

## REGULAR ARTICLE

# Theoretical Treatment of Ultrafast Decay of Excited Vibronic States in the Improved Adiabatic Approximation

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**Abstract:** In the present paper, the non-radiative transition  $S_1 \rightarrow S_0$  of pyrazine was investigated by employing the improved Born-Oppenheimer adiabatic approximation, in which the conical intersection is shown to be avoided. Vibrational frequencies, normal coordinates, and non-adiabatic coupling matrix elements were obtained by *ab initio* quantum chemical methods. Calculated rate constants of internal conversion  $S_1 \rightarrow S_0$  are  $\tau_{(v=0)}=61.7$  ps and  $\tau_{(v=1)}=61.2$  ps in good agreement with the experimental findings.

**Keywords:** Pyrazine; Born-Oppenheimer approximation; internal conversion; DFT

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## 1. Introduction

Pyrazine is a diazine molecule, and its electronic structures, ultraviolet absorption spectra and internal conversions have been studied theoretically and experimentally over half a century.[1-4] The electronic spectroscopy and ultrafast dynamical processes of other diazine molecules such as pyrimidine and pyridazine have also been a very interesting subject due to its rich excited-state dynamical and photochemical properties.[5-8] Substituting a pair of nitrogen atoms for carbon ones at the *para*-position in the benzene molecule, pyrazine has a different electronic structure from benzene. As a symmetrical molecule with point group  $D_{2h}$ , the first excited state  $S_1$  of pyrazine has a  $n\pi^*$  electronic configuration.

Pyrazine molecule has been studied by both theoretical simulations and experimental

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measurements for its low-lying excited states with applications of photophysics and photochemistry. Internal conversion process of pyrazine is described by Domcke and his co-workers through *ab initio* calculations which combined with mathematical models in the 1980s,[9] Domcke et al. proposed an ultrafast internal conversion after  $S_2$  state excitation through conical intersection,[10-13] and the corresponding lifetime was estimated by *ab initio* calculations to be about 20fs.[14] Knee firstly determined experimental results for  $S_1$  state lifetime to be about 110 ps for the vibrationless excitation,[15] and about 100 ps for the vibrationally excited  $S_1$  state, reported by Suzuki.[16, 17] V. Stert[18] The results show that the lifetime of  $S_2$  state due to internal conversion to the lower electronic states was about 20 fs.

Since the development of femtosecond lasers and their application to photochemistry and photophysics, the pump-probe experiments have become a powerful technique to study the femtosecond time-resolved spectroscopies and femtosecond dynamical processes. It is due to its numerous dynamical processes in biology and chemistry and physics are in femtosecond time scale. A main purpose of this paper is to analyze the experimental results of ultrafast dynamical processes by using the improved Born-Oppenheimer adiabatic approximation. Therefore, the experimental results of Suzuki's group[16, 17] will be analyzed and the improved Born-Oppenheimer adiabatic approximation will be employed to calculate the lifetime of vibronic states of pyrazine.

## 2. Computational methods and theoretical details

The improved Born-Oppenheimer adiabatic approximation is briefly described in the following.[19] Notice that the molecular Schrödinger equation is given by

$$\hat{H}\psi(Q,r) = \hat{E}\psi(Q,r), \quad (1)$$

where

$$\hat{H} = \hat{T}_n + \hat{T}_e + V(Q,r) = \hat{T}_n + \hat{H}_e, \quad (2)$$

and

$$\hat{H}_e\Phi_a(Q,r) = U_a(Q)\Phi_a(Q,r), \quad (3)$$

We shall let

$$\psi(Q,r) = \sum_a \Theta_a(Q)\Phi_a(Q,r), \quad (4)$$

where

$$\hat{T}_n\Theta_a\Phi_a = \Phi_a\hat{T}_n\Theta_a + \Theta_a\hat{T}_n\Phi_a - \hbar^2 \sum_i \frac{\partial\Theta_a}{\partial Q_i} \frac{\partial\Phi_a}{\partial Q_i}, \quad (5)$$