Resonance-enhanced multi-photon ionization spectrum of NO in 575—680 nm wavelength region

Guiyin Zhang (张贵银)[1], Yidong Jin (靳一东)[1], and Lianshui Zhang (张连水)[2]

[1]*College of Mathematics and Physics, North China Electric Power University, Baoding 071003*
[2]*College of Physics Science and Technology, Hebei University, Baoding 071002*

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The multi-photon ionization spectrum of NO in the wavelength region of 575—680 nm is obtained with an optical parameter generator and amplifier (OPG/OPA) pumped by a picosecond Nd:YAG laser as radiation source. The banded structure of the spectrum indicates that NO molecule is ionized in resonant manner and the peaks of the spectrum are assigned to the transition of NO molecule from the ground electronic state to $A^2\Sigma$ ($v' = 0, 1, 2, 3$), $E^2\Sigma$ ($v' = 0, 1, 2$), $F^2\Delta$ ($v' = 0, 1, 2, 3$) and $H^2\Sigma$ ($v' = 0, 1, 2$) intermediate resonant ones. The molecule constants about NO ($A^2\Sigma$, $E^2\Sigma$, $F^2\Delta$, $H^2\Sigma$) states are calculated from the center wavelength of the spectrum. It is also found that owing to the special electron configuration of NO, this molecule does not follow the normal transition selection rule of the diatomic molecule during the multi-photon process.

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NO is a primary air pollutant that comes from high temperature combustion processes. It can react with O_3 and produce NO_2. This reaction not only destructs the ozone layer, but also plays key role in the formation of acid rain and photochemical smog. It is hazardous to the health of the general population also. So the detection and measurement of NO is very important in the study of combustion chemistry and environmental pollution. There is much progress in the detection technique, especially for multi-photon ionization spectroscopy method that was developed in recent years[1−5]. The method of multi-photon ionization spectroscopy, which is based on detecting the ions generated from the excitation of the atoms and molecules, is a sensitive detection technique. A characteristic feature of this technique from a spectroscopic point of view is the enhancement by the resonant intermediate states. Since the ionization efficiency is strongly enhanced when the energy of one or more photons is in resonance with real intermediate states, it is possible to measure the spectrum of the intermediate state by scanning the wavelength of the excitation laser. This provides information about not only molecular states and molecular structures, but also the reaction dynamics. One of the advantages of this technique is to study the transitions that are single-photon forbidden. There are many reports about the applications of this technique[3−8]. In this paper, the resonance-enhanced multi-photon ionization (REMPI) spectrum of NO in the wavelength region of 575—680 nm is obtained with a tunable high power laser as the radiation source. The ionization pathway of NO molecule is determined by measuring the intensity of the signal versus the laser intensity together with theoretical calculation.

The experiment setup is similar to that in our previous work[7]. Briefly, an optical parameter generator and amplifier (POG/OPA) pumped by a Nd:YAG laser is used to provide tunable radiation in the wavelength range of 420—680 nm. The laser is operated at 10 Hz with a linewidth of ~ 6 cm^{-1}. The pulse duration is 35 ps. The pulse energy ranges from 0.2 to 0.9 mJ and is monitored by a photoelectric diode (PD) during scanning. The laser beam is focused on the center of two electrodes with a 9-mm gap by lens with 150-mm focal length. The diameter of the focus spot is about 0.5 mm in the laser-gas interaction region and the collection voltage is 100 V. The signal from the detection electrodes is amplified by a 10× amplifier and then inputted to the boxcar. The output of the boxcar is recorded by a computer for storage and later analysis. Both of the signals from the electrode and the PD are displayed by a Tektronix digitizer oscilloscope during the experiments. A mechanical pump makes a vacuum pressure of 3×10^{-3} Pa in the sample cell.

Figure 1 is a typical NO multi-photon ionization (MPI) spectrum recorded in the wavelength region of 575—680 nm with 266-Pa gas pressure and 100-V collection voltage. It is obvious that the spectrum is composed of banded structure. So NO molecule must be ionized in resonant manner.

The potential curves of a few lower electronic states of NO molecule are shown in Fig. 2. The ionization potential of NO molecule is about 74688 cm^{-1}, while the energy of the 575—680 nm photon is 14706—17391 cm^{-1}, NO molecule must absorb five photons to exceed

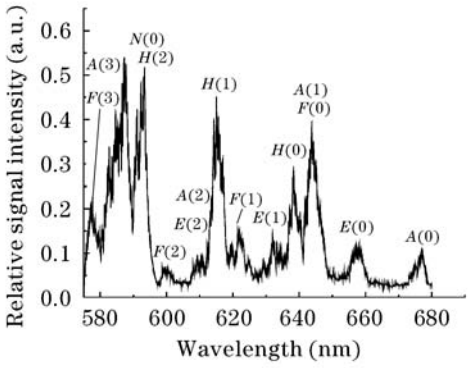

Fig. 1. NO REMPI spectrum in the range of 575—680 nm.

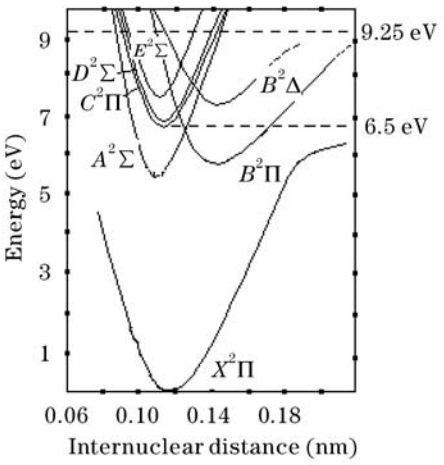

Fig. 2. Potential curves of NO molecule.

ionization limit. To verify this deduction, we measured the ion signal intensity versus the laser intensity at the 638.3-nm radiation wavelength and with 266-Pa pressure also, the result showed a power of 4.8. The near quintic dependence indicates a five-photon process further. Then NO molecule can be ionized through (1+4), (2+3), (3+2), or (4+1) resonance-enhanced multi-photon process. The total energy of two photons with 575—680 nm wavelength is 29412—34783 cm^{-1}, which is lower than the energy of the first excited electronic state. So the (1+4) and (2+3) resonant multi-photon processes can be abandoned. Supposing that NO molecule is ionized through (3+2) resonant multi-photon process, then according to the total energy of the three photons in the wavelength region and the corresponding transition selection rule, the intermediate resonant state must be $A^2\Sigma$ (the energy of the second excited state $C^2\Pi$ is higher than 53324 cm^{-1}). According to the vibronic transition formula of diatomic molecule[9]

$$\tilde{\nu} = \tilde{\nu}_{00} + \omega'_{\mathrm{e}}(v' + \frac{1}{2}) - \omega'_{\mathrm{e}}\chi'_{\mathrm{e}}(v' + \frac{1}{2})^2$$

$$-\omega''_{\mathrm{e}}(v'' + \frac{1}{2}) + \omega''_{\mathrm{e}}\chi''_{\mathrm{e}}(v'' + \frac{1}{2})^2, \qquad (1)$$

the center wavelength of three photon transition from the ground electronic state to $A^2\Sigma$ can be calculated. In Eq. (1), $\tilde{\nu}$ and $\tilde{\nu}_{00}$ are the frequency and foundational frequency of transition with in unit of cm^{-1} respectively; ω'_{e}, $\omega'_{\mathrm{e}}\chi'_{\mathrm{e}}$ and ω''_{e}, $\omega''_{\mathrm{e}}\chi''_{\mathrm{e}}$ are vibration constants of $A^2\Sigma$ and $X^2\Pi$ electronic states; v', v'' are vibration quantum numbers for excited and ground states respectively. The calculation results are listed in Table 1. Comparing the experimental results with the calculation ones, the spectral bands of $A(0) - A(3)$ can be assigned to $A^2\Sigma$ ($v' = 0 - 3$) intermediate resonant state and through a (3+2) REMPI process. The ionization pathway can be indicated as

$$\mathrm{NO}(X^2\Pi\,(v'' = 0)) \xrightarrow{3h\nu} \mathrm{NO}(A^2\Sigma) \xrightarrow{2h\nu} \mathrm{NO}^+ + e. \qquad (2)$$

On the assumption that the unassigned spectral lines come from (4+1) REMPI process, similarly, according to Eq. (1), these lines can be ascribed to $E^2\Sigma$, $H^2\Sigma$, and $F^2\Delta \leftarrow X^2\Pi$ ($v'' = 0$) transitions. This is shown in Table 2. The ionization processes are shown as

$$X^2\Pi \xrightarrow{4h\nu} \left\{ \begin{array}{c} E^2\Sigma \\ H^2\Sigma \\ F^2\Delta \end{array} \right\} \xrightarrow{1h\nu} \mathrm{NO}^+ + e. \qquad (3)$$

Also, the transition wavelengths via valance $B^2\Pi_{1/2,3/2}$ ($v' = 16$) resonant state are 644.4 and 644.3 nm. These are very near to those of $A^2\Sigma$ ($v' = 1$) and $F^2\Delta$ ($v' = 0$) resonant states. The superposition of these lines induces that the spectral line corresponding to the transition from the $X^2\Pi$ ($v'' = 0$) level to $F^2\Delta$ ($v' = 0$) is the strongest in the $F^2\Delta$ ($v' = 0 - 3$) series (this line is not the strongest according to the Frank-Condon principle).

The oscillation frequency and the force constants of the ground vibration levels of $A^2\Sigma$, $E^2\Sigma$, $F^2\Delta$, and $H^2\Sigma$ states can be calculated based on the wavelength of the peak together with Eq. (1). The results shown in Table 3 conform to the reported ones[9]. The error is mainly due to the inaccuracy of the position of the peaks.

Table 1. Wavelengths of $A^2\Sigma$ ($v' = 0 - 3$) $\leftarrow$ $X^2\Pi$ ($v'' = 0$) Transitions

v'	Theory		Experiment
	λ_1 (nm)	λ_3 (nm)	λ'_3 (nm)
0	226.2	678.7	678.1
1	214.7	644.1	644.0
2	204.3	612.9	613.2
3	194.8	584.5	584.8

λ_1: wavelength of single-photon transition; λ_3 and λ'_3: wavelengths of three-photon transitions.

Table 2. Assignments of the Spectral Lines

Line	Peak Wavelength (nm)	λ'_4 (nm)	Intermediate Resonant State
$E(0)$	657.3	657.2	$E^2\Sigma$ ($v' = 0$)
$E(1)$	632.1	632.5	$E^2\Sigma$ ($v' = 1$)
$E(2)$	609.3	609.6	$E^2\Sigma$ ($v' = 2$)
$F(0)$	644.1	644.5	$F^2\Delta$ ($v' = 0$)
$F(1)$	620.6	620.8	$F^2\Delta$ ($v' = 1$)
$F(2)$	598.7	598.5	$F^2\Delta$ ($v' = 2$)
$F(3)$	577.6	577.8	$F^2\Delta$ ($v' = 3$)
$H(0)$	638.3	638.3	$H^2\Sigma$ ($v' = 0$)
$H(1)$	615.0	615.1	$H^2\Sigma$ ($v' = 1$)
$H(2)$	593.3	593.7	$H^2\Sigma$ ($v' = 2$)

λ'_4: wavelength for four-photon transition.

Table 3. Oscillation Frequencies (ω_{e}) and Force Constants (k_{e}) of NO $A^2\Sigma$, $E^2\Sigma$, $F^2\Delta$, and $H^2\Sigma$ States

State	ω_{e} (cm^{-1})		k_{e} ($\mathrm{N{\cdot}m}^{-1}$)	
	Experiment	Ref. [9]	Experiment	Ref. [9]
$A^2\Sigma$	2353	2371	2259	2299
$E^2\Sigma$	2397	2374	2344	2301
$F^2\Delta$	2383	2394	2317	2338
$H^2\Sigma$	2377	2339	2305	2232

According to the selection rule for four-photon transition of diatomic molecule $\Delta\Lambda = 0, \pm 2, \pm 4$, the ionization pathway (expression (3)) is an optical forbidden transition in the four-photon process. But these processes are realized in this work. This is owing to the special electronic configuration of NO. As known, the electronic structure of NO molecule is alkali metals alike. There is only one electron in their outer valence shell. The electrons in the inner shell constitute a closed configuration. Thus most of the NO excited states are Rydberg ones. These are similar to the characteristics of the atoms with one valence electron. So NO molecule ought to follow the transition selection rule of alkali metals atom during the four-photon process, that is, $\Delta l = 0, \pm 2, \pm 4$. Because the outer valence electron of the ground electronic state $X^2\Pi$ of NO molecule is d-orbit alike, while it is in $4s$, $3d$, and $4d$ orbits when excited to $E^2\Sigma$, $F^2\Delta$, and $H^2\Sigma$ states. So the $E^2\Sigma$, $H^2\Sigma$, and $F^2\Delta \leftarrow X^2\Pi$ transitions are allowable by the transition selection rule of atoms with one valence electron.

The REMPI detection technique is based on sensing the ion signal from the ionization of the sample. Using the OPG/OPA pumped by a Nd:YAG laser as the excitation source, NO is ionized though five-photon ionization process and via $A^2\Sigma$, $E^2\Sigma$, $F^2\Delta$, and $H^2\Sigma$ intermediate resonant states. The molecular constants of these states are obtained from the ionization spectrum. One can wish to get more information of the higher excited states of NO by improving the resolving ability of the instrument. This indicates that the technique of REMPI is a suitable method for studying the high excited states of the molecules.

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