

NEXAFS and MS-AES spectroscopy of the C 1s and Cl 2p excitation and ionization of chlorobenzene: production of dicationic species.

Supporting Information

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Complementary TDDFT calculations have been performed at the carbon *K*-edge of chlorobenzene to compare with the RASPT2 results. The resulting spectrum is shown in Figure S1 vis-à-vis with the RASPT2 one. The TDDFT calculations were performed with the Turbomole program package¹ using the hybrid functional B3-LYP² and Aldrich's def2-TZVPP basis set³. The computational details of the RASPT2 calculation are given in the main manuscript. The resulting TDDFT excitation energies and oscillator strengths are collected in Table S1.

The two calculations show different number of states contributing to the first band in the experimental spectrum. The dominant orbital compositions for the first three states obtained with TDDFT are given in Table S2. The TDDFT orbitals are plotted in Table S3.

Notice that, according to the RASPT2 calculation, the dominant composition of the two states obtained at 285.68 and 285.95 eV mix the first TDDFT state, dominated by the $5a_1 \rightarrow 5b_2$ transition, with the following ones dominated by the $2b_1 \rightarrow 2a_2$ and $1b_1 \rightarrow 2a_2$ transitions. The mixture of these three states into two electronic states, as obtained in the RASPT2 calculation, could be causing an overestimated splitting of 0.27 eV between the first two RASPT2 states. We believe that the inclusion of a full valence active space into the RAS2 space, for example, would prevent such mixing of states. However, a full valence active space for chlorobenzene, which has 58 electrons is impractical for a RASPT2 calculation using a large basis set.

Another difference between RASPT2 and TDDFT is on the spectral band labeled **C** in Figure S1. RASPT2 shows a distinct peak at 287.46 eV assigned to $5a_1 \rightarrow 16a_1$ (σ^*) (see Table 1 on the main text) whereas TDDFT shows a few weak peaks in the region between 276.2 and 276.8 eV, being the state $1b_1 \rightarrow 16a_1$ (σ^*) the most intense in this region, with oscillator strength 0.0085 (peak **C** in Table S1). It is noteworthy that the transition $5a_1 \rightarrow 16a_1$ is also found in the TDDFT spectrum very close to the $1b_1 \rightarrow 16a_1$ state, with energy 276.41 eV and oscillator strength 0.0003.

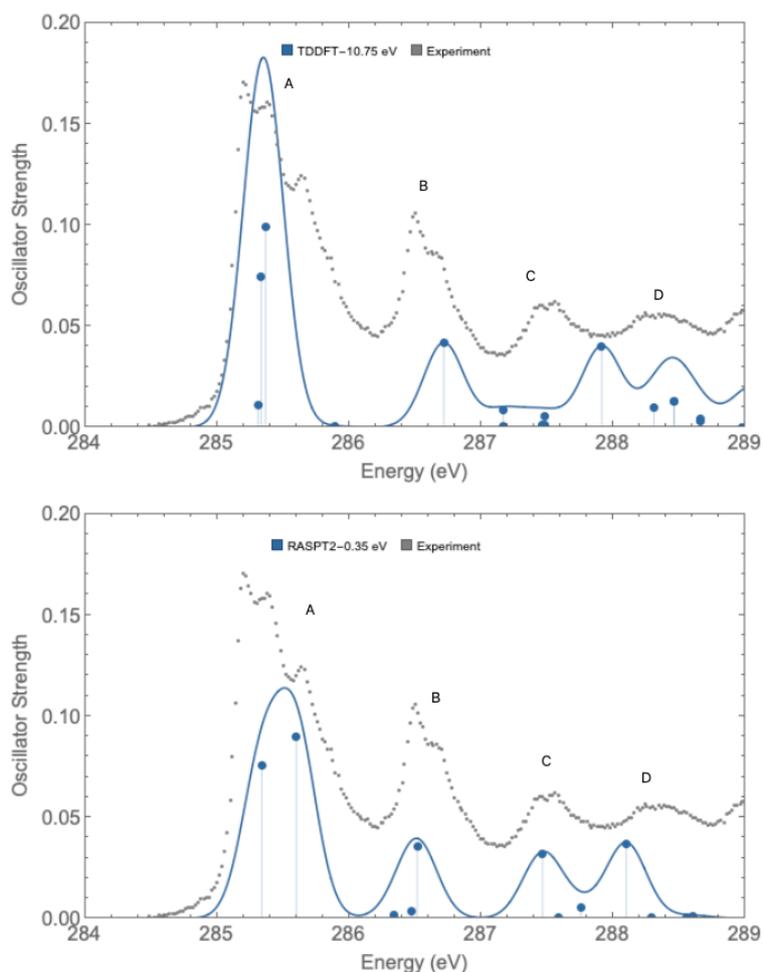


Figure S1. TDDFT (top panel) and RASPT2 (bottom panel) spectra of chlorobenzene. The energies have been shifted by the amount indicated in the legend to align with the center of band **A** of the experiment.

Structure	Energy (eV)	Oscillator Strength	Assignment (Dominant contribution only)
A	274.56	0.0111	$5a_1 \rightarrow 5b_2 (\pi^*)$
A	274.58	0.0742	$2b_1 \rightarrow 2a_2 (\pi^*)$
A	274.61	0.0987	$1b_1 \rightarrow 2a_2 (\pi^*)$
B	275.97	0.0417	$2a_1 \rightarrow 5b_2 (\pi^*)$
C	276.42	0.0085	$1b_1 \rightarrow 16a_1 (\sigma^*)$
D	277.16	0.0398	$2a_1 \rightarrow 16a_1 (\sigma^*)$

Table S1. TDDFT C 1s excitation energies and oscillator strengths.

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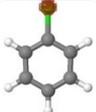
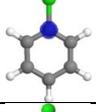
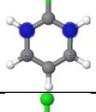
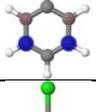
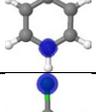
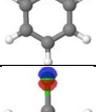
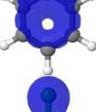
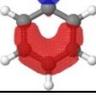
Dominant contributions: 274.58 eV
occ. orbital  virt. orbital  |coeff.|^2
  5 a1         5 b2         87.1
  2 b1         2 a2          5.6

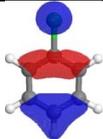
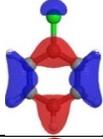
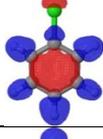
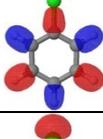
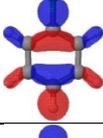
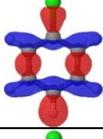
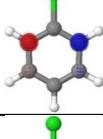
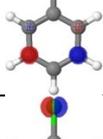
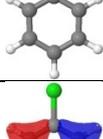
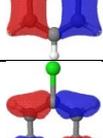
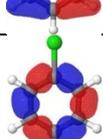
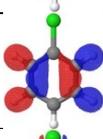
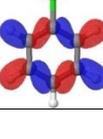
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occ. orbital  virt. orbital  |coeff.|^2
  2 b1         2 a2         56.4
  1 b1         2 a2         16.0
  4 a1         5 b2         15.4

Dominant contributions: 274.64 eV
occ. orbital  virt. orbital  |coeff.|^2
  1 b1         2 a2         59.5
  3 a1         5 b2         19.4
  2 b1         2 a2         16.9

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Table S2. Orbital compositions of the three TDDFT states contributing to band A. Consult Figure-1 in the main text for the C 1s and π^* orbitals plots.

Occupied orbitals	Energy (a.u.)	Orbital
1 a ₁	-101.523	
2 a ₁	-10.2402	
3 a ₁	-10.1904	
4 a ₁	-10.1896	
5 a ₁	-10.1860	
6 a ₁	-9.45513	
7 a ₁	-7.21665	
8 a ₁	-0.89057	
9 a ₁	-0.83663	

10 a ₁	-0.73671	
11 a ₁	-0.60396	
12 a ₁	-0.52888	
13 a ₁	-0.47047	
14 a ₁	-0.43351	
15 a ₁	-0.36643	
1 b ₁	-10.1905	
2 b ₁	-10.1896	
3 b ₁	-7.20800	
4 b ₁	-0.76143	
5 b ₁	-0.62229	
6 b ₁	-0.47220	
7 b ₁	-0.43723	
8 b ₁	-0.36545	

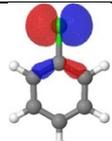
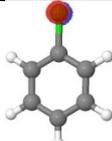
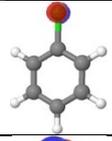
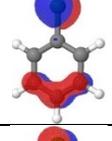
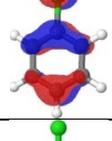
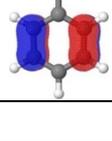
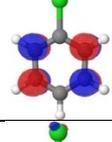
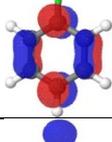
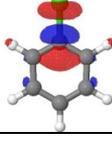
9 b ₁	-0.31336	
1 b ₂	-7.20833	
2 b ₂	-0.39932	
3 b ₂	-0.33644	
4 b ₂ (HOMO)	-0.25202	
1 a ₂ (HOMO-1)	-0.26995	
-- Virtual		
2 a ₂ (LUMO)	-0.02678	
5 b ₂ (LUMO+1)	-0.02484	
16 a ₁ (LUMO+2)	0.018109	

Table S3. TDDFT orbitals of chlorobenzene up to LUMO+2.

References

- [1] TURBOMOLE, V6.2 2010, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
- [2] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623-11627.
- [3] F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 7 (2005) 3297-305.