HIGH RESOLUTION SPECTROSCOPY OF INDOLE DERIVATIVES NEAR CONICAL INTERSECTIONS: TRYPTAMINE AND INDOLE

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The rotationally resolved spectra of vibronic bands of indole and tryptamine in the region between the electronic origin and 1000 cm^{-1} have been analyzed using an evolutionary strategy (ES) approach. The lowest two excited singlet states of the title compounds, which are labeled by ^{1}L$_b$ and ^{1}L$_a$ following the nomenclature by Platt are characterized regarding their excitation energies, geometric structures and their orientation of transition dipole moments (TDM). While the favorable orientation of the transition dipole moment nearly along the main inertial axes in tryptamine makes the assignments of vibronic bands to certain electronic states straightforward, indole poses a much more difficult problem. Here the TDM is oriented to lie between the a and b inertial axes, what causes an uncertainty of the sign of the TDM. This problem can be overcome by fitting the intensities in the vibronic spectrum to a model Hamiltonian, which includes axis reorientation using the ES approach. From the relative sign of the TDM angle with the axis reorientation angle a distinction between both electronic states can be made.

A conical intersection (CI) between ^{1}L$_b$ and ^{1}L$_a$ states in indole is calculated using DFT/MRCI to be located 2000 cm^{-1} above the ^{1}L$_b$ origin, thus perturbing only slightly the vibronic spectrum of indole. For tryptamine the CI is calculated to be less than 1000 cm^{-1} above the ^{1}L$_b$ origin and strong perturbation of the vibronic spectrum is expected and observed.

The vibronic coupling between ^{1}L$_b$ and ^{1}L$_a$ states is calculated using Franck-Condon-Herzberg-Teller theory. The derivatives of the transition dipole moments with respect to the normal coordinates are computed numerical at the DFT/MRCI level of theory. Computed spectra for indole and tryptamine show very good agreement with the experimental ones.