Nonadiabatic rotational excitaton of benzene
by double pulse intense laser fields

(IMS) ○Daeyul Baek, Hirokazu Hasegawa, Yasuhiro Ohshima

1. Introduction

Recently, Meijer et al. [1] pointed out that it may be possible to control a rotational state distribution via NAREX [2] processes using double pulse excitation. However, these experimental studies on NAREX processes have been limited to only the diatomic molecule. In the present study, we investigate the rotational excitation process of benzene molecules by varying the time delay between two intense femtosecond pulses. The rotational state distributions after the double pulses excitation are probed by a (1+1) resonance enhanced multiphoton ionization technique.

The state distribution depends on the time delay of double pulse and shows characteristic beat patterns. The analysis of the beat signals reveals that the rotational excitation processes are different to each other for initial states with different J and/or K.

2. Experiment

The fundamental output from a femtosecond Ti:sapphire laser system (820 nm, 1~2 mJ/pulse, 1 kHz) is divided into double pulses of identical energies with a variable time delay τ. These pump pulses are collinearly focused onto jet-cooled benzene molecules in a molecular beam to induce nonadiabatic rotational excitation. A linear chirp is applied to stretch the pulse duration (35 fs for transform limited) to 160 fs by adjusting the compressor grating. Here, a high pressure pulsed valve with a stagnation pressure of 90 atm is incorporated for an efficient rotational cooling of molecules. After ~100 ns of the interaction with the pump pulse, the probe pulse from a nanosecond frequency-doubled dye laser (258 nm, 10 μJ/pulse, $\Delta E = 0.05$ cm^{-1}) ionizes benzene molecules by 1+1 resonance enhanced multiphoton ionization via the $S_1 \leftarrow S_0 \ 6_0^1$ transition. The generated benzene cations are detected by a time-of-flight mass spectrometer (TOF-MS). The polarization direction of the pump and the probe pulses is set to be parallel to each other, and along with the ion-extraction field in the TOF-MS. The probe pulse was tightly focused with an $f = 170$ mm lens, while the pump pulse was loosely focused by an $f = 300$ mm lens and its focal position was slightly shifted from the probed region by ~10 mm to maximize the laser beam overlap.

3. Results and Discussions

The state distribution depends on the time delay of double pulse and shows characteristic beat pattern. In order to investigate the NAREX dynamics of the benzene molecule, we measured the dependence of the rotational state distribution on the delay time for the states of $J_K = 0_0, 2_0, 1_1, 2_1, 3_1, 2_2, 3_2, 4_2, 3_3,$ and 4_3. The example of this dynamics is shown in Figs. 1 and 2. Fig. 1 shows the dependence of the benzene ion yield on the delay for $J = 2, 3, 4$ with $K = 2$. We consider the following model to explain the observed beat signals. The rotational wave packet generated after the interaction with the first pulse of the double pulse pair at $t = 0$ can be written as the follow:
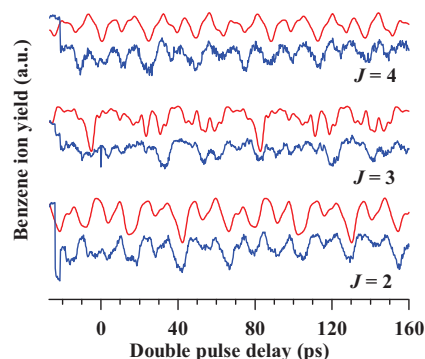

Fig. 1. The experimental (bule line) and simulated (red line) delay dependence of the rotational state population for $J = 2, 3, 4$ with $K = 2$.

$$\left|\Psi(t)\right\rangle = \sum_J A_{J_iJ}e^{i\delta_{J_iJ}}e^{-i\omega_{JK_i}t}\left|JK_iM_i\right\rangle \tag{1}$$

Here, $\omega_{JK_i}=E_{JK_i}/\hbar$, A_{J_iJ} and δ_{J_iJ} are the angular frequency, amplitude and phase of each $\left|JK_iM_i\right\rangle$ state in the rotational wave packet. If the second pump pulse is irradiated onto the molecule at $t=\tau$, the wave packet represented in Eq. (1) is modified as [3],

$$\left|\Psi(t;\tau)\right\rangle = \sum_J B_{J_iJ}(\tau)e^{-i\omega_{JK_i}t}\left|JK_iM_i\right\rangle \tag{2}$$

where, $B_{J_iJ}(\tau)$ is the transition amplitude from $\left|J_iK_iM_i\right\rangle$ to $\left|JK_iM_i\right\rangle$ by the interaction with the double pulse. The rotational state population, as observed beat signals in Fig. 1, is proportional to $\left|B_{J_iJ}(\tau)\right|^2$. The explicit form is as follows:

$$\left|B_{J_iJ}(\tau)\right|^2 = \sum_{J'} A_{J_iJ'}^2 A_{J'J}^2 + 2\sum_{J'>J''} A_{J_iJ'}A_{J'J}A_{J_iJ''}A_{J''J}\cos(\Delta\omega_{J'J''}\tau + \Delta_{J_iJ}^{J''J'}) \tag{3}$$

where $\Delta\omega_{J'J''} = \omega_{J'K_i} - \omega_{J''K_i}$ and $\Delta_{J_iJ}^{J''J'} = \delta_{J_iJ'} + \delta_{J''J} - \delta_{J_iJ''} - \delta_{J'J}$. The information on the phase and amplitudes of the rotational wave packet can be obtained from the Fourier-transformed spectrum of Eq. (3). The peaks of the FT spectrum appear at $\Delta\omega_{J'J''}$ with the intensity of $2A_{J_iJ'}A_{J'J}A_{J_iJ''}A_{J''J}$ and with the phase $\Delta_{J_iJ}^{J''J'}$.

Accordingly, the components of the rotational eigenstates included in the wave packet and the coupling strength between rotational eigenstates can be obtained by the observed beat signals. Fig. 2(a) displays the Fourier transformed signal of the observed beat signals for $J = 2, 3, 4$. As expected, the peaks appear at the positions corresponding to the rotational energy differences. The peak assignments are also shown in Fig. 2(b). Our experimental result supports the theoretical prediction about the rotational excitation process.
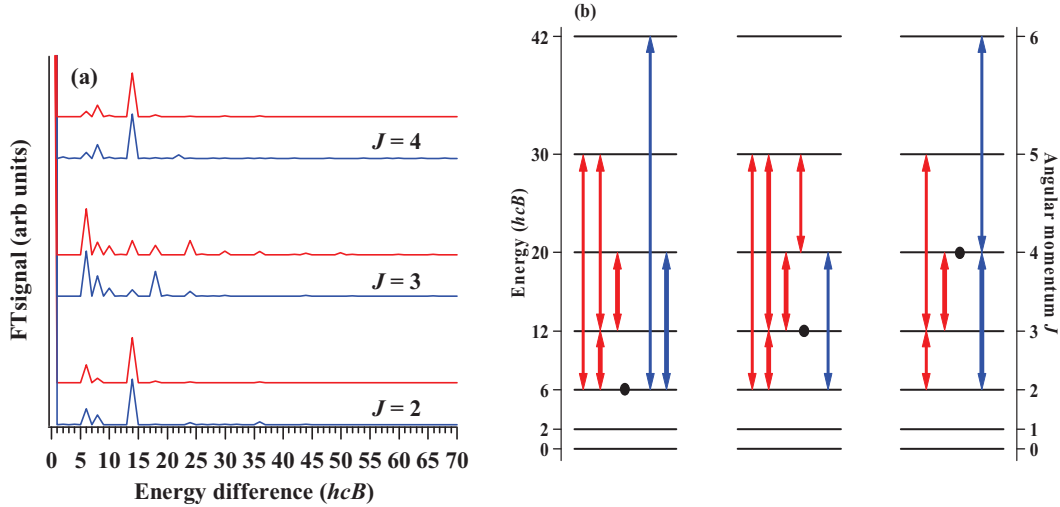

Fig. 2. (a) Fourier-transformed signal of the experimental (bule line) and simulated (red line) delay dependent behavior of the rotational state population for $J = 2, 3, 4$ with $K = 2$, as shown in Fig. 1. (b) Rotational-energy diagram of each probed state (●).

4. Reference

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