Radiative de-excitation of vibrationally excited C_2^-

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Hot molecules isolated in the vacuum environment dissipate their internal energy solely though emission of IR photons, which thereby govern the stability and reactivity of such molecules, for example those in the interstellar space. In general, the radiative cooling of hot homonuclear diatomic molecules is very slow because vibrational transitions are dipole forbidden. In fact, hydrogen molecules require approximately 10^6 s for such transitions[1]. C_2^- is an exception that can be cooled much more efficiently via electronic transitions between the ground state $X^2\Sigma_g^+$ and the low-lying excited state $A^2\Pi_u$, as schematically shown in Fig. 1. The timescales of the transitions from X to A and from A to X are theoretically predicted to be on the orders of ms and μs, respectively[2], whereas these values have not been experimentally confirmed.

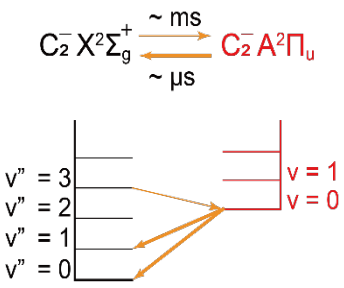

Fig. 1 De-excitation pathways of C_2^- from $v'' = 3$ in the X state.

In this study, we stored C_2^- beam in an electrostatic ion storage ring (TMU E-ring) and observed the time evolution of populations of vibrational states ($v'' = 0 – 7$) in the X state up to 60 ms. To determine the wavelength for monitoring the desired ro-vibrational state, excitation spectra of the laser-induced electron detachment were measured at a fixed ion storage time. These measurements were conducted using either one-photon or two-photon excitation, depending on the vibrational states, in the wavelength region corresponding to the $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ transitions. The well-resolved peaks in the obtained spectra were assigned to the initial and final ro-vibrational states aided by the PGOPHER code[3].

The storage time dependences of the electron detachment yields are shown in Fig. 2, which demonstrate decreases in the populations at the high vibrational states and increases at the low vibrational states[4]. The time profiles agree well with the simulated time evolution of the populations based on the theoretical rates[2] and the Boltzmann distribution at the vibrational temperature of 4500 K in the ion source.

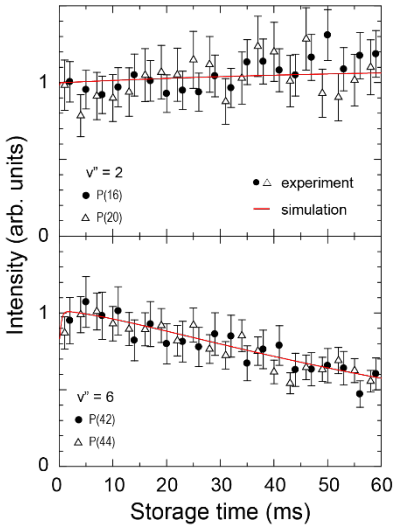

Fig. 2 The Storage time dependences of the electron detachment yields at $v'' = 2$ (top) and $v'' = 6$ (bottom) in the X state. Red lines are the simulated time profiles.

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