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MESSENGER TAGGING SPECTROSCOPY

Project: C3

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Messenger tagging spectroscopy is a spectroscopic method in which adducts between molecule of interest and another molecule or atom are formed to indirectly detect absorptions.

Background

In absorption spectroscopy in condensed matter, the absorption behavior is influenced by the environment of the analyte molecule. Additionally, there are usually a multitude of molecules actually present in the sample (e.g. protonated, deprotonated). To exclude environmental effects and to select specific molecules, it is advantageous to conduct measurements in the gas phase.

This is possible by transferring the ions of interest into the gas phase using mass spectrometry methods. In this way it is also possible to select an ion based on its mass-to-charge ratio (m/z).

However, it becomes apparent that the ion density is no longer sufficient to directly measure the attenuation of the light. For this reason, photodissociation methods are utilized. In these methods, the dissociation of the ion is used as an indicator of absorption. However, in conventional photodissociation measurements, part of the molecule must fragment, often achievable only through multiphoton processes. Messenger tagging spectroscopy provides a solution. With this method, single-photon absorption spectra can be recorded.

Measurement procedure

The ions ($M^{+/-}$) are generated in the gas-phase, mass-selected and cooled. Through collisions with an equally cold tagging gas (e.g., CH_4, H_2, N_2, He), adducts (e.g., [$M^{+/-}$…He_n]) are formed. Since the tag is only weakly bound, it can be easily detached by the energy supplied from an absorption ([$M^{+/-}$…Tag] + hν → $M^{+/-}$ + Tag).[1] Therefore, it is now possible to irradiate the tagged molecules with light of a known wavelength using a tunable laser system and detect the loss of the tag using mass spectrometric methods.

Choice of the tag

When choosing the tag, it should be noted that those which least affect the absorption spectrum (e.g., N_2, He) usually require a more complex instrumental setup to achieve the necessary low temperatures of the ions. Consequently, it is necessary to choose the tag according to the given conditions. The noble gas helium has the least influence on the absorption spectrum, but is experimentally the most demanding. It is useful, for example, for obtaining laboratory data for potential candidates for the carriers of diffuse interstellar bands.[2] Less demanding tags like CH_4 can be useful for searching with probes on icy moons in our solar system for (already tagged) molecules.[3] Additionally, charged tags such as tetramethylammonium can be used to measure neutral molecules that are otherwise inaccessible to mass spectrometry.

References

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(3) Terry, L. M.; Klumb, M. K.; Nemchick, D. J.; Hodyss, R.; Maiwald, F.; Weber, J. M. Cryogenic Ion Vibrational Spectroscopy of Protonated Valine: Messenger Tag Effects. **2024**.