

Static and dynamic quantum mechanical methods for exact interpretation of Infrared Multiple Photon Dissociation Spectra: current state and development perspectives

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Introduction

The advances in gas phase vibrational spectroscopy of mass-selected ions, Cold Ion IR spectroscopy, especially infrared multiple photon dissociation (IRMPD) provide fundamental information for characterization and understanding of the chemical state, the structure and dynamics of gas-phase biomolecules. Additional tool for suitable and exact interpretation and band assignment of an experimental spectrum is the theoretical approaches through available quantum mechanical computational codes, based on algorithms involving the double-harmonic normal mode approximation. These are being often used in conjunction with a density functional theory (DFT) based method.

The implementation of these methods and approaches will be presented through review of articles referring to glycine as the smallest and the simplest amino acid that been continuously drawing the attention of the scientific community. The obtained experimental spectra of glycine and the attempts for their suitable interpretation and band assignment are of great interest for many scientific areas. Therefore, in this work we will highlight the current knowledge, advantages and drawbacks in the currently used experimental and theoretical methods. We will also pinpoint the aspects in which significant new contributions to this field of work can be added by implementation of our own approaches.

Review of current state

The infrared multiple photodissociation (IRMPD) spectroscopic technique has enabled numerous size-selected species to be explored in details. Such method is usually applied employing a weakly bound so called "molecular messenger" to "tag" the investigated ion, using H₂, He, Ne, Ar as typical examples of tags that attach to ions at very low temperatures and that can be detached upon absorption of one or more IR photons. Exact assignment of vibrational modes is an important step in the interpretation of spectrum obtained with these experimental techniques. Most of the band assignments, are usually based on empirical arguments and on the "chemical intuition". Any serious attempt to provide exact and in-depth understanding of molecular force fields should be based on sound theoretical analysis and argumentation (Polfer, 2011).

IRMPD as an experimental approach provides an insight in the nature and localization of posttranslational modifications (PTMs) affecting single amino acids and peptides. The advantages of this method are presented through several PTM containing amino acids and peptides which have been characterized by IRMPD in gas phase. IRMPD spectroscopy takes advantage of the high sensitivity and resolution of MS/MS, but it is not a proteomics tool. Provides detailed structural information for the isolated species of interest in the gas phase, such as individual ions or in a carefully controlled

microsolvation state. Integration with X-ray crystallography and NMR spectroscopy in the structural analysis of biomolecules and reactive intermediates, to elucidate the relationship between structure and biological function (Maitre et al., 2020).

The native-like structures of protonated glycine and peptide Gly₃H⁺ were elucidated using cold ion IR spectroscopy of these biomolecules hydrated by a controlled number of water molecules. In doing so, the focus is kept on the differences in the structures of the hydrated complexes generated directly from an aqueous solution or produced by cryogenic condensation of water onto the gas-phase glycine (Saparbaev et al., 2021).

Using IRMPD is reported IR spectra of cold, protonated glycine tagged with He or between 1 and 14 H₂ molecules. Theoretical approach is conducted simultaneously with density functional theory (DFT) – based method, using second order Møller-Plesset perturbation theory in the double-harmonic normal mode approximation. Only harmonic theory calculations which are scaled to bring the calculated free OH stretch of protonated glycine with a helium atom attached into agreement with the free OH stretch observed in the experimental spectrum of this same ion (Masson et al., 2015).

Discussion and perspective

Experimental results obtained with most of the modern sophisticated techniques, interpreted within the quantum mechanical representation of the structure of matter, provide information about the distance between energy levels of a certain type. In the case of the IRMPD technique, these are vibrational energy levels. However, the data obtained directly from the experiment do not indicate the nature and type of these energy levels. Therefore, for the correct interpretation of the data, serious theoretical support is necessary, which in recent years is practically a necessity in the scientific literature. In the present works in the field of IRMPD spectroscopy, the theoretical support mainly consists in performing routine calculations based on the theory of function of the electron density in the so-called double harmonic approximation. Such calculations contain several assumptions inherent in all static theoretical methods (based only on the potential energy surface of the studied molecular systems).

The shortcomings of these computational methods can be approached for a further development. In the static approach, the total anharmonic vibration potentials of the relevant intra- and intermolecular modes can be calculated, and the vibration Schrödinger equation would be solved sequentially, thus obtaining the anharmonic vibration frequencies, there will be no work in

harmonious approximation. Dynamic calculations, on the other hand, can be performed on a series of statistical-physical simulations (with the Monte-Carlo methods or molecular dynamics) at final temperatures, which correspond to the conditions in which the experiments are performed in reality. Sequentially, with proper mathematical processing of the generated trajectories, the total final temperature spectrograms can be calculated, which inherently contain the effects due to the anharmonicity of the movements.

Conclusion

Most of the theoretical approaches coupled with IRMPD spectroscopy are simple and straightforward, automated in the available quantum mechanical computational codes, based on algorithms involving the double-harmonic normal mode approximation, and are being used often in conjunction with a density functional theory (DFT) – based method. Such calculations contain several assumptions inherent in all static theoretical methods (based only on the potential energy surface of the studied molecular systems). There is a firm evidence that systematic errors inherent to widely used DFT methods may cancel out with those due to the harmonic approximation. Therefore an attempt will be made to make a substantial contribution to the development and implementation of new computational methods that would not have these shortcomings.

References

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