

REVISITING THE RO-VIBRATIONAL SPECTRA OF $C_2H_3^+$ WITH LEAK-OUT-SPECTROSCOPY

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High-resolution ro-vibrational spectroscopy of molecular ions was pioneered by the Oka group¹. Spectra of many carbo-cations and other species were recorded for the first time. Traditional absorption spectroscopy of molecular ions created in a plasma is a formidable task because it is difficult to pull out the signal of the ion of interest from a plethora of lines associated with other species also created in the plasma.

Action spectroscopy of mass selected ions is an alternative method which overcomes this difficulty. In addition, the trapped ions can be cooled with the help of Helium buffer gas which simplifies the spectrum substantially. In this work, we report on the ro-vibrational spectrum of ν_6 antisymmetric CH stretching band of $C_2H_3^+$ using the new method of leak-out-spectroscopy (LOS)². For our study, $C_2H_3^+$ is produced in a storage ion source (SIS) from acetylene. The mass selected species are then stored in a 22-pole ion trap where they are cooled to 12 K. After excitation with a CW IR-OPO, vibrational energy is transferred eventually into kinetic energy via collisions with Neon atoms. The trapping potentials are arranged such that the fast ions resulting from this process are leaving the trap and are detected. A spectrum is generated by recording the number of these ions as a function of the excitation frequency.

The P-, Q- and R-branches of the $C_2H_3^+$ spectrum can easily be identified from the raw data³. The spectrum is sparse enough to assign most of the lines belonging to one initial J value. In LOS only one specific isomer is kicked-out from the trap. Due to inelastic collisions with the buffer gas all ions of this class can be removed from the trap. By analysing the ion fraction left in the trap it is thus possible to determine the ortho to para (o/p) ratio of $C_2H_3^+$ and whether there are other (structural) isomers present in the trap. This opens new ways of assigning and analysing spectra. The determination of the o/p ratio of $C_2H_3^+$ shall serve as a direct distinction between the classical (C_{2V}) and the non-classical (D_{3h}) structure of this carbo-cation.

¹[doi:10.1021/jp4035826](https://doi.org/10.1021/jp4035826), T. Oka, *J. Phys. Chem. A*, **117**(39), 9308–9313 (2013).

²[doi:10.1021/acs.jpca.2c05767](https://doi.org/10.1021/acs.jpca.2c05767), P. C. Schmid, O. Asvany, T. Salomon, S. Thorwirth, and S. Schlemmer, *J. Phys. Chem. A*, **126**(43), 8111–8117 (2022).

³[doi:10.1021/j100042a042](https://doi.org/10.1021/j100042a042), C. M. Gabrys, D. Uy, M.-F. Jagod, T. Oka, and T. Amano, *The Journal of Physical Chemistry*, **99**(42), 15611–15623 (1995).