STIMULATED EMISSION PUMPING-POPULATION TRANSFER SPECTROSCOPY OF JET-COOLED SEROTONIN

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Serotonin (5-hydroxytryptamine) possesses the same flexible ethylamine side chain as tryptamine, differing from it by the addition of a hydroxyl group in the 5-position on the indole ring. Conformational isomerization can therefore occur by reorientation of the ethylamine side chain, hindered rotation of the OH group, or a combination of the two. Building on our recently completed study of the conformation-specific spectroscopy of serotonin,[a]. we report here the results of a study of the energy thresholds to isomerization in serotonin using stimulated emission pumping-population transfer (SEP-PT) spectroscopy. The method involves selective excitation of conformer X early in the supersonic free jet by SEP to produce ground state X with well-defined internal energy E. Following re-cooling of the excited molecules, conformer Y is interrogated selectively downstream in the expansion using laser-induced fluorescence. As the dump laser wavelength is tuned to higher vibrational levels in the ground state, the first transition that produces a gain in the population of conformer Y sets the energy threshold to X$\rightarrow$Y conformational isomerization. Energy thresholds for all seven A$\rightarrow$X channels are determined (where SERO(A) is the lowest energy conformer of serotonin), and compared against the corresponding signal in the A$\rightarrow$A reactant channel. The barriers that involve hindered rotation of the ethylamine side chain are generally similar to those in TRA, while the energy threshold to hindered rotation of the OH group is determined to be $569 < E_{\mathrm{thresh}} < 890\,\mathrm{cm}^{-1}$. When conformational change involves motion of both sub-groups, the observed threshold is the larger of the two thresholds observed for the two sub-group isomerizations. These results will be compared to predictions of the relative energies of the minima and transition states from *ab initio* theory.

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[a]T. A. LeGreve, E. E. Baquero and T. S. Zwier *J. Am. Chem. Soc. (in press).*