Supplementary materials

O K^{-1} main line/shake-up ratio in CO_2

We report the experimental O K^{-1} spectra of the CO_2 molecule recorded at a photon energy of 625 eV. Intensity ratio between main and shake-up lines are estimated. Note that for the shake-up region, one should not associate a given fit function with a unique shake-up transition (see for example the fit function labeled "0" which clearly accounts for more than one shake-up line).

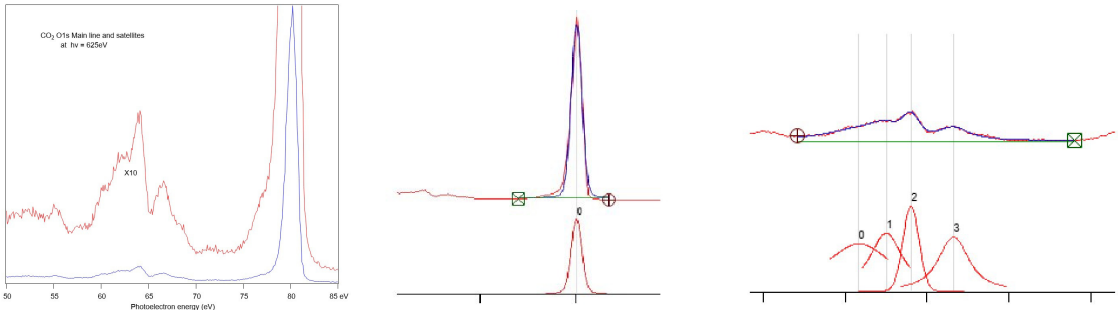

FIG. 1: Left: Experimental O K^{-1} spectrum of CO_2 recorded for a photon energy of 625 eV. Center: Experimental and Voigt fit of the main peak of the O K^{-1} spectrum of CO_2. Right: Experimental and Voigt fit of the main shake-up region of the O K^{-1} spectrum of CO_2.

TABLE I: Area of the functions used to fit the O K^{-1} spectrum of CO_2

	Main line	Peak 0	Peak 1	Peak 2	Peak 3
Area	55031	5825.4	3364.2	1609.6	2725.5
Area ratio (with respect to main line)	1.0	0.106	0.061	0.029	0.049

Vibrational profile of the main peak of the C K^{-1} spectrum of CO

We applied the computational approach described in the main body of the paper to compute the vibrational profile associated with the main peak of the C K^{-1} spectrum of CO. The computed profile is in very good agrement with the experimental one despite a slight overestimation of the Franck-Condon width due to the harmonic approximation.

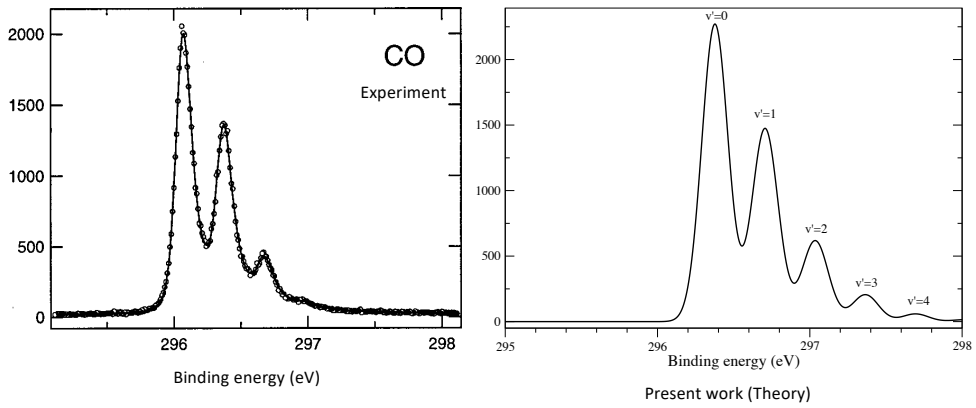

FIG. 2: Left: Experimental vibrational profile of the main peak of the C K^{-1} spectrum of CO (extracted from Ref. [T. Darrah-Thomas, *et. al.*, J. Chem. Phys 118, 10221 (2002)]) Right: Vibrational profile of the main peak of the C K^{-1} spectrum of CO computed using the computational method presented in the main body of the paper.