Coherent rotational dynamics of molecules induced by intense ultrafast laser fields

Hirokazu Hasegawa and Yasuhiro Ohshima

Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, and
The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, Japan

E-mail: ohshima@ims.ac.jp

Abstract. Coherent rotational dynamics of gas-phase molecules induced by the excitation with an intense nonresonant ultrafast laser field is discussed. In particular, utilities of quantum-state resolved spectroscopic probe after the nonadiabatic rotational excitation (NAREX) by the ultrafast pulse(s) are described with an example of double-pulse excitation experiments on NO, which provide detailed information on excitation pathways in NAREX. Future prospects of the present method are briefly discussed.

1. Introduction

When a gaseous molecular sample is irradiated by an intense nonresonant ultrafast laser pulse, the laser field exerts a torque that aligns the molecular axis along the laser polarization vector, due to the interaction with the molecular anisotropic polarizability. The process, now commonly termed as “nonadiabatic molecular alignment,” has been attracting much attention because of interesting physics involved and possible broader applications [1]. Here the field–molecule interaction only remains in much shorter duration than the characteristic time for molecular rotation, and thus the nonadiabatic alignment is inherently accomplished by nonadiabatic rotational excitation (NAREX), where rotation of the molecules is coherently excited to create a rotational quantum wavepacket (WP), a non-stationary superposition of rotational eigenstates.

While most of the previous studies have been devoted to exploring the degree of molecular alignment and its time evolution by using various real-time measurements [2–6], the state distribution in NAREX has not been focused on despite of the following physical significances. First, details concerning the excitation process during exposure to laser fields are encoded in the state distribution. Second, molecules in highly anisotropic states exerted to NAREX will be particularly useful for studies on, e.g., quantum-state resolved collision or reaction dynamics. Third, NAREX can become a competent tool for changing and controlling the rotational state distribution of molecules, especially when recent elaborate methods, i.e., double-pulse pair [7–9] and shaped pulse [10,11], are invoked.

Recently, we have developed a method for measurements of the rotational-state distribution of a molecule irradiated by a nonresonant femtosecond (fs) laser pulse by utilizing a frequency-domain spectroscopic probe with almost full quantum-state resolution [12–14]. Two different classes of molecules have been examined so far; a diatomic molecule, nitric oxide (NO), and a symmetric-top molecule, benzene (C₆H₆). They have been selected primarily because of easy access for probing

1 To whom any correspondence should be addressed.
distributions by resonant-enhanced multiphoton ionization (REMPI). The present manuscript describes some details of the experimental study on NO. In particular, utilities of double-pulse excitation are demonstrated to provide definite information on excitation pathways in NAREX.

2. Experimental
A pulsed molecular beam containing a trace amount of a NO diluted in a He or Ne buffer gas was produced in a differentially pumped vacuum chamber. The rotational temperature of a molecular ensemble in the beam was adiabatically cooled to < 2 K. The molecular beam was then irradiated with the fundamental output (~ 800 nm) from a fs Ti:Sapphire laser system (150 fs duration with 1 mJ/pulse) operated at 1 kHz. This ultrafast pulse is referred as a pump hereafter. In the case of double-pulse excitation experiments, the output from the fs laser systems is divided into a nearly isoc-enegetic pulse pair with a variable time delay by using a Michelson interferometer. After the excitation with the pump pulse(s), molecules were ionized via (1 + 1) REMPI by the probe pulse (~ 226 nm) from the frequency-doubled output of a nanosecond XeCl excimer laser-pumped dye laser system. The bandwidth of the probe pulse was 0.4 cm$^{-1}$. The generated molecular ions are detected by a time-of-flight mass spectrometer (TOF-MS). The time delay between the pump and the probe pulses is fixed to 100 ns. Since the observed REMPI excitation spectra unchanged when the pump-probe delay time was varied down to 50 ns, collisional rotational relaxation is negligible. The polarization direction of the pump and the probe pulses were set to be parallel to each other, and along the ion-extraction field in the TOF-MS ionization region. In order to probe only a molecular ensemble exposed by a uniform pump pulse field, the probe pulse was kept as weak as possible ($\leq 10 \mu J$/pulse) and tightly focused with a plano-convex lens with $f = 170$ mm, while the pump pulse was loosely focused by a plano-convex lens with $f = 300$ mm and its focal position was slightly shifted from the probe region.

3. Results and discussions
Figure 1 shows the (1+1) REMPI excitation spectra of A $^3\Sigma^+$ – X $^2\Pi_{1/2}$ (0, 0) band of NO, recorded at various pump pulse energies, along with the corresponding rotational-state distributions in the X state.

![Figure 1](image)

**Figure 1.** Left: Excitation spectra of NO, recorded after the irradiation of pump pulse with various energies. Right: Observed and calculated rotational-state distributions.
The delay-time dependence of the rotational-state distribution after the double-pulse excitation was examined as the REMPI signals for each transition with different $J$ values in the $P_{11}(J)$ branch, as shown in Figure 2. Characteristic modulations in population are observed against the delay. The observed modulations result from the interference between the rotational eigenstates constructing the WP. Accordingly, information on the eigenstate components constituting the WP and the coupling strength between them can be extracted from the modulated signals. Figure 2 also displays the Fourier-transformed spectra of the observed beat signals for $J = 1.5 – 6.5$. Peaks appear at the positions corresponding to the rotational energy differences. The peak assignments are also shown in the top of Figure 2 (right). This figure shows that the rotational eigenstates constructing the WP can be classified into two groups. One group referred as group I, which is composed of $J = 2.5, 4.5,$ and $6.5$, has the common peaks such as $8B, 16B, 24B,$ and $40B$. On the other hand, another group named as group II, which is made from $J = 1.5, 3.5,$ and $5.5$, has the common peaks such as $3B, 12B, 15B, 20B,$ and $32B$.

The existence of two groups in the wave packet can be explained by the fact that the coupling matrix elements with $\Delta J = \pm 2$ are larger than those with $\Delta J = \pm 1$. Consequently, the initial $J = 0.5$ state is strongly coupled to $J = 2.5$. And then, the produced $J = 2.5$ state is also excited to $J = 4.5$ by the $\Delta J = \pm 2$ interaction. As the results, the excitation chain, $J = 0.5 \rightarrow 2.5 \rightarrow 4.5 \rightarrow 6.5 \rightarrow \ldots$, makes the group I. The group II is constructed by a similar interaction chain, $J = 0.5 \rightarrow 1.5 \rightarrow 3.5 \rightarrow 5.5 \rightarrow \ldots$, starting with relatively weak interaction between $J = 0.5$ and $1.5$ through the $\Delta J = \pm 1$ interaction. The coupling between the two groups is very weak because of the substantially small $\Delta J = \pm 1$ interaction. The delay-time dependence of the rotational-state distribution was also calculated by numerically solving the time-dependent Schrödinger equation. The results are represented also in Figures 1 and 2. The agreement between the experiment and the calculation is remarkably good. The similar results have been reported separately by Meijer et al. [15].

The delay-time dependence of the rotational-state distribution exhibits a noteworthy feature. The state distribution changes periodically with the interval of 20 ps. This revival time is twice larger than well known value, $T_{rev} = 1/(2Bc)$ [1–7]. This difference originates from the energy level structure of NO. For a linear molecule in non-degenerate electronic states, such as $N_2$, $O_2$, and $CO_2$, the angular momentum $J$ is an integer. Thus the rotational energy, $E_J/\hbar c = 0, 2B, 6B, 12B, \ldots, B(J+1)$, has the greatest common measure (GCM) of $2B$. The rotational WP is invariant under the time evolution from

**Figure 2.** Left: Population dependence of each rotational state of NO on the time delay of double pump pulses. Right: Fourier-transformed signals of delay-dependent rotational population.
t to $t + T_{\text{rev}}$ because $\exp\left(-iE_{\text{rev}}T_{\text{rev}}/\hbar\right) = 1$. On the other hand, molecules in degenerate electronic states, such as NO and OH, have a half integer angular momentum $J$. The rotational energy is expressed as: $E_{r} = B, 4B, 9B, \ldots, B(J + 1/2)^{2}$, with the GCM of $B$. The rotational WP of those molecules returns to the initial value by time evolution from $t$ to $t + 1/(Bc)$. Whether the total angular momentum $J$ is integer or half integer plays an essential role for the full revival time being $T_{\text{rev}} = 1/(2Bc)$ or $1/(Bc)$. The observed period of 20 ps for NO agrees well with $1/(Bc) = 19.7$ ps calculated with the precisely known value of $B = 1.696 \text{ cm}^{-1}$.

4. Conclusion

As clearly demonstrated in the previous section, the quantum-state resolved probe after the NAREX by an intense nonresonant ultrafast laser field can afford an indispensable insight into the NAREX process, in particular, when the double-pulse excitation is applied. One of the big advantages of the present method is its state selectivity. We can follow the individual NAREX processes from different initial states by selecting appropriate states to be probed out from a mixed ensemble. By contrast, almost all the previously adopted methods [1–11] rely on the measurements of polar angular distribution averaged over the molecular ensemble, and thus meet difficulty in separating individual processes. In addition, the double-pulse excitation can be extended to reconstructing the rotational WP, which is created by the single pulse of the excitation pair. Such an experimental WP reconstruction has been successfully demonstrated quite recently by the authors’ group [14].

Furthermore, nonadiabatic interaction with a nonresonant intense ultrafast laser field can coherently excite the other degree of freedom for molecular motions, i.e., vibration. Realization of such a nonadiabatic vibrational excitation (NAVEX) and the resultant creation of a vibrational WP is definitely the next step to be proceeded. We have extended the research into this direction.

Acknowledgments

This work was partly supported by Grants-in-Aid from MEXT Japan (18244120, 18750020, and 20050032), and the RIKEN-IMS joint program on “Extreme Photonics”. An additional financial support from the Mitsubishi Foundation is also appreciated.

[1] Stapelfeldt H and Seideman T 2003 Rev. Mod. Phys. 75 543
[2] Rosca-Pruna F and Vrakking, M J J 2002 J. Chem. Phys. 116 6567, 6579
[3] Dooley P W, Litvinyuk I V, Lee K F, Rayner D M, Spanner M, Villeneuve D M, and Corkum P B 2003 Phys. Rev. A 68 023406
[4] Péronne E, Poulsen M D, Bisgaard C Z, Stapelfeldt H and Seideman T 2003 Phys. Rev. Lett. 91 043003
[5] Miyazaki K, Kaku M, Miyaji G, Abdurrouf A and Faisal F H M 2005 Phys. Rev. Lett. 95 243903
[6] Stavros V G, Harel E and Leone S R 2005 J. Chem. Phys. 122 064301
[7] Bisgaard C Z, Viftrup S S and Stapelfeldt H 2006 Phys. Rev. A 73 053410
[8] Lee K F, Villeneuve D M, Corkum P B and Shapiro E A 2004 Phys. Rev. Lett. 93 233601
[9] Lee K F, Shapiro E A, Villeneuve D M and Corkum P B 2006 Phys. Rev. A 73 033403
[10] Renard M, Hertz E, Guérin S, Jauslin H R, Lavorel B and Faucher O 2005 Phys. Rev. A 72 025401
[11] Horn C, Wollenhaupt M, Krug M, Baumert T, de Nalda R and Bañares L 2006 Phys. Rev. A 73 013410
[12] Hasegawa H and Ohshima Y 2006 Phys. Rev. A 74 061401
[13] Hasegawa H and Ohshima Y 2008 Chem. Phys. Lett. 454 148
[14] Hasegawa H and Ohshima Y 2008 Phys. Rev. Lett. 101 053002
[15] Meijer A S, Zhang Y, Parker D H, van der Zande W J, Gijsbertsen A and Vrakking M J J 2007 Phys. Rev. A 76 023411