Low frequency backbone vibrations of individual conformational isomers: Tryptamine

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The low frequency vibrations of the ethylamino backbone of six conformers of tryptamine have been studied in the ground and excited states using dispersed fluorescence spectroscopy, rotationally resolved laser induced fluorescence, and ab initio calculations. Four low frequency vibrational modes of the backbone, which involve torsional and librational motions of the ethylamino group, have been identified. The three anti conformers show a substantially different vibrational pattern than the four conformers in which the amino group is in gauche position with respect to the pyrrole and the phenyl ring, respectively. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357593]

I. INTRODUCTION

The three aromatic amino acid residues that are primarily responsible for the inherent fluorescence of proteins are tryptophan, tyrosine, and phenylalanine. In solution, tryptophan shows the highest fluorescence yield of the three chromophores. Tryptamine (see Fig. 1), which is the decarboxylation product of the amino acid tryptophan, has a very rich potential energy landscape, which is governed by torsional motions of the ethylamino backbone. Since these low frequency backbone vibrations are a probe of the molecular surrounding of the chromophore, we attempt to systemize these vibrations by means of laser induced fluorescence and dispersed emission spectroscopy.

For the nomenclature of the different tryptamine conformers, we use the scheme proposed by Carney and Zwier. Out of the 27 possible conformers of tryptamine (3×3×3 from rotation about τ1, τ2, and τ3 in Fig. 1) the 18 which have the ethylamino group in the aromatic plane have much higher ground state energies. The remaining nine conformers in which the ethylamino group is in gauche position to the phenyl (pyrrole) ring are called Gph (Gpy). Conformers in which the ethylamino group is pointing away from the indole chromophore are called anti. The orientation of the amino lone pair is given by the descriptors “up,” “ph,” “py,” “out,” and “in,” depending if the lone pair points upwards, to the phenyl side, to the pyrrole side, away from the indole ring, or down to the indole ring. The two in conformers have so far not been observed experimentally and will not be treated in the present study.

Philips and Levy performed laser induced fluorescence (LIF) spectroscopy with a spectral resolution of 0.07 cm⁻¹ and obtained the first rotationally resolved electronic spectra of seven different conformers. Later this work was extended to the triply deuterated conformers in the same group. In the groups of Nguyen et al. and Schmitt et al. rotationally resolved spectra of tryptamine were taken at a resolution of about 0.01 cm⁻¹, mainly limited by the experimental Doppler width and the Lorentzian width of the rovibronic transitions. Nguyen et al. found all seven conformers that were described by Philips and Levy, while Schmitt et al. could only determine six different conformers, although the missing one [C(2) in the paper of Philips and Levy] has nearly the same intensity as the directly neighbored C(1) conformer. In the meantime we were able to spot the reason for this discrepancy. By using successively larger nozzle diameters, the C(2) intensity could be increased considerably. This finding shows that the relative amount of each conformer in the molecular beam in governed not only by the relative energies of the conformers but also by kinetic effects in the early phase of the expansion. Using rotational coherence spectroscopy Connell et al. investigated five conformers of tryptamine and found two different recurrence times for the C conformer, one being similar to D and the other to F. The permanent dipole moments of four tryptamine conformers were determined in a recent study by Nguyen and Pratt, using the Stark effect on rotationally resolved electronic spectra. The ground states of the A and B conformers of tryptamine have also been studied using microwave spectroscopy.

Dispersed fluorescence (DF) spectroscopy is a very useful method to observe vibrational energy levels over a wide energy range. Especially the investigation of the very low frequency region (terahertz region) is straightforward, while other spectroscopic (absorption) techniques are technologically demanding, mainly because bright stable terahertz sources are still not available commercially.

Since the π ← π transition of tryptamine is mainly localized in the indole ring, only little Franck-Condon (FC) activity is expected from the ethylamino backbone vibrations. The low frequency vibrations of tryptamine are interesting, because they reflect the interaction between the backbone and the indole chromophore in relation to the different conformers and may be related to peptide folding in larger systems. In the present publication we will determine and assign the backbone vibrations of six tryptamine conformers in the electronic ground and excited states and compare the experimental results to ab initio calculations.