THE CONICAL INTERSECTIONS BETWEEN ^1L_b and ^1L_a STATES IN TRYPTAMINE AND INDOLE

Ch. BRAND, *Institut für Physikalische Chemie I, Heinrich-Heine-Universität, Universitätsstraße 26.43.02.43 D-40225 Düsseldorf, Germany*; J. KÜPPER, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany*; W. LEO MEERTS, *Molecular and Biophysics Group, Institute for Molecules and Materials,Radboud University, 6500 GL Nijmegen, The Netherlands*; D. W. PRATT, *University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260, USA*; JÖRG TATCHEN, *Chemical Physics Department, Weizmann Institute of Science, 76100 Rehovot, Israel*; and M. SCHMITT, *Institut für Physikalische Chemie I, Heinrich-Heine-Universität, Universitätsstraße 26.43.02.43 D-40225 Düsseldorf, Germany*.

The absorption spectrum of the lowest two excited singlet states of indole and tryptamine are calculated using Franck-Condon-Herzberg-Teller (FCHT) theory. The derivatives of the transition dipole moments with respect to the normal coordinates are computed numerically at the combined density functional theory multi-reference configuration interaction (DFT/MRCI) level of theory. All valence electrons were correlated in the MRCI runs and the eigenvalues and eigenvectors of the lowest singlet state were determined. The initial set of reference configuration state functions was generated automatically in a complete active space type procedure (including all single and double excitations from the five highest occupied molecular orbitals in the KS determinant to the five lowest virtual orbitals) and was then iteratively improved. The HT integrals are obtained from Doktorovs recursive relations used for the calculation of the FC integrals. A conical intersection (CI) between ^1L_b and ^1L_a states in indole is calculated using DFT/MRCI to be located 2000 cm^{-1} above the ^1L_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 ^1L_b origin and strong perturbation of the vibronic spectrum is expected and observed.