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

Jian Lei, Rongxing He

Key Laboratory of Luminescence and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China.

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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

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
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 \textit{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 \textit{ab initio} calculations to be about $20$ fs.[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. \textbf{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

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

where

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

and

$$\hat{H}_c \Phi_a(Q,r) = U_a(Q)\Phi_a(Q,r),$$

We shall let

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

where

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