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Cavity Ring-Down Spectroscopy of Carbon-Chain Radicals

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Abstract. Cavity ring-down spectroscopy is a powerful new spectroscopic technique which is used to study transient species.



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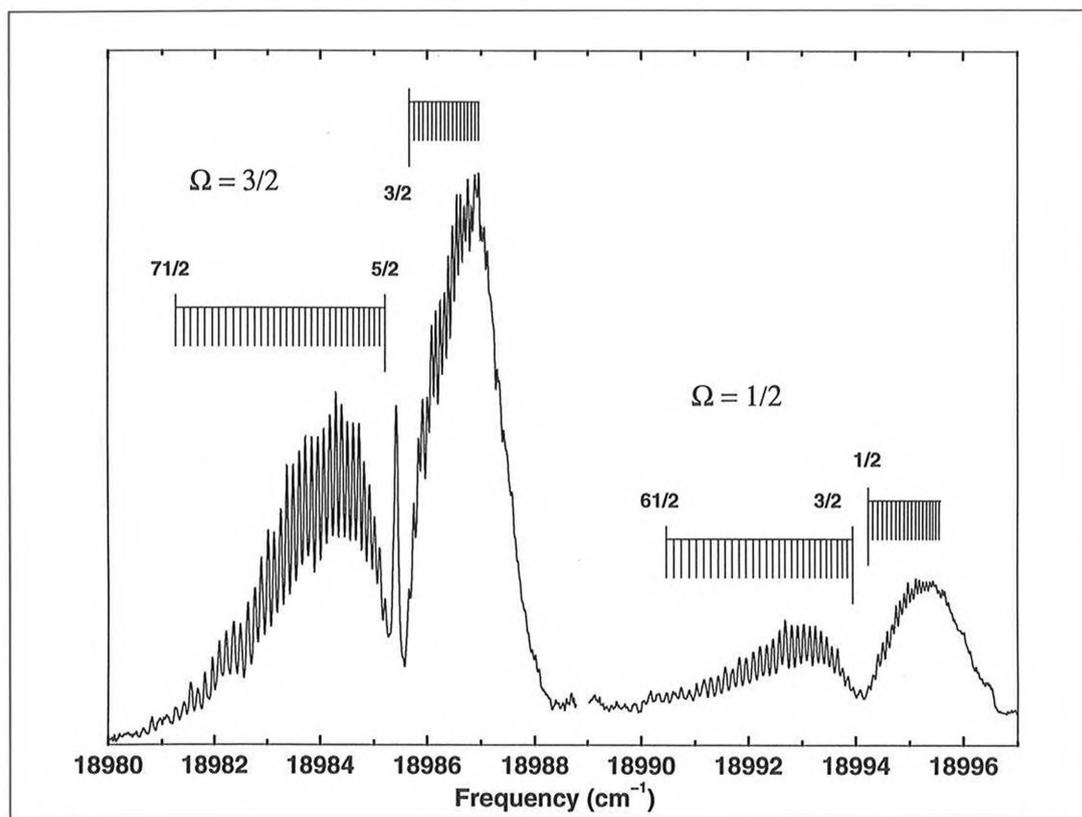


Figure. The two rotationally resolved spin-orbit components of the ${}^2\Pi \leftarrow X^2\Pi$ electronic origin-band transition of linear C_6H , measured by cavity ring-down spectroscopy in an adiabatically cooled supersonic plasma ($T_{rot} < 15$ K)

Transient molecules, such as radicals and ions, play a key role in many processes, varying from atmospheric and interstellar chemistry to combustion and biochemistry. This high reactivity, however, also complicates systematic spectroscopic studies – especially in the gas phase – as it is hard to generate high concentrations under controlled laboratory conditions. A new technique that overcomes these problems is based on cavity ring-down spectroscopy in a pulsed slit nozzle, incorporating a discharge in a high-pressure supersonic expansion [1].

Tunable light from a pulsed laser system is coupled into a stable optical resonator that is formed by two highly reflective ($R > 99.99\%$) plano-concave mirrors. The rate of light leaking out of the cavity is detected by a photo-multiplier and has an envelope which is simply a first-order decay $\exp[-t/\tau]$, τ being the ring-down time. By recording the ring-down time, the rate rather than the magnitude of the absorption is measured, and, consequently, this technique has several important advantages compared to conventional absorption techniques [2]. In addition, the very long absorption pathlengths – up to 100 km – that are obtained by confining a light pulse typically 20 to 80 μs to the cavity, make the technique ideal for the study of unstable species. The latter are generated in a supersonic plasma that is formed in the throat of a slit nozzle mount-

ed inside the cavity. This type of nozzle provides a *Doppler*-free environment and combines high molecular densities with an effective adiabatic cooling. When laser light is absorbed by the radicals in the plasma, the ring-down time decreases and recording τ as function of the frequency yields the molecular spectrum. This is demonstrated in the *Fig.* for the rotationally resolved origin band of the ${}^2\Pi \leftarrow X^2\Pi$ electronic transition of C_6H .

Guided by electronic absorption spectra obtained in mass-selective matrix experiments [3], the method has been used to study long linear carbon-chain radicals, typically of the form $C_{2n}H$, $HC_{2n}H^+$, $NC_{2n}N^+$ or HC_nN^+ [4][5] with up to ten carbon atoms in one chain. The spectra provide a firm base from which to spectroscopically characterize radical carbon species, and in addition they allow the determination of the absolute origin-band positions in the gas phase, which is important, especially, from an astrophysical point of view [5].

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- [1] T. Motylewski, H. Linnartz, *Rev. Sci. Instrum.* **1999**, *70*, 1305.
- [2] A. O'Keefe, D.A.G. Deacon, *Rev. Sci. Instrum.* **1988**, *59*, 2544.
- [3] J.P. Maier, *J. Phys. Chem.* **1998**, *102*, 3462.
- [4] H. Linnartz, T. Motylewski, J.P. Maier, *J. Chem. Phys.* **1998**, *109*, 2819.
- [5] D.A. Kirkwood, H. Linnartz, M. Grutter, O. Dopfer, T. Motylewski, M. Pachkov, M. Tulej, M. Wyss, J.P. Maier, *Faraday Discuss. Chem. Soc.* **1998**, *109*, 109.