Ultrafast Photoelectron Spectroscopy of Electron–Ion Wave Packets in Rydberg N_2

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Abstract: Time-resolved photoelectron spectroscopy of N_2 Rydberg using single-order high harmonics at 80 nm reveals ultrafast wavepacket dynamics (~3 fs) of both Rydberg electron and the corresponding N_2^+ core as the beating oscillation (~ 300 fs).
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1. Introduction

Recent developments of laser high-order harmonics generation have enabled us to employ ultrashort laser pulse as a probe for accessing atomic/molecular Rydberg states lying in EUV. Although Rydberg electrons often exhibit rather slow dynamics due to the motion in larger orbit around the ion core, the orbit period of Rydberg states with $n_{\mathrm{eff}} \sim 10$ (n_{eff} : the effective principle quantum number) becomes femto- to pico-second time scales on which the dynamics corresponds to nuclear motions such as vibration and rotation. Therefore, unlike atomic systems, such molecular Rydberg wave packet exhibits more complex dynamics because Rydberg electrons do not follow nuclear motions and Born-Oppenheimer approximation is no longer hold. Here, we have applied time-resolved EUV photoelectron spectroscopy to Rydberg wave packets dynamics of N_2 in different electronic states by using single-order harmonics at 80 nm (pump) and ultrashort laser pulse at 800 nm (probe). The present study clearly demonstrates the importance of the interplay between nuclear and electron motions for the deeper understanding molecular Rydberg wave packet dynamics.

2. Experiment

The output of a regenerative Ti:Sapphire laser system (800 nm, 2 mJ/pulse, 1 kHz) was split into two pulses with a power ratio of 90:10. The main NIR pulse was frequency-doubled by using a BBO crystal to generate an UV pulse at 400 nm. A set of chirped mirrors were used to compensate the dispersion by the air and the window materials. Ultrashort EUV pulses at 80 nm were generated as the 5th order harmonics of the fundamental UV pulses by focusing them into a gas cell filled with Kr gas (~ 10 Torr) as the nonlinear medium. The co-propagating fundamental and harmonics of other orders were filtered out by using an indium foil (0.1 μm) [1]. The EUV pulses ($\Delta\tau \sim 70$ fs) were used to excite N_2 in the ground vibronic state to several Rydberg states converging to the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states of N_2^+ ion (Fig. 1(a)). The rest of the NIR pulse ($\Delta\tau \sim 50$ fs) was used to probe the subsequent wave packet dynamics by librating the Rydberg electron from the ion core. The photoelectrons produced in the interaction region were detected by using a magnetic bottle type spectrometer with the typical electron energy resolution of $E/\Delta E = 50$ for $E < 100$ eV.

3. Results and discussion

Figure 1(b) shows a photoelectron spectrum at the pump-probe time delay of $\Delta t = 190$ fs. It displays five peaks with an energy spacing of ~ 0.27 eV. This vibrational progression is assigned to the v' = 0–4 levels of the $X^2\Sigma_g^+$ states of the N_2^+ ion; the three extra peaks (v' = 2–4) are identified in addition to the other two peaks (v' = 0, 1) which are seen in the conventional He I photoelectron spectrum [2]. The relative peak intensities of the vibrational progression are simulated by taking into account Franck-Condon factors between each terminated vibrational level and the Rydberg levels of 9pπ(v' = 0), 6pπ(1), 5pπ(2), 4pπ(1), and 8f(0) converging to $X^2\Sigma_g^+$ as well as 3dδ(1) converging to $A^2\Pi_u$ [3]. The experiment is well reproduced by the simulated result shown in Fig. 1(c) where the 3dδ(1) state is included in the calculation. This result shows that the two-color two-photon ionization of N_2 proceeds mainly through the 3dδ(1) Rydberg state.

Figure 1(d) shows the integrated intensity of the v'=0 peak as a function of the pump-probe time delay. The modulation in intensity is clearly observed with a period of ~ 300 fs up to $\Delta t = 1000$ fs. The oscillation period for the v'=0 peak corresponds to the coherent dynamics between the $X^2\Sigma_g^+$ 9pπ(0) and $A^2\Pi_u$ 3dδ(1) states according to the simulation in Fig. 1(c). The period of Rydberg electron wave packet dynamics is calculated to be $T_{\mathrm{el}} = 2.99$ fs from

the energy difference (ΔE_{el} = 1.375 eV) between the 9pπ and 3dδ Rydberg levels while the ion-core wave packet dynamics oscillates with a period of T_{core} = 3.02 fs according to that of ΔE_{core} = 1.369 eV between the $X^2\Sigma_g^+(v' = 0)$ and $A^2\Pi_u(v' = 1)$ states. Although the both periods are much smaller than the observed one, the beating period is calculated to be $T_{beat} = (1/T_{el} - 1/T_{core})^{-1}$ = 300 fs, which agrees well with the experiment. This result shows that the observed dynamics is a result of a superposition of (i) Rydberg electron motion, (ii) electron motion in the ion core, and (iii) vibrations of the ion core.

4. Summary

Ultrafast dynamics of molecular N_2 Rydberg wave packet is investigated by time-resolved photoelectron spectroscopy using single-order laser harmonics at 80 nm. The observed coherent dynamics is interpreted as a result of the beating between Rydberg electron and ion-core wavepackets. The present study shows a Rydberg electron wavepacket may serve as a strobe to probe ultrafast dynamics in the ion core..

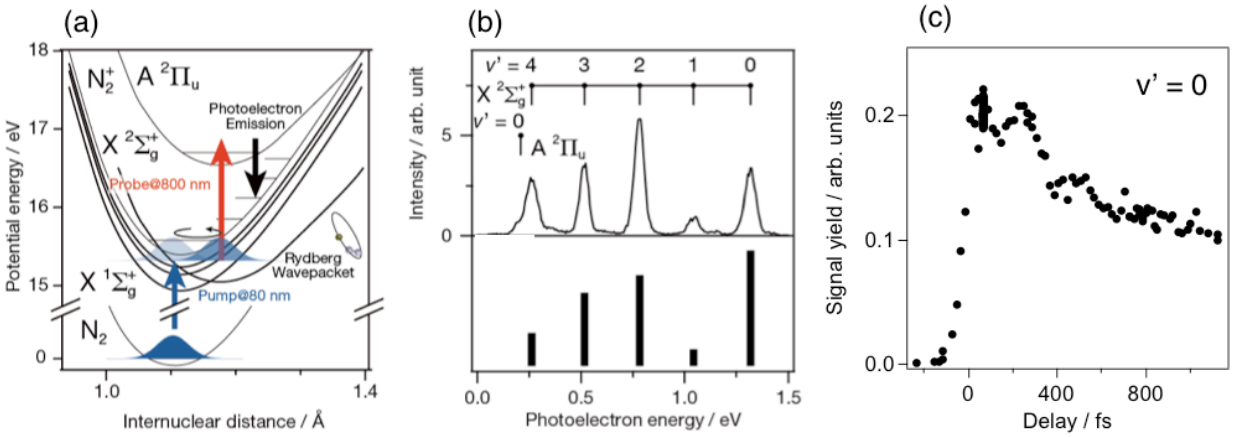

Fig. 1. (a) Schematic diagram of two-color two-photon ionization of N_2 by using pump pulse at 80 nm and probe pulse at 800 nm. (b)(upper) Photoelectron spectrum at the pump-probe time delay of 190 fs. (lower) Relative transition probabilities including Franck-Condon factor from intermediate Rydberg states to the terminated vibrational states in the electronic ground state of N_2^+. (c) Signal intensity for the v' = 0 peak as a function of pump-probe time delay. Oscillations with a period of ~ 300 fs are clearly identified.

References

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