IDENTIFICATION AND CHARACTERISATION OF REACTIVE MOLECULES: INTERPLAY OF AB INITIO CALCULATIONS AND SPECTROSCOPIC STUDIES.

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High-level ab initio calculations can guide the spectroscopic identification of new species by providing reliable predictions for their stability and their spectroscopic properties. When using vibration-rotation spectroscopy, a standard theoretical approach involves the ab initio computation of harmonic and anharmonic force fields followed by a rovibrational perturbation treatment to yield the familiar spectroscopic parameters. The lecture will first review the current status of this approach, in particular with regard to the convergence of the theoretical results with respect to improved correlation treatments and basis set extension. In collaboration with experimental groups, we have applied this approach to study a number of small reactive molecules, including difluorovinylidene $F_2C=C$, silaethene $H_2Si=CH_2$, difluorosilanethione $F_2Si=S$, and thiophosphenous fluoride FP=S. Some examples of these joint investigations will be discussed. The final part of the lecture will address the usefulness and the limitations of density functional theory in studying vibration-rotation spectra, with emphasis on the characterisation of new transition metal species such as nonclassical homoleptic carbonyl cations.