

# Initial Phase in Quantum Beat Created via Ultrafast Internal Conversion of Pyrazine

Yoshi-Ichi Suzuki<sup>1,2</sup> and Toshinori Suzuki<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto Japan

<sup>2</sup>RIKEN Center for Advanced Photonics, RIKEN, Wako Japan  
yoshi-ichi.suzuki@kuchem.kyoto-u.ac.jp

**Abstract:** We present a simple interpretation for the phase-shifted quantum beat that is created on the lower electronic state from the higher state upon a nonradiative transition, using the classical mechanics and harmonic potentials.

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## 1. Introduction

Molecular photoabsorption spectra at the UV region are often broad and less structured because, for highly excited states of polyatomic molecules, a nonradiative decay to the lower or ground states generally takes place (Fig. 1a). It is also still difficult to obtain a converged result by *ab initio* calculations. Time-resolved photoelectron imaging [1] is a convincing method to investigate ultrafast change in electronic states. We observed rapid change in photoelectron angular distribution for the  $S_2$  excited state pyrazine within 30 fs [2–4] (Figs. 1b and 1c). This change is interpreted as the internal conversion from the  $S_2$  to  $S_1$  state, confirmed by calculations [5]. In addition, after 50 fs photoelectron signal exhibits quantum beat with frequency of  $560\text{ cm}^{-1}$ . This oscillation is assigned to  $Q_{6a}$  ( $583\text{ cm}^{-1}$  in  $S_1$ ) mode, which has long been expected theoretically. The oscillation exhibits a peculiar phase shift (Fig. 1b). This is another evidence for the transition  $S_2$ - $S_1$  because for the direct excitation to the  $S_1$  state the phase shift is not expected other than the 0 or  $\pi$  radians [6–8].

The purpose of this study is to elucidate the phase shift in the quantum beat, using the classical mechanics and the potential energy curves of the excited states. It would be natural to assume that the phase shift is related to the lifetime of the  $S_2$  state. The recurrence of the electronic state ( $S_2 \leftrightarrow S_1$ ) has never been observed in the gas phase experiment, although it is expected in the theory including a few vibrational modes. We assume that the internal conversion  $S_2 \rightarrow S_1$  is an irreversible process. The relation between the lifetime and the phase shift would be useful to obtain information on the dynamics near the zero time delay at which the pump and probe pulses overlap temporally and the signal may contain an intense probe-pump signal due to, for instance, the  $S_3$  state in Fig. 1b. Because the molecular  $S_0$  and  $S_1$  states have usually well defined vibrational levels, the vibrational wave packet will be created via internal conversion of the  $S_n$  states ( $n \geq 1$ ) and they can be observed by the short wavelength lasers [9, 10].

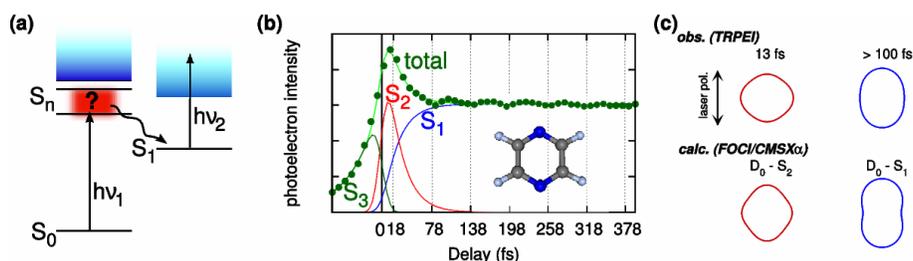


Fig. 1. (a) Schematic view of time-resolved photoelectron spectroscopy for molecular excited states. (b) Photoelectron intensity of two photon ionization of pyrazine as a function of pump-probe delay [2]. Dotted lines indicate the minima of photoelectron intensity. (c) Observed [2] and calculated [5] photoelectron angular distributions.

## 2. Results and Discussion

Figure 2(a) shows a schematic potential energy curves of pyrazine  $S_0$ ,  $S_1$ ,  $S_2$  and  $D_0$  states. The molecular structure is initially assumed to be the equilibrium geometry of  $S_0$ . The molecule is excited instantaneously to  $S_2$  with no momentum. Then, the geometry changes toward the equilibrium geometry of  $S_2$  and moves onto the  $S_1$  surface suddenly at  $\tau$ , lifetime of  $S_2$ . The phase shift of quantum beat upon photoionization from  $S_1$  to  $D_0(v=0)$  is affected by the relative positions of the equilibrium geometries of  $S_0$  and  $D_0$ . In our case (Fig. 2), the phase shift is expected to be  $\pi$  when  $\tau=0$ , *i.e.* oscillatory component  $\propto \cos(\omega t + \pi)$ . The classical motion on the  $S_2$  and  $S_1$  potential curves is described, respectively, by  $Q(t) = -Q_{eq2} \cos(\omega_2 t) + Q_{eq2}$  ( $t < \tau$ ) and  $Q(t) = A \cos(\omega_1 t + \varphi + \pi) + Q_{eq1}$  ( $t \geq \tau$ ), where

the equilibrium geometries and frequencies of the  $S_n$  state are denoted by  $Q_{\text{eq}n}$  and  $\omega_n$ , respectively.  $\varphi$  is a function of  $\tau$ ,  $\omega_1$ ,  $\omega_2$ ,  $Q_{\text{eq}1}$ , and  $Q_{\text{eq}2}$ . It is derived as  $\varphi = \tan^{-1}(s/c)$  by connecting  $Q$  and  $dQ/dt$  at  $\tau$ , where

$$c = (Q_{\text{eq}2} - Q_{\text{eq}1}) \cos(\omega_1 \tau) - Q_{\text{eq}2} [\cos(\omega_1 \tau) \cos(\omega_2 \tau) + \sin(\omega_1 \tau) \sin(\omega_2 \tau) \omega_2 / \omega_1], \quad (1)$$

$$s = (Q_{\text{eq}2} - Q_{\text{eq}1}) \sin(\omega_1 \tau) - Q_{\text{eq}2} [\sin(\omega_1 \tau) \cos(\omega_2 \tau) - \cos(\omega_1 \tau) \sin(\omega_2 \tau) \omega_2 / \omega_1]. \quad (2)$$

In the following discussion, we assume  $\omega_1 = \omega_2$ . Using theoretical values for  $Q_{\text{eq}1}$  and  $Q_{\text{eq}2}$  [8] and observed  $\tau$  and  $\omega_1$ , the phase shift is obtained as 2.6 radians, corresponding to 25 fs in delay time. This agrees reasonably well with 18 fs observed (Fig. 1).

In order to examine the sensitivity of the phase shift to the potential energy curves, we calculated the classical amplitude of oscillation for the  $Q_{6a}$  mode of real pyrazine (Fig. 2a) and model one [Fig. 2b]. In Fig. 2b the equilibrium geometry of  $S_2$  is in the same side of  $S_1$  ( $Q_{\text{eq}1} > 0$  and  $Q_{\text{eq}2} > 0$ ) with respect to the  $S_0$  minimum. Figures 2c and 2d show  $Q(t)$  as a function of time. The lifetime of  $S_2$  is varied from 2 to 22 fs. with 5-fs steps. Apparently, for real pyrazine the beat pattern is sensitive to the lifetime. Especially the phase shift is almost exactly proportional to the  $S_2$  lifetime. On the other hand, for the model (Fig. 2d) the  $S_2$  lifetime has nearly no effect on the phase shift. Therefore, we can conclude that the observed phase shift reflects the real potential energy curves of the  $Q_{6a}$  mode of pyrazine.

For further validation of our model, observation of other modes and molecules would be necessary. Due to new developments in light source with short wavelengths [9, 10], it is very promising to observe the multi-mode vibrational quantum beat in the lower or ground states of molecules. There are five totally symmetric modes for pyrazine. According to the theory [11], the  $S_2$  potential energy curves of  $Q_1$ ,  $Q_2$  and  $Q_{9a}$  modes of pyrazine are the same side of  $S_1$  while that of  $Q_{6a}$  and  $Q_{8a}$  are placed on the other side. Werner *et al.* performed theoretical simulation of pyrazine using the *ab initio* nonadiabatic molecular dynamics "on the fly" [12]. The results infer that there is no phase shift for the oscillation along  $Q_1$  mode. This is consistent with our model.

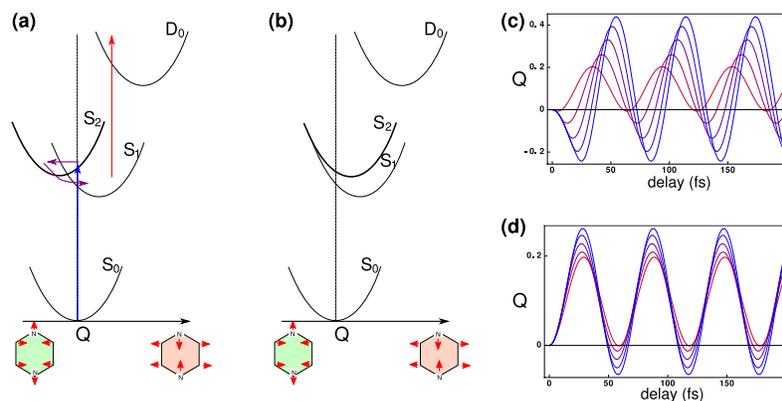


Fig. 2. Schematic potential energy curves of models for the  $S_0$ ,  $S_1$ ,  $S_2$ , and  $D_0$  states. The  $S_2$  curve is in (a) the opposite and (b) the same side of the  $S_1$  curve. Figures (c) and (d) exhibit vibrational motion [see. Eqs. (1) and (2)] for the potential curves (a) and (b), respectively, as a function of delay time and the lifetime of  $S_2$ . The colors indicate different lifetime from red ( $\tau = 2$  fs) to blue (22 fs) with 5-fs steps.

## References

- [1] T. Suzuki, *Annu. Rev. Phys. Chem.* **57**, 555 (2006)
- [2] T. Horio, T. Fuji, Y. Suzuki, and T. Suzuki, *J. Am. Chem. Soc.* **131**, 10392 (2009)
- [3] Y. Suzuki, T. Fuji, T. Horio, and T. Suzuki, *J. Chem. Phys.* **132**, 174302 (2010)
- [4] T. Suzuki and Y. Suzuki "Ultrafast Internal Conversion of Pyrazine via Conical Intersection" in *Advances in multiphoton processes*, S. H. Lin, A. A. Villaeys, and Y. Fujimura, eds., Vol. 21, Chap. 4 (World Scientific, Singapore, 2014)
- [5] Y. Suzuki and T. Suzuki, *J. Chem. Phys.* **137**, 194314 (2012).
- [6] P. M. Felker and A. H. Zewail, *J. Chem. Phys.* **82**, 2961 (1985).
- [7] J. A. Davies and K. L. Reid, *Phys. Rev. Lett.* **109**, 193004 (2012) .
- [8] T. Fuji, Y. Suzuki, T. Horio, and T. Suzuki, *Chem. Asian J.* **6**, 3028 (2011) .
- [9] T. Horio, Roman Spesyvtsev, and T. Suzuki, *Opt. Express* **21**, 22423 (2013) .
- [10] S. Adachi, T. Horio, and T. Suzuki, *Opt. Lett.* **37**, 2118 (2012) .
- [11] A. Raab, G. A. Worth, H.-D. Meyer, and L. S. Cederbaum, *J. Chem. Phys.* **110**, 936 (1999).
- [12] U. Werner, R. Mitrić, and V. Bonačić-Koutecký, *J. Chem. Phys.* **132**, 174301 (2010).