Resonance-enhanced multiphoton ionization of NO via $X^2\Pi \rightarrow A^2\Sigma$ transition

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The resonance-enhanced multiphoton ionization (REMPI) spectrum of NO has been obtained in the range of 420 – 480 nm with a Nd:YAG pumped optical parametric generator and amplifier. The spectral lines can be attributed to NO $X^2\Pi(v''=0,1) \rightarrow A^2\Sigma(v'=0,1)$ transitions. In this wavelength range, NO molecules are ionized via the resonant intermediate state $A^2\Sigma^+$ and by a (2 + 2) REMPI process. The dependence of ion signals on laser intensity and gas pressure is discussed. The variation of the ionization signal versus laser intensity is near quartic. This is in good agreement with theory.

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There is a growing interest in laser-based sensitive monitors of pollutants in the atmosphere in recent years, especially in the detection and monitoring of atmospheric nitrogen oxide compounds[1−3]. Many of these interests stem from the concern with the public health and environment. These compounds play key roles in O_3 destruction, acid rain and photochemical smog formation. NO and NO_2 are the hazardous pollutants emitted mainly from motor vehicles and stationary sources such as thermal power plants and industrial boilers.

Multiphoton ionization spectroscopy (MIS) is a sensitive detection technique. It is based on detecting the ions generated from the excitation of the atoms and molecules. A characteristic feature of multiphoton ionization from a spectroscopic point of view is the enhancement by the resonant intermediate states. Since the ionization efficiency is strongly enhanced, when one or more photons energy is in resonance with real intermediate states, it is possible to measure the intermediate state spectrum by scanning the wavelength of the laser leading to a modulation of the ion current. This provides information about not only molecular states and molecular structures, but also the reaction dynamics. This technique can be used to study the transitions that are single-photon forbidden. There are many reports about the applications of this technique[4−6]. In this paper, the resonance-enhanced multiphoton ionization (REMPI) spectroscopy of NO has been obtained with a tunable high power laser as the radiation source. The effects of laser intensity, gas pressure and collective voltage on the REMPI signals are determined and discussed.

The experimental setup is shown in Fig. 1. A Nd:YAG pumped optical parameter generator and optical parameter amplifier (OPG/A in the figure) operating at 10 Hz and with a linewidth of ~6 cm^{-1} was used to provide tunable radiation in the wavelength range of 420 – 680 nm. The pulse duration is ~35 ps. The pulse energy ranges from 0.2 to 0.9 mJ and was monitored by a photoelectric diode (PD) during scanning. The sample cell consists of a four-arm stainless steel cross with quartz windows mounted on opposing arms of the cell. The laser beam was directed by a 150-mm lens that focused the beam in the center of two electrodes with a 9-mm gap. The beam diameter was about 0.5 mm in the laser-gas interaction region, and the collection voltage was 100 V. The signal from the detection electrodes was amplified and then input to the boxcar together with the signal from the PD. The output of the boxcar was recorded by a computer for storage and analysis. The two signals were displayed by a SR37 double-trace oscilloscope during the experiments. A mechanical pump make a vacuum pressure of 3×10^{-3} Pa in the sample cell.

The physical processes about NO REMPI detection is shown in Fig. 2. At high laser intensities, NO is ionized through a four-photon absorption process. The ionization signal is enhanced at 452 nm via the two-photon resonant intermediate state ($A^2\Sigma^+$). Thus the process is a (2 + 2) REMPI process. Figure 3 is a typical NO REMPI spectrum recorded in the region of 420 – 480 nm with 333-Pa gas pressure and 80-V collection voltage.

According to the vibration term formula[7]

$$T = T_e + \omega_e(v + \frac{1}{2}) + \omega_e\chi_e(v + \frac{1}{2})^2,$$

where T and T_e are the energy of a vibration state and the lowest energy in one electronic state in cm^{-1} as unit,

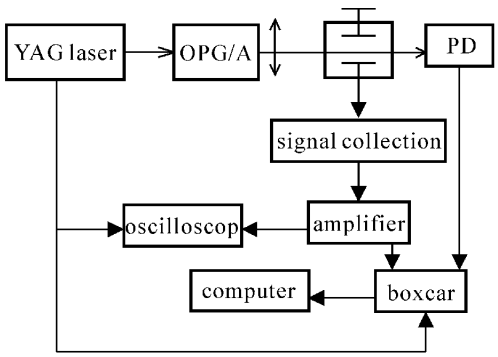

Fig. 1. Experimental setup.

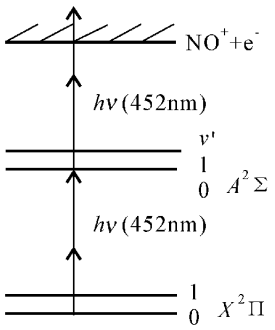

Fig. 2. REMPI process.

respectively; ω_e and $\omega_e\chi_e$ are vibration constants; v is vibration quantum number. The calculated transition wavelengths of NO $X^2\Pi(v''=0,1) \rightarrow A^2\Sigma(v'=0,1)$ band are 226.2, 214.85 nm and 236.22, 223.88 nm, respectively. The peaks in the REMPI spectrum could be attributed to $X^2\Pi \rightarrow A^2\Sigma$ transition. The ionization energy of NO is about 74607.7 cm^{-1}. So in the 420−520 nm wavelength range, a molecule must absorb four photons to exceed ionization limit. From the results of experiments, it can be concluded that the ionization process of NO is REMPI via intermediate $A^2\Sigma$ state. The ionization pathway is

$$\mathrm{NO}(X^2\Pi) \xrightarrow{2h\nu} \mathrm{NO}(A^2\Sigma) \xrightarrow{2h\nu} \mathrm{NO}^+ + e.$$

This consists with the theoretical calculation. At the same time, it is also found that the ionization signals corresponding to $X^2\Pi(v''=0) \rightarrow A^2\Sigma(v'=0,1)$ bands are stronger than $X^2\Pi(v''=1) \rightarrow A^2\Sigma(v'=0,1)$ bands. This is because of the Boltzman distribution of the molecules. At room temperature, most of the molecules lie in the $X^2\Pi(v''=0)$ state. The ground vibration state oscillation frequency of $A^2\Sigma^+$ state can be obtained from the spectrum, which is 2297.38 cm^{-1}. The effective mass of NO molecule is 7.47×10^{-3} kg/mol, and according to the relation

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{m}},$$

the force constant of the ground vibration state of $A^2\Sigma^+$ is 2.32×10^3 N/m.

Figure 4 is the laser energy dependence of ionization signal at 452.3 nm, under the condition of 333-Pa gas pressure and 100-V collection voltage. Fitting the data to the laser energy shows the power being 3.9. The near quartic dependence indicates a four-photon process.

The gas pressure is an important experimental parameter, which affects the collision probability of electrons and ions and the motion of electrons towards the electrode. Figure 5 shows the pressure dependence of ionization signal with fixed laser energy of 100 μJ and 100-V collection voltage at 452.3 and 428 nm, respectively. For both excitation lines, the signal increases to a maximum near 330 Pa. The increase is due to the variation of NO molecule number density with the pressure increasing, whereas the decrease is due to the NO ($A^2\Sigma^+$) quenching and the recombination of NO^+ and electrons when the pressure increases to some extent.

The REMPI detection technique is based on the ion signal from excitation of the sample. Using the optical parameter generator and optical parameter amplifier pumped by a Nd:YAG laser as the excitation source, NO is ionized by (2 + 2) REMPI process by means of $X^2\Pi \rightarrow A^2\Sigma$ transition. There is a suitable pressure for ion detection. Ion detection is accomplished by using a pair of miniature electrodes, which greatly simplifies the instrument and allows for real time and *in situ* monitoring of NO.

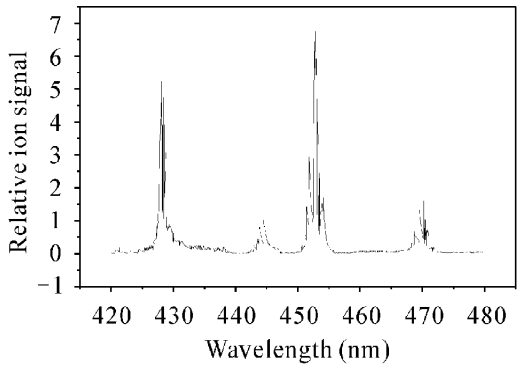

Fig. 3. NO REMPI spectrum in the range of 420 − 480 nm.

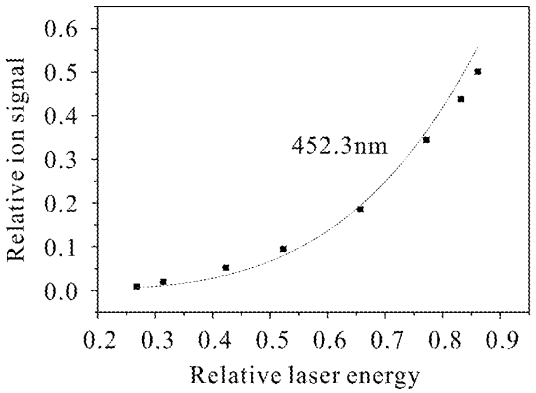

Fig. 4. Ion signal versus laser energy at 452.3 nm.

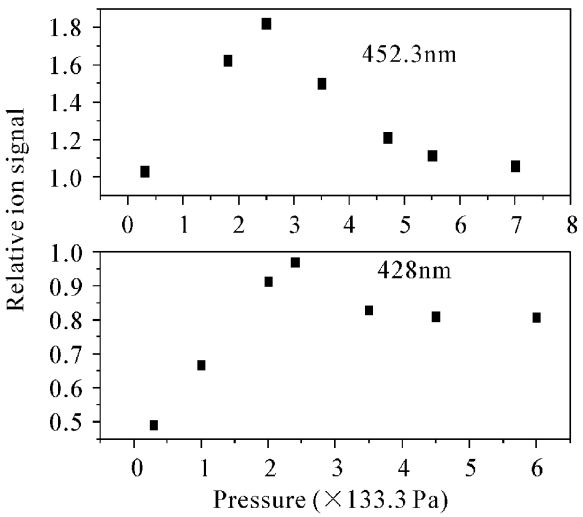

Fig. 5. Ion signal versus pressure.

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