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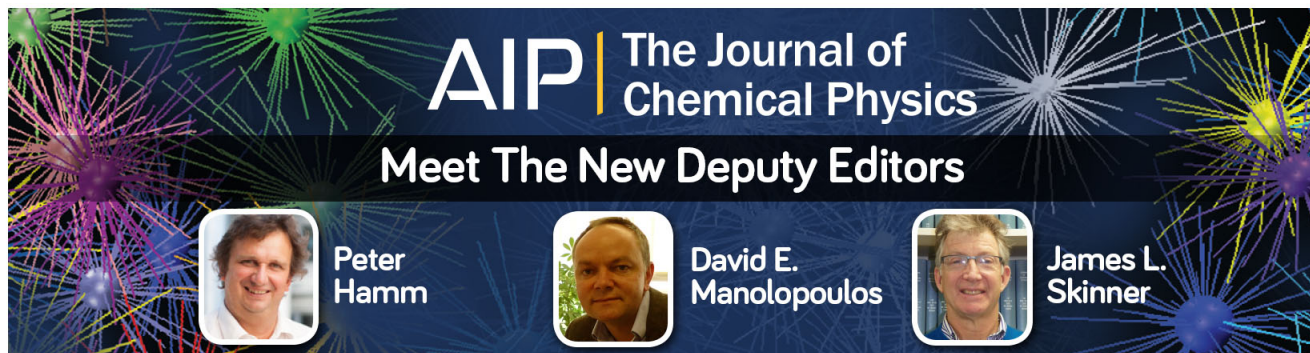
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## Communication: Autodetachment versus internal conversion from the $S_1$ state of the isolated GFP chromophore anion

Christopher W. West, Alex S. Hudson, Steven L. Cobb, and Jan R. R. Verlet<sup>a)</sup>  
 Department of Chemistry, University of Durham, Durham DH1 3LE, United Kingdom

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The anionic form of p-hydroxybenzylidene-2,3-dimethylimidazolinone (HBDI) has been extensively employed as a model of the chromophore of the green fluorescence protein. The bright  $S_1$  excited state  $\text{HBDI}^-$  has a measured lifetime of 1.4 ps in the gas-phase and is dominated by two non-radiative decay mechanisms: internal conversion and autodetachment into the neutral continuum. Here, time-resolved photoelectron spectroscopy has been used to determine the yields of these two channels from which the lifetime for autodetachment was found to be  $\sim 30$  ps. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4819078>]

The discovery of the green fluorescent protein (GFP) and related fluorescent proteins has revolutionised bio-imaging as a marker for *in vivo* studies of biological systems.<sup>1–4</sup> In many fluorescent proteins, the absorption and fluorescence can be attributed to a well-defined chromophore encapsulated in the protein structure.<sup>2,5</sup> For GFP, p-hydroxybenzylidene-2,3-dimethylimidazolinone (HBDI) has commonly been used as the representative chromophore. Fluorescence originates from the anionic form,  $\text{HBDI}^-$ , where the phenoxyl group has been deprotonated (see Fig. 1).<sup>1,6</sup> The photo-physical properties of  $\text{HBDI}^-$  have been extensively studied with the aim of gaining insight into the photophysics of GFP.<sup>7–13</sup> From this perspective, studies on the isolated  $\text{HBDI}^-$  are particularly valuable as these provide detailed information on the intrinsic photophysics to which theoretical studies can be benchmarked.<sup>11,14–28</sup>

An important difference between  $\text{HBDI}^-$  and GFP is that for the latter, the protein environment stabilises the anionic chromophore and increases the detachment energy by several eV.<sup>20,29</sup> For  $\text{HBDI}^-$  in isolation, a number of photoelectron (PE) spectroscopy<sup>17–19</sup> and theoretical studies<sup>15,16,30</sup> have shown that the  $S_1$  state lies very close in energy to the neutral ground state,  $D_0$ , although formally, the  $S_1$  is bound in the Franck-Condon region. Despite this, PE spectra from our group<sup>19</sup> and the Andersen group<sup>17</sup> have shown that autodetachment from the  $S_1$  state is possible, enabled by the finite temperature ( $\sim 300$  K) of  $\text{HBDI}^-$  in these experiments. Autodetachment is an important channel, not only for the interpretation of the action (absorption) spectra of  $\text{HBDI}^-$ , but also for any dynamical studies of the  $S_1$  excited state. The excited state dynamics have recently been probed using time-resolved PE spectroscopy.<sup>14</sup> An overall observed lifetime of 1.4 ps was measured based on the decay of the PE signal following detachment from the  $S_1$  state by a probe pulse at 1.55 eV. However, it was not possible to deconvolute the individual contributions arising from internal conversion and autodetachment. In the present work, through careful measurements of the time-resolved PE spectra, the lifetime of both

decay pathways are determined using the excitation scheme shown in Fig. 1.

The experimental setup and methodology has previously been described in detail.<sup>31–36</sup>  $\text{HBDI}^-$  was synthesized based broadly on published methods.<sup>37</sup> Isolated deprotonated  $\text{HBDI}^-$  ions were produced by electrospray ionisation ( $\sim 1$  mM in MeOH, adjusted to pH 11 by the addition of NaOH). Ions were then stored in a ring-electrode trap and injected at 50 Hz into a time-of-flight mass-spectrometer, where  $\text{HBDI}^-$  ions were mass selected and then irradiated at the centre of a velocity-map-imaging PE spectrometer.<sup>31,38</sup> Femtosecond laser pulses at 2.57 eV (482 nm), 2.48 eV (500 nm), and 2.39 eV (519 nm) served as the pump and 1.55 eV (800 nm) femtosecond pulses probed the population from the  $S_1$  excited state. The polarisation of all pulses was set parallel to the detector. All laser pulses were derived from a commercial femtosecond Ti:sapphire system. The spectral width of visible pulses was on the order of 60 meV (12 nm) full-width at half-maximum (FWHM) and the cross-correlation between pump and probe pulses was on the order of 120 fs. The resolution of the PE spectrometer is  $\sim 5\%$  and has been calibrated using the spectrum of  $\text{I}^-$ .

Figure 2 shows pump-probe PE spectra of  $\text{HBDI}^-$  excited at 2.48 eV (500 nm) with pump-probe delays of  $t = 0$

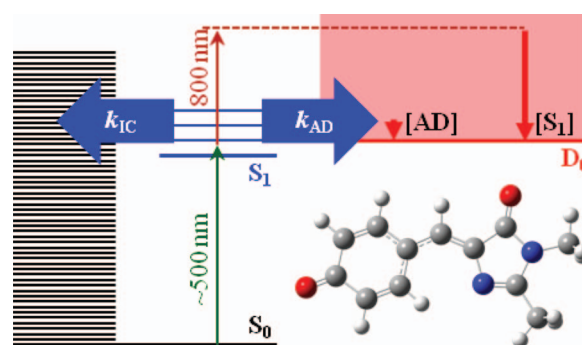


FIG. 1. Excitation scheme for  $\text{HBDI}^-$  indicating the two prominent decay routes: internal conversion (IC) and autodetachment (AD). Also shown is the structure of  $\text{HBDI}^-$ .

<sup>a)</sup>j.r.r.verlet@durham.ac.uk

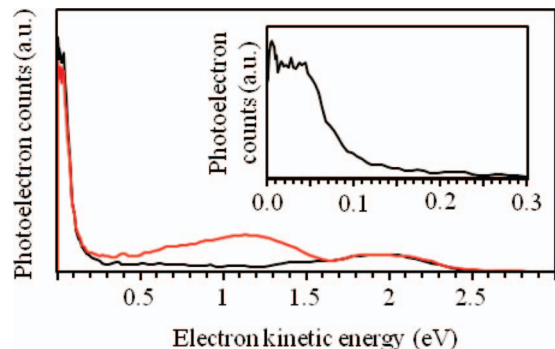


FIG. 2. Time-resolved photoelectron (PE) spectra taken with 2.48 eV pump and 1.55 eV probe pulses at delays of  $t = -2$  ps (black) and  $t = 0$  ps (red). (Inset) The first 300 meV of a PE spectrum taken at 2.48 eV at low VMI voltages.

and  $t = -2$  ps. Similar spectra have been obtained for excitation at 2.57 eV (482 nm) and 2.39 eV (519 nm). Signal levels at 2.39 eV were significantly lower than at higher pump energies. In order to reduce the impact of long-term drifts in the experimental conditions, PE images were collected at each delay for 700 laser shots before toggling between the two delays. Raw PE images were collected until a desired signal level was attained, amounting to  $\sim 4 \times 10^4$  laser shots at 2.57 and 2.48 eV and  $> 2 \times 10^5$  laser shots at 2.39 eV. Photoelectron images were deconvoluted using the polar-orion peeling algorithm.<sup>39</sup>

The PE spectra at  $t = -2$  ps are virtually identical to those recorded with the pump pulse only: the 1.55 eV probe energy is insufficient to directly detach from the ground state and is not resonant with any transitions. At higher intensity, some PE signal can be observed at 1.55 eV, which arises from 2-photon excitation. The main feature of the PE spectra at 2.57, 2.48, and 2.39 eV is an intense peak at low electron kinetic energy ( $eKE$ ). This is highlighted in the inset of Fig. 2, for which the VMI voltage was reduced by a factor of  $\sim 4$ . This feature has previously been assigned to vibrational autodetachment from the  $S_1$  state.<sup>17,19</sup> Although the adiabatic detachment energy ( $\sim 2.6$  eV) lies above the  $S_1$  origin, the 0.3 eV of internal energy due to the finite temperature (300 K)<sup>33</sup> leads to transitions from vibrationally excited states that can overcome the adiabatic energy.

PEs generated by vibrational autodetachment from the  $S_1$  state have low  $eKE$  ( $< 0.1$  eV). This feature is in fact structured (see Fig. 2 inset), with a maximum at about 30 meV. The  $eKE$  of this feature is roughly independent of photon energy.<sup>17</sup> At  $eKE < 10$  meV, an additional PE signal is observed, which we had previously interpreted as originating from thermal electron loss from the ground  $S_0$  state (thermionic emission).<sup>19</sup> The  $t = -2$  ps PE spectra also show a PE feature centred at  $eKE \sim 2$  eV, which arises from two-photon, resonance-enhanced absorption.<sup>19</sup>

The PE spectrum at  $t = 0$  shows a new feature, centred around  $eKE \sim 1.2$  eV, which can be assigned to detachment by the 1.55 eV probe from the  $S_1$  excited state. As shown by experiments performed in our laboratory, this feature evolves in time, reflecting dynamics occurring on the  $S_1$  state, and the integrated PE signal decays on a 1.4 ps time scale.<sup>14</sup> The

statistics, however, were insufficient to characterise any dynamics occurring in the low energy feature, which we have overcome here. At  $t = 0$ , there is a depletion in the low energy feature, which is concomitant with the increase of the pump-probe feature at  $eKE \sim 1.2$  eV. It is clear from Fig. 2 that the total integrated depletion of the low  $eKE$  signal is much smaller than the signal arising from the excited state.

The integrated pump-probe feature which peaks at  $eKE \sim 1.2$  eV is proportional to the population of excited states in  $\text{HBDI}^-$ ,  $[S_1]$ . Its population decay is susceptible to all available decay processes. Internal conversion and autodetachment are expected to dominate as shown schematically in Fig. 1. The *observed* rate constant of the  $S_1$  state measured in time-resolved experiments can be expressed as a sum of the rate constants for all possible decay routes from the excited state,  $i$ :  $k_{\text{obs}} = \tau_{\text{obs}}^{-1} = \sum_i k_i = (1.4 \text{ ps})^{-1}$ . The low  $eKE$  feature is primarily a measure of the  $S_1$  excited states that have undergone autodetachment. Therefore, the integrated depletion of the low  $eKE$  feature in Fig. 2, [AD], is a measure of the population fraction of  $[S_1]$  that has undergone autodetachment. The ratio of the rate constant for autodetachment,  $k_{\text{AD}}$ , to all other decay rates can be expressed as

$$\frac{k_{\text{AD}}}{\sum_{i \neq \text{AD}} k_i} = \frac{[\text{AD}]}{[S_1] - [\text{AD}]}$$

Given that  $k_{\text{obs}} = \sum_i k_i = k_{\text{AD}} + \sum_{i \neq \text{AD}} k_i$ , we can now write that

$$k_{\text{AD}} = \left( k_{\text{obs}} \frac{[\text{AD}]}{[S_1] - [\text{AD}]} \right) \left( 1 + \frac{[\text{AD}]}{[S_1] - [\text{AD}]} \right)^{-1},$$

where we have only considered autodetachment and internal conversion as the decay pathways from the  $S_1$  state. Taking  $[S_1]$  as the integrated PE signal between  $0.15 < eKE < 1.50$  eV and  $[\text{AD}]$  as the integrated PE signal between  $0 < eKE < 0.1$  eV,<sup>40</sup> and using the previously determined<sup>14</sup>  $k_{\text{obs}} = (1.4 \text{ ps})^{-1}$ , the lifetimes for autodetachment and internal conversion can be calculated. At 2.57, 2.48, and 2.39 eV, the autodetachment lifetime is 36, 28, and 33 ps, respectively. These are more than an order of magnitude longer than the observed lifetime so that the true internal conversion lifetime is only slightly longer than 1.4 ps (1.46, 1.47, and 1.46 ps at 2.57, 2.48, and 2.39 eV, respectively).

There are relatively large errors associated with the  $\tau_{\text{AD}}$  and  $\tau_{\text{IC}}$  lifetimes determined here, which we estimate to be on the order of  $\pm 20\%$ . This is in part due to the increased noise generated during image reconstruction at low  $eKE$ .<sup>39</sup> More importantly, however, there is likely to be some overlap between the depleted signal and the  $[S_1]$  signal. Finally, there are additional contributions to the low  $eKE$  feature originating from thermionic emission, which we have neglected.

The relative importance of autodetachment versus internal conversion observed in the current experiments is consistent with the recent work of Bochenkova and Andersen.<sup>16</sup> In this, particular vibrational modes have been identified that are strongly coupled to specific decay pathways. Specifically, a high-frequency mode was correlated with the promotion of vibrational autodetachment into the continuum, while lower-frequency modes associated with torsional motion were

correlated with the promotion of internal conversion. The high-frequency modes are the more Franck-Condon active, but it is the interplay between these two types of modes that leads to a balance between the rate of vibrational autodetachment and internal conversion.<sup>16</sup> Using a statistical model, Bochenkova and Andersen<sup>16</sup> were also able to estimate relative rates  $k_{AD}:k_{IC}$  at 2.48 eV (500 nm) and found that  $k_{AD}:k_{IC} \sim 0.1$ .<sup>16</sup> This is in reasonable agreement with the ratio of  $k_{AD}:k_{IC} \sim 0.05 \pm 0.01$  determined here at 2.48 eV. Given the uncertainties in our experimental measurements, the model of Bochenkova and Andersen<sup>16</sup> seems to have captured much of the underlying physics occurring on the  $S_1$  excited state.

Their model also predicts that, at higher excitation energies, the mode leading to autodetachment is more readily excited and this is expected to result in a sharp increase in the rate of autodetachment. At 2.57 eV (482 nm), the ratio  $k_{AD}:k_{IC}$  was expected to increase to 0.2 and at 2.75 eV (450 nm), autodetachment is expected to account for about half of the parent ion depletion.<sup>16</sup> Our results do not follow this trend, although the spectral window probed here is probably too narrow to conclusively state that the  $k_{AD}:k_{IC}$  is constant as a function of energy. At 2.39 eV, we are exciting well below the  $S_1 \leftarrow S_0$  0-0 transition which is at 2.52 eV (492 nm). At this pump energy, excitation is enabled by the fact that our pulses have a broad spectral profile (FWHM  $\sim 12$  nm) and by the finite temperature of the ground state ions ( $\sim 300$  K). If the spectral overlap of the laser with the action spectrum at 300 K is considered, then it is clear that components of the laser pulse that are significantly blue-shifted drive the transition, although the central energy is at 2.39 eV. Additionally, the initial temperature used in the statistical model by Bochenkova and Andersen<sup>16</sup> was 300 K. Although we estimate the internal temperature of  $\text{HBDI}^-$  in the current experiment to be similar to this, it may be slightly higher and hence a direct comparison must be cautioned. Ideally, we had hoped to perform our experiments at 2.75 eV (450 nm), but this is not possible using our current set-up.

Action spectra from the Jockusch group show that the ratio of electrons formed to fragmentation is  $\sim 1:1$  at 2.57 eV (482 nm).<sup>22,25</sup> The former may be assigned to autodetachment, while the latter must to be a consequence of internal conversion, thus suggesting that  $k_{AD}:k_{IC} \sim 1$  at 2.57 eV (482 nm). This is neither consistent with the ratio determined here nor with that predicted by Bochenkova and Andersen.<sup>16</sup> In the PE spectra at  $eKE < 10$  meV, a peak can be attributed to thermionic emission from the  $S_0$  ground state. In our analysis above, we have neglected to consider the depletion in the peak at  $< 10$  meV. Its depletion at  $t = 0$  is negligible compared to (and convoluted by) the depletion in the peak at  $0.01 < eKE < 0.10$  eV. The small depletion observed indicates that thermionic emission has a much longer lifetime than the vibrational autodetachment and internal conversion, as may be expected.<sup>41-43</sup> The discrepancy between our results and the action spectra from the Jockusch group can, in part, be accounted for by this thermionic emission. We note that we can currently only monitor thermionic electrons over a few 100 ns window (limited by our VMI arrangement). If thermionic emission is much slower than this, which it likely will be, then the true yield of thermionic electrons is not accurately

represented in our experiments and this feature will be much larger than measured here.

In conclusion, we have experimentally determined the lifetimes of electron autodetachment and internal conversion from the  $S_1$  excited state of the HBDI gaseous anion at three excitation wavelengths. The lifetime for autodetachment is on the order of 30 ps following excitation near the maximum of the  $S_1 \leftarrow S_0$  absorption (action) spectrum and is consistent with the calculations by Bochenkova and Andersen.<sup>16</sup> We have also noted the importance of thermionic emission as an operative electron loss channel over long time scales.

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