Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The O $K^{-2}V$ spectrum of CO: the influence of the second core-hole

Supplementary information

D. Koulentianos[a,b,c], S. Carniato[a], R. Püttner[d], J.B. Martins[a], O. Travnikova[a,e], T. Marchenko[a,e], L. Journel[a,e], R. Guillemin[a,e], I. Ismail[a,e], D. Céolin[e], M.N. Piancastelli[a,f], R. Feifel[b], and M. Simon[a,e]

[a]Sorbonne Université, CNRS, Laboratoire de Chimie Physique-Matière et Rayonnement, F-75005 Paris Cedex 05, France
[b]Department of Physics, University of Gothenburg, Origovägen 6B, SE-412 96 Gothenburg, Sweden
[c]Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S Cass Avenue, Lemont, IL 60439, United States of America
[d]Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany
[e]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette Cedex, France
[f]Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden

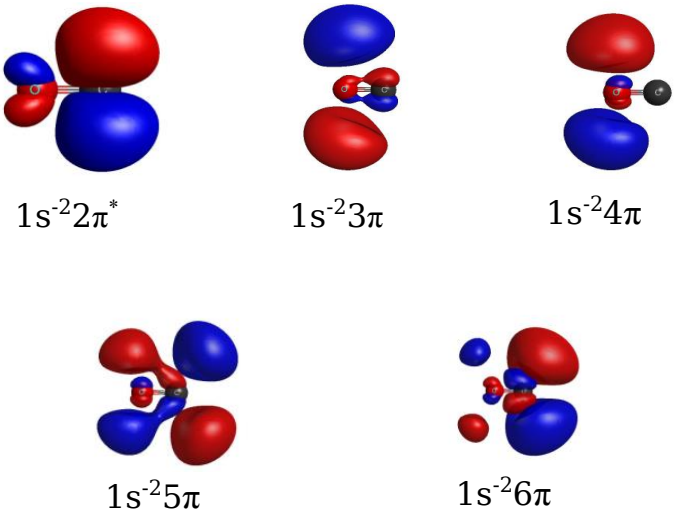

Figure S1: Density plots of the main K^{-2} Hartree-Fock molecular orbitals of Π symmetry, used as initial guess for configuration interaction calculations.

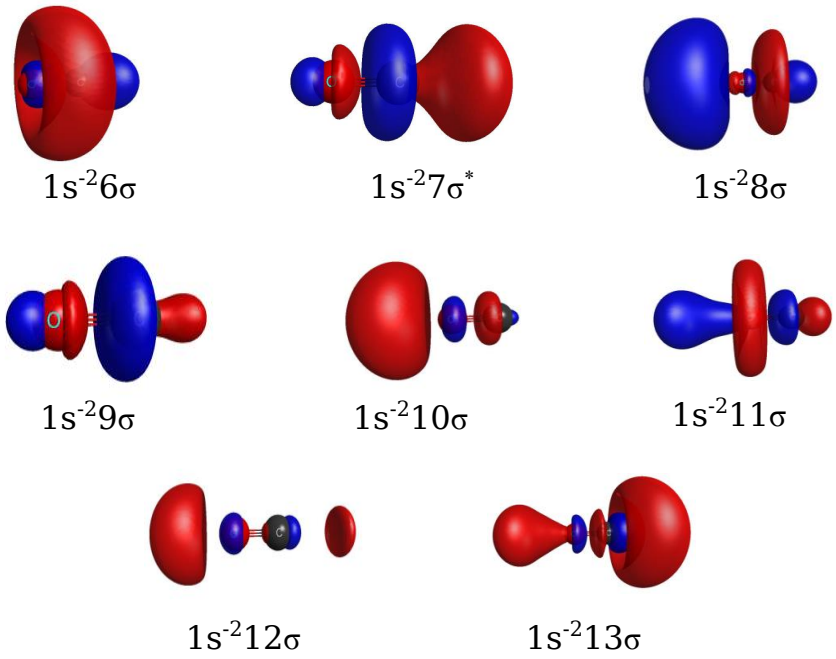

Figure S2: Density plots of the main K^{-2} Hartree-Fock molecular orbitals of Σ symmetry, used as initial guess for configuration interaction calculations.

Table S1: A comparison of the experimentally measured binding energies, $E_{bin,exp}$, with the theoretically predicted values, $E_{bin,theo}$, in a CI level of theory, after a shift of 2.2 eV has been applied to the latter, so that the experimental and theoretical binding energy values for the $K^{-2}2\pi^*$ transition are the same. For each transition the distributions of the dominant configurations, the path of excitation and the theoretical relative intensities are also given. For the paths C and D indicate conjugate and direct shake, respectively. Captial letters indicate strong contributions and small letters minor contributions. If only one letter is given only one processes is possible based on symmetry arguments. The notations π and π' have been used to denote degenerate MOs, which are perpendicular to each other, like π_x and π_y.

Region	$E_{bin,exp}$ (eV)	Label	$E_{bin,theo}$ (eV)	Main configurations	Path	Relative intensities
I	1156.0	$1(^2\Pi)$	1156.0*	$0.96\ 1s^{-2}2\pi^{*1}$	C	1.00
II	1166.0	$1(^2\Sigma^+)$	1165.80	$0.88\ 1s^{-2}6\sigma^1$+0.22 $1s^{-2}7\sigma^{*1}$ +0.20 $1s^{-2}5\sigma^{-1}2\pi^{*2}$ + 0.20 $1s^{-2}5\sigma^{-1}2\pi'^{*2}$)	D/c	1.86
		$2(^2\Sigma^+)$	1166.17	$0.68(1s^{-2}5\sigma^{-1}2\pi^{*2})$ - $0.68(1s^{-2}5\sigma^{-1}2\pi'^{*2})$	–	0
		$3(^2\Sigma^+)$	1167.14	-0.38($1s^{-2}6\sigma^1$) + 0.53($1s^{-2}7\sigma^{*1}$) - 0.16($1s^{-2}8\sigma^1$) -0.48($1s^{-2}5\sigma^{-1}2\pi^{*2}$)- 0.48($1s^{-2}5\sigma^{-1}2\pi'^{*2}$)	C/d	0.20
III	1168.5	$2(^2\Pi)$	1168.40	$0.96(1s^{-2}3\pi^1)$	C	0.11
		$4(^2\Sigma^+)$	1169.11	-0.75($1s^{-2}7\sigma^{*1}$) - 0.42($1s^{-2}5\sigma^{-1}2\pi^{*2}$) - 0.42($1s^{-2}5\sigma^{-1}2\pi'^{*2}$)	D/C	0.58
		$5(^2\Sigma^+)$	1169.57	-0.93($1s^{-2}8\sigma^1$)	C	0.33
IV	1172.2	$6(^2\Sigma^+)$	1171.91	-0.92($1s^{-2}9\sigma^1$)	D/c	0.19
		$3(^2\Pi)$	1172.07	$0.96(1s^{-2}4\pi^1)$	C	0.13
		$7(^2\Sigma^+)$	1172.58	-0.94($1s^{-2}10\sigma^1$)	D/c	0.26
		$4(^2\Pi)$	1173.45	-0.84($1s^{-2}5\pi^1$) + 0.42($1s^{-2}6\pi^1$)	D/C	0.13
		$8(^2\Sigma^+)$	1173.48	$0.91(1s^{-2}11\sigma^1)$	C	0.14
		$9(^2\Sigma^+)$	1174.08	$0.95(1s^{-2}12\sigma^1)$	D/c	0.14
		$5(^2\Pi)$	1174.52	-0.44($1s^{-2}5\pi^1$) - 0.82($1s^{-2}6\pi^1$)	C	0.04
		$10(^2\Sigma^+)$	1174.71	$0.93(1s^{-2}13\sigma^1)$	D/C	0.08
V	1180.0	$6(^2\Pi)$	1182.60	-0.60($1s^{-2}1\pi^{-1}2\pi^{*2}$) - 0.45($1s^{-2}1\pi^{-1}2\pi'^{*2}$) - 0.15($1s^{-2}1\pi'^{-1}2\pi^{*1}2\pi'^{*1}$) - 0.21($1s^{-2}1\pi'^{-1}2\pi^{*1}2\pi'^{*1}$) +0.19($1s^{-2}5\sigma^{-1}2\pi^{*1}8\sigma^1$) - 0.32($1s^{-2}5\sigma^{-1}2\pi^{*1}13\sigma^1$)	C	
VI	1188.0	$11(^2\Sigma^+)$	1187.20	-0.63($1s^{-2}1\pi^{-1}2\pi^{*1}6\sigma^1$) - 0.63($1s^{-2}1\pi'^{-1}2\pi'^{*1}6\sigma^1$) +0.15($1s^{-2}1\pi^{-1}2\pi^{*1}8\sigma^1$) +0.15($1s^{-2}1\pi'^{-1}2\pi'^{*1}8\sigma^1$)	D	
		$12(^2\Sigma^+)$	1189.03	0.28($1s^{-2}1\pi^{-1}2\pi^{*1}6\sigma^1$) + 0.28($1s^{-2}1\pi'^{-1}2\pi'^{*1}6\sigma^1$) +0.23($1s^{-2}5\sigma^{-1}2\pi^{*1}7\pi^1$) + 0.23($1s^{-2}5\sigma^{-1}2\pi'^{*1}7\pi'^1$) +0.24($1s^{-2}5\sigma^{-1}6\sigma^1 7\sigma^{*1}$) + 0.39($1s^{-2}5\sigma^{-1}6\sigma^1 8\sigma^1$) -0.19($1s^{-2}5\sigma^{-1}7\sigma^{*1}8\sigma^1$) + 0.19($1s^{-2}5\sigma^{-1}7\sigma^{*2}$) - 0.26($1s^{-2}5\sigma^{-1}8\sigma^2$) -0.27($1s^{-2}5\sigma^{-2}2\pi^{*2}8\sigma^1$) - 0.27($1s^{-2}5\sigma^{-2}2\pi'^{*2}8\sigma^1$)	D	
		$13(^2\Sigma^+)$	1190.65	0.29($1s^{-2}1\pi^{-1}2\pi^{*1}6\sigma^1$) +0.29($1s^{-2}1\pi'^{-1}2\pi'^{*1}6\sigma^1$) - 0.18($1s^{-2}1\pi^{-1}2\pi^{*1}7\sigma^{*1}$) - 0.18($1s^{-2}1\pi'^{-1}2\pi'^{*1}7\sigma^{*1}$) -0.15($1s^{-2}1\pi^{-1}2\pi^{*1}7\sigma^{*1}$) -0.15($1s^{-2}1\pi'^{-1}2\pi'^{*1}7\sigma^{*1}$) + 0.24($1s^{-2}1\pi^{-1}2\pi^{*1}8\sigma^1$) + 0.24($1s^{-2}1\pi'^{-1}2\pi'^{*1}8\sigma^1$) -0.50($1s^{-2}5\sigma^{-1}6\sigma^1 7\sigma^{*1}$) + 0.24($1s^{-2}5\sigma^{-1}6\sigma^2$)	D	

Table S2: Theoretical results obtained in a HF level of theory showing the initial MOs used as initial guess for the previously reported CI calculations. The assignments of the final $K^{-2}V$ states in single photon transition from the ground molecular state are given in the first column, while the second column describes he main contribution to the final molecular state. Values of the orbitals' mean radius square, the theoretically predicted term value (TV) of the transitions and effective quantum number (n^*) are also given. The atomic orbital character of the different MOs occupied upon core-excitation is given in the six last columns.

Configuration	Main character	$\sqrt{\langle r^2 \rangle}$ (Å)	TV (eV)	n^*	O			C		
					s	p	d	s	p	d
Valence zone (n = 2)										
$1s^{-2}2\pi^*$	$1s^{-2}2\pi_C$	1.44			0.00	0.08	0.12	0.00	0.79	0.01
$1s^{-2}7\sigma^*$	$1s^{-2}2sp_O/2p_C$	3.02			0.31	0.29	0.03	0.07	0.25	0.06
Rydberg zone (n = 3)										
$1s^{-2}6\sigma$	$1s^{-2}(3s_O/3p_C)$	2.07	11.24	2.20	0.70	0.06	0.04	0.03	0.18	0.05
$1s^{-2}3\pi$	$1s^{-2}3p\pi_O$	2.66	7.92	2.62	0.00	0.86	0.02	0.00	0.11	0.00
$1s^{-2}8\sigma$	$1s^{-2}3p\sigma_O$	2.62	8.02	2.61	0.09	0.71	0.03	0.07	0.25	0.06
Rydberg zone (n = 4)										
$1s^{-2}9\sigma$	$1s^{-2}4s_O$	4.98	4.60	3.44	0.80	0.05	0.06	0.04	0.04	0.02
$1s^{-2}4\pi$	$1s^{-2}4p\pi_O$	5.01	4.34	3.54	0.00	0.96	0.02	0.00	0.00	0.02
$1s^{-2}10\sigma$	$1s^{-2}4p\sigma_O$	5.24	4.17	3.61	0.09	0.84	0.05	0.01	0.01	0.00
$1s^{-2}6\pi$	$1s^{-2}4pd\pi_O/p\pi_C$	5.24			0.00	0.33	0.14	0.00	0.47	0.06
$1s^{-2}13\sigma$	$1s^{-2}4p\sigma_O/3d_{z^2O}/p\sigma_C$	5.29			0.12	0.30	0.16	0.06	0.36	0.01
Rydberg zone (n = 5)										
$1s^{-2}11\sigma$	$1s^{-2}5spd\sigma_O$	6.66	4.63	3.98	0.50	0.19	0.17	0.01	0.12	0.01
$1s^{-2}5\pi$	$1s^{-2}5p\pi_O$	7.74	2.86	4.36	0.00	0.82	0.06	0.00	0.08	0.04
$1s^{-2}12\sigma$	$1s^{-2}5sp\sigma_O$	8.08			0.37	0.60	0.01	0.00	0.02	0.00

Table S3: The different $K^{-2}V$ configurations at each spectral region, along with the main character for each of them are tabulated in the second and third column respectively. Theoretical binding energy values calculated at the DFT/B3LYP level of theory, for the different core-ionized core-excited states are given in the fourth column. For the estimation of TVs in the fifth column, the theoretical value of the K^{-2} threshold, given in the last row, has been used. The gradients of the PECs corresponding to the different final states are given in the seventh column and have been used to estimate the FHWM of each spectral feature, in the same way like for Region I (see main text for details).

			DFT/B3LYP (single point)													
Region	Configuration	Main character	Binding energy	TV	$\sqrt{\langle r^2 \rangle}$	Gradient	FWHM	n^*	TV[†]	O			C		
			(eV)	(eV)	(Å)	(eV/Å)	(eV)		(eV)	s	p	d	s	p	d
I	$1s^{-2}2\pi^*$	$1s^{-2}2\pi^*_C$	1153.80	21.04	1.41	−33.2	1.86	-	-	0.00	0.08	0.11	0.00	0.81	0.00
II	$1s^{-2}6\sigma$	$1s^{-2}(3s_O/3p_C)$	1163.44	11.40	1.85	−40.6	2.27	2.08	12.57	0.51	0.03	0.04	0.01	0.32	0.09
III	$1s^{-2}7\sigma^*$	$1s^{-2}(2sp\sigma_O/2p_C)$	1165.56	9.28	2.40	−48.2	2.70	2.38	9.60	0.49	0.14	0.06	0.08	0.16	0.08
	$1s^{-2}3\pi$	$1s^{-2}3p\pi_O$	1166.25	8.59	2.49	−22.6	1.27	2.55	8.40	0.00	0.84	0.02	0.00	0.14	0.00
	$1s^{-2}8\sigma$	$1s^{-2}3p\sigma_O$	1167.16	7.68	2.83	−25.0	1.40	2.70	7.46	0.07	0.81	0.02	0.03	0.06	0.01
IV	$1s^{-2}9\sigma$	$1s^{-2}4s_O/3d_{z^2_O}$	1169.22	5.62	3.79	−33.5	1.88	3.00	6.04	0.50	0.12	0.22	0.03	0.13	0.00
	$1s^{-2}4p\pi$	$1s^{-2}4p\pi_O$	1169.94	4.90	4.41	−25.0	1.40	3.33	4.91	0.00	0.90	0.04	0.00	0.01	0.05
	$1s^{-2}10\sigma$	$1s^{-2}4sp\sigma_O$	1170.22	4.62	4.47	−24.8	1.39	3.25	5.15	0.52	0.36	0.05	0.00	0.06	0.00
	$1s^{-2}11\sigma$	$1s^{-2}5sp\sigma_O$	1171.01	3.83	6.25	−27.9	1.56	3.85	3.67	0.34	0.40	0.05	0.02	0.19	0.00
	$1s^{-2}12\sigma$	$1s^{-2}5sp\sigma_O$	1171.84	3.00	7.11	−25.5	1.43	4.11	3.22	0.75	0.18	0.00	0.02	0.04	0.00
	$1s^{-2}13\sigma$	$1s^{-2}5sp\sigma_O$	1172.34	2.50	7.80	−27.1	1.52	4.38	2.84	0.15	0.65	0.01	0.05	0.13	0.00
	$1s^{-2}5p\pi$	$1s^{-2}5p\pi_O$	1171.96	2.88	8.62	−25.6	1.44	4.60	2.58	0.00	0.94	0.01	0.00	0.05	0.00
V	$1s^{-2}$	-	Exp.: 1178.0 ± 0.8 Theory: 1174.84	-	-	−26.45	1.48	-	-	-	-	-	-	-	-

[†] TV estimated from $13.6 \cdot \frac{Z^{*2}}{n^{*2}}$, for $Z^* = 2$.