LASER PHOTODISSOCIATION SPECTRA OF THE ANILINE-ARGON CATIONIC CLUSTER IN THE NEAR INFRARED

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The near infrared spectra of the ionic complexes with argon of aniline and its doubly deuterated (on the amino group) isotopomer have been measured by laser photodissociation spectroscopy in a molecular beam. They have been assigned to the $D_1(A^2A_2) \leftarrow D_0(X^2B_1)$ electronic transitions within the solvated chromophores.

The spectra were found similar for aniline$(NH_2)^+$-argon and aniline$(ND_2)^+$-argon. They are characterized by a long vibrational progression involving the 6a mode. On the basis of CASSCF calculations, a large change of geometry along the normal coordinate associated to this mode is found, while the amino group is found in the ring plane. Therefore a change of the conjugation of the ring rather than a charge transfer is inferred. This is thought to be the origin of the extent of the progression. In addition ultrafast internal conversion was observed through the broadening of the vibronic bands, and found dependent on the vibrational state in the upper D_1 electronic state.

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