

THE INFLUENCE OF RARE-GAS TAGGING ON THE RENNER-TELLER PERTURBED HCCH⁺ ION PROBED BY CRYOGENIC ACTION SPECTROSCOPY

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Infrared predissociation action spectroscopy in its form as messenger spectroscopy, is a well-established technique to record vibrational spectra of reactive molecular ions. One of its major drawbacks is that the spectrum of the messenger-ion complex is taken as a proxy of that of the bare ion. In particular for small open-shell species, such as the Renner-Teller (RT) affected HCCH⁺, the attachment of the tag may have a significant impact on the spectral features. In order to investigate this effect, we have recorded the vibrational spectra of Ne- and Ar-tagged HCCH⁺ using a cryogenic ion trap end user station at the FELIX laboratory^a, and compared them to previous data of the bare ion obtained with laser induced reactions (LIR) spectroscopy^b. The Ne-attachment led to a shift in band positions and change in relative intensities, while the Ar-attachment even led to a complete quenching of the RT splitting. Whereas for HCCH⁺ LIR offers a tag-free spectroscopic method^b, this is not the case for most other reactive open-shell species. The newly developed leak-out spectroscopy (LOS)^c, seems to provide a much more universal tag-free method. Here we present the application of this method to record the cis-bending of the HCCH⁺ cation (700 cm⁻¹), and demonstrate that the obtained LOS spectrum is equivalent to the previously recorded LIR spectrum. Not only presents this the energetically lowest-lying vibrational mode targeted with LOS so far, but it also shows its potential to overcome the tag problem in other Renner-Teller affected species.

^aJusko, P.; Brünken, S.; Asvany, O.; Thorwirth, S.; Stoffels, A. *et al.* *Faraday Discuss.*, **2019**, 217, 172-202.

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