The role of the A_u ($n\pi^*$) state in the photophysics of pyrazine: a quantum dynamics study.

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The excited state structure and dynamics of pyrazine has attracted considerable attention in the last three decades. It has long been recognized that after UV excitation, the dynamics of the molecule is impacted by strong non-adiabatic effects. In particular, the broad band observed in the $B_{2u}(\pi\pi^*)$ state region of the UV spectrum is an indication of a fast relaxation process[1].

Further theoretical works allowed to interpret this spectral feature as the consequence of the presence a conical intersection between the $B_{2u}(\pi\pi^*)$ and $B_{3u}(n\pi^*)$ states. Several quantum dynamics studies[2,3] based on the KDC vibronic coupling model[4] has succeeded in reproducing the low energy part of the UV spectrum.

However, it is known from high level electronic structure calculations[5] that the dark $A_u(n\pi^*)$ state lies between the $B_{2u}(\pi\pi^*)$ and $B_{3u}(n\pi^*)$ states at the Franck-Condon geometry. The effect of this state on the photophysics of pyrazine has been recently investigated by means of ab-initio calculations[6] as well as on the fly trajectory surface hopping non-adiabatic dynamics simulations[7]. It was shown that, although it has a limited impact on the UV absorption spectrum, it plays an important role in the dynamics of the molecule after excitation to the $B_{2u}(\pi\pi^*)$ state.

The purpose of this work was to pursue the investigation of the role of the $A_u(n\pi^*)$ state on the photophysics of pyrazine by means of wavepacket propagation techniques. A linear vibronic coupling model hamiltonian including the $B_{3u}(n\pi^*)$, $A_u(n\pi^*)$ and $B_{2u}(\pi\pi^*)$ electronic states and the nine most relevant vibrational degrees of freedom was constructed using high level XMCQDPT2[8] electronic structure calculations. Wavepacket propagation calculations based upon this hamiltonian using the MCTDH method[9] were then performed and used to simulate the absorption spectrum as well as the diabatic and adiabatic electronic population dynamics of the system. Our results agree with previous calculations [6,7] and show that the $A_u(n\pi^*)$ state plays an important role in the photophysics of pyrazine.

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