

# Dynamics mechanism of optical-optical double-resonant multiphoton ionization of nitrogen dioxide

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The optical-optical double-resonant multiphoton ionization (OODR-MPI) spectrum of  $\text{NO}_2$  molecule in the 460–605-nm wavelength region of the probe photon is presented. The mechanism of the OODR-MPI of  $\text{NO}_2$  molecule is analyzed. The results show that the resonant features can be assigned to the transitions from the first  $3s\sigma_g$  Rydberg intermediate resonant state to the final  $np\sigma_u$  Rydberg series. The ionization pathway is  $\text{NO}_2 (X^2A_1) \xrightarrow{3h\nu_1} 3s\sigma_g \xrightarrow{h\nu_2} np\sigma_u \xrightarrow{h\nu_2 \text{ or autoionization}} \text{NO}_2^+ + e$ . It is found that the converging potential of the  $np\sigma_u$  Rydberg series and the quantum defect of  $np$  orbit about  $\text{NO}_2$  are  $(78803 \pm 14) \text{ cm}^{-1}$  and  $0.652 \pm 0.014$ , respectively. The bending vibration frequency of  $5p\sigma_u$  state is determined also.

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$\text{NO}_x$  is the major atmospheric pollutant. They are hazardous to the health of the general population and play key role in the formation of acid rain. So the detection and measurement of  $\text{NO}_x$  are very important in the environment science. We have already performed detailed study on  $\text{NO}$  by using varied laser spectroscopy technique and got some useful information for the detection of  $\text{NO}$ <sup>[1–3]</sup>. As for  $\text{NO}_2$ , a lot of work concerning the energy level structure of this molecule has been done<sup>[4–9]</sup>. The results show that there are intersections among the potential curves of the first two excited electronic states  $A^2B_2$ ,  $A^2B_1$ , and the ground one  $X^2A_1$ . This makes these excited states show the property of near continuum absorption in the wavelength region from the red to the near ultraviolet (UV). The continuum absorption facilitates transitions from the bent ground state to the higher excited ones in two or three steps. So the technique of optical-optical double-resonant multiphoton ionization (OODR-MPI) provides a suitable method for the study of the higher excited states. We have collected the OODR-MPI spectrum of  $\text{NO}_2$  molecule in the 460–605-nm wavelength region of the probe photon and found that the spectrum is composed of separated bands. In this paper, the mechanism of the OODR-MPI of  $\text{NO}_2$  molecule is analyzed from the structure of the spectrum and the theoretical calculation. The ionization pathway of the OODR-MPI of  $\text{NO}_2$  with higher power pump laser is decided.

The experimental setup is shown in Fig. 1. The OODR transitions of  $\text{NO}_2$  molecules are induced by two lasers,

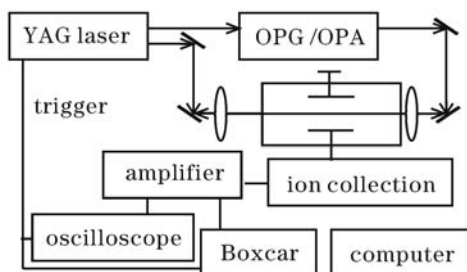


Fig. 1. Experimental setup.

one is a Nd:YAG laser with double-frequency output of 532 nm and the other is an optical parameter generator and optical parameter amplifier (OPG/OPA) pumped by the triple-frequency output 355 nm of the former. The former, which is used as the pump laser (set as  $\omega_1$ ), has duration of 35 ps and runs at a repetition rate of 10 Hz. The intensity can reach  $\sim 10^{10} \text{ W/cm}^2$  when focused by a 30-cm-focal-length lens. The OPG/OPA with tunable region of 420–680 nm is used as probe laser (set as  $\omega_2$ ). The bandwidth is  $6 \text{ cm}^{-1}$  and the output energy is larger than 0.1 mJ. Two electrodes with a separation of 1 cm are of copper and parallel to each other. They are mounted on the two opposite windows of the sample cell and biased at 150 V for collecting the charged particles. The ion signal is fed into an amplifier-Boxcar system, and a computer stores the output of the Boxcar.

The two laser beams are aligned from opposite directions and the probe laser delays 5 ns after the pump one. Both of the laser beams have been attenuated before entering the sample cell in order to avoid producing any ion signal when stimulated by either of them.

Figure 2 shows the OODR-MPI spectrum obtained by scanning the probe laser in the range of 460–605 nm under the condition that both of the pump and probe lasers are focused at the middle of the two electrodes. The gas pressure of  $\text{NO}_2$  is approximately 266 Pa. As can be seen, the spectrum is composed of banded progression.

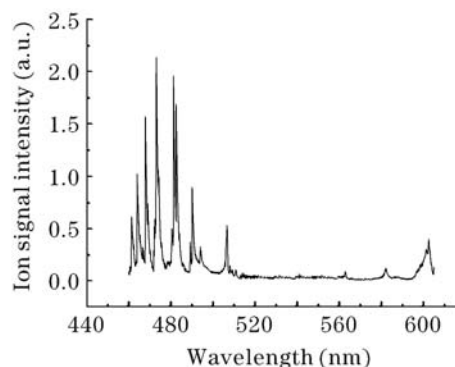


Fig. 2. OODR-MPI spectrum of  $\text{NO}_2$  in 460–605-nm region.

NO<sub>2</sub> molecule must be ionized in resonant manner. This banded structure shows itself as that the spacing of the main spectral peaks becomes monotonically wider, and their intensity shows a trend that increases first and then decreases with increasing wavelength. This is just the property of the spectrum of the Rydberg series<sup>[10]</sup>. So the main peaks of the spectrum must be corresponding to transitions to a Rydberg series.

Giving ascription of the spectrum, the ionization pathway must be first ascertained. The energy levels that relate with the ionization process are shown in Fig. 3. Above the 3sσ<sub>g</sub> Rydberg state, all of the excited states of NO<sub>2</sub> molecule are Rydberg type.

When a long focal lens focuses the pump laser, strong visible fluorescence can be detected<sup>[11]</sup>. It is deduced that NO<sub>2</sub> molecule must be first excited to A<sup>2</sup>B<sub>2</sub> state by one-photon process. This process is named as the first step. The transition following the first step to Rydberg state should take two photons in the wavelength region of the two lasers. So the whole resonant transition processes from the ground state to the Rydberg one can be divided into three types:

- type I: ω<sub>1</sub> + 2ω<sub>2</sub>;
- type II: ω<sub>1</sub> + ω<sub>1</sub> + ω<sub>2</sub>;
- type III: ω<sub>1</sub> + 2ω<sub>1</sub>.

Type I transition denotes a (1 + 2) process. The spectrum corresponding to this process is collected<sup>[12]</sup>. It is different from the one in Fig. 2. So the excitation process of type I is not exist in the ionization process. Type II transition combines the A<sup>2</sup>B<sub>2</sub> state with Rydberg state via an intermediate one. This intermediate state can be one of the high vibration levels of A<sup>2</sup>B<sub>2</sub>, B<sup>2</sup>B<sub>1</sub>, and C<sup>2</sup>A<sub>2</sub>. The transition from A<sup>2</sup>B<sub>2</sub> state to these intermediate states is hard to realize due to the selection rule of optical transition. Another aspect, which supposes this conclusion, is that the UV fluorescence has not been detected during the experiment. So type II transition can be excluded also. Type III transition indicates that NO<sub>2</sub> molecule absorbs three pump photons in resonant manner. The energy of three pump photons is about 56391 cm<sup>-1</sup>. Based on Refs. [13,14] and the calculation, NO<sub>2</sub> molecule can be excited to 3sσ<sub>g</sub> Rydberg

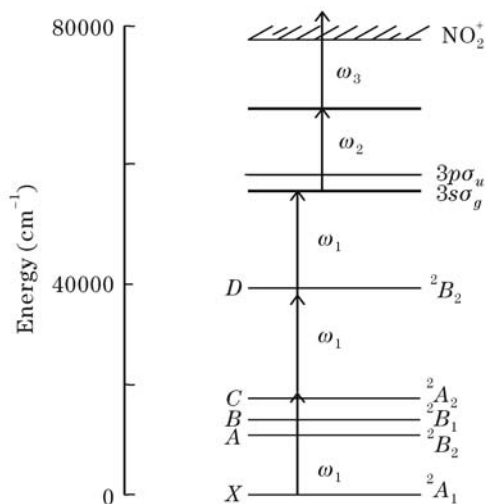


Fig. 3. Relative energy level for OODR-MPI ionization of NO<sub>2</sub>.

state or (0,1,0) vibration level of 3pσ<sub>u</sub> Rydberg state after Type III transition, but the later transition can be eliminated by consulting the structure of the spectrum. It is obvious that the spectrum is composed of only one series. If the later process mentioned above can be realized, then transitions from 3pσ<sub>u</sub> to the s and d Rydberg states are strongly allowed in the light of selection rule of Δl = ±1. It ought to at least present two series in the ionization spectrum, that is sσ, dσ (or dπ) series. So NO<sub>2</sub> molecule ought to be excited to 3sσ<sub>g</sub> Rydberg state by pump photons. This Rydberg state is called the first intermediate resonant state. From this state, NO<sub>2</sub> molecules absorb probe photons to realize ionization.

The adiabatic ionization potential of NO<sub>2</sub> is (77320 ± 20) cm<sup>-1</sup><sup>[15]</sup>. As mentioned above, NO<sub>2</sub> molecule is excited to 3sσ<sub>g</sub> state by pump photons. It ought to absorb two probe photons and via final intermediate resonant state to exceed the ionization potential when the wavelength of the probe photons is longer than 473 nm. Otherwise it needs only one probe photon. Figure 4 is the observed curve of the ion signal versus the laser intensity with the excitation wavelength of 472.9 nm. The linear variation confirms above suppose further.

Because the configuration of NO<sub>2</sub> 3sσ<sub>g</sub> state is linear, the upper state of the following single probe photon resonant transition should be linear structure also. According to the inversion symmetrical selection rules g ↔ u and the selection rules for atoms with single electron Δl = ±1, the upper state ought to be nρσ<sub>u</sub> or nρπ<sub>u</sub>.

From above deduction, the ionization pathway of NO<sub>2</sub> in this OODR-MPI process is

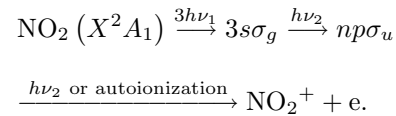


Table 1 lists the wavelengths of the spectral lines and the corresponding energy of (3+1) photons. As is known, the Rydberg series are often described by

$$E = I.P. - \frac{R}{(n - \delta)^2}, \quad (1)$$

where E is the energy of the Rydberg state, I.P. is the limit towards which the states converge, R is the Rydberg constant, n is the principal quantum number, and δ is the quantum defect. A least square fit of the energy in

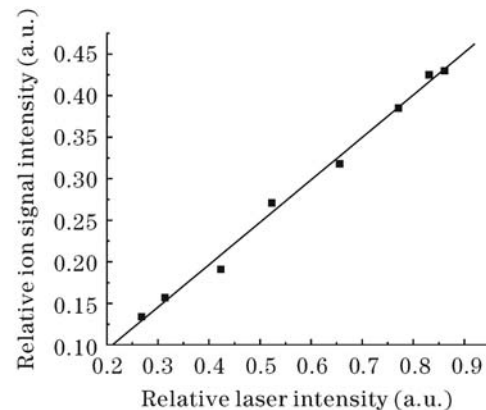


Fig. 4. Ion signal versus laser intensity.

**Table 1. Assignment of the Spectral Lines**

State	Peak Wavelength (nm)	(3+1) Photon Energy (cm <sup>-1</sup> )	Term Value (cm <sup>-1</sup> )
5pσ <sub>u</sub>	602.6	72986	5817
6pσ <sub>u</sub>	...	...	
7pσ <sub>u</sub>	506.7	76127	2676
8pσ <sub>u</sub>	489.9	76803	2000
9pσ <sub>u</sub>	481.0	77181	1622
10pσ <sub>u</sub>	472.9	77537	1266
11pσ <sub>u</sub>	467.6	77777	1026
12pσ <sub>u</sub>	463.8	77952	851
13pσ <sub>u</sub>	461.1	78078	725

**Table 2. Vibration Bands of 5pσ<sub>u</sub> States**

Peak (nm)	(3+1) Photon Energy (cm <sup>-1</sup> )	Energy Difference of Vicinity Peak (cm <sup>-1</sup> )
602.6	72986	0
582.0	73573	587
562.8	74159	1173

Table 1 is in well agreement with an assigned converging potential of  $(78803 \pm 14) \text{ cm}^{-1}$  and a quantum defect of  $0.652 \pm 0.014$ . The value of the quantum defect is consistent with the one of  $np\sigma_u$  series<sup>[15]</sup>, so Fig. 2 could be thought of corresponding to an  $np\sigma_u$  Rydberg series. The term values and assignments of the states are listed in Table 1 also.

The converging potential of  $(78803 \pm 14) \text{ cm}^{-1}$  is higher than that of the adiabatic ionization. This indicates that the  $np\sigma_u$  Rydberg series of NO<sub>2</sub> does not converge to the NO<sub>2</sub><sup>+</sup>X<sup>2</sup>Σ<sub>g</sub><sup>+</sup>(0, 0, 0) level.

Besides the main peaks that are assigned as  $np\sigma_u$  Rydberg series, there are two weak peaks at the positions of 562.8 and 582.0 nm. Taking into account the photon energy which corresponding to the peaks, it appears that the two peaks represent transitions to the vibration levels of the 5pσ<sub>u</sub> state. Table 2 shows the energy difference between two vicinity bands. It presents that the bending vibration frequency of 5pσ<sub>u</sub> state is  $\omega_{e2} = 587 \text{ cm}^{-1}$ . This is consistent with those of Ref. [14].

The dynamic mechanism of OODR-MPI of NO<sub>2</sub> molecule is analyzed. It is found that NO<sub>2</sub> molecule is

ionized though (3 + 1 + 1) multiphoton process and via  $np\sigma_u$  Rydberg final resonant states. The higher converging potential of  $np\sigma_u$  Rydberg series indicates that this Rydberg series does not converge to the ground vibration level of NO<sub>2</sub><sup>+</sup>. The bending vibration frequency of 5pσ<sub>u</sub> state has been gotten also. The results indicate that the technique of OODR-MPI is a suitable method for the study of the higher excited states of polyatomic molecules.

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## References

1. L. Zhang, G. Zhang, X. Yang, X. Zhao, and Y. Li, *Chin. Opt. Lett.* **1**, 438 (2003).
2. G. Zhang, Y. Jin, and L. Zhang, *Chin. Opt. Lett.* **4**, 439 (2006).
3. L. Zhang, G. Zhang, X. Yang, B. Sun, and X. Zhao, *Acta Opt. Sin.* (in Chinese) **24**, 718 (2004).
4. B. Kirmse, A. Delon, and R. Jost, *J. Chem. Phys.* **108**, 6638 (1998).
5. A. Delon and R. Jost, *J. Chem. Phys.* **114**, 331 (2001).
6. F. Santoro, *J. Chem. Phys.* **109**, 1824 (1998).
7. V. Sivakumaran, K. P. Subramanian, and V. Kumar, *J. Quant. Spectro. Rad. Transfer* **69**, 525 (2001).
8. G. Zhang, L. Zhang, and X. Han, *Chin. Opt. Lett.* **3**, 119 (2005).
9. J. Liang, K. Pei, and H. Li, *Chem. Phys. Lett.* **388**, 212 (2004).
10. B. H. Rockney, E. H. Gregory, and E. R. Grant, *J. Chem. Phys.* **78**, 7124 (1983).
11. L. Zhang, B. Sun, G. Zhang, and X. Zhao, *Spectroscopy and Spectral Analysis* (in Chinese) **25**, 416 (2005).
12. G.-Y. Zhang, L.-S. Zhang, B. Sun, X.-F. Han, and W. Yu, *Chin. Phys.* **14**, 524 (2005).
13. G. Herzberg, *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966) p.142, p.602.
14. R. K. Ritchie and A. D. Walsh, *Proc. Roy. Soc. London Ser. A* **267**, 395 (1962).
15. P. Bell, F. Aguirre, E. R. Grant, and S. T. Pratt, *J. Chem. Phys.* **119**, 10146 (2003).