

Ab Initio Quantum Dynamical Study on Ultrafast Nonradiative Transition Pathways of Pyrazine

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Abstract: We theoretically verified the participation of optically dark $n\pi^*$ states other than S_1 in ultrafast internal conversion of pyrazine. Contrary to a recent semiclassical study, our quantum dynamical calculations demonstrated that their contributions are negligible.

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1. Introduction

Pyrazine $C_4H_4N_2$ is a typical azabenzene that undergoes ultrafast nonradiative transitions. They come from the prominent vibronic couplings between two electronic excited states of different characters, i.e., the optically active $\pi\pi^*$ S_2 ($^1B_{2u}$) and almost dark $n\pi^*$ S_1 ($^1B_{3u}$) states in the UV (265 ~ 325 nm) region [1]. Domcke and coworkers proposed on the basis of the results of *ab initio* molecular orbital investigations that the ultrafast nonradiative transition from the S_2 to S_1 state takes place through the conical intersection (CI) between their potential energy surfaces (PESs) [2,3]. Experimentally, Suzuki *et al.* measured the lifetime of the S_2 state (22 ± 3 fs) by pump-probe photoelectron imaging spectroscopy with a 22 fs time resolution and analyzed the observed spectrum under the condition that the nonradiative process from the S_2 to S_1 state occurs [4].

Recently, Werner *et al.* proposed new pathways via optically dark $n\pi^*$ 1A_u and $^1B_{2g}$ states [5]. These dark states were theoretically predicted to be near the S_1 state but there have been no experimental evidence of their existence. Werner *et al.* calculated time-dependent populations of the lowest 1A_u and $^1B_{2g}$ states in addition to those of the S_1 and S_2 states “on the fly” by combining the time-dependent density functional theory with Tully’s stochastic fewest switches surface hopping procedure. Their interesting finding was that the lifetime of the S_2 state was 21.1 fs, which agrees with the experimental value, while at the initial stage the population was preferentially transferred to both the 1A_u and $^1B_{2g}$ states rather than the S_1 state.

The geometrical configurations of CIs between the S_2 state and the 1A_u and $^1B_{2g}$ states have not been theoretically examined to our knowledge. In this study, we quantify the participation of the CIs between the optically active $\pi\pi^*$ S_2 state and the optically dark $n\pi^*$ states in ultrafast internal conversion of pyrazine. “On-the-fly” methods are powerful to search for nuclear dynamics of molecules with multiple vibrational modes but unable to properly describe quantum vibrational coherent behaviors in electronic excited states since they are based on classical equations of motion. We employ the multireference configuration interaction (MRCI) method to obtain reliable PESs of the excited states and the nuclear wave packet (WP) propagation method to solve the nuclear dynamics on the PESs coupled by CIs in restricted vibrational degrees of freedom. The nuclear WP propagation method is applicable to ultrafast nonradiative transitions in aromatic molecules with multiple vibrational modes at the initial stage, in which restricted vibrational modes play an essential role.

2. Computational outline

All electronic structure calculations were carried out with the 6-311++G** Gaussian basis set by using the *ab initio* quantum chemistry program MOLPRO. The geometry of pyrazine was optimized in the electronic ground state S_0 (1A_g) under D_{2h} symmetry constraints at the complete-active-space self-consistent field (CASSCF) level of theory, followed by normal mode analysis. The active space comprised ten electrons distributed among eight orbitals (three π , three π^* , and two lone-pair orbitals). The lowest five singlet electronic states (S_0 to S_4) were state-averaged with equal weights. To take dynamical electron correlation into account, the CASSCF energies were refined at the level of the internally contracted MRCI including single and double excitations (MRCISD).

Two-dimensional PESs were constructed within the subspaces defined by tuning and coupling modes, which span the branching plane of a CI. The vibrational ground-state wave function in the S_0 state was placed on the PES of the optically active S_2 state at the initial time $t = 0$. The subsequent time evolution of the Franck-Condon WP was

performed in the diabatic basis to deal with nonadiabatic couplings by the split-operator method. The resultant diabatic WPs were converted to adiabatic WPs.

3. Results and discussion

We confirmed that the calculated results of geometrical parameters, excitation energies, and vibrational frequencies of pyrazine are in excellent agreement with the experimental data reported by Innes *et al.* [1]. For instance, the vibrational vectors of four selected normal modes are illustrated schematically in Fig. 1. For all of them, the calculated frequency is slightly higher than the experimental one but the difference is only less than 50 cm^{-1} .

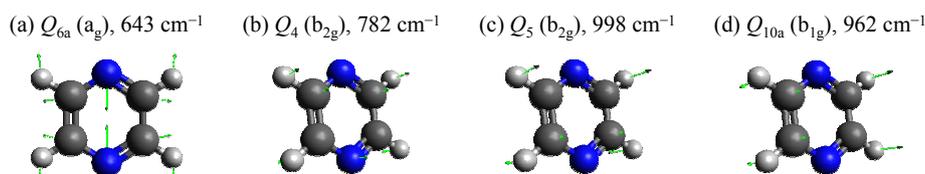


Fig. 1. Vibrational vectors of selected normal modes in the S_0 state of pyrazine. The gray, black, and blue balls represent hydrogen, carbon, and nitrogen atoms, respectively. Harmonic vibrational frequencies were computed at the CASSCF/6-311++G** level of theory.

The time-resolved measurements by Suzuki *et al.* suggested that the Q_{6a} (a_g) in-plane ring deformation mode (Fig. 1a), where pyrazine maintains D_{2h} symmetry, is the dominant tuning mode for the $S_2 \leftarrow S_0$ photoabsorption [4]. The one-dimensional PESs of the S_1 (${}^1B_{3u}$), S_2 (${}^1B_{2u}$), S_3 (1A_u), and S_4 (${}^1B_{2g}$) states along the Q_{6a} mode are depicted in Fig. 2. The S_3 and S_2 states are degenerate at $Q_{6a} = 0.64\text{ u}^{1/2}a_0$, while the S_4 – S_2 and S_2 – S_1 crossings are located farther away at $Q_{6a} = 1.10$ and $-1.21\text{ u}^{1/2}a_0$, respectively. The tail of the Franck-Condon WP covers the S_3 – S_2 crossing but the other crossings are outside the Franck-Condon region. The S_4 state is higher in energy than the S_3 state during the course of propagation to the S_2 – S_1 crossing. Unless a substantial population transfer to the S_3 state takes place by nonadiabatic transition, it is reasonable to conclude that the S_4 state plays a minor role in ultrafast internal conversion of pyrazine.

The Q_4 (b_{2g}) out-of-plane ring bending and Q_5 (b_{2g}) out-of-plane CH bending modes (Figs. 1b and 1c) couple the S_3 (1A_u) and S_2 (${}^1B_{2u}$) states. These modes lower the symmetry of pyrazine to C_{2h} and the irreducible representation of the S_2 state to 1A_u . Figure 3 shows the temporal behaviors in the population of the S_3 state obtained from the nuclear WP simulations on two-dimensional PESs within the Q_{6a} – Q_4 and Q_{6a} – Q_5 subspaces. In both cases, a small fraction of the population is transferred to the S_3 state but its maximum value is less than 0.03, which is much smaller than that in the semiclassical study by Werner *et al.* (~ 0.4) [5]. This indicates that nonadiabatic transitions to the S_3 and S_4 states are negligible. The dominant contribution to ultrafast internal conversion is electronic relaxation through the S_2 – S_1 CI.

The coupling mode between the S_2 (${}^1B_{2u}$) and S_1 (${}^1B_{3u}$) states is the Q_{10a} (b_{1g}) out-of-plane CH bending mode (Fig. 1d). We will also present the detailed analysis of S_2 – S_1 relaxation dynamics within the Q_{6a} – Q_{10a} subspace.

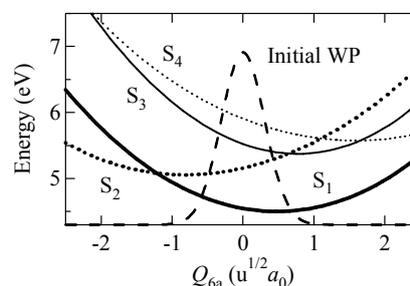


Fig. 2. One-dimensional MRCISD PESs of the S_1 (${}^1B_{3u}$), S_2 (${}^1B_{2u}$), S_3 (1A_u), and S_4 (${}^1B_{2g}$) states along the Q_{6a} mode. Also shown is the probability density of the Franck-Condon WP.

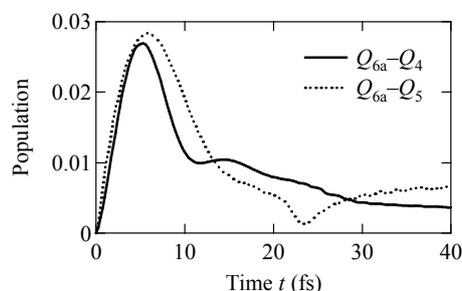


Fig. 3. Temporal behaviors in the population of the S_3 state in the Q_{6a} – Q_4 and Q_{6a} – Q_5 subspaces.

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