Theoretical approach for simulating single photon double core ionization of small molecules

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Double core hole states (DCH states) have been observed as the result of single photon absorption at synchrotron facilities. Still the experimental observation of the formation of these highly excited system remain a challenge mostly because of the very low probabilities of such events (few order of magnitude lower than standard single core hole formation). In this context, developing robust theoretical approach for simulating these events is crucial in order to filter what is actually a signal from what is merely an experimental noise and to assign a final DCH state (the main close shell one and all its valence-valence shake-up excitation satellites) to the coresponding peak.

In the dipolar approximation, the corresponding cross section is proportional to the square of the overlap matrix between the neutral initial state and the K^{-2} double core ionized final state. We show that using the CIPSI [2] selected CI method for computing both initial N electrons and final $N-2$ electrons wave functions lead to good accord between our simulated spectrum and experimental results for small molecules such as (O K^{-2}) CO (Fig.1) and H_2O. We also show that using the second order Epstein-Nesbet perturbative correction to the energy naturaly available in the CIPSI methode leads to a fast convergence of the peak relative energies. For instance in the case of the CO molecule it reduces the number of selected slater determinants needed in the expansion of the ion wave function to achieve convergence from 3.5 million to a mere 500 000 determinants significantly reducing the numerical cost of such calculation.

Finally we show that using two non-orthogonal molecular orbital (MO) basis set for the neutral and the ion wave functions, and using Löwdin rules [3] to compute the overlap, lead to a faster convergence of the peak intensities compared to the case where we use the same MO basis for both, further reducing the numerical needs.

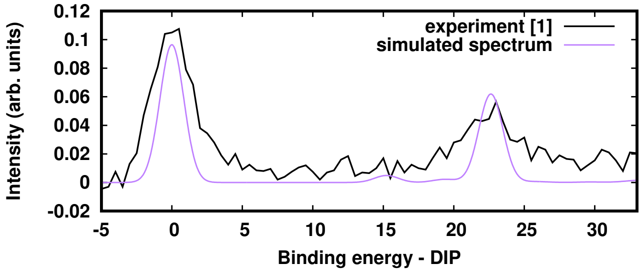

Figure 1: Computed and experimental $O(K^{-2})$ spectrum of the CO molecule.

References

1. Experiment by P. Lablanquie et al.
2. A.Scemama et al., *J. Chem. Theory Comput.* **15** (2019)
3. P.O. Löwdin, *Phys. Rev.* **97** (1955)