

Spectroscopy of benzophenone, xanthone and fluorenone ions: a comparative study

General Background

Benzophenone is the paradigm example for photochemistry which proceeds from a metastable triplet state after the latter was populated by a very rapid non radiative energy transfer from the initially populated singlet state. We have recently investigated the ultrafast dynamics of the triplet formation of the benzophenone isolated species¹. In 2012, we explored the photoionization of this molecule, both experimentally on the DESIRS beamline at SOLEIL and theoretically².

The quantum chemistry calculations that we did on the benzophenone ion showed that the C_2 symmetry of the neutral parent is not preserved in the ion. Indeed, electronic delocalization between the two rings is disconnected and where the positive charge is mainly localised on one ring of the benzophenone ion. Such behaviour is expected to be profoundly changed in close structural molecules such as Fluorenone, Anthrone and Xanthone. These last molecules belong also to the diarylketone family and share the same ionisation mechanism where the electron is removed from the lone pair of the oxygen atom. They differ from benzophenone by the second bridge between the two benzyl rings which is expected to block out-of-plane deformations and should maintain the localisation of the charge on the oxygen atom. The n^{-1} ion state which localizes the charge on the oxygen atom should become the ground ionic state. Its electronic structure is hence similar to that of the neutral triplet state ($n\pi^*$).

Project

Our previous work on the benzophenone cation provided the full vibrational spectroscopy of the ion as well as threshold energies for the lowest fragmentation channels. ² An Ionization Energy of 8.8 ± 0.1 eV was measured whereas the value available in the literature amounts to 9.05 eV ³. Importantly, a striking reactivity has also been discussed in this work besides the expected elimination of a phenyl or a CO group from benzophenone upon single photon ionisation. It corresponds to the ejection of an H atom and was interpreted tentatively as the occurrence of an electrocyclic condensation within the isolated species. Such behaviour might be forbidden in the other molecules, again because of its bridged structure.

To confirm these findings, we measured accurately the ionisation dynamics i.e. the threshold energy of all the opened fragmentation channels of fluorenone and xanthone. For these molecules accurate measurements of the ionization energy and of their low vibronic states is not or not precisely documented yet in the literature³.

During your visit, we propose to finalize the data treatment of the measurement issued from the above mentioned experiments, and to perform the theoretical calculations on the fluorenone and xanthone neutral and ionic molecules. The goal will be to

- Assign the character of the relaxed ionic states as well as its orbital configuration.
- Estimate the adiabatic fragmentation thresholds and identify the observed fragments
- Propose the mechanisms for the unimolecular decomposition decays of these ions
- Perform the comparison of the reactivity of benzophenone, xanthone and fluorenone

At the end, we should be able to publish these results within the current year.

Bibliography

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