Radiative Cooling of Polyyne Anions: C_4H^- and C_6H^- 

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Abstract: The time-dependent photodetachment action spectra of the linear hydrocarbon anions C_4H^- and C_6H^- 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 C_4H^- and C_6H^-, respectively. For C_4H^-, 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

\[ ^{12}C_6H^- - (n = 2, 3) \] ion beams were produced using a cesium sputtering ion source with a \( ^{12}C \)-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) as a set of algorithms for dimensionality reduction, source separation and topic extraction.

Results and analysis

The radiative cooling of C_4H^- and C_6H^- 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 C_4H^- and C_6H^- as a function of ion storage time are shown below.

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

\[ k_s(E) = A_s^{(0)} \sum \rho(E - \hbar \nu_k) \rho(E) \]

where \( k_s \) is the rate constant, \( A_s^{(0)} \) and \( \rho(E) \) are calculated using the Beyer-Swinehart algorithm with scaled harmonic vibrational mode frequencies \( \nu_k \). The SHC model assumes that the only allowed emissions are those where \( \Delta \nu_k = \pm 1 \). The Einstein coefficients \( A_s^{(0)} \) and harmonic vibrational frequency for each mode of \( ^{12}C_4H^- \) and \( ^{12}C_6H^- \) were calculated at the B3LYP/6-311+G(d,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 \( p_s(E) = \sum \nu \rho(E) \).

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

\[ g(E, t = 0) = (\rho(E)e^{-E/k_B T} / (\sum \rho(E)e^{-E/k_B T})) \]

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:

\[ g(E, t + dt) = \sum \rho(E)e^{-E/k_B T} + \sum \rho(E + \hbar \nu_k, t) (1 - e^{-E/k_B T}) \]

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 C_4H^- and 3.0 ± 0.2 s for C_6H^-.

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Reference
