Intrinsic absorption profile and radiative cooling rate of a PAH cation revealed by action spectroscopy in the cryogenic electrostatic storage ring DESIREE

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Abstract. The multi-photon photodissociation (MPD) action spectrum of the coronene cation $(C_{24}H_{12}^+)$ has been measured as a function of storage time up to 60 s in the cryogenic electrostatic storage ring DESIREE. These measurements reveal not only the intrinsic absorption profile of isolated coronene cations, but also the rate at which hot-band absorptions are quenched by radiative cooling. The cooling rate is interpreted using a Simple Harmonic Cascade model of infrared vibrational emission.

Keywords. molecular data, techniques: spectroscopic, ISM: molecules

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1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are thought to be ubiquitous in the Interstellar Medium (ISM), as evidenced by the ubiquitous infrared emission bands associated with their vibrational modes (Tielens 2008). It is widely accepted that this emission arises from PAHs excited by ultraviolet starlight followed by rapid internal conversion to a vibrationally-excited ground electronic state. The rate at which this vibrational energy is discharged through infrared emission is of consequence to the PAH destruction rate under UV irradiation. Laboratory benchmarks of PAH radiative cooling rates (*e.g.* Martin *et al.* (2013)) are thus valuable for refining models of the interstellar carbon cycle, and determining the relative importance of photodestruction and *e.g.* shock processing (Micelotta *et al.* 2010; Stockett *et al.* 2015). Measuring the infrared emission rate of PAHs is challenging as it requires they be isolated in a cold, collision free environment for timescales up to tens of seconds. Recent advances in cryogenic ion beam storage techniques have granted experimental access to such "ultra-slow" processes (Hansen *et al.* 2017; Schmidt *et al.* 2017). Here, we investigate the radiative cooling of coronene cations $(C_{24}H_{12}^+)$ using two-dimensional (*i.e.* storage-time-dependent) multi-photon dissociation (MPD) action spectroscopy (Wolf *et al.* 2016). These experiments were conducted using the DESIREE (Double ElectroStatic Ion Ring ExpEriment) infrastructure located at Stockholm University (Thomas *et al.* 2011). In a previous article, we compared the MPD action spectrum of coronene measured at DESIREE to previous experiments in cryogenic ion traps (Stockett *et al.* 2019). In the present contribution we turn our attention to the infrared radiative cooling rate of hot coronene cations.
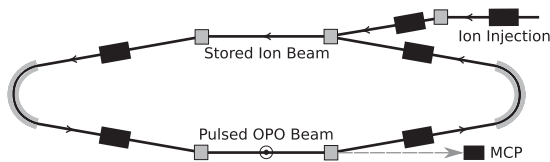
Figure 1. The DESIREE symmetric storage ring. Stored $C_{24}H_{12}^{+}$ ions are irradiated in a crossed-beam geometry in the lower straight section.

2. Experimental methods

The experiment has been described previously by Stockett *et al.* (2019). Briefly, hot coronene cations were produced using a Nielsen-type plasma ion source equipped with a temperature-controlled oven. The ions were accelerated to 15 keV and those with mass-to-charge ratio $m/z = 300$ were selected using a bending magnet. These ions were injected into the so-called "symmetric ring" (one of the two DESIREE storage rings (Thomas *et al.* 2011; Schmidt *et al.* 2013)) and stored for up to one minute. The experimental setup is shown schematically in Figure 1. Stored ions were excited at a 10 Hz repetition rate in one of the straight sections of the ring in a crossed-beam geometry using a tunable wavelength OPO laser system (EKSPLA). Neutral fragments – presumed to mainly be H atoms, the lowest energy dissociation channel for $C_{24}H_{12}^{+}$ (Holm *et al.* 2011) – formed in this section are unaffected by the electrostatic steering fields and fly straight into a micro-channel plate (MCP) detector. The detector signal is gated with a 1 μs width and a delay after the laser firing time corresponding to the flight time from the interaction region to the detector. This eliminates the counting of scattered laser light and strongly suppresses the counting of detector dark noise and background fragmentation events due to collisions between stored ions and residual gas in the ring. The excitation wavelength is stepped in between ion injections, creating a two-dimensional photodissociation action spectrum.

To interpret the changes in the action spectrum over time, we applied a Principal Component Analysis (PCA, Jolliffe (2002)). PCA is a statistical procedure that diagonalizes the covariance matrix of the complete, 2D data set to obtain a set of orthogonal principal components (PCs) and their weightings. The PCs may be thought of as the underlying spectra that describe the 'average' evolution of the MPD action spectrum with ion storage time, with a time-invariant 'background' contribution due to MPD signal from cold ions.

3. Radiative cooling model

We have developed a Simple Harmonic Cascade (SHC) model to describe the infrared radiative cooling of $C_{12}H_{24}^{+}$. The model computes a vibrational density of states ρ using the Beyer-Swinehart algorithm (implemented in Python, after Solano & Mayer (2015)), taking as inputs the vibrational frequencies and infrared intensities provided by the NASA Ames PAH IR Spectroscopic Database (Bauschlicher *et al.* 2018). For a given mode s, the infrared radiative cooling rate coefficient, assuming only transitions where $\Delta v = -1$ are allowed, is (Chandrasekaran *et al.* 2014):

$$k_s(E) = A_s^{10} \sum_{v=1}^{v \leqslant E/h\nu_s} \frac{\rho(E - vh\nu_s)}{\rho(E)}, \tag{3.1}$$

where he summation is over vibrational quantum number v, E is the energy of a given vibrational state, A_s^{10} is the Einstein coefficient for spontaneous emission from $v = 1$ to $v = 0$, and h is Plank's constant. The total infrared radiative cooling rate $k_{tot} = \sum_s k_s$ is
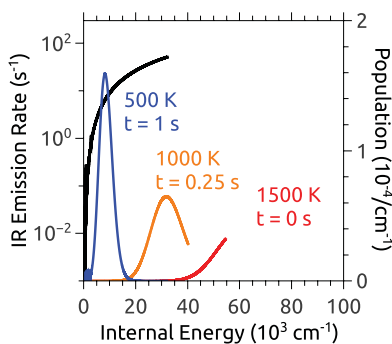
Figure 2. Total IR radiative cooling rate (black line, left axis) and internal energy distributions at various temperatures (colored curves, right axis) for $C_{24}H_{12}^{+}$.

plotted in Figure 2, as are several illustrative vibrational energy distributions. Starting from an initial Boltzmann distribution of vibrational energy $g(E, t=0)$ corresponding to 1500 K – chosen to be just below the energy where dissociation becomes competitive according to Montillaud *et al.* (2013) – the total energy emitted radiatively at each time step is (Kono *et al.* 2018):

$$dE_{tot}/dt = -\int g(E,t) \sum_s h\nu_s k_s dE, \qquad (3.2)$$

where the total energy remaining in the ensemble as a function of time $E_{tot}(t) = \int E g(E,t)dE$ is taken as an indicator of the progress of cooling. Assuming that Internal Vibrational Redistribution (IVR) is fast compared with radiative cooling (Nesbitt & Field 1996), the vibrational energy is statistically redistributed each simulation time step according to a Boltzmann distribution with a temperature associated with the total energy remaining in the system $E_{tot}(t)$. This temperature is found from an empirical equation of state generated from an interpolation of the total internal energy computed for a range of Boltzmann temperatures. Given that the vibrational energy quanta are small and the number of stored ions is large, level occupation numbers were treated as continuous quantities. The simulation time step is dynamically determined based on the IR decay rate of the highest significantly occupied vibrational level. For comparison to experiments, the simulation points are time-averaged with constant bin widths equal to those in the experiment (set by the 10 Hz repetition rate of the OPO laser).

4. Results and Discussion

Figure 3 shows several slices through the two-dimensional MPD action spectrum of $C_{24}H_{12}^{+}$, each representing the absorption at different storage times up to roughly 1 s. At the earliest times (0.01 s after injection into DESIREE, top red spectrum in Figure 3) the absorption is nearly flat. As the ions cool, the contributions to the spectrum from hot-band absorptions dissipate. After a few hundred milliseconds the spectrum converges to the thicker blue line, which is the average of all data recorded after 0.51 s of storage.

Figure 4 shows the relative weight of the hot-band contribution to the MPD action spectrum of $C_{24}H_{12}^{+}$ over 10 s of storage in DESIREE, as determined by Principal Component Analysis (see section 2). Also shown is the result of our Simple Harmonic Cascade simulation, namely the total internal energy $E_{tot}(t)$. For the sake of comparison, a constant offset (an artifact of the PCA) determined from a single-exponential fit (the black line in Figure 4) has been removed from the experimental data. The agreement is
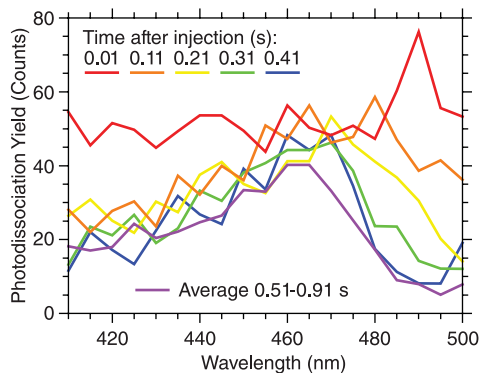
Figure 3. MPD action spectra of $C_{12}H_{24}^{+}$ recorded at different storage times.
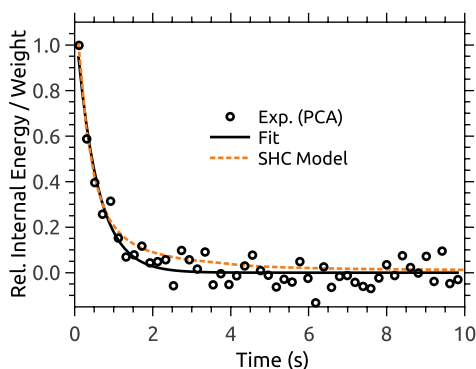

Figure 4. Decay of hot band contribution to MPD action spectrum (black) and total internal energy from SHC simulation (orange).

good, with a single-exponential fit to the experimental data giving a time constant of 0.54 ± 0.05 s and a fit to the time-binned simulation result 0.53 ± 0.02 s.

5. Conclusions

We have presented a novel method for measuring the radiative cooling rate of PAH cations isolated in a cryogenic electrostatic storage ring on time scales up to 10 s. The results are interpreted using a Simple Harmonic Cascade model of infrared radiative cooling of a vibrationally hot ion ensemble. While the agreement between experiment and simulation is satisfying, several aspects of each require further examination before quantitative conclusions should be drawn. On the experimental side, multi-photon effects could skew the action spectrum in favor of hot-band absorption. Our Principal Component Analysis may be subject to selection biases in both the wavelength and time dimensions. Several assumptions of our SHC model can also be questioned. We have neglected effects of anharmonicity (Mackie *et al.* 2018) and recurrent fluorescence following inverse internal conversion (Martin *et al.* 2013). At long times, IVR may not be as efficient as assumed in the model, leading to population becoming trapped in infrared inactive modes. Nevertheless, it seems that even such a simple model can at least qualitatively explain the time-evolution of the MPD action spectrum in terms of hot-band absorptions which are quenched by infrared radiative cooling.

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