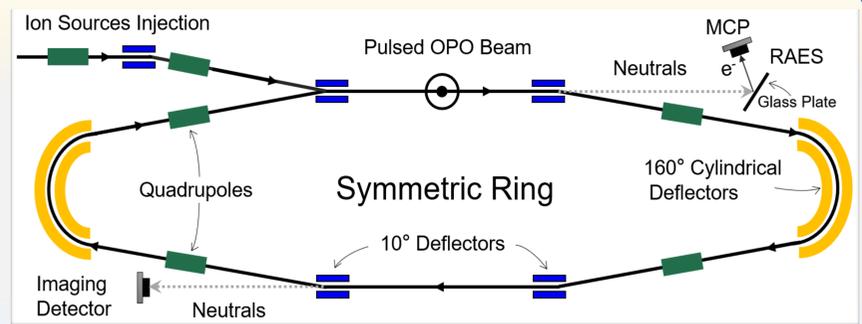


Abstract: The time-dependent photodetachment action spectra of the linear hydrocarbon anions C₄H⁻ and C₆H⁻ are investigated using the cryogenic electrostatic ion storage ring DESIREE. Radiative cooling characteristics of the ions on the millisecond to second timescale are probed by monitoring changes in the spectra as the ions cool by spontaneous infrared (IR) emission. A simple harmonic cascade (SHC) model is used to model the cooling processes. The cooling rates, extracted using Non-negative Matrix Factorization (NMF), are fit with 1/e lifetimes of 19 ± 2 s and 3.0 ± 0.2 s for C₄H⁻ and C₆H⁻, respectively. For C₄H⁻, the adiabatic detachment energy is determined from the cold ions' photodetachment spectra to be 3.45 ± 0.02 eV. The photodetachment spectrum and the ultraslow radiative cooling dynamics interpreted in the present work provide important data for understanding the thermal cooling properties of linear hydrocarbon anions and for refining the formation and destruction processes of these anions in astrochemical models.

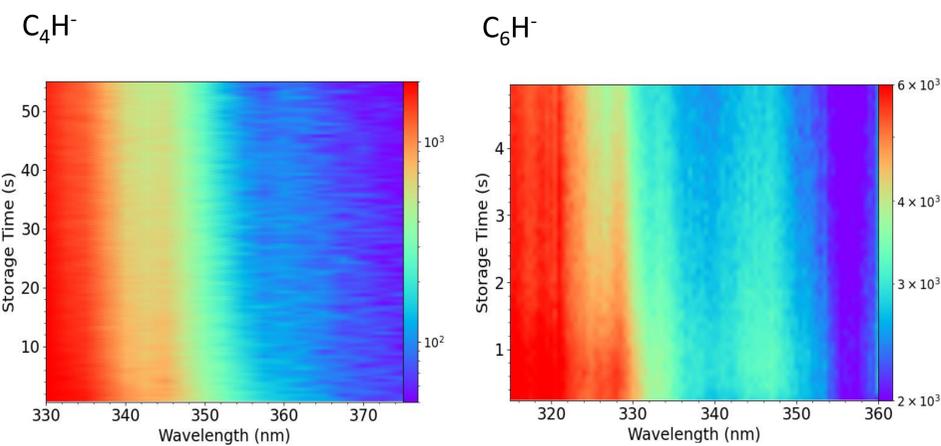
Experiment and method

- ¹³C_{2n}H⁻ (n = 2, 3) ion beams were produced using a cesium sputtering ion source with a ¹³C-enriched graphite cathode, where sputtered carbon clusters react with residual water in the source to form hydrocarbons.
- For the action spectroscopy experiments, a tunable wavelength OPO laser system was used to excite the target ions in a crossed-beams geometry through the ion storage ring.
- The 2D photodetachment action spectra were analyzed using Non-negative Matrix Factorization (NMF) a set of algorithms for dimensionality reduction, source separation and topic extraction.

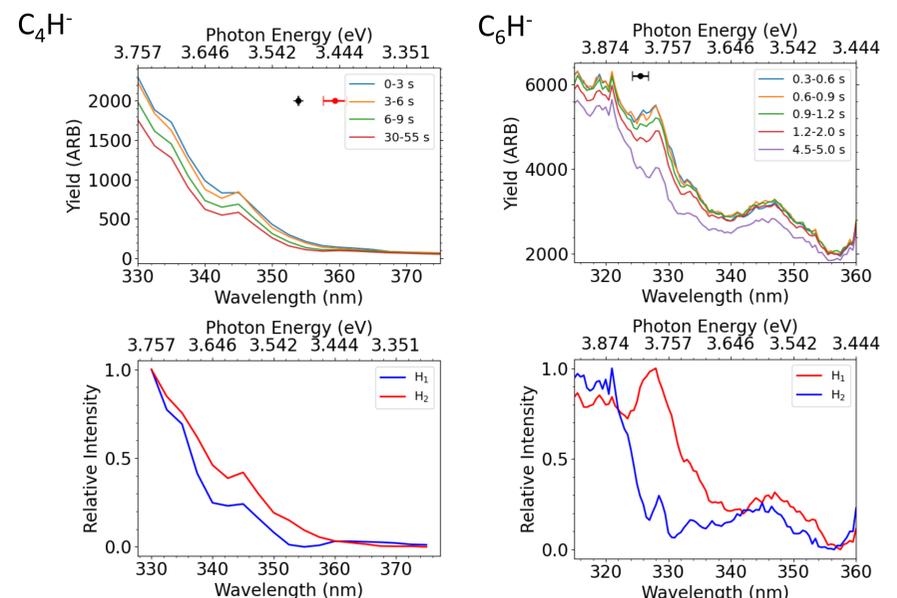


Results and analysis

The radiative cooling of C₄H⁻ and C₆H⁻ is probed using two-dimensional (i.e. storage time and excitation wavelength dependent) photodetachment action spectroscopy as a hot ensemble of stored ions cool during storage. A photodetachment spectrum surveys collected for C₄H⁻ and C₆H⁻ as a function of ion storage time are shown in below.



Time-binned photodetachment spectra for C₄H⁻ and C₆H⁻ in different time slices are shown in the below of upper panel. The data markers represent the ADE (red value from H₁ and black value from previous results). Latent components are extracted from NMF analysis.

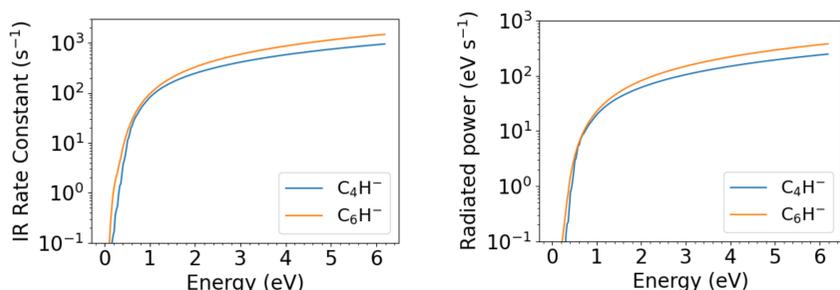


Spontaneous radiative cooling was analyzed using a simple harmonic cascade (SHC) model with the following equation:

$$k_s(E) = A_s^{10} \sum_{v_s=1}^{v_s \leq E/h\nu_s} \frac{\rho(E - v_s h\nu_s)}{\rho(E)}$$

where E is the energy of a given vibrational state, h is Planck's constant, and the summation is over v_s ($v_s = 0$ and $v_s > 1$ are the quantum numbers of the ground state and the vibrational-excited states for the corresponding mode v_s , respectively). The density of vibrational states $\rho(E)$ are calculated using the Beyer-Swinehart algorithm with scaled harmonic vibrational mode frequencies ν_s . The SHC model assumes that the only allowed emissions are those where $\Delta v_s = -1$. The Einstein coefficients A_s^{10} and harmonic vibrational frequency for each mode of ¹³C₄H⁻ and ¹³C₆H⁻ were calculated at the B3LYP//6-311++G(2d,p) level of DFT in Gaussian 16.

The total IR rate constant $k_s(E)$ and radiative power $p_s(E)$ are shown in below, where $p_s(E) = \sum_s h\nu_s k_s(E)$.

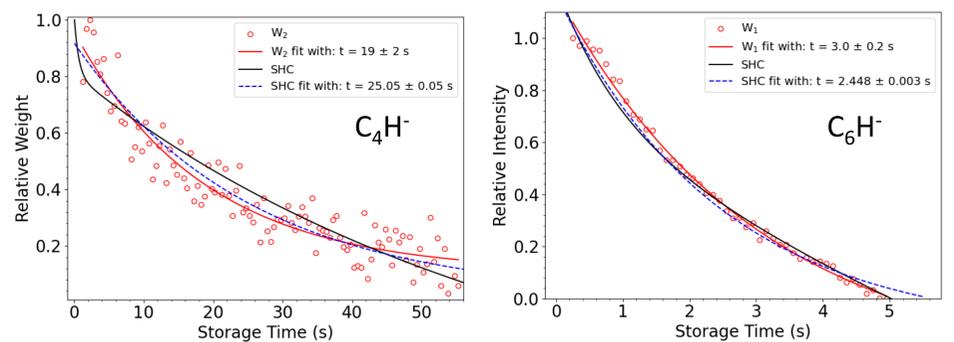


The initial population density $g(E, t = 0)$ can be described as:

$$g(E, t = 0) = (\rho(E) * e^{-E/(k_B T)}) / (\sum_E \rho(E) * e^{-E/(k_B T)})$$

where k_B is Boltzmann constant and T is the temperature determining the initial of the vibrational energy distribution. Radiative cooling processes are the time evolution of the internal energy distribution that is given by the following expression:

$$g(E, t + dt) = \sum_s g(E, t) e^{-k_s(E) dt} + \sum_s g(E + h\nu_s, t) (1 - e^{-k_s(E + h\nu_s) dt})$$



IR radiative cooling rates have been simulated using a Second Harmonic Cascade model in good agreement with experiment. Average cooling lifetimes are 19 ± 2 s for C₄H⁻ and 3.0 ± 0.2 s for C₆H⁻. The adiabatic detachment energies for C₄H⁻ were obtained from the NMF-extracted cold-ion spectrum, giving ADE values of 3.40 ± 0.02 eV by Wigner threshold law.

Acknowledgments

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