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Vibronically state-selective photoisomerization in 5-hydroxytropolone

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Fluorescence excitation, dispersed fluorescence, and population labeling spectra of 5-hydroxytropolone cooled in a supersonic free jet demonstrate that syn-anti photoisomerization in the molecule can be driven with high vibrational state selectivity in either direction (syn ↔ anti).

Over the past two decades, the goal of mode-selective chemistry, in which excitation of motion along a given reaction coordinate enhances formation of a specific product, has been hotly pursued with limited success.1–5 The difficulty is that at chemically relevant excitation energies, intramolecular state mixing is typically so extensive that localizing excitation in the reaction coordinate on a chemically useful timescale is not possible. In recent years, successful mode-selective photodissociation2 and bimolecular3,4 chemistry has been achieved following local mode excitation in H2O and HOD, where state mixing is small even at high energies. Electronic state specificity in photodissociation has also been realized in a few cases in which bond rupture occurs within a few vibrational periods.5 Alternatively, recent advances in coherent control methods have demonstrated its future potential for active laser control of chemical reactivity.6

The well-defined intramolecular reaction coordinate accompanying photoisomerization makes it an apt subject of mode-specific studies.7 In this communication, initial results demonstrating vibronically state-selective photoisomerization in 5-hydroxytropolone are outlined. The molecule is remarkably well suited to the task, demonstrating state selective, reversible photoisomerization in a simple laser-induced fluorescence experiment.

5-hydroxytropolone (5-HOTrOH), shown below, is a symmetrically substituted derivative of tropolone, a pseudo-aromatic molecule which is capable of intramolecular hydrogen-atom tunneling. Tropolone has been the subject of several studies8–12 aimed at understanding the vibrationally state-specific H-atom tunneling splittings. In 5-IIOTrOH, despite the symmetric position of hydroxy substitution, the hydroxy group produces asymmetry in the molecular potential energy surface by virtue of the preference of OH groups for in-plane orientations when attached to aromatics.12,13

Based on our recent work on 5-aminotropolone,14 where the asymmetry of the NHD isotope was sufficient to quench H-atom tunneling in the ground state, one might expect a similar quenching in 5-HOTrOH. In that case, the labels syn and anti can be used to distinguish the two conformations which differ in whether the tunneling and 5-hydroxy hydrogens are on the same or opposite sides of the molecule, respectively. Syn–anti isomerization can then proceed along either of two reaction pathways involving H-atom tunneling or 5-OH torsion through 180 degrees.

Fluorescence excitation, dispersed fluorescence, and population labeling spectra of 5-HOTrOH have been recorded using an apparatus described previously.15 5-HOTrOH was synthesized at Cal State Fullerton using the procedure of Russell, Tanger, and Kosugi.15 The sample is heated to 120 °C, entrained in 2–5 bar helium and cooled in a supersonic free jet. Population labeling (or hole burning) scans identify transitions in 5-HOTrOH out of a specific ground state level. In these scans, a high power laser (operating at 20 Hz) saturates a transition out of a given ground state level. A delayed probe laser (operating at 40 Hz with 100 ns delay) is then tuned through a region of the spectrum. A gated integrator monitors the difference in fluorescence signal from the probe laser with and without the saturation laser present using active baseline subtraction.

An overview fluorescence excitation spectrum of the first 1600 cm⁻¹ of the S₁→S₀ transition of 5-IIOTrOH is shown in Fig. 1. Population labeling scans confirm that the red (Fig. 2) and blue (not shown) origins at 25 047 and
25 533 cm\(^{-1}\) arise from different ground state levels. The transitions above the two origins separate cleanly into two spectra built on these two origins. Dispersed fluorescence spectra of the transitions at 25 047 and 25 533 cm\(^{-1}\) [Figs. 3(a) and 4(a), respectively] are very similar to one another and to the origin transition in tropolone,\(^{10}\) confirming them as distinct origins due to syn and anti isomers of 5-HOTrOH.

From this data alone, one might surmise that the asymmetry of the hydroxy substituent is sufficient to localize the tunneling H atom in both \(S_0\) and \(S_1\) states in either of two wells, syn or anti to the 5-hydroxy hydrogen atom. In the limit of high barriers to both H-atom tunneling and O–H torsion, these two isomers would be decoupled from one another, each exhibiting its own characteristic vibrational structure.

Figures 2(b) and 2(c) identify two weak transitions in the population labeling scans 236 cm\(^{-1}\) above the red origin ("red+236") and 236 cm\(^{-1}\) below the blue origin ("blue−236"). The dispersed fluorescence from the (blue−236) transition [Fig. 3(b)] is identical to that from the red origin [Fig. 3(a)]. Thus, the (blue−236) and red origin transitions have a common excited state level though they arise from ground state zero point levels due to different isomers. Similarly, the (red+236) and blue origin transitions (Fig. 4) have a common excited state level despite being accessed from different isomeric ground states. As shown schematically in Fig. 5(a), the (red+236) and (blue−236) transitions are thus "cross-over" transitions which promote syn (anti) ground state molecules to what
is predominantly an anti (syn) excited state zero point level. The frequencies of these transitions, together with the 486 cm$^{-1}$ separation between the red and blue origins, determine the relative energies of the zero point levels of the isomers in both $S_0$ and $S_1$. As indicated in Fig. 5(a), the isomer responsible for the red origin has a ground state zero point level 250 cm$^{-1}$ higher in energy than the other isomer. In $S_1$, the relative stabilities reverse, with an energy difference of 236 cm$^{-1}$.

The spectra do not determine which isomer (syn or anti) is responsible for which spectrum. However, both experiment$^{17}$ and computation$^{18}$ on other vinyl alcohols indicate that the lower energy isomer in the ground state points the hydroxy H atom toward the adjacent double bond in the ring. In 5-HOTrOH this is the syn isomer. Preliminary ab initio calculations on 5-HOTrOH also predict a global minimum at the syn ground state geometry.$^{19}$ Thus, in the remainder of the paper we will call the blue $0_0$ level syn and the red $0_0$ level anti.

The dispersed fluorescence spectrum from the syn $S_1$ origin [Fig. 4(a)] confirms that the weak syn$\rightarrow$anti crossover transitions observed in the excitation spectrum are also observed in emission. The transitions marked by tie lines in the emission from syn $0_0$ [Fig. 4(a)] are due to anti ground state levels, with the weak anti $0_0$ level located 250 cm$^{-1}$ above the $0_0$ level of the syn isomer. The fact that syn$\rightarrow$anti transitions appear with nonzero Franck–Condon factors indicates that the excited state levels possess mixed syn and anti character, i.e.,

$$\psi_{\text{exc}}(\nu') = \alpha \psi_{\text{syn}} + \beta \psi_{\text{anti}}.$$ 

Based on the intensities in the fluorescence excitation and dispersed fluorescence spectra, the probability distributions for the red $0_0$ and blue $0_0$ excited state levels are shown in schematic form in Fig. 6(a) and 6(b).

The existence of these nominally syn$\rightarrow$anti transitions provides an explanation for other anomalies in the fluorescence excitation and population labeling scans. For instance, the set of five transitions marked by an asterisk in Fig. 1 begin 84 cm$^{-1}$ above the blue origin, an energy too low to be ascribed to vibrations built on the blue origin. Nevertheless, the population labeling spectra prove that these levels arise from the same ground state level as the blue origin. Figure 6(b) shows a corresponding set transitions originating from the anti zero point level which begin 320 cm$^{-1}$ (i.e., 84+236) above the red origin and match one-for-one with the blue transitions. These pairs of transitions possess identical dispersed fluorescence spectra (not shown), proving that they arise from common excited state vibronic levels. Thus the low frequency transitions in the blue spectrum (i.e., out of the syn ground state) are accessing vibrational levels nominally in the anti well.

While a full analysis of the syn$\rightarrow$anti state mixing of these and other levels above the two origins will be given elsewhere,$^{20}$ it is qualitatively obvious from Fig. 6 that those transitions which are large in the blue spectrum (out of the syn ground state) are small in the red spectrum (out of the anti ground state) and vice versa. This varying degree of syn/anti mixing is also reflected in the intensity of emission out of these mixed levels to ground state levels within the syn and anti wells. Preliminary analysis of the
dispersed emission from a number of vibronic levels in the spectrum indicates that excited state levels vary from nearly pure syn to highly mixed to nearly pure anti in character.

In summary, 5-HOTrOH provides a clear example of vibronic state selectivity in photoisomerization. While weak, the (red+236) and (blue-236) “cross-over” transitions involve excitation out of an anti (syn) ground state 0_0 level to the 0^* excited state level of dominant syn (anti) character. Emission to the ground state from this level thus completes a cycle of excitation/emission which transforms the syn (anti) isomer into the anti (syn) isomer. Furthermore, one suspects that nonradiative processes from these excited state levels will also result in predominant formation of the same isomer as fluorescence produces. The clear observation of the syn-anti transitions in population labeling scans indicates that the transitions can be partially or completely saturated with pulses from conventional dye lasers, causing a significant fraction of the ground state population of a given isomer to undergo photoisomerization. Furthermore, the process is reversible by simple choice of excitation wavelength. The molecule thus shows the potential, at least, for acting as a wavelength-selected, reversible molecular switch.  

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8344  Letters to the Editor