on Pt(111) because of a striking similarity of the vibrational data. This system has been well characterized by thermokinetic, structural, and vibrational studies, which suggest adsorption of oxygen with its molecular axis parallel to the surface[17] and a severely weakened O-O bond[18] leading to considerable bond lengthening[17] and potential-well anharmonicities.[19] We note also in this comparsion a similar low intensity of low-frequency modes assignable to M-O_2 or M-CO stretching and bending vibrations. The comparison of the vibrational values for these two molecules in Table I shows not only similar frequency shifts of the O-O and C-O stretch fundamentals from their gas-phase values (ν_{ad}/ν_{gas}) but also comparable anharmonicity parameters X_e. It is worth noting that *the bond anharmonicities for both systems predict far lower bond energies than estimated from bond-order versus fundamental-frequency relationships of diatomic molecules.*[7] The reason for this discrepancy can likely be found in the strong delocalization of the C-O or O-O stretching vibration, which is a result of the strong metal-molecule interactions. This will lead to large frequency shifts due to mechanical renormalization and vibrational coupling between the dipole and its image in the surface.[4] In addition, the vibrational motion will cause large charge fluctuations between metal and molecule as the molecular bond is shortening or lengthening,[20] thus accounting for the observed large dynamic dipole moment of the C-O stretch. A further consequence of this side-on–bonding mode should be a distinct change in the position and shift of the highest molecular orbitals of CO (4σ, 5σ, 1π, and $2\pi^*$). Unfortunately, no direct comparison with existing photoemission and Penning ionization data is possible at present because of the higher CO coverages in these experiments,[21,22] which do not allow isolation of this particular adsorption state.

Finally, we postulate that this side-on–bonding mode of CO is a *precursor state to CO dissociation.* Strong potential-well anharmonicities, as in the present case, are generally observed for predissociation states in gas-phase spectroscopy.[23] Furthermore, our isotopic scrambling data in Fig. 2 indicate that C-O bond breaking must have occurred prior to desorption. That such a dissociation process occurs preferentially for molecules in the side-on–bonding mode has been shown experimentally for metal carbonyls[24] and molecular oxygen adsorbed on Pt(111),[6] as well as predicted theoretically for CO adsorbed on nickel.[25,26]

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