Response to the comment by C.T. Campbell on: Interaction of carbon dioxide with clean and oxygenated Cu(110) surfaces, by T. Schneider and W. Hirschwald [1]

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We should like to make clear in the following, that the observed CO desorption following CO_2 adsorption at 85 K is not an experimental artefact, but due to CO_2 interaction with the Cu(110) surface.

In his comment Campbell alleges two possible sources of CO adsorption: first, the possibility of impurities in the adsorbed CO_2 (mass 48) and second, dissociation on hot filaments or other active surfaces. In the adsorbing gas we detected no other impurities than the molecules of mass 46 and 44, due to $C^{18}O^{16}O$ and $C^{16}O_2$, respectively.

The amount of CO *adsorption* due to CO_2 exposures of 400 and 50 L was experimentally determined by exposing CO_2 at temperatures well above its desorption peak (100 K) and well below the CO peak (220 K), e.g. at 150 K. It was found to be less than 10% at 400 L and less than 5% at 50 L of the CO coverage due to CO_2 adsorption and interaction at 85 K. All CO desorption spectra following CO_2 adsorption at 85 K were corrected for these contributions during the computational routine.

Further experimental evidence of CO_2 dissociation is the development of the known (2×1) LEED structure of the oxygenated Cu(110) surface, induced by adsorption of CO_2 at 85 K and subsequent heating to 300 K, which is higher than the CO desorption temperature. Additionally it was confirmed by AES, that the only remaining species at the surface was oxygen.

As already referred to in ref. [1], the main difference between the experimental conditions of our and Campbell's study was the adsorption temperature (85 K versus 110 K, with the CO_2 desorption peak maximum at 100 K). We agree with Campbell, that sticking coefficients should not be different by several orders of magnitude. But as the peak maximum of molecular CO_2 desorption appears at 100 K, the resulting CO_2 coverages differ strongly ($\theta_{CO_2} \approx 0.13$ at 85 K and 5×10^{-8} mbar, from isotherms, recently measured [2]).

We admit, that an influence of defects cannot be excluded, as our measurements are performed with high sensitivity (differentially pumped and shielded mass spectrometer) at rather low coverages ($\theta \approx 0.001-0.1$). If dissociation occurs at a small amount of more active sites of the Cu(110) surface like kinks, steps, vacancies or others, weakly bonded, adsorbed CO_2 could diffuse to and subsequently dissociate at these sites.

That CO_2 dissociation is possible on the stepped Cu(311) surface was demonstrated recently by Fu and Somorjai [3]. Otto et al. [4] confirmed both the occurrence of adsorbed CO_2 and a bent $CO_2^{\delta-}$ species (assumed precursor to dissociation) on rough copper films even at 40 K.

The facts given above: (a) adsorption below the temperature of the desorption peak maximum, (b) possible influence of defects and (c) detection of small coverages with high sensitivity, might explain the differences between our results and Campbells observations and reconcile them to a certain degree.

Our statement, that CO_2 exhibits nearly 100% dissociation on the clean Cu(110) surface, is valid only for very small total coverages ($\theta \lesssim 0.005$). According to equilibrium measurements [2] the amount of molecularly adsorbed CO_2 is much higher and the percentage of dissociation correspondingly diminishes.

References

[1] T. Schneider and W. Hirschwald, Catal. Lett. 14 (1992) 197.
[2] K.H. Ernst, K. Christmann and D. Schlatterbeck, unpublished.
[3] S.S. Fu and G.A. Somorjai, Surf. Sci. 262 (1992) 68.
[4] D. Diesing, W. Akemann and A. Otto, Proc. DPG-Tagung (VI) 27 Regensburg (1992) 871.

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