Action Spectroscopy in Cold Ion Traps

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Action spectroscopy in cold ion traps is one of the brilliant techniques invented by Dieter Gerlich already in the early 1990s. Its tool box grew tremendously over the last 20-30 years [1]. In Cologne we concentrated on applying the method of laser induced reactions (LIR) to astrophysical relevant ions such as H_3^+ and its isotopic siblings, CH_3^+, CH^+, C_3H^+ and many others. Some of these species were identified in space based on our laboratory measurements.

Often we promote a chemical reaction by excitation of a molecular vibration. For this purpose, we use light from the free electron laser (FELIX, Nijmegen) to cover a very wide spectral range and obtain a full account of the vibrational modes. Rotationally resolved infrared spectra become available with the use of narrow bandwidth infrared cw-OPO systems and QCLs. In recent years the technique of vibrational excitation was “only” used as a detector for addressing a specific ion. In these double resonance experiments microwaves, Millimeter- or submm-waves are used to change the population of the rotational states of the ion ensemble in the trap. As a result of this double resonance approach, pure rotational spectra in very high resolution open yet another door for action spectroscopy.

One focus of our work is concerned with ions which exhibit large amplitude motions (LAM) in more than one degree of freedom. Recently we studied the vibrational pre-dissociation of the $He\text{-}H_3^+$ complex in our COLtrap instrument in high-resolution [2]. High level electronic structure calculations of the potential energy surface followed by the computation of the vibrational-rotation-tunneling (VRT) states of the $He\text{-}H_3^+$ enabled an assignment of the many experimental lines [3]. We succeeded to reconstruct the energy term diagram of the lowest energy states of this floppy system just based on the experimental lines and compared this with the theoretical results. The term diagrams obtained have a clear and simple structure which can be explained treating the complex as a diatomic molecule with Coriolis interaction.

Very recently we recorded a high-resolution infrared spectrum of the enigmatic protonated water dimer. The spectra are extremely rich because of the numerous tunnelling motions involved in this molecule. We will present those spectra and discuss the current state of assignment and interpretation. Our results seem to support that the central proton is indeed shared between the two water molecules in agreement with the suggested Zundel structure.

References

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