INFRARED PHOTODISSOCATION OF A WATER MOLECULE FROM A FLEXIBLE MOLECULE- H_2O COMPLEX: RATES AND CONFORMATIONAL PRODUCT YIELDS FOLLOWING XH STRETCH EXCITATION

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Infrared-ultraviolet hole-filling spectroscopy has been used to study IR-induced dissociation in competition with isomerization in tryptamine-$(H_2O)_1$ and tryptamine-$(D_2O)_1$ complexes. Upon complexation of a single water molecule, the seven conformational isomers of tryptamine collapse to a single structure that retains the same ethylamine side chain conformation present in the most highly populated conformer of tryptamine monomer. Infrared excitation of the tryptamine-water complex was carried out using a series of infrared absorptions spanning the range from 2470 to 3715 cm^{-1}. Our goal was to determine the conformational product yields and rates of dissociation of the complex as a function of internal energy over this range. The observed threshold for dissocation occurred at 2872 cm^{-1} (tryptamine-$(H_2O)_1$) and 2869 cm^{-1} (tryptamine(d_n)-$(D_2O)_1$), with no dissociation occuring on the timescale of the experiment at 2745 cm^{-1}. The dissociation time constants varied from 250 ns for the 2869 cm^{-1} band of (tryptamine(d_n)-$(D_2O)_1$), to 25 ns for the 2872 cm^{-1} band of (tryptamine-$(H_2O)_1$. This steep dependence with deuterium substitution is likely a zero-point energy effect on the dissociation energy that places the deuterated complex nearer to the dissociation limit. At all higher energies, the dissociation lifetime was shorter than the pulse duration of our lasers (8 nsec). At all wavelengths, the observed products in the presence of collisions are dominated by conformers A and B with small contributions from the other minor conformers. Interestingly, right at threshold (tryptamine(d_n)-$(D_2O)_1$) at 2869 cm^{-1}, only conformer A is formed in the absence of collisions with helium, while both A and B are observed in the presence of collisions. Comparison of experimental data to *ab initio* computed barriers and binding energies will be made, and the use of the method to test RRKM rate theory applied to dissociation in competition with conformational isomerization will be discussed.