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# Dissociation and radiative stabilization of the indene cation: The nature of the C–H bond and astrochemical implications

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## AFFILIATIONS

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## ABSTRACT

Indene ( $C_9H_8$ ) is the only polycyclic pure hydrocarbon identified in the interstellar medium to date, with an observed abundance orders of magnitude higher than predicted by astrochemical models. The dissociation and radiative stabilization of vibrationally hot indene cations are investigated by measuring the time-dependent neutral particle emission rate from ions in a cryogenic ion-beam storage ring for up to 100 ms. Time-resolved measurements of the kinetic energy released upon hydrogen atom loss from  $C_9H_8^+$ , analyzed in view of a model of tunneling through a potential energy barrier, provide the dissociation rate coefficient. Master equation simulations of the dissociation in competition with vibrational and electronic radiative cooling reproduce the measured dissociation rate. We find that radiative stabilization arrests one of the main  $C_9H_8$  destruction channels included in astrochemical models, helping to rationalize its high observed abundance.

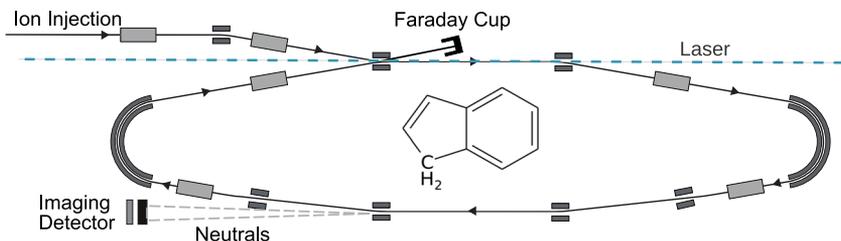
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## I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have long been thought to be ubiquitous in the interstellar medium (ISM). This is based on the infrared emission bands observed by astronomers at wavelengths coincident with their characteristic vibrational transition energies.<sup>1</sup> However, these bands are common to PAHs as a class and have proven difficult to assign to specific PAH molecules. It was only in the past few years that indene,<sup>2,3</sup> 2-cyanoindene,<sup>4</sup> and two isomers of cyano-naphthalene<sup>5</sup> were identified in space in the Taurus molecular cloud, TMC-1 by comparing astronomical microwave spectra with known rotational emission lines. Very recently, several larger cyano-functionalized PAHs have been identified by the same methods.<sup>6,7</sup> Interestingly, the observed interstellar abundance of indene ( $C_9H_8$ , Fig. 1), the only polycyclic pure hydrocarbon identified to date, was more than four orders of magnitude higher than predicted by astrochemical modeling.<sup>4</sup> These models

neglect radiative cooling and assume that PAHs are rapidly broken down into linear fragments following ionizing collisions with small cations including  $C^+$  and  $H_3^+$ .<sup>5</sup> Several recent studies have examined the spectroscopy and stability of indene<sup>8,9</sup> and its primary degradation product, indenyl, under astrophysically relevant conditions.<sup>10,11</sup>

A previous study<sup>12</sup> on 1-cyanonaphthalene by some of the present authors found that the energized cation is efficiently stabilized by recurrent fluorescence (RF)—the emission of optical photons from thermally excited electronic states.<sup>13,14</sup> This rapid radiative cooling closes some of the destruction pathways included in astrochemical models that underpredicted the abundance of that molecule in TMC-1 by six orders of magnitude.<sup>5</sup> Numerous laboratory studies have confirmed that RF, rather than infrared photon emission from vibrational relaxation, is the primary radiative stabilization mechanism for PAH cations,<sup>12,15–22</sup> with few exceptions.<sup>23</sup>



**FIG. 1.** DESIREE electrostatic ion-beam storage ring. Neutral fragments formed in the lower straight section are not constrained by the storage ring's electric fields and impact on a detector. The inset shows the structure of indene noting the  $sp^3$  functional group.

We present a study of the unimolecular dissociation and radiative stabilization of the indene radical cation,  $C_9H_8^+$ ,  $Ind^+$ . The dissociation rate coefficient and activation energy are determined from time-resolved measurements of kinetic energy release distributions of an ensemble of vibrationally excited ions isolated in a cryogenic ion-beam storage ring. RF rate coefficients are calculated based on *ab initio* molecular dynamics simulations. Master equation modeling including dissociation, RF, and infrared vibrational radiative cooling processes closely reproduces the measured absolute dissociation rate of the stored ion ensemble. We find that  $Ind^+$ , in contrast to fully  $sp^2$ -hybridized PAH cations, cools mainly by IR photon emission, with at most a small contribution from RF. Nevertheless, we find that  $Ind^+$  can be expected to be radiatively stabilized following charge-exchange reactions between  $C^+$  and neutral indene, one of the most important destruction channels for PAHs included in astrochemical models of molecular clouds.

## II. METHODS

### A. Experiments

Experiments were conducted using the DESIREE (Double ElectroStatic Ion Ring ExpERiment) cryogenic ion-beam storage ring infrastructure located at Stockholm University<sup>24,25</sup> using procedures similar to earlier experiments on cyano-naphthalene.<sup>12</sup> Indene (Sigma-Aldrich, >99%) vapor was introduced into an electron cyclotron resonance (ECR, Panteknik Monogan) ion source. The ECR source produces molecular ions with high internal energies. Positive ions were extracted from the source, accelerated to 86 keV, and those with  $m/z = 116$  were selected with a bending magnet. Ion beams were stored using electrostatic deflectors in the storage ring depicted in Fig. 1. Neutral fragments emitted from vibrationally hot ions in the lower straight section of the ring (see Fig. 1) impinged on a 75 mm diameter Z-stack microchannel plate detector (Photonis) with a phosphor screen anode (phosphor type P24). The position and time of each detected fragment were recorded using a Timepix3 hybrid pixel detector (Amsterdam Scientific) located outside of the DESIREE vacuum chamber. At the end of each storage cycle, the beam was dumped into a Faraday cup coupled to a fast amplifier for current normalization.

To analyze the kinetic energy released during dissociation, the event data from the Timepix were first binned according to time after ionization, with a bin width equal to the revolution period of the ions around the ring. Two dimensional histograms of the detector images for each revolution were centered and azimuthally integrated using the PyAbel package.<sup>26</sup> The resulting time-dependent radial intensity distributions were then further averaged over time windows with widths linearly increasing with storage time to

improve signal-to-noise at late times where the count rate is low. The radial intensity distribution includes contributions from neutral fragments emitted along the straight section of the storage ring and projected onto the detector plane (see Fig. 1). We fit analytic kinetic energy release (KER) distribution models to this final projected distribution by first applying a matrix transformation from energy to radial distance considering, for each energy bin, the range of radii over which the differential intensity will be spread given the finite length of the straight section. The projection of this spherically symmetric distribution onto the detector plane is achieved with a one-dimensional forward Abel transform. For more information on the analysis, see the Appendix.

While our numerical analysis of the KER is based on fits to the detector-plane radial intensity distribution, selected KER distributions are shown in Sec. III to facilitate comparison to the literature. To account for the numerical error introduced by the inverse Abel transform, we invert and average 128 radial distributions with intensities normally distributed according to the measured distribution and its counting statistics. The resulting distribution is calibrated assuming that all neutrals are emitted from the midpoint of the straight section, i.e.,

$$\varepsilon(\rho) = \frac{m_{neut}}{m_{cat}} E_{acc} \left( \frac{\rho}{L_{mid}} \right)^2, \quad (1)$$

where  $\varepsilon(\rho)$  is the KER associated with the radius  $\rho$ ,  $m_{neut}$  and  $m_{cat}$  are the masses of the neutral and cationic reaction products,  $E_{acc} = 86$  keV is the beam energy, and  $L_{mid} = 1.7$  m is the distance from the detector to the mid-point of the straight section. This leads to some distortion of the plotted KER distribution (see the Appendix).

A photo-activation technique was employed to probe the evolution of the internal energy distribution on longer timescales, after the initially hot ions have all either dissociated or been radiatively stabilized. In these experiments, light from a wavelength-tunable optical parametric oscillator laser system was overlapped collinearly with the stored ion beam, as shown in Fig. 1. Following rapid internal conversion and intramolecular vibrational redistribution, photo-activation increases the vibrational energy of the excited ions by a known, fixed amount (the photon energy). Photo-activated ions are thus re-heated to energies above the dissociation threshold, and neutral fragments are again emitted and detected using the same procedures detailed above for the source-heated ions.

### B. Quantum chemical calculations

The vibrational frequencies and infrared intensities of  $Ind^+$  were calculated at the LC- $\omega$ HPBE/cc-pVTZ level in Gaussian.<sup>27</sup> The

infrared emission rate coefficients were computed using the simple harmonic cascade (SHC) approximation,<sup>28</sup>

$$k_s^{IR} = A_s^{IR} \sum_{\nu=1}^{\nu \leq E/h\nu_s} \frac{\rho(E - \nu h\nu_s)}{\rho(E)}, \quad (2)$$

where  $\nu$  is the vibrational quantum number and  $h\nu_s$  and  $A_s$  are the transition energy and Einstein coefficient of vibrational mode  $s$ , respectively. The density of vibrational states  $\rho(E)$  is calculated using the Beyer–Swinehart algorithm.<sup>29</sup> The SHC model considers only  $\nu \rightarrow \nu - 1$  fundamental transitions, and the transition energies and level densities are assumed to be harmonic. However, we use anharmonic (VPT2) fundamental frequencies and intensities in our simulations, as these have been shown to better reproduce experiments.<sup>30</sup>

The RF emission rate coefficients are parameterized as<sup>14</sup>

$$k_j^{RF}(E) = A_j^{RF} \frac{\rho(E - E_j)}{\rho(E)}, \quad (3)$$

where  $E_j$  and  $A_j^{RF}$  are the transition energy and Einstein coefficient of the  $D_j \leftarrow D_0$  electronic transition.

Quantitative studies, by the present collaboration as well as others, have generally found that Eq. (3) drastically underestimates RF cooling rates when the parameters  $E_j$  and  $A_j^{RF}$  are estimated using quantum chemical methods such as TD-DFT.<sup>15,19</sup> It was previously reported that this discrepancy could be narrowed by consideration of Herzberg–Teller (HT) vibronic coupling, which greatly increases the transition probability of the lowest-energy optical transition of PAHs.<sup>12</sup> HT simulations of open-shell systems remain a challenge for computational chemistry programs, and recently, a more generally applicable method based on molecular dynamics simulations has been introduced.<sup>11</sup>

Here, we performed temperature-dependent *ab initio* molecular dynamics (AIMD)<sup>31</sup> at the  $\omega$ B97X-D/cc-pVTZ level of theory,<sup>32,33</sup> with canonical sampling through velocity rescaling.<sup>34</sup> Trajectories at given initial temperatures, converted to vibrational energies according to the caloric curve based on the state density, were run for 1 ps in 0.5 fs steps, with the vertical transition energies and oscillator strengths for the  $D_j \leftarrow D_0$  states computed at each step. The RF rate coefficients for fixed thermal energies  $E$  were then calculated and time-averaged for each trajectory.

Dissociation energies for H-loss from the  $sp^3$  site were performed using the DSD-PBEP86-D3(BJ)/def2-TZVPP and CCSD(T)/cc-pVTZ theories.

### C. Master equation simulations

Our approach to master equation simulations of PAH cooling dynamics has been described previously.<sup>19</sup> The vibrational energy distribution  $g(E, t)$  of the ensemble is initialized as a normalized Boltzmann distribution at  $t = 0$ . The master equation propagates the distribution according to

$$\begin{aligned} \frac{d}{dt}g(E, t) = & -k^{diss}(E)g(E, t) \\ & + \sum_s [k_s^{IR}(E + h\nu_s)g(E + h\nu_s, t) - k_s^{IR}(E)g(E, t)] \\ & + \sum_j [k_j^{RF}(E + E_j)g(E + E_j, t) - k_j^{RF}(E)g(E, t)]. \quad (4) \end{aligned}$$

The first term gives the depletion of the population by unimolecular dissociation. On the next line, the first term in brackets represents  $\nu + 1 \rightarrow \nu$  vibrational emission from levels above  $E$ , while the second is  $\nu \rightarrow \nu - 1$  emission to levels below  $E$ . Similarly, the terms on the third line account for RF emission from the electronically excited states  $D_j$  ( $j = 1, 2, 3$ ) to the ground state  $D_0$ . The time step  $dt$  is chosen to match the experimental data, with 32 extra points prior to the first experimental time bin to account for ion decays during the transit time from the ion source to the storage ring. The dissociation rate is given by  $\Gamma(t) = \int k^{diss}(E)g(E, t)dE$ .

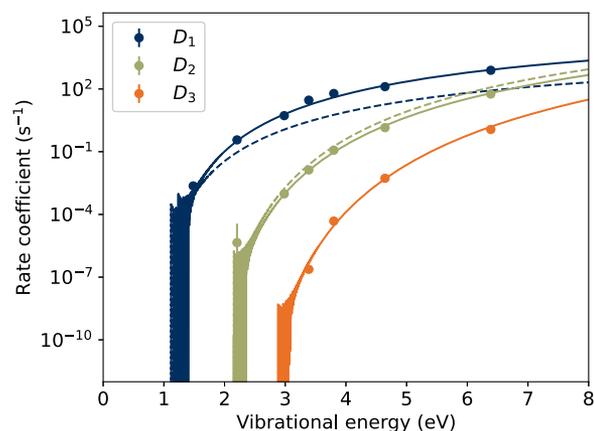
## III. RESULTS

### A. Recurrent fluorescence rate coefficients

Our calculated RF rate coefficients, based on our AIMD simulations, are presented in Fig. 2. The solid curves are fits of Eq. (3) to the points that are time averaged values from AIMD trajectories with given initial temperatures. The fit parameters  $E_j$  and  $f_{j0}$  are given in Table I, along with experimental and calculated values<sup>35</sup> from Chalyavi *et al.* Prior to fitting, the  $D_n$  state energies in the AIMD simulations were scaled by a factor of 1.03 so that the resulting value of  $E_2$  agrees with the 0–0 transition energy Chalyavi *et al.* measured using He-tagging messenger spectroscopy.<sup>35</sup> Chu *et al.* reported<sup>36</sup> a nearly identical energy of this transition at 17 379.3  $\text{cm}^{-1}$  for bare  $\text{Ind}^+$ , while Nagy *et al.* found<sup>37</sup> 17 249  $\text{cm}^{-1}$  in a Ne matrix. Significantly, the oscillator strength of the  $D_1 \leftarrow D_0$  transition is an order of magnitude greater in our AIMD simulation than in the TD-DFT calculations of Chalyavi *et al.*, leading to a commensurately increased RF rate coefficient.

### B. Kinetic energy release

The velocity distribution of the neutral products, integrated over the first eight revolutions of the stored ions in DESIREE ( $t = 56\text{--}242 \mu\text{s}$  after ionization), is shown in Fig. 3. The distribution is bimodal with the dominant component with higher mean



**FIG. 2.** RF rate coefficients for the lowest three electronic transitions of  $\text{Ind}^+$ . The points are the time-averaged values from individual AIMD trajectories at fixed internal energies. The solid curves are fits of Eq. (3). The dashed curves for  $D_1$  and  $D_2$  are calculated rate coefficients using the TD-DFT values from Chalyavi *et al.*<sup>35</sup>

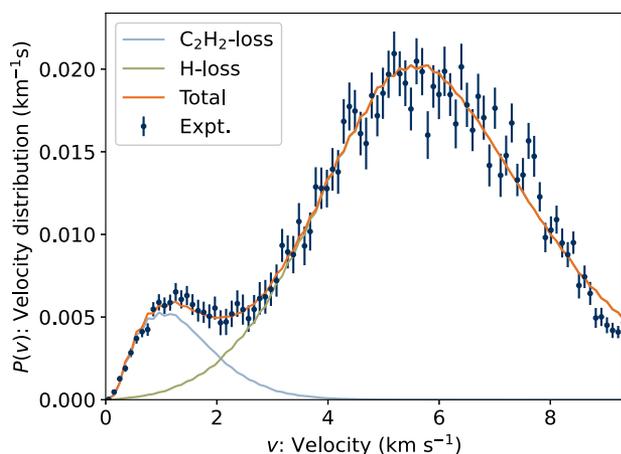
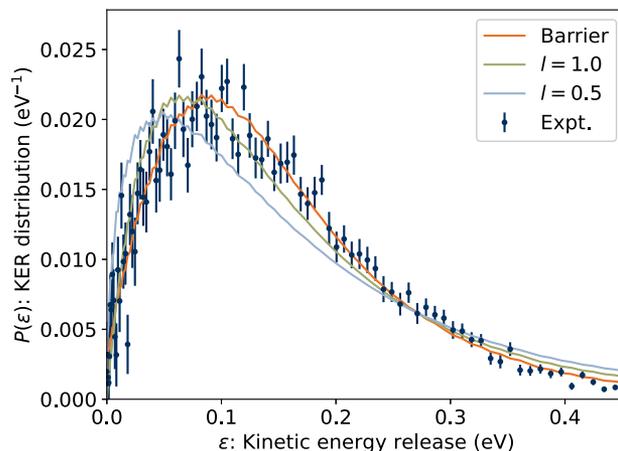
**TABLE I.** Transition energies  $E_j$  ( $\text{cm}^{-1}$ ) and oscillator strengths  $f_0$  for  $D_j \leftarrow D_0$  transitions in  $\text{Ind}^+$ .

$j$	This work (AIMD)		Chalyavi <i>et al.</i> <sup>35</sup>		
	$E_j$	$f_0$	$E_j$ exp.	$E_j$ calc.	$f_0$ calc.
1	10 000(300)	0.006(1)		9026	0.0004
2	17 400(100)	0.030(3)	17 379(15)	20 243	0.0563
3	23 300(300)	0.05(3)		26 971	0.0000

velocity being due to H-loss from  $\text{Ind}^+$ . We attribute the low-velocity component to  $\text{C}_2\text{H}_2$ -loss from  $^{13}\text{C}$ -indenyl ( $^{13}\text{C}^{12}\text{C}_8\text{H}_7^+$ ), which has the same mass-to-charge ratio as our ion of interest ( $^{12}\text{C}_9\text{H}_8^+$ ). Owing to its fully  $sp^2$ -hybridized structure, the indenyl cation  $[\text{Ind-H}]^+$  has a higher dissociation energy for H-loss than  $\text{Ind}^+$  and was found to decay exclusively by  $\text{C}_2\text{H}_2$ -loss in previous experiments at DESIREE.<sup>11</sup> Given that the dissociation threshold energy for  $\text{C}_2\text{H}_2$ -loss from  $\text{Ind}^+$  is significantly higher than for H-loss, we do not expect these channels to be competitive on such long timescales.<sup>38</sup> We can also rule out sequential fragmentation processes in which stored  $\text{Ind}^+$  first loses an H atom to form  $[\text{Ind-H}]^+$  and then fragments again by  $\text{C}_2\text{H}_2$ -loss. This is because ions with such high internal energies as to undergo multi-fragmentation would not survive to the point of mass selection by the bending magnet.

To handle the  $[\text{Ind-H}]^+$  contamination in our analysis of the KER distributions, a separate measurement was made of all- $^{12}\text{C}$   $[\text{Ind-H}]^+$  under the same experimental conditions, giving the shape parameters needed to fit the combined distributions in Fig. 3. As the dissociation of  $[\text{Ind-H}]^+$  is quenched much more rapidly than that of  $\text{Ind}^+$  (see Sec. III D), the parameters for  $\text{Ind}^+$  were obtained by integrating the KER distributions over the 25–50 ms time window, as shown in Fig. 4.

The kinetic energy released in H-loss reactions of hydrocarbons has long been known to be anomalously large,<sup>39</sup> and the shape of

**FIG. 3.** Velocity distribution of neutral products emitted from stored ion beam 56–242  $\mu\text{s}$  after ionization. The smooth curves are fits of Eq. (5). H-loss is from  $\text{Ind}^+$ , while  $\text{C}_2\text{H}_2$ -loss is from contaminant  $[\text{Ind-H}]^+$  with one  $^{13}\text{C}$  atom.**FIG. 4.** KER distribution of  $\text{Ind}^+$  integrated over the 25–50 ms time window following ionization in an ECR ion source. The solid curves are fits of Eqs. (5) and (6).

the KER distribution is notoriously difficult to model.<sup>40</sup> The reaction generally shows no reverse activation barrier, and indeed, no energy gap in the KER distribution is observed. However, the emission of low-energy ( $<0.05$  eV) H atoms is notably suppressed, skewing the distribution beyond what can be readily accommodated by otherwise successful models.<sup>39</sup> In their study of the benzene cation, Gridelet *et al.* argue that the high KER is due to the difference in electronic configurations of the reactant and product states.<sup>40</sup> The non-adiabatic character of the reaction requires passage through a conical intersection to a dissociative state of the appropriate symmetry, which Gridelet *et al.* show can qualitatively be understood as tunneling through a modified centrifugal barrier.

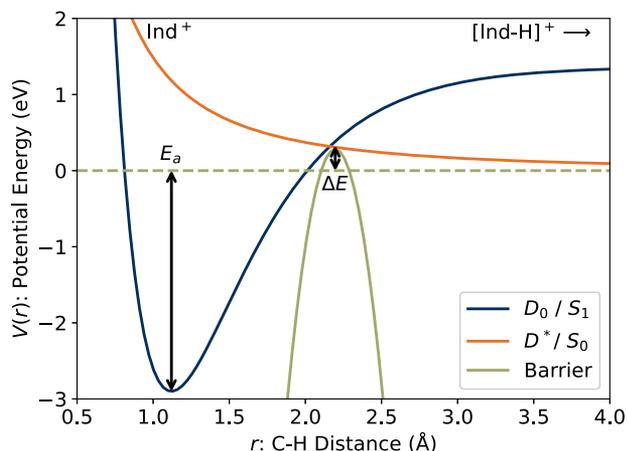
Following Gridelet *et al.*, the dissociation pathway of H-loss from  $\text{Ind}^+$  is illustrated in Fig. 5. The ground  $D_0$  state of  $\text{Ind}^+$  crosses a dissociative  $D^*$  state, which becomes the ground  $S_0$  state of  $[\text{Ind-H}]^+$ , at a conical intersection. The  $D_0$  potential energy curve is drawn as a Morse potential with the frequency of the aliphatic CH stretch and the  $D^*$  as a centrifugal potential for the  $\text{H} \cdots [\text{Ind-H}]^+$  system. The crossing is treated as a potential barrier with the shape of an inverted parabola of height  $\Delta E$  above the asymptotic energy of the  $D^*/S_0$  state. The activation energy  $E_a$  is the difference between this asymptotic energy and the minimum of  $D_0$ .

Our measured KER distributions were fit by the model of Hansen,<sup>41</sup> who considered tunneling and reflection from a potential barrier given by an inverted parabola as a model of a transition state. The shape of the KER distribution in this model is given by

$$P(\varepsilon) = \frac{e^{\beta'} e^{-(\varepsilon - \Delta E)/k_B T_p}}{e^{\beta'} + 1}, \quad (5)$$

where  $\beta' = 4\pi \frac{\Delta E}{\hbar\omega} \left( \sqrt{\frac{\varepsilon}{\Delta E}} - 1 \right)$ ,

where  $\varepsilon$  is the kinetic energy release,  $\Delta E$  is the height of the barrier above the product channel,  $T_p$  is the temperature of the product ion, and  $\hbar\omega$  is related to the curvature of the transition state. The fitted



**FIG. 5.** Modeled dissociation pathway for H-loss from  $\text{Ind}^+$ . The conical intersection of electronic states along the reaction coordinate is approximated as an inverted parabolic barrier.

curve labeled “Barrier” in Fig. 4 returned  $\Delta E = 0.33(8)$  eV, which is large compared to the typical KER. This is in contrast to the case of a reverse reaction barrier where  $\Delta E$  is measured as the gap between 0 eV and the onset of the KER distribution.<sup>41,42</sup>

For comparison, we have included fits of the measured KER distribution to the conventional “model-free” expression,<sup>42,43</sup>

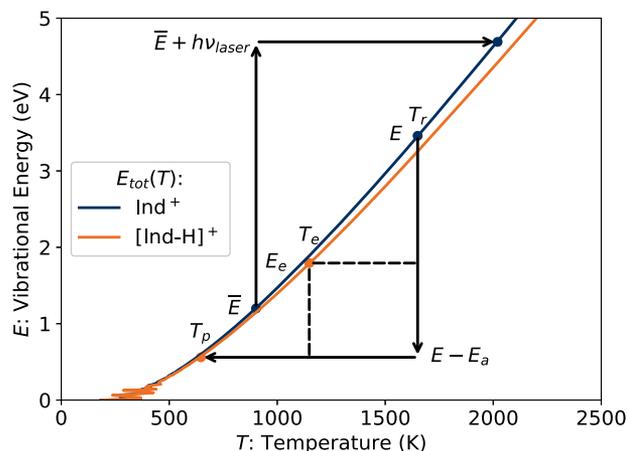
$$P(\varepsilon) \propto \varepsilon^l e^{-\varepsilon/k_B T_p}, \quad (6)$$

where the parameter  $l$  characterizes the interaction between the products. For the Langevin ion/induced-dipole interaction,  $l = 0.5$ , while  $l = 1$  corresponds to the limiting case of a hard sphere. Neither agree with the experimental data as well as the Hansen barrier model. The best agreement between the model-free expression and the measured KER distribution (not shown) is obtained when  $l$  is allowed to take the non-physical value of 1.4, which is associated with the anomalously high KER of H-loss reactions from hydrocarbons.<sup>39,40</sup> We thus adopt the Hansen model for the rest of our analysis.

The time-dependent temperature of the decaying ions is determined from the analysis of KER distributions. The temperature of an isolated molecule having total vibrational energy  $E$  is that of a fictitious Boltzmann distribution with a mean energy<sup>44</sup> equal to  $E$ . One must distinguish between the temperature of the reactant  $T_r$ , corresponding to a vibrational energy  $E$ , the product temperature  $T_p$ , with internal energy  $E - E_a$ , and the effective emission temperature  $T_e$ , which reconciles the canonical and microcanonical descriptions of the rate coefficient,

$$k^{\text{diss}} = A e^{-E_a/k_B T_e} = A \frac{\rho(E - E_a)}{\rho(E)}. \quad (7)$$

According to finite heat bath theory,<sup>45</sup>  $T_e \approx (T_r + T_p)/2$ . The relationship between these quantities is illustrated in Fig. 6. The

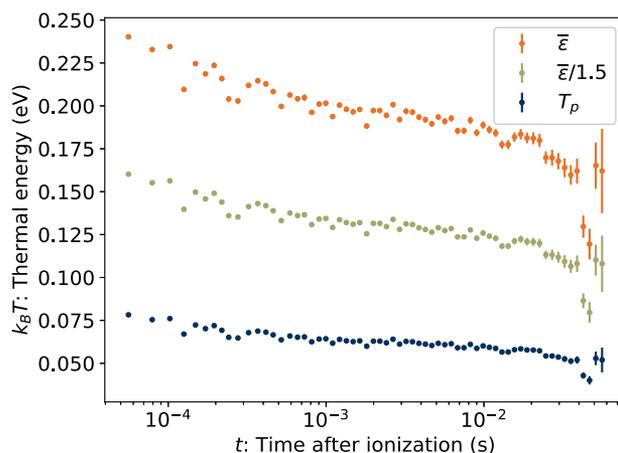


**FIG. 6.** Caloric curves  $E_{\text{tot}}(T)$  for  $\text{Ind}^+$  and  $[\text{Ind-H}]^+$ . Examples of microcanonical temperatures and energies of ions before, during, and after fragmentation (see the text) are indicated. The mean energy of the ions before and after laser excitation is also illustrated.

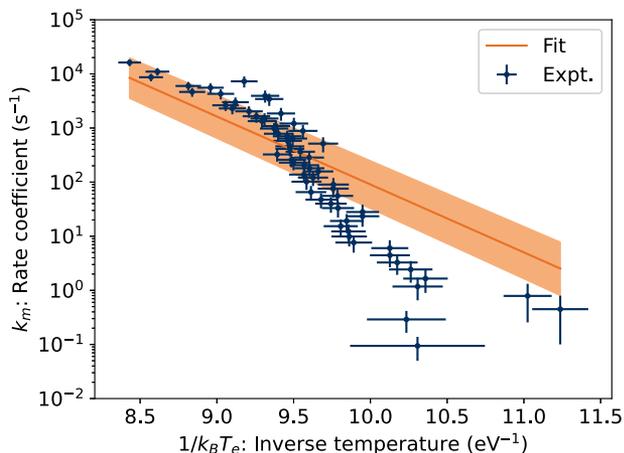
KER distribution gives information about  $T_p$ .<sup>45</sup> In the model-free approach [Eq. (6)], the average KER is a measure of the temperature,

$$\bar{\varepsilon} = \int \varepsilon P(\varepsilon) d\varepsilon / \int P(\varepsilon) d\varepsilon = (l + 1)k_B T_p. \quad (8)$$

For the Langevin interaction,  $l = 0.5$ , and so  $\bar{\varepsilon} = 1.5k_B T_p$ . In the absence of tunneling corrections, these two methods of determining the product temperature usually agree. As shown in Fig. 7, we find  $\bar{\varepsilon}$  to be roughly a factor of three higher than the temperature returned by a fit of Eq. (5), portending a non-physical value of  $l \approx 2$ . Finding the model-free approach insufficient once again, we proceed with the values of  $T_p$  obtained from Eq. (5).



**FIG. 7.** Product thermal energies for dissociation of  $\text{Ind}^+$  obtained from fits of Eq. (5) to measured KER distributions.



**FIG. 8.** Arrhenius plot for H-loss from  $\text{Ind}^+$ . The effective emission temperatures  $T_e$  are determined from fits of Eq. (5) to the measured KER distributions, with corrections for the finite heat bath [Eq. (11)]. The most-probable dissociation rate coefficient  $k_m$  is determined from the measured count rate using Eq. (10). The solid line is a fit of Eq. (9), with the shaded area indicating the 68% confidence interval.

### C. Dissociation rate coefficient

We determine the Arrhenius parameters of the dissociation rate coefficient from a fit to the measured data of the expression

$$\log(k_m) = \log(A) - E_a/k_B T_e. \quad (9)$$

The most probable dissociation rate coefficient  $k_m(t)$  observed at time  $t$  is given by

$$k_m(t) = \phi_H(t)R(t)/r_0, \quad (10)$$

where  $\phi_H(t)$  is the fraction of counts due to H-loss, determined from the fit to the KER distribution,  $R(t)$  is the total count rate, and  $r_0$  is a dimensionless normalization constant (see Sec. III D). To determine the effective emission temperature  $T_e$ , the energy of the decaying ions  $E_e$  is calculated as part of the fit from the KER distributions using the computed caloric curve  $E_{tot}(T_e)$  for the product  $[\text{Ind-H}]^+$  and the second order finite heat bath correction,<sup>44</sup>

$$E_e = E_{tot}(T_p) + \frac{E_a}{2} - \frac{E_a^2}{12(E_{tot}(T_p) + E_a)}. \quad (11)$$

From  $E_e$ , the emission temperature  $T_e$  is computed from the caloric curve of the reactant  $\text{Ind}^+$ .

From the fit shown in Fig. 8, we find the activation energy  $E_a = 2.9(1)$  eV and the pre-exponential factor  $A = 3.3(5) \times 10^{14} \text{ s}^{-1}$ . It is clear that the simple Arrhenius model is not an ideal description of the measured dissociation rate coefficient. This may be attributed to both experimental challenges, such as the separation of the  $\text{Ind}^+$  and  $[\text{Ind-H}]^+$  contributions to the KER distribution, and to the questionable applicability of classical kinetic theory to complex quantum tunneling processes. However, the resulting parameters are in line with expectations and, as will be shown in Secs. III D–III F, reproduce other experimental observables.

Our activation energy agrees with the 2.6(4) eV found by West *et al.* for  $\text{Ind}^+$  using a photo-electron photo-ion coincidence technique.<sup>38</sup> A weighted average of threshold energies for  $sp^3$ -hybridized H atom losses from six different PAH cations determined by similar methods give  $E_a = 2.4(4)$  eV.<sup>38,46,47</sup> Our own quantum chemical calculations found dissociation energies for H-loss from  $\text{Ind}^+$  of 2.8 eV at both the DSD-PBEP86-D3(BJ)/def2-TZVPP and CCSD(T)/cc-pVTZ levels of theory, in good agreement with our measured value.

The pre-exponential factor is close to the “universal” Gspann value of  $1.6 \times 10^{15} \text{ s}^{-1}$  for the evaporation of atomic and molecular clusters.<sup>39</sup> In an RRKM framework, our value of  $A$  corresponds to an activation entropy of  $\Delta S_{1000\text{K}}^\ddagger = 14(1) \text{ J K}^{-1} \text{ mol}^{-1}$ , consistent with a loose transition state. West *et al.*<sup>38</sup> give  $\Delta S_{1000\text{K}}^\ddagger = -2 \pm 38 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $\text{Ind}^+$  and an average value<sup>38,46,47</sup> for  $sp^3$ -hybridized H-losses of  $\Delta S_{1000\text{K}}^\ddagger = 44 \pm 20 \text{ J K}^{-1} \text{ mol}^{-1}$ .

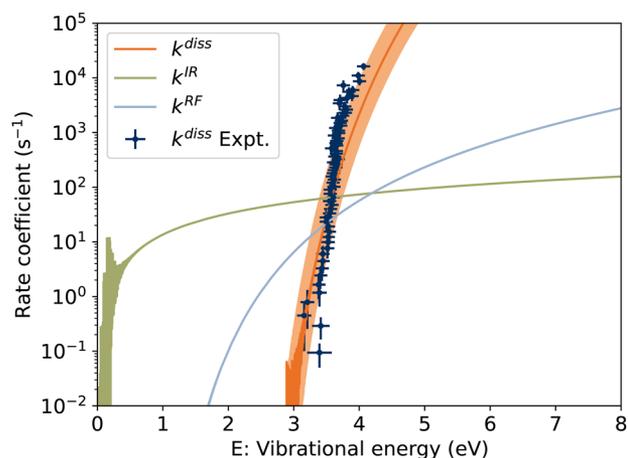
Taking instead a detailed balance perspective, the cross section for H atom capture by the indenyl cation is given by<sup>44</sup>

$$\sigma_c = \frac{\pi^2 \hbar^3}{2\mu(k_B T_p)^2} A, \quad (12)$$

where  $\mu$  is the reduced mass. For the average product temperatures determined from the fit to the KER distributions [Eq. (5)], Eq. (12) gives  $\sigma_c = 1.2(2) \text{ \AA}^2$ . This may be compared to the Langevin cross section, which gives an upper limit on the reaction rate,<sup>44</sup>

$$\sigma_L = \pi \sqrt{\frac{\pi \alpha q_e^2 k_e}{2k_B T_d}}, \quad (13)$$

where  $\alpha = 0.667 \text{ \AA}^3$  is the polarizability volume of the H atom fragment,  $q_e$  is the elementary charge, and  $k_e = 1/4\pi\epsilon_0$ . This yields  $\sigma_L = 49.2(1) \text{ \AA}^2$ , which is comparable to the geometric cross section of indene.<sup>8</sup> Thus, our measured dissociation rate for  $\text{Ind}^+$  implies a formation rate more than an order of magnitude below the Langevin rate.



**FIG. 9.** Rate coefficients for  $\text{Ind}^+$ : dissociation by H-loss  $k^{diss}(E)$  determined from KER distributions, IR vibrational radiative cooling  $k^{IR}(E)$  from the SHC model [Eq. (2)], and recurrent fluorescence  $k^{RF}(E)$  from AIMD simulations (Fig. 2).

Our experimentally determined microcanonical dissociation rate coefficient  $k^{diss}(E) = k_m(t)$  is plotted in Fig. 9 as a function of the vibrational energy of the reactant,  $E = E_{tot}(T_p) + E_a$ , along with our calculated radiative cooling rate coefficients  $k^{IR}(E)$  and  $k^{RF}(E)$ .

#### D. Dissociation rate

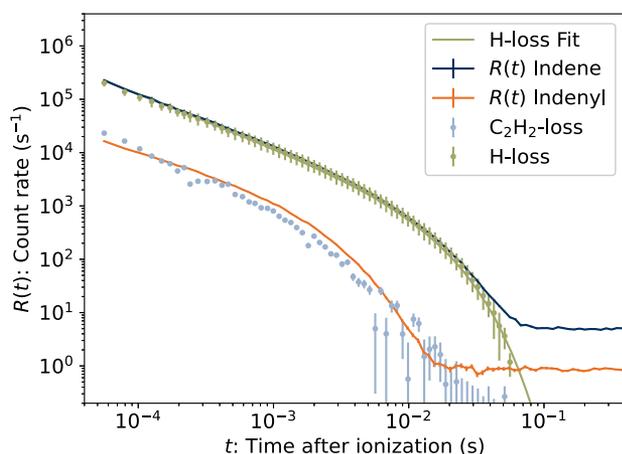
The total neutral product count rate  $R(t)$  for  $\text{Ind}^+$  ions stored in DESIREE is shown in Fig. 10 (blue curve). For the first few milliseconds after injection, the rate follows a power-law  $R(t) \propto t^{-1}$ , indicative of a broad internal energy distribution.<sup>48</sup> After about 10 ms, the rate begins to deviate from the power law trend, as radiative cooling becomes competitive with dissociation. After 100 ms, a constant rate is observed due to dissociation of stored ions induced by collisions with the residual gas in the ring.

The total count rate  $R(t)$  is divided into contributions from H-loss from  $\text{C}_9\text{H}_8^+$  (green symbols in Fig. 10) and  $\text{C}_2\text{H}_2$ -loss from the contaminant  $^{13}\text{C}^{12}\text{C}_8\text{H}_7^+$  (blue symbols) according to fits of the KER distribution as in Fig. 3. The count rate for a separate measurement of pure  $^{12}\text{C}$  indenyl ( $\text{C}_9\text{H}_7^+$ ), scaled to that of the  $\text{C}_2\text{H}_2$ -loss contamination signal, is included for comparison (orange curve). It is clear that H-loss from  $\text{Ind}^+$  is the dominant contribution to  $R(t)$ , and the  $\text{C}_2\text{H}_2$ -loss channel will therefore be neglected in the remaining analysis.

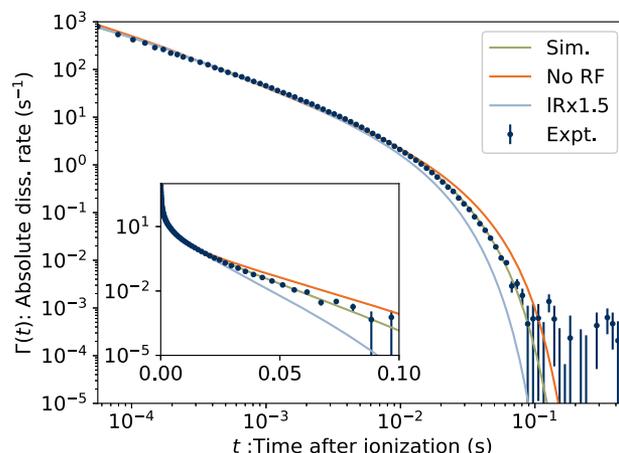
The spontaneous decay rate  $R(t)$  was fit with

$$R(t) = r_0 t^{-1} e^{-k_c t}, \quad (14)$$

in which the dimensionless constant  $r_0$  collects all the experimental parameters and  $k_c$  is the critical rate coefficient where cooling competes with dissociation. The value of  $k_c$  according to the fit is  $78(1) \text{ s}^{-1}$ , which is lower than the values obtained for other cationic, pure PAHs to date, which range from  $460(30) \text{ s}^{-1}$  for naphthalene<sup>20</sup> to over  $1000 \text{ s}^{-1}$  for tetracene.<sup>22</sup> This can be explained by low dissociation threshold energy for loss of the labile  $sp^3$  hybridized



**FIG. 10.** Measured total count rate  $R(t)$  of neutral fragments of  $\text{Ind}^+$ . Points are partial yields of H and  $\text{C}_2\text{H}_2$  determined from fits of KER distributions. Scaled count rate for  $[\text{Ind-H}]^+$ , measured separately, is plotted for comparison to the  $\text{C}_2\text{H}_2$  yield. We attribute the  $\text{C}_2\text{H}_2$  contribution to  $^{13}\text{C}[\text{Ind-H}]^+$  co-stored with isobaric  $\text{Ind}^+$ .



**FIG. 11.** Normalized spontaneous decay rate  $\Gamma(t)$  [Eq. (15)] of  $\text{Ind}^+$ . The solid curves are the results of master equation simulations for three different assumptions about the radiative cooling rates. “Sim.”: rates as calculated with full model described in this work; “No RF”:  $k^{RF}$  set to zero; “IR  $\times 1.5$ ”:  $k^{RF}$  as calculated,  $k^{IR}$  increased by a factor of 1.5. Inset with linear time axis.

H atom. The fully  $sp^2$ -hybridized perylene cation  $\text{C}_{20}\text{H}_{12}^+$ , for example, decays mainly by H-loss but with a higher dissociation energy of  $4.8(6) \text{ eV}$ ,<sup>47</sup> resulting in a value of  $k_c = 450(2) \text{ s}^{-1}$ .<sup>19</sup> Critical rate coefficients on the order of  $100 \text{ s}^{-1}$  have been determined for other functionalized PAH cations and explained by infrared radiative cooling,<sup>23</sup> with larger values being interpreted as evidence for RF.<sup>12</sup>

The absolute, per-particle dissociation rate  $\Gamma(t)$  is related to the measured count rate  $R(t)$  by

$$\Gamma(t) = \frac{f_{rev} q_e}{\eta_{det} G I_{avg}} R(t), \quad (15)$$

where  $f_{rev} = 43.07 \text{ kHz}$  is the revolution frequency of the ions in the storage ring,  $q_e$  is the elementary charge,  $\eta_{det}$  is the detector efficiency,  $G = 0.11$  is the fraction of the circumference of the storage ring visible to the detector (see Fig. 1), and  $I_{avg} = 160(1) \text{ pA}$  is the average ion beam current measured at the end of each storage cycle.

Results of our master equation simulations compared to the measured dissociation rate  $\Gamma(t)$  are presented in Fig. 11. Simulations were run for a range of temperatures  $T_0$ , specifying the initial, Boltzmannian distribution of vibrational energies of the ensemble. The detector efficiency  $\eta_{det}$  was also taken as a free parameter. The simulation that best reproduced the measured data had  $T_0 = 1650(40) \text{ K}$  and  $\eta_{det} = 0.113(1)$ . This temperature is comparable to that obtained for other PAHs using the same experimental and modeling techniques, and the derived detector efficiency is reasonable for hydrogen atoms with  $\approx 740 \text{ eV}$  kinetic energy in the lab frame as in the present experiment.<sup>19,49</sup>

Two alternative simulation results are also presented in Fig. 11. In the first, to test our hypothesis that vibrational motion enhances the RF rate, we turn off RF in the simulation. The best fitting simulation under these conditions [ $T = 1800(100) \text{ K}$  and  $\eta_{det} = 0.101(2)$ ] diverges from the measured rate after a few tens of milliseconds. This

shows that RF plays a role in the simulated cooling dynamics despite the RF rate coefficient being lower than for IR cooling in the energy window probed in our experiment. A second scenario leaves RF in place but increases the IR cooling rate by a factor of 1.5. Differences in the IR rates on this scale are sometimes noted between different levels of theory.<sup>30</sup> Again, the best fitting simulation [ $T = 1670(40)$  K and  $\eta_{\text{det}} = 0.108(1)$ ] diverges from the measured data, but in the opposite direction. Thus, an overestimate of the RF rate coefficient could be compensated for by an underestimate of the IR rate coefficient. We conclude that RF makes, at most, a small contribution to the radiative stabilization of indene cations.

### E. On the connection between measured rates and rate coefficients

In our analysis of the dissociation rate, we make the assumption that the measured decay rate  $R(t)$  is directly proportional to the dissociation rate coefficient of the ions dissociating at time  $t$  [Eq. (10)] and that the constant of proportionality  $r_0$  is determined from the fit of Eq. (14) to  $R(t)$ . This is motivated by the fact that  $k^{\text{diss}}(E)$  increases rapidly with energy, so that the ensemble averaged decay rate is dominated by ions with energies  $E_m(t)$  at the high-energy front of the internal energy distribution, i.e.,  $R(t) \propto k_m(t) \equiv k^{\text{diss}}(E_m(t))$ , where we take the values of  $E_m(t)$  to be those obtained from the KER distributions, as described in Sec. III C. We name the fraction of ions with  $E \approx E_m(t)$  to be  $\gamma_0(t)$ , which can also be written as the ensemble averaged destruction probability,

$$\gamma_0(t) = \int g(E, t) (1 - e^{-k^{\text{diss}}(E)t}) dE / \int g(E, t) dE. \quad (16)$$

Here, we take  $\gamma_0$  to be constant and define

$$r_0 = \gamma_0 \frac{\eta_{\text{det}} G I_{\text{avg}}}{f_{\text{rev}} q_e}. \quad (17)$$

From Eqs. (10), (15), and (17),  $\Gamma(t) = \gamma_0 k_m(t)$ . The assumption that  $\gamma_0$  is constant is equivalent to assuming that the number of stored ions is constant and equal to the ion beam current  $I_{\text{avg}}$  measured at the end of the storage cycle. This condition is typically fulfilled in storage ring experiments, where only a few percent of the ions in the stored ensemble have sufficient energy to decay prior to the onset of radiative cooling.

In the context of thermal electron emission from fullerene anions, Hansen<sup>50</sup> developed a model including the following expression for  $\gamma_0$  (recast in our symbols):

$$\Gamma(t) = \gamma_0 k_m(t) = g(E_m(t), t) \frac{E_a C}{t [\ln(At)]^2}, \quad (18)$$

where  $g(E_m(t), t)$  and the heat capacity  $C$  are assumed to be constant, and the most-likely rate coefficient is given by  $k_m(t) = t^{-1}$ . Solving instead for  $g(E_m(t), t)$ , and using our values for  $E_m(t)$  obtained from the KER distributions, and our Arrhenius parameters  $A$  and  $E_a$  determined from the fit of Eq. (9), we obtain the vibrational energy distribution of ions that dissociated during the experiment, denoted  $g^\dagger(E)$ ,<sup>23</sup> plotted in Fig. 12. Here, we assume a constant heat capacity  $C = 45/k_B$  and again take the detector efficiency as a free parameter to obtain agreement with the  $g^\dagger(E)$  distribution computed in our best-fitting master equation simulation. We find

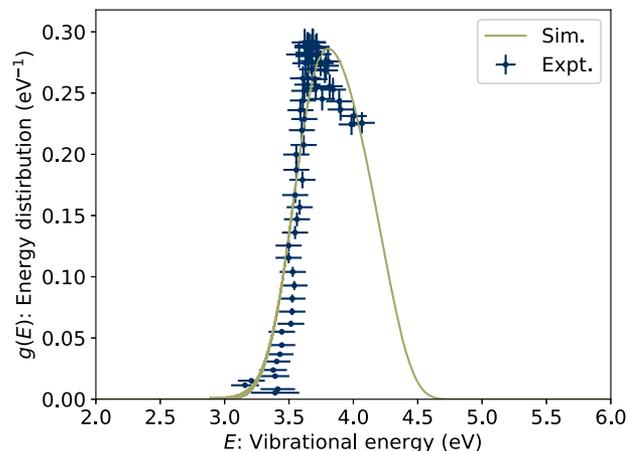


FIG. 12. Internal energy distribution  $g^\dagger(E)$  of dissociating  $\text{Ind}^+$  from Eq. (18) (points) and from our master equation modeling (solid curve).

$\eta_{\text{det}} = 0.095(2)$ , which is similar to the values found comparing the simulated and measured dissociation rates (Sec. III D). The qualitative agreement in the shape of the distributions and the quantitative agreement of their magnitudes validate our assumption in Eq. (10) that the measured dissociation rate  $R(t)$  can be treated as being directly proportional to the dissociation rate coefficient  $k_m(t)$ .

### F. Radiative cooling

Only a fraction of the ions injected into the DESIREE storage ring decay by the dissociation process discussed so far. Most will continue to circulate while cooling by emission of thermal radiation. The evolution of the internal energy distribution of the stored ions  $g(E, t)$  can be tracked with laser probing techniques.<sup>19,21,51,52</sup> Figure 13 shows the yield of neutral fragments  $S$  as a function of time following laser excitation  $t_{\text{after}}$  with  $h\nu_{\text{laser}} = 3.75$  eV (330 nm) and 3.49 eV (355 nm) photons, for a laser firing time of  $t = 0.6$  s.

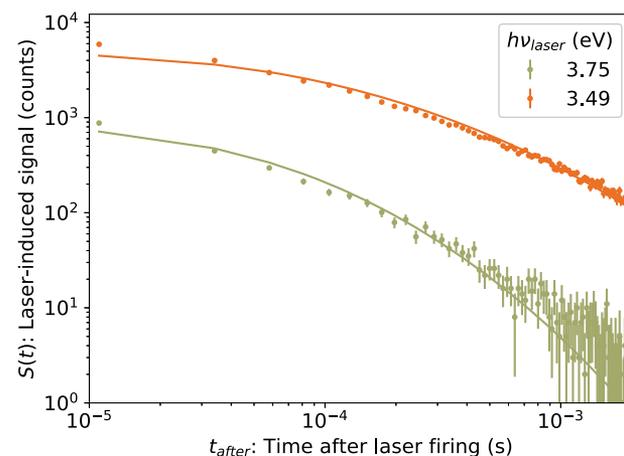


FIG. 13. Laser-induced neutral fragment yield  $S(t_{\text{after}})$  of  $\text{Ind}^+$  for two different laser excitation energies at the same laser firing time  $t = 0.6$  s.

To analyze the laser-induced dissociation rates, we fit a simplified model,

$$S(t_{\text{after}}) = s_0 \int k^{\text{diss}}(E) g_T(E) e^{-k^{\text{tot}} t_{\text{after}}} dE, \quad (19)$$

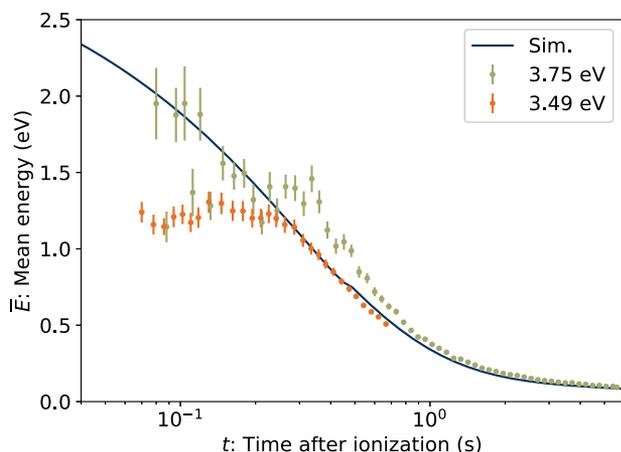
where  $s_0$  includes the absorption probability and the various experimental parameters and  $g_T$  is a Boltzmann distribution with the temperature  $T$ , shifted by the laser photon energy  $h\nu_{\text{laser}}$  and  $k^{\text{tot}} = k^{\text{diss}} + k^{\text{IR}} + k^{\text{RF}}$ . The solid lines in Fig. 13 are fits of Eq. (19). In contrast to our master equation simulations detailed above, this model neglects the re-distributive effect of radiative cooling. Essentially, it assumes that a single photon is always sufficient to quench dissociation and may thus underestimate the dissociation rate for the hottest ions. This would not appear to be a serious issue. A fit of Eq. (19) to the spontaneous dissociation rate gave  $T = 1695(5)$  K, which is consistent with the more accurate master equation approach given in Sec. III D.

The mean energies  $\bar{E}$  of the Boltzmann distributions fit to the laser-induced decay curves are plotted in Fig. 14. Good agreement is generally found between these fitted energies and the mean energy of the ensemble in our master equation simulation, which best fits the spontaneous dissociation rate (solid curve in Fig. 14).

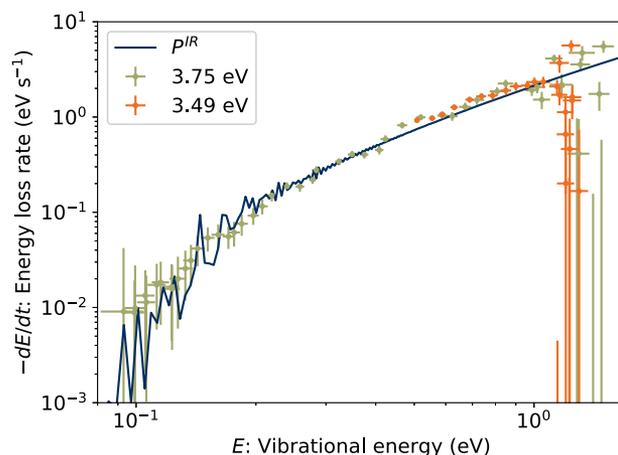
The energy loss rate due to radiative cooling is computed as the time derivative of  $\bar{E}$ , plotted in Fig. 15. Good agreement is found with the calculated total vibrational radiative power  $P^{\text{IR}} = \sum_s K_s^{\text{IR}} h\nu_s$ , supporting the accuracy of our calculated rate coefficients, which, as discussed in Sec. III D, imply a minor role for RF in the radiative stabilization of  $\text{Ind}^+$ .

### G. Astrochemical implications

Astrochemical models routinely underestimate the observed abundances of small PAHs in TMC-1.<sup>2,5</sup> The main destruction mechanism included in these models is collisions with the cations  $\text{H}^+$ ,  $\text{He}^+$ ,  $\text{C}^+$ ,  $\text{H}_3^+$ , and  $\text{HCO}^+$ , which are assumed to lead inexorably to complete degradation of the PAHs into small linear fragments.<sup>5</sup>

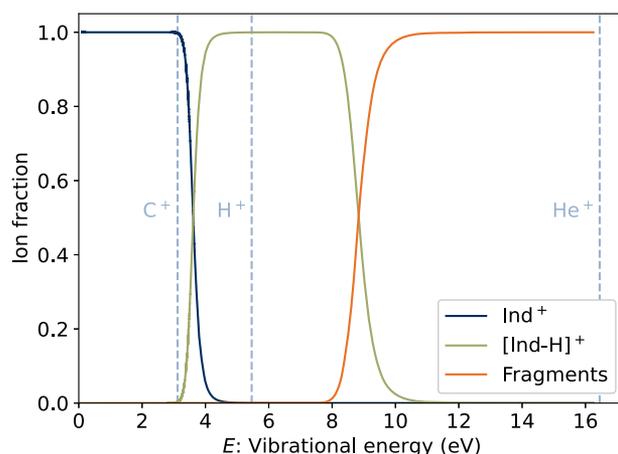


**FIG. 14.** Mean energies of the Boltzmann model [Eq. (19)] fitted to the measured  $S(t_{\text{after}})$  curves for  $\text{Ind}^+$  at two different laser photon energies. The solid line is the mean energy of the ensemble in our best-fitting master equation simulation (see Sec. III D).



**FIG. 15.** Energy loss rate for  $\text{Ind}^+$  computed as the gradient of the fitted  $\bar{E}$  values (Fig. 14). The solid curve is the vibrational radiative power.

These models may be improved by including more complete product breakdown reactions. In Fig. 16, we give a breakdown diagram for indene following ionizing collisions based on the dissociation and radiative cooling rate coefficients for  $\text{Ind}^+$  (Fig. 9) and  $[\text{Ind-H}]^+$  from Ref. 11. At the low temperatures ( $\sim 10$  K) prevalent in TMC-1, the atomic cations will undergo electron transfer at large distances with negligible translational-to-vibrational energy transfer,<sup>53</sup> leaving the ionized PAH with a maximum internal excitation energy equal to the difference in the ionization potentials (the molecular cations will lead to proton transfer). Note that these maximal energy transfers, given as vertical dashed lines in Fig. 16, are extremely unlikely in distant electron-transfer reactions. With its relatively low ionization potential (11.26 eV), charge transfer forming carbon atoms occurs at shorter distances and will lead to greater heating of the  $\text{Ind}^+$



**FIG. 16.** Breakdown diagram for products of ionizing collisions between neutral Ind and atomic cations included in astrochemical models. The dashed vertical lines indicate the maximum energy transferred to  $\text{Ind}^+$  for each atomic collision partner.

product. Collisions with  $C^+$  are thus considered the most important PAH-destruction channels in many astrochemical models.<sup>54,55</sup> However, given the 8.14 eV ionization potential of Ind,<sup>38</sup> such collisions yield a maximal energy transfer of 3.12 eV. This is unlikely to induce dissociation of  $Ind^+$ , which is stabilized by radiative cooling up to a critical energy of 3.6 eV, where the dissociation and radiative rate coefficients are equal. Charge exchange reactions with protons could transfer sufficient energy to induce H-loss from  $Ind^+$ , yielding  $[Ind-H]^+$ , although, as stated above, such high high-energy transfers are rather unlikely in distant electron-transfer reactions. Collision with  $He^+$  could potentially transfer sufficient energy to further break down  $[Ind-H]^+$ . However, the second ionization potential of Ind, at 21.8(1) eV,<sup>56</sup> is low enough that formation of  $Ind^{2+}$  may be competitive.

It seems clear that collisions between PAHs and atomic cations in molecular clouds will primarily produce radiatively stabilized PAH cations. Previous studies have found that these cations do not react with  $H_2$  and react mainly by association with H, N, and O atoms to form larger cationic molecules.<sup>57,58</sup> Destruction of PAH cations in dark clouds is expected mainly in recombination reactions with free electrons<sup>59</sup> or mutual neutralization with anions including PAH anions.<sup>60</sup> However, given that neutral PAHs may also be radiatively stabilized by RF,<sup>11</sup> it is not obvious that extensive fragmentation should be expected following recombination.

#### IV. CONCLUSION

Through analysis of the kinetic energy released upon H atom loss from indene cations, we determine a dissociation rate coefficient consistent with results of an earlier photodissociation study.<sup>38</sup> The shape of the KER distribution is consistent with a qualitative model of tunneling through an intersection of potential energy surfaces.<sup>40,41</sup> More experiments on H-loss reactions for other hydrocarbons are needed to assess how general this phenomenon might be.

Using our best estimates of the vibrational and electronic radiative cooling rate coefficients, combined with the dissociation rate coefficient deduced from the present experiments, we find a limited role for recurrent fluorescence in the stabilization of indene cations. This is noteworthy as RF has been found to be the dominant cooling mechanism of nearly all PAH cations investigated experimentally to date.<sup>12,15–22</sup> Still, we conclude that the IR radiative cooling rate is sufficiently high to prevent dissociation following ionizing collisions with carbon cations. This may partly explain the high observed abundance of indene in interstellar clouds,<sup>3</sup> demonstrating the importance of radiative stabilization of small PAHs in astrochemical reaction networks.

#### SUPPLEMENTARY MATERIAL

The [supplementary material](#) is available for this article in the form of a spreadsheet listing the computed vibrational frequencies and infrared intensities, the vibrational level density, the caloric curve, the calculated rate coefficients for vibrational and electronic radiative cooling, and the fitted dissociation rate coefficient of  $Ind^+$ .

#### ACKNOWLEDGMENTS

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#### AUTHOR DECLARATIONS

##### Conflict of Interest

The authors have no conflicts to disclose.

##### Author Contributions

**M. H. Stockett:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal). **A. Subramani:** Formal analysis (equal); Investigation (equal); Writing – review & editing (equal). **C. Liu:** Formal analysis (equal); Investigation (equal); Writing – review & editing (equal). **S. J. P. Marlton:** Formal analysis (equal); Investigation (equal); Writing – review & editing (equal). **E. K. Ashworth:** Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Resources (equal); Writing – review & editing (equal). **H. Cederquist:** Funding acquisition (equal); Resources (equal); Writing – review & editing (equal). **H. Zettergren:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – review & editing (equal). **J. N. Bull:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Supervision (equal); Writing – review & editing (equal).

#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### NOMENCLATURE

$A^{diss}$	Pre-exponential factor determined from $k_m(t)$ and $T_p$ [Eq. (9)]
$E_a$	Activation energy determined from $k_m(t)$ and $T_p$ [Eq. (9)]

$E_e$	Energy of decaying ions [Eq. (11)]
$E_{tot}(T)$	Caloric curve computed from vibrational level density $\rho(E)$
$\bar{E}$	Mean energy of stored ion ensemble prior to laser activation. Determined from the fit of Eq. (19) to $S(t_{after})$
$h\nu_{laser}$	Laser photon energy
$k^{diss}(E)$	Model dissociation rate coefficient [Eq. (7)] using fitted values of $A^{diss}$ and $E_a$
$k^{IR}(E)$	Vibrational (infrared) emission rate coefficient [Eq. (2)] from SHC model
$k_m(t)$	Most probable rate coefficient observed at time $t$ [Eq. (10)]
$k^{RF}(E)$	Recurrent fluorescence rate coefficient [Eq. (3)] using parameters from AIMD simulations
$R(t)$	Measured spontaneous dissociation rate
$T_0$	Canonical temperature characterizing stored ion ensemble. Determined from fitting $R(t)$ with results of master equation simulations
$T_e$	Microcanonical emission temperature of decaying ions $\approx (T_r + T_p)/2$
$T_p$	Microcanonical temperature of product with energy $E - E_a$ . Determined from fits of Eq. (5) to measured KER distributions
$T_r$	Microcanonical temperature of reactant with energy $E$
$\Gamma(t)$	Absolute, per particle dissociation rate [Eq. (15)]
$\Delta E$	Barrier height. Determined from fit of Eq. (5) to measured KER distribution at late times

## APPENDIX: MATRIX TRANSFORMS

Here, we describe the implementation of matrix transforms used to compute the following:

1. the total density distribution of the Newton sphere consisting of contributions from neutral particles emitted with a given kinetic energy distribution along a linear segment normal to the image plane, and
2. the forward Abel transform between the Newton sphere density distribution and the radial intensity distribution in the image plane.

These matrix transforms are used to fit model kinetic energy release (KER) distributions  $P(\varepsilon)$  to measured radial intensity distributions  $P(r)$  measured with a two-dimensional microchannel plate detector after linear translation of the expanding Newton sphere from the point of reaction to the detector plane. This approach is preferred as the measured  $P(r)$  distributions have well-defined uncertainties given by counting statistics, while inverting the transforms inevitably introduces new errors.

### 1. Spatial transform

For a point source, there is a one-to-one relationship between the velocity of an emitted particle and the radius of the Newton sphere at a given time after emission. In particle imaging experiments, where the lab-frame velocity of the reactant ion is much

higher than the velocity of the fragment in the center-of-mass frame, the relevant time after emission corresponds to a translation of the center of the Newton sphere to the detector plane, and the kinetic energy of the particle maps directly to spherical radius  $\rho$ , given by

$$\varepsilon(\rho, L) = \frac{m_{neut}}{m_{cat}} E_{acc} \left( \frac{\rho}{L} \right)^2, \quad (\text{A1})$$

where  $L$  is the distance from the point of decay to the detector. The Newton sphere density  $P(\rho) = \frac{\partial k^{diss}}{\partial \rho}$  may be obtained from the KER distribution  $P(\varepsilon) = \frac{\partial k^{diss}}{\partial \varepsilon}$  by

$$P(\rho) = \frac{\partial \varepsilon}{\partial \rho} P(\varepsilon) = \frac{2\varepsilon}{\rho} P(\varepsilon), \quad (\text{A2})$$

where Eq. (A1) was used.

In DESIREE, particles are emitted along a linear segment with a length  $L_{SS} = 0.96$  m, which is comparable to the distance  $L_{mid} = 1.7$  m from the midpoint of this segment to the detector. Thus, the density at a radius  $\rho_i$  ( $i = 0, 1, \dots, n$ , where  $n$  is the radius of the detector in pixels) of the cumulative Newton sphere includes contributions from energies ranging from  $\varepsilon_{j_{min}}(\rho_i) = \varepsilon(\rho_i, L_{max})$  to  $\varepsilon_{j_{max}}(\rho_i) = \varepsilon(\rho_i, L_{min})$ , where  $L_{max} = L_{mid} + L_{SS}/2$  and  $L_{min} = L_{mid} - L_{SS}/2$ . Equation (A2) thus becomes the weighted average,

$$P(\rho_i) = \sum_{j=j_{min}}^{j_{max}} \mathcal{F}_{ij} P(\varepsilon_j), \quad (\text{A3})$$

where

$$\mathcal{F}_{ij} = \frac{2\varepsilon_j}{\rho_i(j_{max} - j_{min})}. \quad (\text{A4})$$

We define our energy coordinate vector  $\varepsilon_j$  ( $j = 0, 1, \dots, n$ ) to span the range from  $\varepsilon_{j_{min}}(\rho_0)$  to  $\varepsilon_{j_{max}}(\rho_n)$ . We choose the  $\varepsilon_i$  to increase quadratically, to maintain the scaling of Eq. (A1).

In Fig. 17, we show the results of several transformations of a model KER distribution into integrated Newton sphere density distributions using  $\mathcal{F}$  matrices with varying lengths of the emitting segment  $L_{SS}$ . The model distribution is of the form of Eq. (5) using the parameters found from the fit to the late-time KER distribution of  $\text{Ind}^+$  (Fig. 4). The actual value of  $L_{SS}$  in DESIREE is 960 mm, leading to a density distribution that is notably distorted relative to that from a point source.

Unfortunately, the  $\mathcal{F}$  matrix is ill-conditioned and cannot be inverted. In order to plot KER distributions, it is thus necessary to perform a pseudo-calibration by Eq. (A1) with  $L = L_{mid}$ . As shown in Fig. 18, this results in distorted KER distributions for emitting segments of finite length. We reiterate that all numerical results are obtained by fitting of the radial intensity in the detector plane, which, because it only requires the forward transform, is not affected by this distortion.

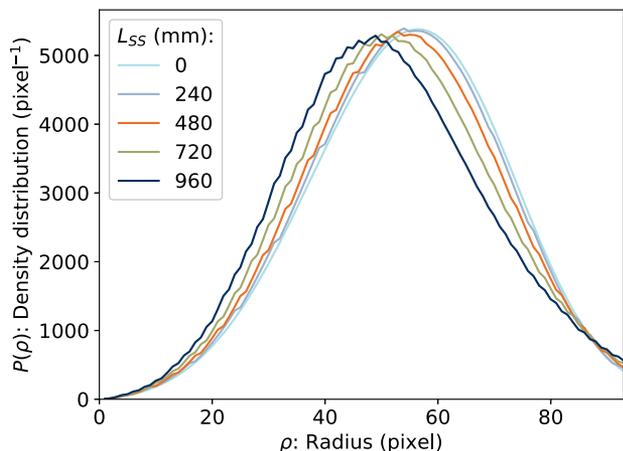


FIG. 17. Transformations of a model KER distribution to integrated Newton sphere density for varying lengths of the emitting segment  $L_{SS}$ .

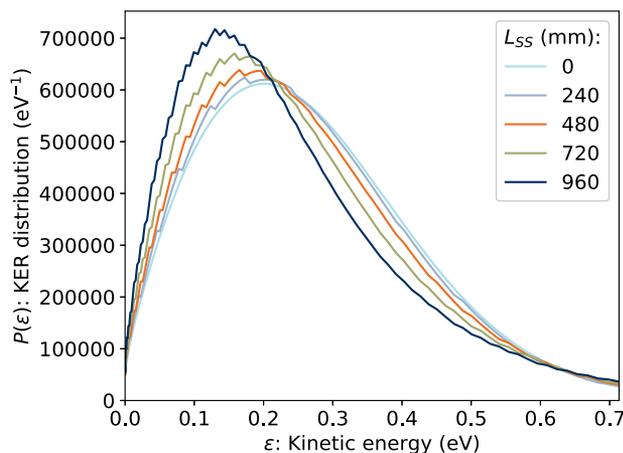


FIG. 18. Pseudo-calibrations of transformed model KER distribution for varying lengths of the emitting segment  $L_{SS}$ .

## 2. Abel transform

The Abel transform of a one-dimensional distribution  $f(\rho)$  is given by

$$F(r) = \int_{\rho}^{\infty} \frac{2\rho f(\rho)}{\sqrt{\rho^2 - r^2}} dr. \quad (\text{A5})$$

We operate on the Newton sphere density distribution integrated over solid angle,  $P(\rho) = 4\pi\rho^2 f(\rho)$ , and thus desire a matrix approximating the integral

$$F(r) = \int_{\rho}^{\infty} \frac{P(\rho)}{2\pi\rho\sqrt{\rho^2 - r^2}} dr. \quad (\text{A6})$$

We may naively take this matrix to be

$$\mathcal{A}_{ij} = \frac{1}{2\pi\rho_i\sqrt{\rho_i^2 - r_j^2}} \quad (i \geq j) \quad (\text{A7})$$

and  $\mathcal{A}_{ij} = 0$  for  $i < j$ , for two coordinate vectors  $\rho_i = r_i = i$  for  $i = 0, 1, \dots, (n_{pix} - 1)$ , where  $n_{pix}$  is the width of the detector in pixels. This is problematic near the main diagonal, so instead we define the coordinate vectors,

$$r_i = \rho_i - \delta \quad (0 < \delta < 1), \quad (\text{A8})$$

with  $\delta$  being an adjustable parameter. Still, we have a problem with  $\mathcal{A}_{00}$ , which we take to be a second adjustable parameter. The numerical value of these parameters is found by least squares fitting, either to analytical functions with known Abel transforms or to real data using the two-dimensional Abel transform algorithms included in the PyAbel package.<sup>26</sup> We find that  $\delta = 0.35$  and  $\mathcal{A}_{00} = 0.8$  generally produce good results. Finally, to obtain the azimuthally integrated radial intensity on the detector,  $P(r)$ , we rescale  $F(r)$  by the diagonal matrix,

$$\mathcal{R}_{ii} = 2\pi r_i. \quad (\text{A9})$$

In Fig. 19, we show a comparison of forward Abel transforms using the complete matrix transform  $\mathcal{R}\mathcal{A}$  and the PyAbel package. Both start from the model distribution  $P(\rho)$  from Fig. 17 (for  $L_{SS} = 960$  mm). For PyAbel, the Hansen–Law algorithm was employed, with other options giving nearly identical results. The

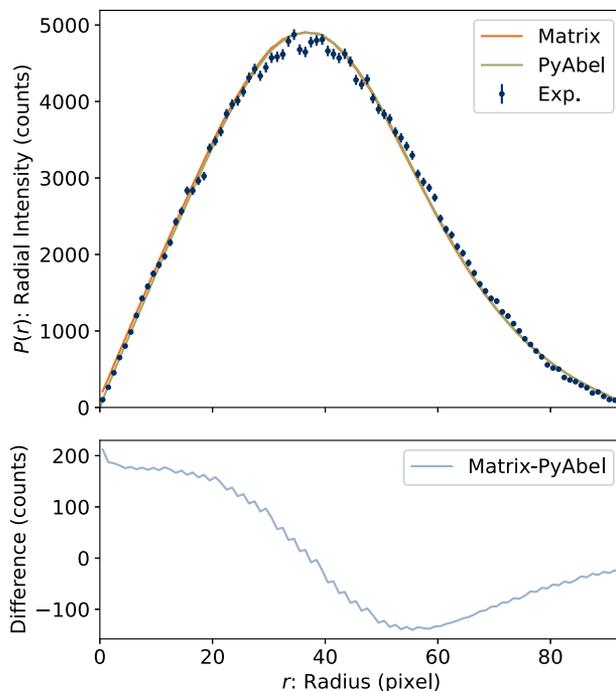


FIG. 19. Comparison of forward Abel transform methods for the model KER distribution and the measured radial intensity distribution of  $\text{In}^+$ .

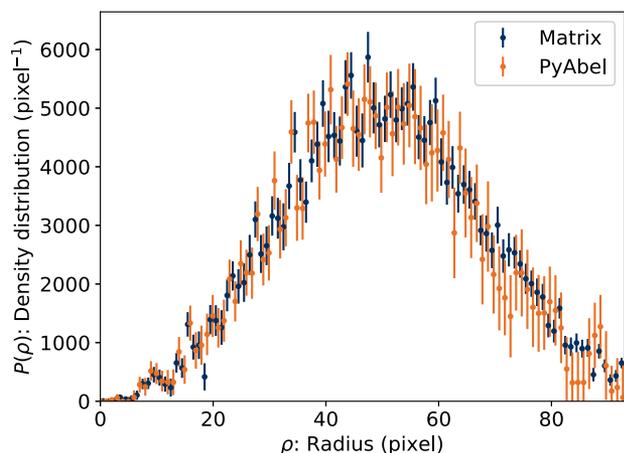


FIG. 20. Comparison of reverse Abel transform methods for the measured radial intensity distribution of  $\text{Ind}^+$ .

differences in the resulting  $P(r)$  distributions are smaller than the experimental uncertainties.

With the given choices of  $\delta$  and  $\mathcal{A}_{00}$ , the transform matrix is readily inverted using the standard Moore–Penrose algorithm. By reduction of dimensionality and cancellation of counting uncertainties by azimuthal integration prior to inversion, the matrix implementation of the reverse Abel transform outperforms the benchmark PyAbel routine. As described in Sec. II A, the uncertainty in the density distribution  $P(\rho)$  is found by inverting and averaging 128  $P(r)$  distributions with intensities normally distributed according to the measured distribution and its counting statistics. Applying this same approach using PyAbel, which operates on the full 2D image rather than the radial intensity distribution, takes 60 times longer than the matrix method. As shown in Fig. 20, the PyAbel result is also noisier.

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