

Multi-reference Approach to the Computation of Double-Core-Hole Spectra

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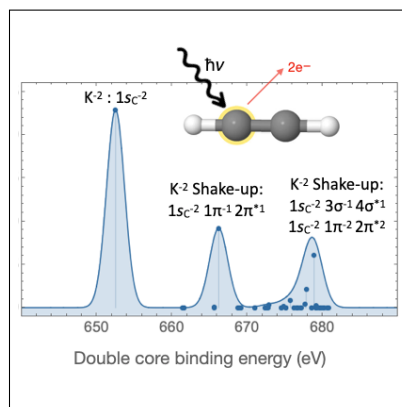
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Abstract

Double-Core Hole (DCH) states of small molecules are assessed with the restricted active space self-consistent field (RASSCF) and multi-state restricted active space perturbation theory of second order (MS-RASPT2) approximations. To ensure an unbiased description of the relaxation and correlation effects on the DCH states, the neutral ground state and DCH wave functions are optimized separately, whereas the spectral intensities are computed with a biorthonormalized set of molecular orbitals within the state-interaction (SI) approximation. Accurate shake-up satellites binding energies and intensities of double-core-ionized states (K^{-2}) are obtained for H_2O , N_2 , CO and C_2H_{2n} ($n=1-3$). The results are analyzed in details and show excellent agreement with recent experimental data.

Graphical TOC Entry



Keywords

Photoionization, DCH, Shake-up, satellites

With the advent of the newest generation of x-ray sources, double core-shell photoionization spectroscopy has been reported with unprecedented resolution either from two-photon photoelectron spectroscopy using x-ray free electron laser (X-FEL) radiation¹⁻⁶ or with single x-ray photon at synchrotron facilities.⁷⁻¹⁶ Single-site double core hole (ssDCH or K^{-2}) spectroscopy has gained special attention due to, among others, its chemical specificity and enhanced sensitivity to chemical environment when compared to single core hole (SCH) spectroscopy.² The high sensitivity of ssDCH spectroscopy to chemical environment has been demonstrated, for example, in the K^{-2} spectra of the C_2H_{2n} ($n=1-3$) series, where the shift in binding energy of the first peak of C_2H_4 relative to C_2H_2 was measured to be $\Delta E_{C_2H_4/C_2H_2} = -2.1$ eV,¹⁷ versus the value $\Delta E_{C_2H_4/C_2H_2} = 0.9$ eV obtained from the SCH spectra.¹⁸ Its characteristics upraise ssDCH spectroscopy as one of the most promising techniques to chemical analysis. However, in contrast to SCH spectroscopy,¹⁹⁻²² it has been widely demonstrated that some of the most important features of a typical DCH spectrum arise from strong shake-up satellite states,^{14,17,23} which stem from excitation of one or more outer electrons in combination with the photoionization of two core electrons located on the same atom. Shake-up satellite states have intrinsic multielectronic character and it is strongly affected by relaxation and correlation effects.²⁴⁻²⁶ Therefore, its accurate computation depends on the appropriateness of the computational method to be used in dealing with these effects.

Relaxation and correlation effects are in principle different concepts. Electronic relaxation is regarded as the shrinking of the electron cloud in response to the formation of a deep core hole. Correlation, on the other hand, is a theoretical concept associated with deviations from the independent particle picture. Put in simple terms, it can be assessed by the difference between a mean field Hartree-Fock (HF) calculation and the full configuration-interaction (Full-CI) result in the limit that the basis set approaches completeness. It may be worth recalling that even relaxation can be considered a correlation effect, and not separately treated. Indeed, in several many-body schemes aiming at describing ionization, like algebraic-

diagrammatic construction (ADC)^{27–29} or equation-of-motion coupled cluster (EOM-CC) theory,^{30–32} relaxation is treated as pure correlation. In the context of ssDCH spectra, a few computational strategies have been proposed. Pioneering studies by Cederbaum *et al.*^{33–35} have shown the extraordinary sensitivity of ssDCH states even before any experimental technique could allow their observation with the resolution level that we have today. A seminal work by Ågren and Jensen³⁶ described the relaxation and correlation contributions to double core ionization energies, and how one could compute them using multi-configuration self-consistent field (MCSCF) wave-functions,^{37–39} in particular, the restrict active space (RAS) approach.³⁸ RAS constitutes a threefold division of the correlation orbital space, denoted RAS1, RAS2 and RAS3.

A number of theoretical works aimed at double core hole states have been reported over the past few years, employing different levels of theory, ranging from time-dependent density functional theory (TD-DFT),^{40,41} DFT,^{6,42–44} and Δ SCF,^{6,45} to MCSCF,^{6,42–44,46} Delta Coupled Cluster (Δ CC),⁴⁷ and many-body Green’s function.^{45,48,49} Most of these works, however, were limited to the computation of double core ionization potentials. A previous attempt to compute the ssDCH spectra of the CO molecule using the RAS approach was presented by Tashiro *et al.*,⁵⁰ but a too simple approximation on the transition amplitudes prevented the authors from reproducing the spectra at a satisfactory level.

It was only recently that an accurate method to compute ssDCH binding energies as well as spectral strengths was proposed by Ferté *et al.* and applied to the CO molecule.²³ The method combines a CI approach using perturbative selection (CIPSI)^{51,52} with the computation of transition amplitudes using two sets of non-orthogonal molecular orbitals. One set was obtained from a restricted HF calculation on the ground state configuration; the second (relaxed) set was generated from a non-Aufbau SCF calculation with two electrons removed from the core orbital. At this approximation level, dubbed NOTA+CIPSI by the authors, the oxygen double core edge spectrum of carbon monoxide was obtained in excellent agreement with the experimental data.

In the present work, we propose a multi-reference protocol to compute ssDCH spectra using the restricted active space self-consistent field (RASSCF) approach³⁸ as well as multi-state restricted active space perturbation theory of second order (MS-RASPT2).^{53–56} In our approach, the transition amplitudes are obtained within the sudden approximation using a biorthonormalized set of molecular orbitals, where the ground state and the double core hole states are obtained from different RASSCF calculations. This ensures an unbiased representation of the initial and final states and an appropriate description of the relaxation and correlation effects associated with the shake-up satellites of a ssDCH spectrum. Moreover, the use of a biorthonormalized orbital set⁵⁷ significantly simplifies the computation of matrix elements between different states, reducing the computational cost of such calculations.

In detail, we consider a molecule with N electrons initially in its ground state $|\Psi_i^N\rangle$. Following the single-channel approximation, we represent the wave-function $|\Psi_f^N\rangle$ of the final state where two electrons have been ejected into the continuum as an antisymmetrized product of the wave-function of the molecular (bound) $(N-2)$ double-core-hole final state, $|\Psi_f^{N-2}\rangle$, and the continuum wave-function $|\psi^{el}(\vec{k}_1, \vec{k}_2)\rangle$, of the two photoelectrons with asymptotic momenta \vec{k}_1 and \vec{k}_2 ,

$$|\Psi_f^N\rangle = \hat{\mathcal{A}}(N) |\Psi_f^{N-2} \psi^{el}(\vec{k}_1, \vec{k}_2)\rangle \quad (1)$$

where $\hat{\mathcal{A}}(N)$ is the N -electron antisymmetrizer operator.

Within the dipole approximation, the differential cross-section connecting the initial state and the final state wave-function – in atomic units and in the length gauge – is given by

$$\frac{d^2\sigma}{d\vec{k}_1 d\vec{k}_2} = 4\pi^2 \alpha \omega |\vec{D}_{if}|^2 \quad (2)$$

where $\vec{D}_{if} = \langle \Psi_i^N | \vec{\mu} | \Psi_f^N \rangle$ is the dipole transition moment, α is the fine-structure constant, and ω is the energy of the incident photon.

In the sudden approximation,⁵⁸ the transition, or spectral, strengths associated with a

peak in the ssDCH spectrum can be estimated as

$$\begin{aligned} |T_{i \rightarrow f}|^2 &\propto |\langle \Psi_f^{N-2} | a_{1s}^\alpha a_{1s}^\beta | \Psi_i^N \rangle|^2 \\ &= |\langle \Psi_A^{N-2} | \Psi_B^{N-2} \rangle|^2 \end{aligned} \quad (3)$$

where a_{1s}^σ is the second-quantization annihilation operator of the electron of spin σ in orbital $1s$.

As highlighted by the second equality in Eq. (3), the spectral strengths correspond to overlap matrix elements between two $(N-2)$ electron wave functions. By using a biorthonormalized set of molecular orbitals in Eq. (3), as done in the RASSI method,^{57,59} the computation of these matrix elements is very efficient and straightforward, as it would be to compute the overlaps with a common orthonormal molecular orbital basis.

The RASSI method has been used to compute matrix elements over distinct (biorthonormal) molecular orbital (MO) sets of inner-shell states with great success.⁶⁰⁻⁶² To briefly recapitulate the attributes of the RASSI method,^{57,59} let us first write the matrix elements between two distinct optimized wave functions Ψ_A and Ψ_B described by a CI expansion of Slater determinant functions (SDF) or spin-adapted configuration state functions (CSF), Φ^A and Φ^B , constructed from the sets of molecular orbitals $\{\phi^A\}$ and $\{\phi^B\}$ (Ψ_A and Ψ_B can be generalized to the case of CASSCF or RASSCF wave-functions)

$$\Psi_A = \sum_{\mu} C_{\mu}^A \Phi_{\mu}^A, \quad \Phi_{\mu}^A = a_p^{\dagger} \dots a_s^{\dagger} |\text{vac}\rangle \quad (4)$$

$$\Psi_B = \sum_{\nu} C_{\nu}^B \Phi_{\nu}^B, \quad \Phi_{\nu}^B = a_q^{\dagger} \dots a_r^{\dagger} |\text{vac}\rangle \quad (5)$$

where μ is a lists of occupied orbitals $(p\dots s)$, and similarly for ν .

The overlap matrix between the wave functions can be written as

$$\langle \Psi_A | \Psi_B \rangle = \sum_{\mu\nu} C_{\mu}^A C_{\nu}^B S_{\mu\nu} \quad (6)$$

with $S_{\mu\nu}$ as the overlap matrix elements between two SDF, $S_{\mu\nu} = \langle \Phi_\mu^A | \Phi_\nu^B \rangle$. The overlap matrix S becomes the unit matrix provided that the two sets of spin-orbitals are biorthonormal, i.e. $\langle \phi_p^A | \phi_q^B \rangle = \delta_{pq}$.⁵⁷ When this is not the case, like in the work of Ferté *et al.*,²³ the more complicated Löwdin's rules have to be used to compute $\langle \phi_p^A | \phi_q^B \rangle$ and then $S_{\mu\nu}$.⁶³

However, it is possible to find a set of non-unitary orbital transformations which transforms $\{\phi^A\}$, $\{\phi^B\}$, $\{C^A\}$, $\{C^B\} \rightarrow \{\widetilde{\phi}^A\}$, $\{\widetilde{\phi}^B\}$, $\{\widetilde{C}^A\}$, $\{\widetilde{C}^B\}$, such that the MO overlap $\langle \widetilde{\phi}_p^A | \widetilde{\phi}_q^B \rangle = \delta_{pq}$, while the wave functions Ψ_A and Ψ_B remain the same. Using these biorthonormally-transformed orbital sets allow us to employ simpler equations for overlap matrix elements between the two different wave functions, as if one common orthonormal orbital set is used, that is,

$$\langle \Psi_A | \Psi_B \rangle = \sum_{\mu} \widetilde{C}_{\mu}^A \widetilde{C}_{\mu}^B \quad (7)$$

We have implemented the computation of the spectral strength of Eq. (3) according to Eq. (7) within the RASSI framework^{57,59} in a locally modified version of the OpenMolcas program package⁶⁴ by using:

$$\begin{aligned} |\Psi_A\rangle &= |\Psi_{\text{DCH}}^{N-2}\rangle \\ |\Psi_B\rangle &= a_{1s}^{\alpha} a_{1s}^{\beta} |\Psi_{\text{GS}}^N\rangle \end{aligned} \quad (8)$$

where $|\Psi_{\text{DCH}}^{N-2}\rangle$ is the double core-holed wave function and $a_{1s}^{\alpha} a_{1s}^{\beta} |\Psi_{\text{GS}}^N\rangle$ is the ground-state wave function with the core spin-orbitals' occupations annihilated. As anticipated, we used RASSCF³⁸ to compute the ground and DCH states and subsequently improved them with MS-RASPT2 in order to include dynamic correlation effects.⁵³⁻⁵⁶ Thus, the two sets of MO orbitals $\{\phi^A\}$ and $\{\phi^B\}$ are biorthogonalized, followed by application of the annihilators to the GS wave function, which then simplifies the computation of the overlap, Eq. (7).

The approximation in Eq. (3) assumes that the kinetic energy dependence of the transition moment and, thus, the interaction between the two photoelectrons and the $(N - 2)$

bound wave-function is negligible. The sudden approximation should be a good approximation for high kinetic energies of the photoelectrons, as it generally happens to be the case far above the double core ionization potential.

We tested our approach by computing the ssDCH spectra of CO, H₂O, N₂ and of the C₂H_{2n} ($n=1-3$) series, and comparing our results with available experimental data.^{15,17,23} An imaginary level shift of 0.45 hartree was applied to avoid intruder state singularities in the RASPT2 calculations. Within the framework of the state interaction approximation, where a basis of biorthogonal orbital set is used to compute the matrix elements, we were able to optimize the ground state and DCH wave functions in separate calculations, securing a unbiased description of the relaxation and correlation effects. The correlated consistent augmented triple zeta basis (aug-cc-pVTZ) set of Dunning and coworkers^{65,66} was employed throughout, with additional core-augmented functions (aug-cc-pCVTZ) for oxygen and nitrogen, only when they are the relevant core edges. Douglas-Kroll-Hess scalar relativistic effects⁶⁷ up to the second order were incorporated in all our calculations.

Since the selection of orbitals to form the RASSCF active space is system dependent, it is often necessary to test more than one active space until the desired result is reached. In Table 1 we report the active spaces of each molecule used in this work. The RAS approach can be used to avoid the variational collapse of the wave-function to a low-lying state. The RAS1 space contains the core-shell orbital where double hole condition is enforced, while RAS2 is used for complete electron distribution. RAS3 was kept empty. For the N₂ and C₂H_{2n} ($n=1-3$) molecules, where the core orbitals are delocalized, we localized the core orbitals using the Boys method.⁶⁸ The DCH states were computed by state averaging over 15 final singlet states for H₂O, 30 singlet states for CO, 40 singlet states for N₂, and 50 singlet states for each member of the C₂H_{2n} series.

All calculations were carried out at the experimental ground-state equilibrium geometries from the NIST Chemistry webBook database.⁶⁹ To ease the comparison with the experimental results, the sticks spectra are convoluted with a Gaussian broadening of half-width-at-

half-maximum (HWHM) between 0.5 and 1.5 eV, depending on the experimental spectrum that we were comparing with. Additionally, the theoretical spectra were shifted by a value Δ indicated in the figures, in order to match the experimental position of the first peak. The experimental data points reproduced in our figures were digitized from the original references using WebPlotDigitizer.⁷⁰ Herein, we will discuss only RASPT2 results. For RASSCF results, see the Supporting Information.

Table 1: Active spaces used in the RASSCF/RASPT2 calculations.

Molecule	Abelian point group	RAS1	RAS2	# electrons/# orbitals
H ₂ O	C_{2v}	$1a_1$ ($1s_O$)	2-7 a_1 , 1-3 b_1 , 1-3 b_2	RAS(10/13)
CO (O K ⁻²)	C_{2v}	$1a_1$ ($1s_O$)	4-7 a_1 , 1-3 b_1 , 1-3 b_2	RAS(10/11)
CO (C K ⁻²)	C_{2v}	$2a_1$ ($1s_C$)	4-7 a_1 , 1-3 b_1 , 1-3 b_2	RAS(10/11)
N ₂	D_{2h}	$1a_g$ ($1s_N$)	2-4 a_g , $1b_{2g}$, $1b_{3g}$, $1-2b_{2u}$, $1-2b_{3u}$, $1-3b_{1u}$	RAS(12/13)
C ₂ H ₂	D_{2h}	$1a_g$ ($1s_C$)	2-4 a_g , $1b_{2g}$, $1b_{3g}$, $1-2b_{2u}$, $1-2b_{3u}$, $2-3b_{1u}$	RAS(12/12)
C ₂ H ₄	D_{2h}	$1a_g$ ($1s_C$)	2-4 a_g , $1b_{2g}$, $1-2b_{3g}$, $1-2b_{2u}$, $1-2b_{3u}$, $2-3b_{1u}$	RAS(14/13)
C ₂ H ₆	C_{2h}	$1a_g$ ($1s_C$)	2-6 a_g , $1-2a_u$, $1-2b_g$, $2-5b_u$	RAS(16/13)

In Figure 1 and Table 2, we present the theoretical results for the K⁻² spectra of H₂O, N₂, and CO. The experimental points (in red) were digitized from Ref. 15 (H₂O), Ref. 17 (N₂), and Refs. 17, 23 (CO). The ground-state HF occupied molecular orbitals are indicated as: (H₂O) $1s_O^2$, $2a_1^2$, $1b_2^2$, $3a_1^2$, $1b_1^2$; (N₂) $1s_N^2$, $1s_N^2$, $1\sigma_{2s}^2$, $2\sigma^2$, $3\sigma^2$, $1\pi^4$ and (CO) $1s_O^2$, $1s_C^2$, $1\sigma_{2s}^2$, $2\sigma^2$, $1\pi^4$, $3\sigma^2$.

Table 2: RASPT2 K^{-2} binding energies (BE) and spectral strengths of the main peaks of CO (C and O edges), H_2O and N_2 .

Molecule	State Label	BE (eV)	BE Exp. (eV)	$ T_{i \rightarrow f} ^2$
H_2O	A	1172.90	1171.0 ± 1^{15}	0.2148
	B	1198.42	-	0.0226
	C	1202.62	-	0.0626
	D	1206.44	-	0.0644
	E	1208.06	-	0.1053
N_2	A	900.37	902.5 ± 1^{17}	0.2360
	B	916.97	919.0 ± 1^{17}	0.0878
	C	928.68	-	0.0144
	D	930.36	-	0.0125
CO(K^{-2})	A	1177.20	1178.0 ± 0.8^{23}	0.2319
	B	1192.69	-	0.0094
	C	1196.56	-	0.0150
	D	1199.81	1200.6 ± 0.8^{23}	0.0366
	E	1200.29	1200.6 ± 0.8^{23}	0.0835
	F	1214.31	-	0.0206
	G	1216.57	-	0.0365
C(K^{-2})O	A	665.76	666.7 ± 1^{17}	0.3123
	B	682.32	682.2 ± 1^{17}	0.0676
	C	693.56	-	0.0318
	D	696.25	-	0.0239
	E	698.32	-	0.0235

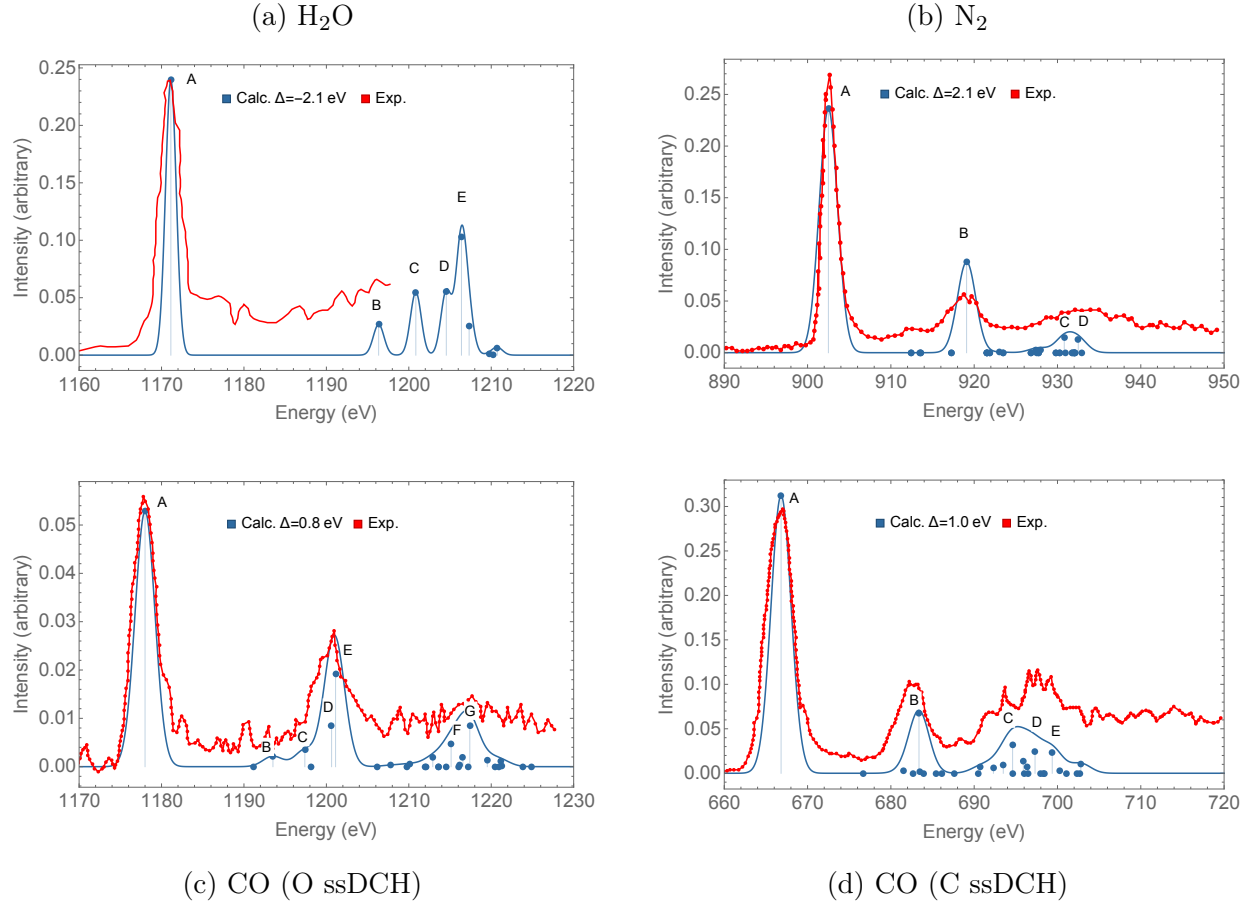


Figure 1: RASPT2 K^{-2} spectra of H_2O , N_2 , and CO . The experimental points were extracted from Ref. 15 for H_2O , Ref. 17 for N_2 , and Refs. 17,23 for CO . The aug-cc-pCVTZ basis was used for the atom where the double core hole resides, and aug-cc-pVTZ on the remaining atoms. The theoretical spectra were shifted by Δ , whose value given in the legends, to match the position of the first experimental peak. The stick spectra were broadened with Gaussian functions using a HWHM of 0.7 eV for H_2O and of 1.1 eV for N_2 and CO .

The computed K^{-2} spectrum of H_2O , shown in Fig. 1a, exhibits five main peaks labeled from A-E, with binding energies and spectral strengths listed in Table 2. Peak A corresponds to a double photoionization from the oxygen's $1s$ orbital, where the weight of the major configuration in the CI expansion is $0.96(1s_O^{-2})$.⁷¹ The spectral strength computed with the approximation given by Eq. (3) is a monopolar transition between the initial ground state and a final double core state. As a consequence, the more similar the final state is to the ground state configuration, the more intense the transition will be. This also means that almost pure double-core photoionized final states will have more overlap with the ground state than multi-configurational DCH shake-up states. Therefore, we in general expect the pure double-core photoionized state to be the most intense peak in the DCH spectrum. The main CI configurations and weights of the shake-up satellite peaks B, C and D are, respectively: $0.96(1s_O^{-2}3a_1^{-1}4a_1^1)$, $0.87(1s_O^{-2}1b_2^{-1}2b_2^1)$ and $0.79(1s_O^{-2}1b_1^{-1}2b_1^1)$. The multi-configuration character of peak E is more pronounced than for its predecessors, being $0.62(1s_O^{-2}3a_1^{-1}7a_1^1) + 0.16(1s_O^{-2}3a_1^{-1}6a_1^1) + 0.12(1s_O^{-2}1b_1^{-1}2b_1^1)$, where the orbitals 6-7 a_1 are Rydberg orbitals of s type. Notice that we are only showing configurations with weights higher than 0.1 (10%) in the CI expansion, which means that a large number of CI configurations, important to recover relaxation/correlation effects, are not listed here. Unfortunately, the available experimental data¹⁵ only cover a limited energy range, from 1160 to 1200 eV, where it is impossible to observe all the computed shake-up satellites. However, one can notice an increase in the experimental intensity after 1190 eV, where the first satellite, labeled B, appears.

The K^{-2} spectrum of N_2 is shown in Fig. 1b together with experimental data.¹⁷ Overall, the agreement between theory and experiment is good. The four main peaks contributing to the spectrum are labeled A-D and their binding energies and spectral strengths are listed in Table 2. Peak A has a major contribution from the double photoionization from one of the N $1s$ orbital. The weight of the $1s_N^{-2}$ configuration in the CI expansion is 0.81. Peak B corresponds to the $1s_N^{-2}$ hole and a $\pi \rightarrow \pi^*$ valence excitation, with main CI configuration and weight $0.68(1s_N^{-2}1\pi^{-1}\pi^{*1})$, and dozens of other configurations with weights less than 0.1.

The binding energy of this peak is in good agreement with experiment, although its intensity is higher, which might be due to energy dissipation or nuclear relaxation effects not taken into account in our calculations. Peaks C and D belong to the high energy region of the spectrum, where a broad and flat band is observed at around 930 eV. Both states C and D present strong multi-configuration character, with two electrons removed from the N $1s$ orbital followed by a $2\sigma \rightarrow \sigma^*$ (C) or $3\sigma \rightarrow \sigma^*$ (D) valence excitations.

The K^{-2} spectra of CO were computed both at the oxygen and carbon edges. The results are presented in Figures 1c and 1d alongside with experimental data.^{17,23} In both cases, the agreement between the experimental results and the theoretical spectra is very good, if not excellent. The experimental profile of the O K^{-2} spectrum shows three prominent features, the first being a strong peak centered at 1178 eV, followed by a broad peak at 1200 eV and a very broad and weak band around 1220 eV. The spectrum shown in Fig. 1c displays seven main contributing 'sticks' that we labeled from A-G. The corresponding binding energies and spectral strengths can be consulted in Table 2. Peak A corresponds, as usual, to the double photoionization from the O $1s$ orbital with weight of the main configuration in the CI expansion $0.90(1s_O^{-2})$. In the second region of the spectrum, centered at 1200 eV, we identify four peaks, B-E, where E is the brighter. The shake-up satellite state B is associated with the main CI configurations $0.82(1s_O^{-2}3\sigma^{-2}2\pi^{*2})$, whereas peak C is associated with the main configurations $0.61(1s_O^{-2}3\sigma^{-1}4\sigma^{*1}) + 0.22(1s_O^{-2}1\pi^{-1}2\pi^{*1})$. The shake-up satellites D and E are associated with the main CI configurations $0.38(1s_O^{-2}3\sigma^{-1}4\sigma^{*1}) + 0.10(1s_O^{-2}3\sigma^{-1}5\sigma^{*1}) + 0.38(1s_O^{-2}1\pi^{-1}2\pi^{*1})$ for peak D, and the main CI configurations $0.44(1s_O^{-2}3\sigma^{-1}4\sigma^{*1}) + 0.13(1s_O^{-2}3\sigma^{-1}5\sigma^{*1}) + 0.22(1s_O^{-2}1\pi^{-1}2\pi^{*1})$ for peak E. Overall, the relative intensities between peaks A and D-E are in excellent agreement with those from the experimental spectrum, which we attribute to the optimal description of the non-orthogonal states given by the RASPT2/state-interaction approximation.⁵⁹ Our theoretical assignments and binding energies for the oxygen K^{-2} spectrum of CO agree well with the results obtained by Ferté et al. using the NOTA+CIPSI approach.²³ The last region around 1215 eV is dominated

by the satellite states F and G, with main configurations $0.70(1s_O^{-2}1\pi^{-1}3\pi^{*1})$ for F, and $0.43(1s_O^{-2}2\sigma^{-1}4\sigma^{*1}) + 0.20(1s_O^{-2}3\sigma^{-1}4\sigma^{*1}1\pi^{-1}3\pi^{*1})$ for G.

The C K^{-2} spectrum of CO is shown in Fig. 1d. As the experiment shows,¹⁷ the C K^{-2} spectrum is also characterized by three main regions. The first important feature is an intense peak centered at 665 eV, followed by a weaker peak centered at 682 eV, and a broad region above 690 eV with many distinct unsolved structures. One can notice that the experimental spectrum at the carbon edge is less noisy than the one at the oxygen edge, which makes it easier to identify the shake-up satellites structures in the spectrum. The first feature, labeled A in Fig. 1d and Table 2, is again the pure double photoionization from the C $1s$ orbital, with weight of the major configuration in the CI expansion being $0.84(1s_C^{-2})$. Peak B is characterized by the main configurations $0.21(1s_C^{-2}3\sigma^{-1}4\sigma^{*1}) + 0.50(1s_C^{-2}1\pi^{-1}2\pi^{*1})$ and a large number of secondary configurations with small weights. The upper region of the spectrum, after 690 eV, presents a large number of shake-up satellites, of which we selected three with relevant intensities and labeled them C-E. Peaks C-E present strong multi-excitation character where a large number of singles and doubles valence $1s_C^0\sigma \rightarrow \sigma^*$ and $1s_C^0\pi \rightarrow \pi^*$ excitations can be identified. Nonetheless, peaks C-E demonstrate good agreement with the aggregate experimental structures present in this region C K^{-2} spectrum of CO.

Having demonstrated the accuracy of our method for the K^{-2} spectra of H_2O , N_2 and CO, we now characterize the spectra of ethyne, ethene and ethane. In Figure 2 we show the computed K^{-2} spectra plotted alongside with experiment.¹⁷ The binding energies and spectral strengths are listed in Table 3. The occupied orbitals in the HF ground state are: $1s_C^2, 1s_C^2, 1\sigma_{2s}^2, 2\sigma_{C-C}^2, 3\sigma_{C-C}^2, 1\pi^4$ for C_2H_2 ; $1s_C^2, 1s_C^2, 1\sigma_{2s}^2, 2\sigma_{C-C}^2, 3\sigma_{sp^2}^2, 4\sigma_{C-C}^2, 5\sigma_{sp^2}^2, 1\pi^2$ for C_2H_4 and $1s_C^2, 1s_C^2, 1\sigma_{2s}^2, 2\sigma_{C-C}^2, 3\sigma_{sp^3}^2, 4\sigma_{sp^3}^2, 5\sigma_{C-C}^2, 6\sigma_{CH}^2, 7\sigma_{CH}^2$ for C_2H_6 .

The experimental spectrum of C_2H_2 ¹⁷ shows three well separated features: a bright peak centered at 652 eV, labeled peak A in Figure 2a, followed by a second peak centered at 666 eV, labeled B, and a broad and relatively weak structure starting at around 675 eV. We

obtained two peaks contributing to this last region that we labeled C and D. The binding energies and intensities can be consulted in Table 3. The relative energies and intensities between the peaks A and B look very precise, while our computed peak D is slightly more intense than the corresponding experimental one. Overall, we find good agreement between the experiment and the computed results throughout the spectrum. Peak A is a pure double photoionization from the C 1s orbital. The weight of the major configuration in the CI expansion is $0.82(1s_C^{-2})$. The shake-up peak B is associated with the main CI configurations and weights $0.08(1s_C^{-2}) + 0.68(1s_C^{-2}1\pi^{-1}2\pi^{*1})$ and a number of other configurations with small weights. Peak C is associated with the main configuration $0.56(1s_C^{-2}3\sigma^{-1}4\sigma^{*1})$, while peak D is mainly associated with the multi-excited configurations $0.62(1s_C^{-2}1\pi^{-2}2\pi^{*2})$.

The K^{-2} spectrum of C_2H_4 is displayed in Fig. 2b. The first peak, labeled A, has weight $0.95(1s_C^{-2})$ in the CI expansion. It was experimentally observed¹⁷ that the first peak of the C_2H_4 K^{-2} spectrum is red-shifted with respect to peak A in the K^{-2} spectrum of C_2H_2 . The experimental red-shift ($\Delta E_{C_2H_4/C_2H_2}$) is -2.1 ± 0.2 eV, while the computed red-shift is -2.5 eV (cf. Table 3). Moreover, the relative binding energies and intensities between peaks A and B accurately reproduce the experimental profile. Peak B is a shake-up satellite associated with the main CI configurations $0.86(1s_C^{-2}1\pi^{-1}2\pi^{*1})$ and a large number of secondary configurations with small weights. The weak peaks C and D belong to the region above 670 eV with various small and scattered structures, where it is very difficult to characterize individual contributions from the experiment. These peaks are associated with the main CI configurations: (peak C) $0.44(1s_C^{-2}3\sigma_{sp^2}^{-1}\sigma_{CH}^{*1}) + 0.25(1s_C^{-2}4\sigma_{CC}^{-1}\sigma_{CC}^{*1}) + 0.10(1s_C^{-2}5\sigma_{sp^2}^{-1}\sigma_{CH}^{*1}1\pi^{-1}2\pi^{*1})$ and (peak D) $0.16(1s_C^{-2}3\sigma_{sp^2}^{-1}\sigma_{CH}^{*1}) + 0.25(1s_C^{-2}3\sigma_{sp^2}^{-1}\sigma_{CC}^{*1})$.

The K^{-2} spectrum of C_2H_6 is a bit simpler than those of the unsaturated species, featuring only one single, strong, peak, labeled A, and a broad and weak region above 660 eV. Once again, the first peak is related to a pure double photoionized C 1s state. The weak peaks labeled B and C are associated with the main CI configurations (B) $0.25(1s_C^{-2}5\sigma_{CC}^{-1}\sigma_{CC}^{*1}) + 0.16(1s_C^{-2}5\sigma_{CC}^{-1}\sigma_{Ryd. s}^{*1})$ and (C) $0.23(1s_C^{-2}2\sigma_{CC}^{-1}\sigma_{CC}^{*1}) + 0.18(1s_C^{-2}2\sigma_{CC}^{-1}\sigma_{CH}^{*1}) + 0.12(1s_C^{-2}4\sigma_{sp^3}^{-1}\sigma_{CH}^{*1})$.

The computed red-shift on the peak A ($\Delta E_{\text{C}_2\text{H}_6/\text{C}_2\text{H}_2}$) is -2.4 eV, whereas the experimental value is -1.9 ± 0.2 eV.¹⁷ Both the $\Delta E_{\text{C}_2\text{H}_4/\text{C}_2\text{H}_2}$ and $\Delta E_{\text{C}_2\text{H}_6/\text{C}_2\text{H}_2}$ are in good agreement with the experiment showing a slightly smaller $\Delta E_{\text{C}_2\text{H}_6/\text{C}_2\text{H}_2}$ than the $\Delta E_{\text{C}_2\text{H}_4/\text{C}_2\text{H}_2}$ value. In Figure 2d we compare the results for the C_2H_{2n} ($n=1-3$) K^{-2} spectra jointly, where the shifts of peak A are clearly apparent. As a general remark, we were able to reproduce and characterize the main experimental features in the K^{-2} spectra of C_2H_{2n} ($n=1-3$) with excellent accuracy.

To summarize, we have presented a highly accurate method to compute the ssDCH spectra of general molecular systems, i.e., ssDCH binding energies and transition amplitudes. It is based on the calculation of (non-orthogonal) multi-reference wave-functions, conveniently obtained using the RASSCF³⁷⁻³⁹ and MS-RASPT2^{55,56} methods. The transition amplitudes are estimated in the sudden approximation limit⁵⁸ by means of a monopolar matrix element $|T_{i \rightarrow f}|^2$, which is very efficiently computed within the state-interaction⁵⁷ framework using biorthonormalized molecular orbital sets. We were capable of reproducing the main experimental features of the K^{-2} spectra of H_2O , N_2 , CO and the C_2H_{2n} ($n = 1 - 3$) molecules with excellent agreement with experimental results. The method is also quite practical, as we averaged a relatively small number of DCH states – that is, between 20 and 50 states.

In perspective, we believe that the flexibility of the RASSCF method will permit us to apply our protocol to more challenging cases, for instance DCH states of bi-metal transition metal complexes,⁴⁰ or imaging nuclear trajectories necessary to compute nuclear dynamics effects of organic molecules. We are currently exploring whether one can use the same RASSCF/State-Interaction framework to obtain the pre-edge DCH spectra,⁸ coupling the direct and conjugate Dyson orbitals with an accurate continuum wave-function obtained at the (TD)DFT level on a B-spline basis.²⁴ A detailed report of the pre-edge DCH methodology will be presented elsewhere.

Table 3: K^{-2} binding energies and intensity of the main peaks of C_2H_{2n} ($n=1-3$) computed at the RASPT2 level. The experimental results were obtained from Ref. 17.

Molecule	State Label	BE (eV)	BE Exp. (eV)	$ T_{i \rightarrow f} ^2$
C_2H_2	A	651.81	652.5 ± 0.5	0.2297
	B	665.51	666.5 ± 0.5	0.0914
	C	677.15	-	0.0230
	D	678.20	-	0.0604
C_2H_4	A	649.32	650.4 ± 0.5	0.1942
	B	659.56	660.5 ± 0.5	0.0993
	C	671.09	-	0.0118
	D	674.02	-	0.0294
C_2H_6	A	649.42	650.5 ± 0.5	0.2373
	B	666.69	-	0.0104
	C	671.72	-	0.0222
$\Delta E_{C_2H_4/C_2H_2}$		-2.5	-2.1 ± 0.2	
$\Delta E_{C_2H_6/C_2H_2}$		-2.4	-1.9 ± 0.2	

Acknowledgement

B.N.C.T and S.C. acknowledge financial support from the Independent Research Fund Denmark–Natural Sciences, DFF-RP2 Grant No. 7014-00258B.

Supporting Information Available

RASSCF results for all molecular systems considered.

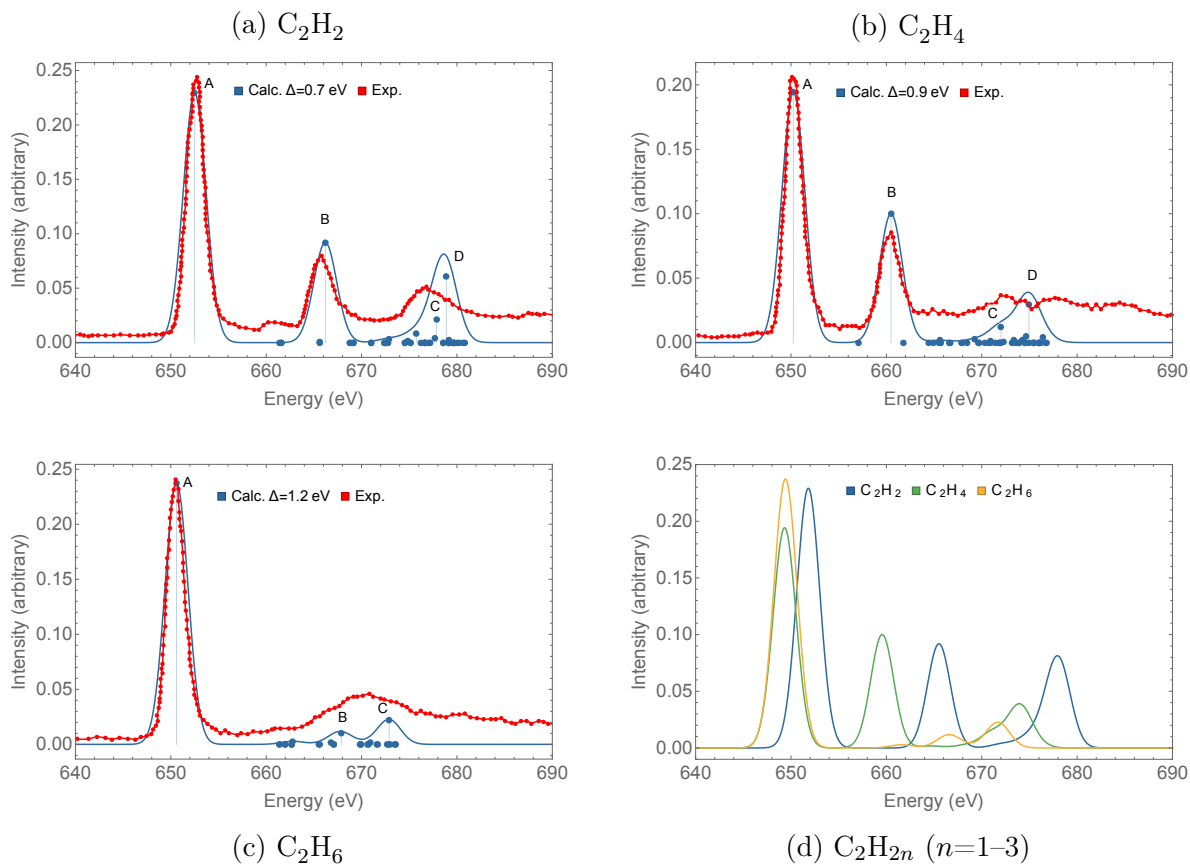


Figure 2: RASPT2 K^{-2} spectra of C_2H_{2n} ($n=1-3$). The experimental points were re-digitized from Ref. 17. The aug-cc-pVTZ basis set was used on all atoms. The rigid shifts Δ used to align the computed spectra with the position of the first experimental peak are given in legend. The stick spectra were broadened using Gaussian functions with $\text{HWHM} = 1.1$ eV.

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