

# Valence ionization spectra of transition metal compounds: SAC-CI study

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Valence ionization spectra of several transition metal compounds were studied with the symmetry-adapted cluster configuration interaction (SAC-CI) method. We have calculated the ionization potentials and photo-ionization strengths (monopole intensities) of metal carbonyls ( $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Ni}(\text{CO})_4$ ) and ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ ). With the theoretical SAC-CI spectroscopy, we assigned the peaks of the experimental UV-photoelectron (UPS) and Penning-ionization spectra.

For many transition metal compounds, the valence ionization spectra are grouped into the peaks in two regions. The peaks in the lower-energy region are mainly assigned as the ionizations of metal  $d$ -electrons. The peaks in the higher-energy region are dominantly characterized as ligand ionizations. For accurate descriptions of the ionization potentials, not only electron correlations and orbital reorganizations, but also their coupling are important. The SAC-CI method can efficiently describe these effects because the methodology is based on the cluster expansion.

Table 1 shows the ionization potential of ferrocene. In the lower energy states, doubly excited configurations strongly mixed to the one-electron ionization of ion  $3d$  orbitals. The two-electron shake-up processes are essential even in these lower states. Koopmans picture, which is based on the one-electron orbital theory, cannot explain even the trends of the ionization character of ferrocene. As shown in the Figure 1, the SAC-CI method well reproduced the experimental UPS spectrum.

Table 1: Ionization potential of ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ ) (in eV)

State	Nature	Koopmans	SAC-CI	Exptl.
$1^2E_2'$	$3d(\text{Fe}) + (\text{double})^a$	11.42	6.38	6.86
$1^2A_1'$	$3d(\text{Fe}) + (\text{double})^a$	9.24	7.20	7.23
$1^2E_1'$	$3d(\text{Fe}) + \pi(\text{Cp})^b$	13.80	8.62	8.72
$1^2E_1''$	$3d(\text{Fe}) + \pi(\text{Cp})$	9.27	8.99	9.14
$1^2A_2''$	$4p(\text{Fe}) + \pi(\text{Cp})$	13.71	11.69	
$1^2E_2''$	$\sigma(\text{Cp})$	11.43	12.28	12.2
$2^2E_2'$	$\sigma(\text{Cp})$	14.32	12.42	
$1^2E_1'$	$\sigma(\text{Cp})$	14.98	13.08	13.0
$2^2A_1'$	$\pi(\text{Cp})$	15.23	13.17	
$2^2E_1''$	$\sigma(\text{Cp})$	15.13	13.28	13.46

<sup>a</sup>Doubly excited configurations. <sup>b</sup>Cp =  $\text{C}_5\text{H}_5$

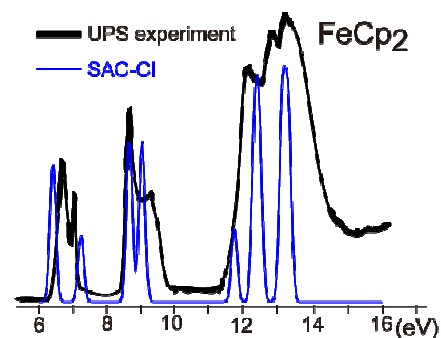


Figure 1: Theoretical and experimental ionization spectrum of ferrocene.