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Communication: Autodetachment versus internal conversion from the S₁ state of the isolated GFP chromophore anion

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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 S₁ excited state 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 ~30 ps.

The experimental setup and methodology has previously been described in detail. HBDI was synthesized based broadly on published methods. Isolated deprotonated HBDI⁻ ions were produced by electrospray ionisation (~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 HBDI⁻ ions were mass selected and then irradiated at the centre of a velocity-map-imaging PE spectrometer. 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 S₁ 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 ~5% and has been calibrated using the spectrum of I⁻.

Figure 2 shows pump-probe PE spectra of HBDI⁻ excited at 2.48 eV (500 nm) with pump-probe delays of t = 0 ps. A clear decay of the PE signal is observed with a lifetime of ~30 ps, indicating the two prominent decay routes: internal conversion (IC) and autodetachment (AD). Also shown is the structure of HBDI⁻.

FIG. 1. Excitation scheme for HBDI⁻ indicating the two prominent decay routes: internal conversion (IC) and autodetachment (AD). Also shown is the structure of HBDI⁻.
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-onion peeling algorithm.\(^{39}\)

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.\(^{17,19}\) 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)\(^{33}\) 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.\(^{17}\) At eKE < 10 meV, an additional PE signal is observed, which we had previously interpreted as originating from thermal electron loss from the ground state (thermionic emission).\(^{19}\) 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.\(^{19}\)

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.\(^{14}\) 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 exited state.

The integrated pump-probe feature which peaks at eKE \( \sim 1.2 \) eV is proportional to the population of excited states in HBDF\(^-\), [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

\[
\frac{k_{\text{AD}}}{\sum_{i \neq \text{AD}} k_i} = \frac{[\text{AD}]}{[\text{S}_1] - [\text{AD}]},
\]

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

\[
k_{\text{AD}} = \left( \frac{[\text{AD}]}{[\text{S}_1] - [\text{AD}]} \right) \left( 1 + \frac{[\text{AD}]}{[\text{S}_1] - [\text{AD}]} \right)^{-1},
\]

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 [AD] as the integrated PE signal between 0 < eKE < 0.1 eV,\(^{40}\) and using the previously determined\(^{14}\) \( k_{\text{obs}} = (1.4 \text{ ps})^{-1} \), 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.\(^{39}\) 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.\(^{16}\) 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.\textsuperscript{16} Using a statistical model, Bochenkova and Andersen\textsuperscript{16} were also able to estimate relative rates $k_{AD}/k_{IC}$ at 2.48 eV (500 nm) and found that $k_{AD}/k_{IC} \sim 0.1$.\textsuperscript{16} 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\textsuperscript{16} 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.\textsuperscript{16} 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 ($\sim 300 \text{ K}$). 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\textsuperscript{16} was 300 K. Although we estimate the internal temperature of 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 $\sim 1$ at 2.57 eV (482 nm).\textsuperscript{22, 25} The former may be assigned to autodetachment, while the latter must to be a consequence of interplay between these two types of modes that leads to a balance between the rate of vibrational autodetachment and internal conversion.\textsuperscript{16} Using a statistical model, Bochenkova and Andersen\textsuperscript{16} were also able to estimate relative rates $k_{AD}/k_{IC}$ at 2.48 eV (500 nm) and found that $k_{AD}/k_{IC} \sim 0.1$.\textsuperscript{16} 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\textsuperscript{16} seems to have captured much of the underlying physics occurring on the $S_1$ excited state.

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.\textsuperscript{16} We have also noted the importance of thermionic emission as an operative electron loss channel over long time scales.

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The integration ranges defining $S_1$ for excitation at 2.38 and 2.57 eV were $0.15 < eKE < 1.40$ eV and $0.15 < eKE < 1.60$ eV, respectively, reflecting that fact that the maximum of the pump-probe feature shifts to higher $eKE$. The integration range for that of the vibrational autodetachment stays roughly unchanged at the different photon energies used.