Vol 14 No 3, March 2005
1009-1963/2005/14(03)/0524-05

Chinese Physics

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Optical–optical double-resonant multiphoton ionization spectra of Rydberg states of nitrogen dioxide*

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(Received 22 December 2003; revised manuscript received 29 November 2004)

The optical–optical double-resonant multiphoton ionization (OODR-MPI) technique has been applied to the study of the Rydberg states of nitrogen dioxide. The results show that, although the OODR-MPI spectra of NO_2 are composed of regular progression bands at different pump laser intensities, their ionization pathways are different. The NO_2 molecule is ionized through the (3+1+1) double-resonant process as the pump laser intensity is in a high value, or else it is through the (1+2+1) process. The final resonant states in the two ionizing processes have been attributed to different Rydberg states.

Keywords: OODR-MPI, nitrogen dioxide, Rydberg states
PACC: 3335, 3300, 3380K, 3380E

1. Introduction

The NO_2 molecule has long been of chemical interest because it is an active molecule of nonzero spin and has many special properties. There are many theoretical and experimental reports concerning the spectra of NO_2.[1−10] It has been shown that there is a conical intersection between the ground state X^2A_1 and the first excited state A^2B_2.[1] A Renner–Teller effect between the ground state X^2A_1 and the second excited state B^2B_1 is also present.[2] The effects mentioned above make the absorption of NO_2 in the visible region very complex. The absorption spectrum is nearly continuous and the radiation lifetime of the excited state is anomalously long.[3−5] Although the molecular spectra of NO_2 have been studied extensively for many years, many uncertainties still exist because of its extremely complicated structure, especially in its higher Rydberg states. Ritchie and Walsh[6] have measured the ultraviolet (UV) absorption spectrum of NO_2 and shown that the main transition involved in the 165–135nm region can be classified as $E^2\Sigma_u$ Rydberg state. Mass spectrometric studies of the ionization behaviour at different experimental conditions show that the dissociation ionization of NO_2 is governed not only by the laser wavelength and intensity, but also by laser pulse duration.[8,9] Tong and Li[10] have studied the near-threshold structure due to inner-shell excitation of the NO_2 molecule. Li and co-workers[11,12] also gave a detailed information of the Rydberg energy level structure of the molecule. The near continuity of the valence states that extends from the red to the near-UV region facilitates transitions from the bent ground state to the linear Rydberg states in two or three steps, each step being optical resonant. In this paper, the optical–optical double-resonant multiphoton ionization (OODR-MPI) processes of Rydberg states of NO_2 are investigated at different exciting laser intensities. The ionization spectrum which contains a progression of $\sim$613cm^{-1} intervals in the energy region 61000–66000cm^{-1} is assigned to the transition via $E^2\Sigma_u$ Rydberg state, while the other in the energy range 76000–78300cm^{-1} with unequal interval progression is assigned to the transition via high-lying members of the $np\sigma_u$ Rydberg series. The pathway of the excitation and ionization is determined as well.

2. Experimental setup

*Project supported by the Natural Science Foundation of Hebei Province, China (Grant No 102090).
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The experimental setup, as shown in Fig.1, is similar to that reported in Ref.[13]. Briefly, the OODR-MPI transitions of NO_2 molecules are induced by two lasers, one is a Nd:YAG (France Quantel Company, YG900) laser with double-frequency output of 532nm; and the other is an equipment for optical parameter generator and optical parameter amplifier (OPG/OPA, EKSPLA Company, PG401VIR) pumped by the triple-frequency output 355nm of the Nd:YAG laser. The intensity of the Nd:YAG laser is $\sim 10^8 W \cdot cm^{-2}$. It can reach $\sim 10^{10} W \cdot cm^{-2}$ when focused by a 30cm focal length lens. This laser used as the pump laser(ω_1) has a duration of 35ps and run at a repetition rate of 10Hz. The tunable wavelength of the OPG/OPA, which is used as the probe laser(ω_2), is 420–680nm. The bandwidth of the probe laser is $6cm^{-1}$ and the output energy is larger than 0.1mJ. The probe laser beams are focused (by a 10cm focal length lens) on to the middle point of the distance between two electrodes, which is 1cm long. The electrodes mounted on the two opposite windows of the sample cell are made of copper and are parallel to each other. They are biased at 150V for collecting the charged particles. The ion signal is fed into an amplifier-Boxcar (Stanford Research, SRS280/255) system. A computer stores the output of the Boxcar, and the ion signal is displayed on a digital oscilloscope (Tektronix, TDS3052) during the experiments. The gas pressure of nitrogen dioxide is approximately 266Pa.

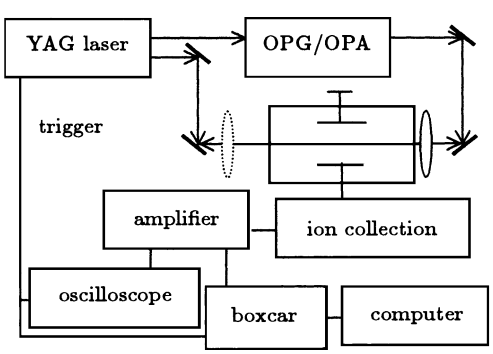


Fig.1. Experimental setup.

The two laser beams are aligned from opposite directions and the probe laser delays 5ns after the pump laser. 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 the two lasers.

3. Experimental results and discussion

3.1. The OODR-MPI spectrum

Figure 2 shows a portion of one OODR spectrum obtained by scanning the probe laser in the range of 420–475nm under the condition that the pump laser is unfocused and the probe laser is focused on the centre of the pump laser beam. Figure 3 shows another OODR-MPI spectrum obtained in the wavelength region of 455–515nm under the condition that both pump and probe lasers are focused at the same point. As can be seen, the two spectra are both composed of a regular progression. But their structure is different. So the ionization processes under the two different experimental conditions must be via different final resonant states.

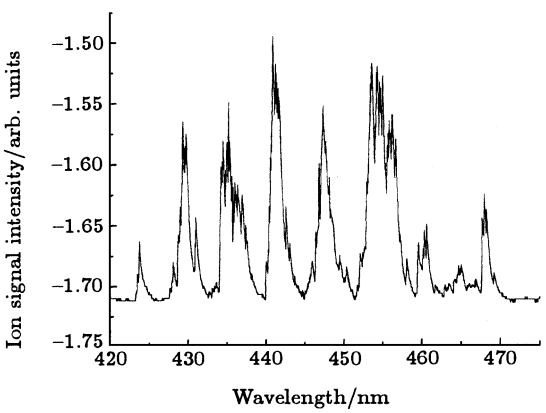


Fig.2. OODR-MPI spectrum of NO_2 (the pump laser beam is unfocused).

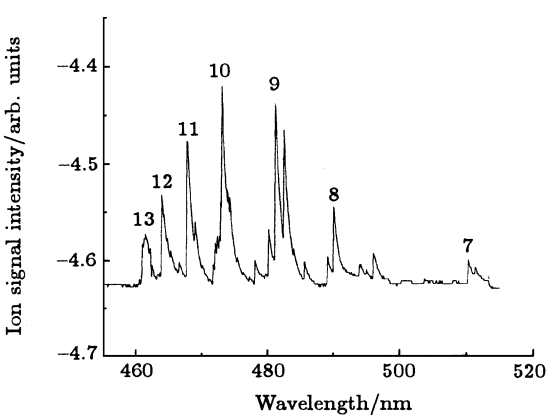


Fig.3. OODR-MPI spectrum of NO_2 (the pump laser beam is focused).

3.2. OODR transition for equal interval progression in Fig.2

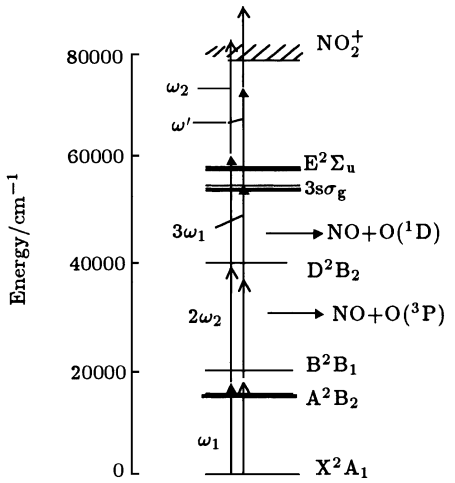


Fig.4. Diagram showing the relative energy levels for OODR-MPI of NO_2.

To give a transition ascription of the spectrum in Fig.2, it should be determined which excited states are in resonance with the absorbing photons during the ionization process. The energy levels related with the ionization process are shown in Fig.4. Because very strong visible fluorescence can be detected when unfocused pump laser irradiates the sample cell, we can conclude that the NO_2 molecule is excited to the appropriate level of the first excited A^2B_2 state by absorbing one pump ω_2 laser (ω_1) photon. Since the adiabatic ionization potential of the NO_2 molecule is about 9.78eV(78882cm^{-1}),[14] it should take three photons for the ionization from the first excited state in the wavelength region of 420–475nm. Taking into account the interval (–300cm^{-1}) of the vibration progression and the spectroscopic data[14] of the NO_2 molecules, the spectrum is inconsistent with the mechanism of single-photon resonance. So the (1+1+2) resonant ionization process can be excluded. The spectrum can be explained only in terms of the (1+2+1) resonant ionization manner. Table 1 shows the positions of the peaks and the corresponding (1+2) photons energies. According to the result of Fig.4, it can be postulated that the final resonant state is Rydberg $E^2\Sigma_u$ state. The progression with regular interval is correlated with a Rydberg state. This accords with the characteristic of the spectral structure associated with a Rydberg state of the polyatomic molecule.[15,16]

The vibronic energy of the undegenerate level in first approximation is[14]

$$T_{ev} = T_e + \sum_{i=1}^{3} \omega_{ei}\left(v_i + \frac{1}{2}\right), \qquad (1)$$

where T_e is the electronic energy with cm^{-1} as units, v_i is the vibration quantum numbers, ω_{ei} is the vibration frequencies. For the three vibration modes of NO_2, the vibration frequencies are ω'_{e1}=1420cm^{-1}, ω'_{e2}=597cm^{-1}, ω'_{e3}=1680cm^{-1}[17] and the electronic energy T_e=58309cm^{-1} for $E^2\Sigma_u$ state.[14] The corresponding vibration bands of the ionization peaks in Fig.2 are shown in Table 1. It can be seen that the ionization peaks could be attributed to $E^2\Sigma \leftarrow A^2B_2 \leftarrow X^2A_1$ (1+2) transitions. Then the ionization of the NO_2 molecules must undergo a (1+2+1) process, i.e. the ionization pathway is

$$NO_2\left(X^2A_1\right) \xrightarrow{h\nu_1} NO_2(A^2B_2) \xrightarrow{2h\nu_2} NO_2\left(E^2\Sigma_u\right) \xrightarrow{h\nu_2} NO_2^+ + e.$$

Table 1. Assignment of the vibration bands in Fig.2.

peak/nm	(1+2)photon energy/cm^{-1}	$E^2\Sigma_u$ energy level/cm^{-1}	assignment
424.1	65956	65925	(2,8,0)
429.7	65341	65328	(2,7,0)
435.4	64732	64731	(2,6,0)
441.3	64118	64134	(2,5,0)
447.2	63519	63537	(2,4,0)
453.3	62918	62940	(2,3,0)
460.0	62275	62343	(2,2,0)
468.5	61486	61520	(1,3,0)

The symmetric stretching and bending vibration frequencies at $E^2\Sigma_u$ state obtained from the above ionization spectrum are ω'_{e1}=1418cm^{-1}, ω'_{e2}=613cm^{-1} respectively, which are consistent with those in Ref.[17].

The bond angle and the N–O bond length of the NO_2 molecule in A^2B_2 state are 102^o and 0.126nm,[18] while their values are 180° and 0.113nm[6] at $E^2\Sigma_u$ Rydberg state respectively. The transition possibility at their band origins is a small value in the light of the Franck–Condon principle, because the electron should undergo a transition from the bent state to the linear

upper state with a decrease in N–O length. Actually, the band origin has not appeared in the spectrum of Fig.2. As shown in the spectrum also, the peaks at 435.4 and 453.3nm are broader than others. The possible reason is that in addition to the resonance at $E^2\Sigma_u$ state, there may be a resonance at the second photon levels, where those belong to the D^2B_2 state are broadened by pre-dissociation. The weak peak at 464.7nm cannot be identified definitely. This needs further investigations.

3.3. The affirmation of the npσ_u Rydberg series

The fact that the spectrum in Fig.3 demonstrates a different structure from that in Fig.2 shows that the ionization dynamics of NO_2 pumped by a focused laser beam is different from that under an unfocused condition. Under the condition of higher pump laser intensity, the NO_2 molecule can be excited to higher excited states through absorbing more than one pump photon. As can be seen, the spacing of the spectral peaks becomes monotonically wider, and their intensity shows a trend to increase first and then decrease with increasing wavelength. The main peaks of the spectrum must be corresponding to transitions to a Rydberg series.[17] It is therefore reasonable to postulate that the ion signal comes from a (3+1+1) double-resonant process. The NO_2 molecule will be first excited to $3s\sigma_g$ Rydberg state by absorbing three pump photons ($56391cm^{-1}$).[6] The Rydberg series correlated with the main peaks should lie in the energy region of the single probe photon.

The Rydberg series can be formulated as

$$E = \mathrm{IP} - \frac{R}{(n-\delta)^2}, \tag{2}$$

where E is the energy of the Rydberg state, IP the ionization potential, R the Rydberg constant, n the principal quantum number, and δ the quantum defect. The value of δ is about 1 for s-type orbit, 0.7 for p-type orbit, and 0.1–0.3 for d-type orbit.[17] Since the NO_2 molecules are excited to $3s\sigma_g$ Rydberg state by a pump laser, photo-selection rules restrict the upper state to be npσ_u state in the following single-photon transition. Suppose δ=0.7, and IP=$78882cm^{-1}$, the peaks in Fig.3 can be assigned to a Rydberg series with formula (2), which are given in Table 2.

Table 2. Assignment of the peaks in Fig.3.

State	Peak wavelength/nm	(3+1)photon energy/cm^{-1}	calculated energy/cm^{-1}
$7p\sigma_u$	509.9	76004	76117
$8p\sigma_u$	489.9	76803	76822
$9p\sigma_u$	481.0	77181	77289
$10p\sigma_u$	472.9	77537	77613
$11p\sigma_u$	467.6	77777	77847
$12p\sigma_u$	463.8	77952	78022
$13p\sigma_u$	461.1	78078	78156

The curve of (3+1) photon energy versus n is plotted in Fig.5. The adiabatic ionization potential and the quantum defect can be obtained through a least-square fit. The values of IP and δ is $(78813 \pm 22)cm^{-1}$ and 0.71 ± 0.05 respectively. It has been reported that the value of the adiabatic ionization potential of NO_2 is $78760cm^{-1}$, determined through resonance-enhanced multiphoton ionization mass spectrometric method.[19] Electron impact experiment gives it a value of $79285cm^{-1}$.[14] Our result is well consistent with that reported. Giving a precise adiabatic ionization potential of NO_2 is difficult. Since NO_2 is a bent molecule in the ground electronic state, and NO_2^+ is a linear molecule, the changing from a bent molecule to a linear ion makes the Franck–Condon factor for the transition from the low vibration level of the ground state to the one of the ionic state to be pretty small. The experiment reported in this paper shows a simple method for the measurement of IP for those molecules resemble to NO_2.

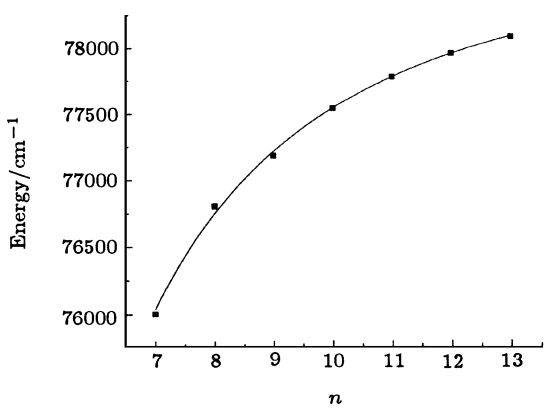


Fig.5. Fitting of the experimental data.

4. Conclusion

The REMPI spectra of nitrogen dioxide generated in OODR manner are recorded and its ionization pathway is analysed. It has been recognized that NO_2 molecules can be ionized by (1+2+1) or (3+1+1) double resonant process via different Rydberg final resonant states. Furthermore, several spectroscopic constants for NO_2 are determined in our experiment.

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