

# Coupled cluster study of the near-edge absorption fine structure spectra of small molecules containing carbon and oxygen up to the ionization limit.

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## Introduction

In X-ray absorption spectroscopy the ejection of a core electron is initiated by the absorption of an x-ray photon, inducing an excitation to bound states. Such core excitations exhibit strong relaxation effects and there are many states that can be reached upon the excitation, so a correct theoretical description of the processes can be especially challenging. In order to meet these challenges, the performance of the coupled cluster (CC) hierarchy with core valence separation (CVS)[1] have been evaluated. Amongst the electronic methods available, the CC ones are generally considered some of the most accurate, where the correct physical description of the quantum mechanical system can be approached in a systematic manner. Implemented with the response theory gives a reliable theoretical framework in which relaxation effects are taken into account by means of an accurate treatment of electron correlation in both the ground and excited state. Moreover, the simulation of the vibronic progressions associated to each electronic transition allows a more direct and detailed comparison with experiment.

## Methods

The hierarchy CCS (coupled-cluster singles), CC2 (coupled cluster singles and approximate doubles) and CCSD (coupled cluster singles and doubles) with core valence separation in the Dalton code [2] has been used to compute both core excitations and ionization potentials. Optimized structures for both ground and core-excited states were obtained with Cfour [3]. Different Dunning correlation consistent basis sets, further enriched with Rydberg-type basis functions, were used. The potential energy surfaces (PES) of the ground state and the core-excited states have been modeled with a quadratic expansion around their minima (adiabatic Hessian approach [4]) and the vibronic structure of the absorption spectra has been computed in Franck-Condon approximation, adopting both the time-independent [5] and the time dependent [6] methods implemented in the development version of the FCclasses code[7].

## Discussion

The ability of the coupled cluster hierarchy of methods CCS, CC2 and CCSD to accurately reproduce the near-edge absorption fine structure of formaldehyde, carbonyl fluoride, formyl fluoride and formic acid, including the region of Rydberg transitions and the core-ionization limits, has been investigated. In order to fully reproduce the experimental data[8], the vibronic structure of formaldehyde at the C edge and the O edge has been resolved.

## Conclusion

The CCSD method has been found to yield spectra in good agreement with experiment when basis sets of at least augmented triple zeta quality are used and Rydberg-type functions are added. The small discrepancy in absolute energy for the most accurate calculations as compared to experiments can be ascribed to the finite basis sets and truncation of the CC excitation manifold. We can demonstrate that CCSD gives excellent spectral features, while CC2 yields good agreement to experiments only for the most intense features. A good match with the experimental findings indicate that the adopted level of theory is able to correctly predict the differences between the initial and final state PES, in terms of displacement of the equilibrium geometry and changes in the composition and frequency of the normal modes.

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