SERS of CO₂ on Cold-Deposited Cu: An Electronic Effect at a Minority of Surface Sites

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We compare the results of surface enhanced Raman scattering (SERS) and infrared reflection absorption spectroscopy (IRRAS) of carbon dioxide (CO₂) on cold-deposited copper films. The SERS spectra of CO₂ on copper films deposited at 40 K display neutral species at SERS active sites with bands not observed by Raman spectroscopy of CO₂ gas, but identical to the loss bands of gaseous CO₂ in electron energy loss spectroscopy. The absence of one component of the Fermi doublet of CO₂ in SERS proves that the local electromagnetic field enhancement at SERS active sites cannot deliver signals above the noise level. The activated anionic CO₂⁻ is observed by transient electron transfer from the anionic molecule to the copper metal at a subgroup of SERS active sites, which are annealed below 200 K. The IRRAS spectra show only the expected infrared (IR) active modes of neutral CO₂ representing the “majority species” of adsorbed CO₂.

I. Introduction

SERS is a surface optical effect known since more than 25 years; see the geminating bibliography by Chang and Furtak. The discussion on the electronic contribution by transient charge transfer is still controversial, whereas the enhancement by increased local electromagnetic (EM) field in plasmonic resonances is generally accepted. At metal surfaces in ultrahigh vacuum, it is hard to prove the involvement of transient charge transfer effects. This is more easily achieved at electrode surfaces because the electrode potential can be varied, thus shifting the electronic levels of an adsorbed molecule with respect to the Fermi level in the electrode. The usual method of Raman excitation profiles cannot differentiate with certainty between plasmonic resonances and the electronic contribution to SERS.

For CO₂ however, the vibrational selectivity of SERS provides clear evidence for an electronic mechanism. Here we discuss previous SERS results in a new way using recent electron energy loss and infrared spectroscopic results.

II. Discussion

At first glance, one would expect nothing exciting for the neutral linear molecule O=C=O. For gas phase CO₂, infrared spectroscopy yields the double generate O=C=O bending mode and Raman spectroscopy yields only the Fermi resonance doublet composed by the symmetric C=O stretch vibration and the second harmonic O=C=O bending mode. The lower frequency component (in gas phase at 1286 cm⁻¹) will be denoted FRI and the higher frequency component (in gas phase at 1388 cm⁻¹) FRII. The IRRAS spectrum of CO₂ adsorbed on cold-deposited Cu films in the upper part of Figure 1 displays a splitting of the double degenerate bending mode and the antisymmetric stretch mode with nonsymmetric line shape depending on exposure, probably reflecting the disordered Cu surface. The broad structure near 2100 cm⁻¹ is caused by CO contamination.

The SERS results and the assignment of the bands to neutral and anionic CO₂⁻ on the substrates sapphire, potassium, cold-deposited copper, and cold-deposited copper annealed at 200 K have been described extensively in ref 10; see also the Supporting Information.

Figure 2 shows spectra and integrated band intensities as a function of exposure in the range of the Fermi resonance and the bending mode. The anionic CO₂⁻ species have a higher bonding enthalpy to the copper surface than the neutral species; hence, the bands of the anionic species have higher intensity at low exposures, see Figure 2b. All bands including FRII are broad and asymmetric, probably caused by strong electronic damping of the internal vibrations of CO₂ at SERS active sites. Possibly the weak broad structure at about 1267 cm⁻¹ (see Figures 1 and 2a) is the FRI band. Only at an exposure of 20
L also narrow bands of FRI at 1275 cm\(^{-1}\) and FRII at 1382 cm\(^{-1}\) appear, in close agreement with the Fermi doublet of CO\(_2\) condensed on sapphire.

At the time of publication,\(^{10,11}\) it was not clear why only the higher component FII of the Fermi resonance appeared strongly and why the Raman forbidden bending mode was observed. Now a consistent electronic enhancement mechanism is indicated by comparison with the inelastic cross sections of electron scattering by gaseous CO\(_2\) in the energy range of 0 - 5 eV, including the \(2\Pi_u\) shape resonance at 2 - 5 eV\(^{12,13,16}\) and the so-called virtual state \(2\Sigma\) of anionic CO\(_2^-\) below 1 eV\(^{17}\) in Figure 3.

The cross sections of the Fermi doublet components below 1 eV display at decreasing electron energy an increase for FRII with and a negligible contribution of FRI. This experimental result in Figure 3 has been corroborated by theory.\(^{17}\) The selection rules in the \(2\Pi_u\) shape resonance and the virtual state \(2\Sigma\) forbid the excitation of the antisymmetric stretch mode. The relatively strong cross section of the antisymmetric stretch mode \(\nu_s(CO_2^-)\) at low electron energies is probably caused by a comparatively long-range electron interaction with the dynamic electric dipole of the antisymmetric stretch mode. This interaction will be shielded at the surface. The SERS spectra can easily be explained with the electronic energy scheme in Figure 4.

The value of about 3.5 eV of the Coulomb relaxation in Figure 4 has been inferred from two-photon-emission spectroscopy\(^{18}\) of CO on Cu(111) and the resonant low energy electron scattering in CO gas.\(^{19}\)

Within the coherent Raman process the “hot electron” created by laser photon annihilation will temporarily occupy the virtual state \(\Sigma\) of the directly adsorbed CO\(_2\) species and excite the various vibrational bands according to the cross sections in Figure 3 at energies below 0.5 eV. These are the bending mode

and the higher frequency mode FRII. This explains the SERS spectrum of CO\(_2\) on Cu in Figure 1, especially the observation of the bending mode which is not Raman active for free CO\(_2\) and of only the higher frequency band FII of the Fermi dyad. If the transient formation of anionic CO\(_2^-\) did not exist, strong EM enhancement should show both FRI and FRII. But the near absence of the FRI component in SERS (indicated as “hot electron”) is the Fermi energy plus laser photon energy of 1.92 eV. All energies are up to scale.

The SERS spectrum of CO\(_2\) on Cu films cold-condensed at 40 K (Figure 1) contains a second couple of lines, which coincide with the positions of the CO\(_2^-\) bands observed on
potassium, see the Supporting Information. These bands indicate the existence of the bent form of anionic CO$_2^-$, now permanently charged with one electron.$^{21}$ The bending and symmetric stretching mode of the anionic form are observed by the transient transfer of the extra electron from CO$_2$ to the metal, because these two nuclear motions are involved in the configurational change toward the linear molecular form of neutral CO$_2$. This direction of photoinduced charge transfer is similar to the mechanism found in SERS of CN$^-$ on silver electrodes.$^{7,8}$ When a cold-deposited Cu film, cryocondensed at 40 K, annealed at 200 K, and recooled to 40 K, is exposed to CO$_2$, then the anionic CO$_2^-$ is no more observed, only the bending modes and FRII of neutral CO$_2$ persist. Apparently, the adsorption sites on Cu where CO$_2$ is activated to its anionic shape are annealed below 200 K. Apparently, these “chemically active sites” form a subgroup of the “SERS active sites”.$^{22}$ The fact, that the infrared active bending and symmetric stretch modes of anionic CO$_2$ is not observed in IRRAS (see Figure 1) corroborates the assignment of the bonding of these two nuclear motions are involved in the configurational change toward the linear molecular form of neutral CO$_2$. This resembles the case of NO exposure of cold-deposited Cu: SERS provides high spectroscopic sensitivity and is focusing on the “chemical active sites” covered with N$_2$, N$_2$O, O$_{ads}$, but shows no NO, whereas with IRRAS only adsorbed NO was observed.

III. Conclusions

All spectral SERS features of neutral CO$_2$ on SERS active sites of cold-deposited Cu involve transient electron transfer from Cu to CO$_2$, leading to a temporary virtual $^3\Sigma$ state of anionic CO$_2$. This can be proven by a comparison of the SERS spectra with low electron energy loss spectra of gaseous CO$_2$. The EM enhancement alone may deliver very weak Raman signals from species not adsorbed at SERS active sites, but this is not certain. On Cu films deposited at 40 K also a stable form of anionic CO$_2^-$ is observed by SERS, involving transient electron transfer from anionic CO$_2^-$ to Cu. The adsorption sites of the stable anionic CO$_2$ are lost by annealing the film to 200 K, whereas SERS of neutral CO$_2$ is still observed after recoiling to 40 K (see the supporting material). IRRAS observes the infrared active modes of the majority species of neutral CO$_2$ adsorbed on cold-deposited Cu, whereas SERS is focusing on a minority of surface sites on the atomically rough Cu surface.

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Supporting Information Available: SERS spectra of CO$_2$ on potassium, nonannealed and annealed cold-deposited Cu with assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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