4C07

Molecular-Frame Photoelectron Angular Distribution of Nitric Oxide Studied by Time-Resolved Photoelectron Imaging

(RIKEN) Tang Ying, Takuya Horio, Yoshi-ichi Suzuki, and Toshinori Suzuki

Introduction

Photoionization is important as the most fundamental photo-induced processes. In addition, understanding of photoionization process is indispensable for interpreting time-resolved photoelectron imaging to capture ultrafast dynamics of molecules. Nitric Oxide is the benchmark system for photoionization studies. It is the only molecule for which photoinoization dynamical parameters (PDPs) in ultraviolet photoionization (the magnitudes and phases of the ionization transition dipole moment) have been reported both theoretically and experimentally. However, the experimental result has been reported only for photoelectron kinetic energy (PKE) of 0.18 eV by a single research group [1]. This fact illustrates the limited understanding of photoionization dynamics. Here, we take a new strategy for studying photoionization dynamics at the level of molecular-frame photoelectron angular distribution (MF-PAD) examine the photoionization dynamics of NO in the energy range 1.33-0.05 eV, attempting deeper understanding of this benchmark system.

In the present work, we constructed new theoretical framework for time-resolved photoelectron imaging to extract photoionization dynamical parameters. The laboratory-frame photoelectron angular distribution (LF-PAD) of aligned molecules is expressed as follows [2]:

$$\frac{d\sigma}{d\Omega} \propto \sum_{LM_L}\sum_{KQ}\sum_{k_\gamma q_\gamma}\sum_{\Lambda p}(-1)^{L-M_L}\begin{pmatrix} K & L & k_\gamma \\ Q & -M_L & q_\gamma \end{pmatrix} \times \rho^{\gamma_{pr}}_{k_\gamma q_\gamma}\tilde{A}^{\gamma_{pu}}_{KQ\Lambda p}(\Delta t) b_{KLk_\gamma \Lambda p}(E) Y_{LM}(\theta_k, \varphi_k), \quad (1)$$

$\tilde{A}^{\gamma_{pu}}_{KQ\Lambda p}$ is the alignment parameter, $b_{KLk_\gamma \Lambda p}$ is the expansion coefficient determined by an experiment.

In (1+1') REMPI with parallel polarizations of the pump and probe light, LF-PAD is expressed as follows [3]:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_0}{4\pi}[1 + \beta_2(t)P_2(\cos\theta) + \beta_4(t)P_4(\cos\theta)], \quad (2)$$

The experimental observables β_L can be expanded with the alignment parameters $\tilde{A}^{\gamma_{pu}}_{KQ\Lambda p}$ and the photoionization dynamical factors $b_{KLk_\gamma \Lambda p}$ which contain the photoionization transition dipole matrix elements in the molecular frame:

$$\beta_L(\Delta t, E, \gamma_{pu}, \gamma_{pr}) \propto \sqrt{2L+1}\sum_{KQ}\sum_{k_\gamma q_\gamma}\sum_{\Lambda p}(-1)^L\begin{pmatrix} K & L & k_\gamma \\ Q & 0 & q_\gamma \end{pmatrix} \times \rho^{\gamma_{pr}}_{k_\gamma q_\gamma}\tilde{A}^{\gamma_{pu}}_{KQ\Lambda p}(\Delta t, \tau_{pr}) b_{KLk_\gamma \Lambda p}(E), \quad (3)$$

In our measurements, the standard deviations of β_2 and β_4 were at the unprecedented levels of less than 0.03, which enable us to extract 11 photoionization dynamical parameters (PDPs).

Experiment

The pump laser (226 nm) excites jet-cooled NO to the A (3sσ Rydberg) state, and they are ionized by the probe laser (242-323 nm, PKE: 1.33-0.05 eV) after a variable delay time Δt. The photoelectrons are accelerated and projected onto a position-sensitive detector. The images are recorded by a CMOS camera synchronized with a 1 kHz laser, and the real-time center-of-gravity (COG) calculation is performed to find the accurate positions where photoelectrons hit on the detector. Due to the propensity rule of Δv=0 upon ionization from the A state to the cation, the

change of the probe wavelength is directly reflected to the change of PKE. We observed photoelectron images for each probe wavelength and each delay time, and extracted integral photoionization intensity σ_0, and two anisotropy parameters β_2 and β_4.

Results and Discussion

Fig. 1 shows the typical results for PKE of 0.9 eV, in which the rotational wave packet revival features are clearly identified with the full and half revival time of 8.4 and 4.2 ps. The time-dependence of σ_0 shows that ionization occurs more efficiently via parallel than perpendicular transition: we extracted $b_{02200}(E)$ factor with accuracy of <0.01 from σ_0.

For highly accurate determinations of $b_{KLk_r\Lambda p}$, we concentrated our measurements of β_2 and β_4 around the full and half revival times, as shown in Fig. 2. From the experimentally determined $b_{KLk_r\Lambda p}$ and the scattering phases taken from the MQDT analysis of high Rydberg states, we obtained 7 transition dipole matrix elements. With these parameters, MF-PADs are calculated as shown in Fig. 3.

Thus, we have successfully determined MF-PADs in photoionization of NO from $A(^2\Sigma^+)$ state by a novel experimental approach of time-resolved photoelectron imaging. The method can be extended to other systems. The extracted photoionization dynamics parameters were in reasonable agreement with Zare [1], while the agreement was poorer with existing theoretical predictions. This clearly suggests necessity of improvement of theoretical methods. Although, we are unable to identify specifically which theoretical problem causes the discrepancy, it would be clarified by further theoretical studies. Near threshold variation of MF-PADs is predominantly determined by the Coulomb phases, however, the present study uncovered fast modulations of $b_{02200}(E)$ parameters, that is beyond a simple one-electron model of photoionization dynamics.

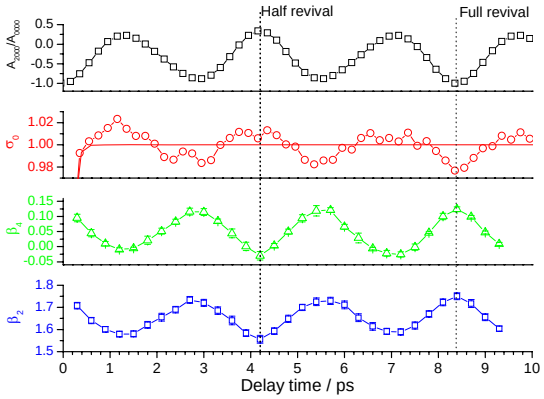

Fig. 1. σ_0, β_2 and β_4 as a function of the pump-probe time delay.

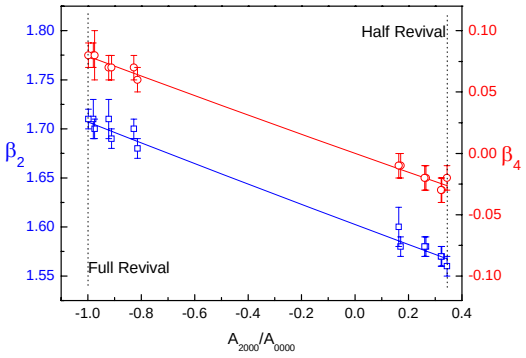

Fig. 2. β_2 and β_4 as a function of alignment parameter A_{2000}/A_{0000}.

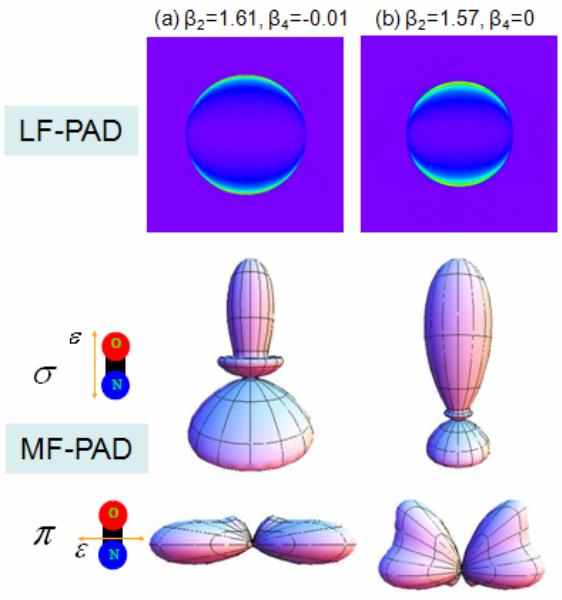

Fig. 3. LF-PADs and MF-PADs at PKE of (a) 1.33 eV and (b) 0.27 eV.

References

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