Magnetic field effect on highly excited states near ionization potential of nitric oxide

Ken Takazawa*

Tsukuba Magnet Laboratory, National Institute for Materials Science, 3-13 Sakura, Tsukuba 305-0003, Japan

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Abstract

Fluorescence excitation spectra due to the $A^2\Sigma^+ - X^2\Pi$ transition of gaseous nitric oxide (NO) were measured in magnetic fields, $H$, ranging from $0 \leq H \leq 10$ T. Lines in the observed spectra were assigned by using quantum mechanical calculations. Based on the assignment, two-color resonance-enhanced multiphoton ionization spectra via a single Zeeman sublevel in the $A$ state were measured to observe the effect of magnetic fields on electronic states near the ionization potential (IP). Complicated structures due to strong $n$- and $l$-mixing in highly excited Rydberg states were observed below the IP. It was found that new resonance appears above the IP for $H \geq 4$ T. By using a semi-classical calculation, this resonance was assigned to the quasi-Landau resonance, which was observed for the first time in molecules.

$^*$ Tel.: +81-29-863-5487; fax: +81-29-863-5599.
E-mail address: takazawa.ken@nims.go.jp (K. Takazawa).

1. Introduction

Recent progress in magnet technology enables the use of magnetic fields, $H$, for molecular spectroscopy that exceed 10 T. We measured electronic spectra of gaseous nitric oxide (NO) by using a superconducting magnet capable of generating magnetic fields up to 10 T, [1] and by using a water-cooled resistive magnet capable of generating magnetic fields up to 25 T [2]. The high magnetic fields revealed fine structures of the Zeeman sublevels, which cannot be resolved with magnetic fields of 2 T, which are typical for resistive magnets used for molecular spectroscopy. For $H \geq 10$ T, the Zeeman shift of the rotational level in the electronic ground state (the $X$ state) of NO reaches the same extent as the energy difference between adjacent rotational levels. Therefore, strong interactions between the rotational levels were observed, indicating that the rotational motion of the molecule is significantly influenced by the magnetic field. Relative to the binding energy, however, such high magnetic fields still represent only a small perturbation of the orbital motion of an electron.

The Zeeman shift caused by a 10 T magnetic field is on the order of meV, even for NO, which is a paramagnetic molecule ($S = 1/2$). This Zeeman shift is only less than 0.1% of the binding energy of the electron. Therefore, the orbital motion of the electron in the electronic ground state is not significantly influenced by magnetic fields that can be generated in a laboratory.

The Rydberg state of a molecule is an atomic-like excited state, in which one electron is excited to a high-$n$ orbital ($n$ : principal quantum number). Thus, similar to a hydrogen atom, the energy of the Rydberg state can be expressed as

$$E = IP - R(n - \delta)^2$$

where IP is the ionization potential, $R$ is the Rydberg constant, and $\delta$ is the quantum defect, respectively. Rydberg states, therefore, are composed of a series of states, which converge to IP at $n = \infty$. High-$n$ Rydberg states in a magnetic field are of particular interest because of the low binding energy of the electron. The Coulomb force that attracts the Rydberg electron to the core (positively charged molecular ion) is proportional to $n^{-3}$, and the energy difference between adjacent $n$ levels is proportional to $n^{-5}$ [3]. In the $n = 29$ Rydberg state, the Coulomb force on the Rydberg electron is of the same
order as the Lorenz force from a 10 T magnetic field. Therefore, a 10 T magnetic field is not a small perturbation for the Rydberg state; the orbital motion of the electron is strongly influenced by the Lorenz force and the levels with different \( n \) are strongly mixed (\( n \)-mixing) because of the small energy gap.

Although the electronic structure of high-\( n \) Rydberg atoms in a magnetic field has been studied by many people [4], few studies on molecules have been made. In addition to the electronic structure, high-\( n \) Rydberg molecules in a magnetic field are interesting because of the magnetic field effects on the molecular dynamics, which occur only in molecules, such as predissociation, and rotational and vibrational autoionization. Quantum defect theory, which is commonly used to describe these processes, [5] indicates that the rate of these processes is proportional to \( n^{-3} \) and decreases with increasing \( l \) (\( l \): quantum number of orbital angular momentum). Because of the strong \( n \)- and \( l \)-mixing caused by magnetic fields, it is expected that in high-\( n \) Rydberg states the rates of predissociation and autoionization can be varied by applying a magnetic field.

Two-color resonance-enhanced multi-photon ionization (REMPI) spectroscopy is useful for studying high-\( n \) Rydberg states of molecules. In this technique, the ground state molecule is excited to a specific rotational level in the first excited state (the A state) by a first laser. A second laser is used to excite the molecule in the A state to a high-\( n \) Rydberg state. The transition to the Rydberg state is observed by detecting ions produced from Rydberg molecules by collisional ionization and autoionization. Because the molecules in the single rotational level in the A state are created with the first laser, the spectrum is simplified due to the selection rule of the transition. This simplification greatly aids analysis of the spectrum.

The first step to apply two-color REMPI spectroscopy to molecules in magnetic fields is to determine the A–X transitions in magnetic fields, so that molecules can be excited to specific Zeeman sublevels in the A state with the first laser. We built a setup for measuring the fluorescence excitation spectra for \( 0 \leq H \leq 10 \) T. Using this setup, we observed the A–X transition of NO, and all lines in the spectra were assigned by using a quantum-mechanical calculation [1]. We also developed a setup for two-color REMPI spectroscopy in magnetic fields. Based on the assignment of the A–X transitions, the two-color REMPI spectra of the high-\( n \) Rydberg state of NO was measured for \( 0 \leq H \leq 10 \) T. It was found that the electronic structure near the IP was significantly influenced by magnetic fields [6]. In this paper, measurements of the magnetic field effect on the highly excited states of NO are summarized and the electronic structure near the IP is discussed using a semi-classical calculation.

2. Experimental

2.1. Fluorescence excitation spectra

Fig. 1 shows a setup for measuring fluorescence excitation spectra in magnetic fields. A superconducting magnet was used to generate a maximum field of 10 T in
a 100 mm diameter, room-temperature bore. The NO pressure in the chamber inside the bore was maintained at 40 mTorr by controlling the NO flow rate. A dye laser was pumped by using an Xe–Cl excimer laser operated at 10 Hz. The output of the dye laser was frequency-doubled and focused on the sample gas with a lens. The frequency of the laser was scanned in the energy region of the A–X transition. The laser resolution was about 0.1 cm$^{-1}$ (FWHM). Selection rules of the electronic transition in a magnetic field are given by

\[
\Delta M = 0 \ (H \parallel E),
\]

\[
\Delta M = \pm 1 \ (H \perp E),
\]

where $M$ is the projection of the total angular momentum, $J$, along a laboratory fixed-Z axis, $H$ is the magnetic field along the Z axis, and $E$ is the laser polarization. A laser polarized parallel to the magnetic field was used to observe $\Delta M = 0$ transitions. Fluorescence from excited molecules was collected by a lens and detected by using a photomultiplier. The photomultiplier was mounted 2 m away to avoid the effects of stray fields. The signal was integrated with a boxcar integrator and recorded with a computer.

2.2. Two-color REMPI spectra

The setup for measuring two-color REMPI spectra is shown in Fig. 2. The magnet was the same superconducting magnet used for measuring the fluorescence excitation spectra. A chamber containing a pair of electrodes inside was attached to the magnet. The NO pressure in the chamber was maintained at 80 mTorr. Two dye lasers were pumped by using split outputs from an Xe–Cl excimer laser. The outputs of the dye lasers were frequency-doubled and coaxially focused in the middle of the electrodes. The first laser, $\nu_1$, was used to excite molecules to a specific Zeeman sublevel in the A state. The second laser, $\nu_2$, was scanned in the energy region of the transition from the A state to the high-$n$ Rydberg states. Laser $\nu_2$ was polarized perpendicular to the magnetic field to observe $\Delta M = \pm 1$ transitions. 5 ms after laser excitation, a +15 V voltage was applied to the electrode to detect ions produced from the Rydberg molecule. A 5 µs delay was used to avoid electric field effects on molecules at laser excitation. The ion signal was amplified by using a current amplifier, integrated with a boxcar integrator, and recorded with a computer.

3. Results and discussion

3.1. A–X transitions in magnetic fields

Fig. 3 shows the fluorescence excitation spectra due to the $A$ $^2\Sigma^+ (v' = 0) \rightarrow X^2\Pi_{3/2}(v'' = 0)$ transition for $0 \leq H \leq 10 \text{T}$ ($v$: vibrational quantum number). The assignment of the rotational lines is shown at the top of Fig. 3. The $P_{21}$ rotational branch was observed in the spectrum measured at $H = 0$. Spectra measured at $H \geq 4 \text{T}$. 

![Fig. 2. Setup for measuring two-color REMPI spectra in magnetic fields. ER: Electrode. BS: Beam splitter.](image-url)
show complicated structures due to large Zeeman splitting. With increasing $H$, each rotational line splits into two components and each of the components further splits into several lines.

To assign the lines in the spectra, the rotational energy levels in the magnetic fields were calculated, as described elsewhere [1]. Briefly, the matrix elements of the Hamiltonian, including the Zeeman interaction, $H_{\text{Zeeman}} = \mu_B (L_Z + 2S_Z) H$, were written by using the representation of the Hund’s case (a) basis set [7] for both the $\text{A}^2\Sigma^+$ and $\text{X}^2\Pi$ states. Here, $\mu_B$ is the Bohr magneton and $H$ is the magnetic field intensity. The Hamiltonians were diagonalized numerically. $J$ varied from 0.5 to 19.5 and $M$ varied from $-|J|$ to $|J|$. The rotational constants in the $\text{A}^2\Sigma^+$ and $\text{X}^2\Pi$ states and the spin-orbit coupling constant in the $\text{X}^2\Pi$ state were taken from Ref. [7]. Fig. 4 shows calculated transition energies of the $P_{21}$ branch for $0 \leq H \leq 10$ T, together with observed

![Fig. 3. Fluorescence excitation spectra of the $P_{21}$ branch of the $\text{A}^2\Sigma (v' = 0) - \text{X}^2\Pi (v'' = 0)$ transition for $0 \leq H \leq 10$ T. The laser was polarized parallel to the magnetic field ($\Delta M = 0$).](image)

![Fig. 4. Calculated transition energies of the $P_{21}$ branch, with magnetic fields overlaid on the spectra.](image)
spectra. Our calculations well reproduced the position of the observed lines, indicating that the lines observed in the spectra were assigned.

3.2. Highly excited states near IP

The assignment of the A–X transition in magnetic fields allowed us to measure the two-color REMPI spectra, by using a single Zeeman sublevel in the A state as an intermediate state of the excitation. Fig. 5 shows the excitation diagram. The first laser was used to excite the ground state molecule to the $J = 2.5$, $M = −1.5$ Zeeman sublevel in the vibrational excited state ($v = 1$) in the A state (the spectra due to the A $^{2}Σ^+$ ($v' = 1$)–$X^2Π$ ($v'' = 0$) state are not shown). Because the A state of NO is the Rydberg state ($3σr$), the operative selection rule for transition to a higher Rydberg state is $Δv = 0$. Therefore, the transition to the Rydberg states that converge to the IP$_0$ ($v = 1$) are allowed (IP$_0$ ($v = 1$) ; $v = 1$ level of cation). As shown in Fig. 5, the high-$n$ Rydberg states converging to IP$_0$ ($v = 1$) are energetically above the lowest ionization potential, IP$_0$, which corresponds to the $v = 0$ level of the cation. Thus, in addition to collisional ionization, molecules in those states can ionize by autoionization. Because of the high ionization efficiency due to two ionization processes, the transition to the Rydberg states can be detected with high sensitivity.

Fig. 6 shows two-color REMPI spectra measured after exciting the $v = 1$, $J = 2.5$, $M = −1.5$ Zeeman sublevel in the A $^{2}Σ^+$ state by using laser $ν_1$ for $0 ≤ H ≤ 10$ T. Levels with $M = −2.5$ and $M = −0.5$ are observable due to the $ΔM = ±1$ selection rule. For $H = 0$, an increase in the ion signal at 77050 cm$^{-1}$ (corresponding to the IP$_0$ ($v = 1$)) were observed, and below the ionization potential the Rydberg states converging to the IP$_0$ ($v = 1$) were also observed. These Rydberg states were assigned to $ns$ ($δ = 1.2$) and $np$ ($δ = 0.66$) series by Anezaki et al. [8]. Assignments of the Rydberg states are shown in Fig. 6. With increasing magnetic field, Rydberg states show complicated level splitting, reflecting the large Zeeman shift of the high-$n$ Rydberg states. However, the most dramatic feature of the spectra is an appearance of periodic modulations of the signal intensity above the IP for $H ≈ 4$ T.

It is well known that the Schrödinger equation for a Rydberg atom in a magnetic field is non-separable and, as a result, cannot be solved analytically. Many theoretical attempts have been made to obtain the solution of this problem because a Rydberg atom in a magnetic field is one of the best systems with which to study quantum chaos [4,9]. The motion of a Rydberg electron in a magnetic field is classically chaotic when $H$ and $n$ satisfy certain conditions. Although calculations with modern supercomputers successfully reproduce energy levels of simple atoms, such as hydrogen, it is difficult to calculate energy levels of Rydberg molecules because of the complicated structure of the energy levels due to rotation and vibration. To analyze the spectra of NO, therefore, we used a semi-classical calculation that was developed to calculate resonance structures of high-$n$ Rydberg atoms in a magnetic field [10–12]. Using cylindrical coordinates, the potential for the Rydberg electron in a magnetic field is given by

$$V(ρ,Z) = (m^2 − 1/4)ρ^2/2 − (ρ^2 + Z^2)^{−1/2} − mH/2 + H^2ρ^2/8.$$  (3)
Because the electron is excited near the IP, the electron can move freely in the Z direction, although the motion in the X–Y plane is bound by the magnetic field. Therefore, the motion in the Z direction does not contribute significantly to the resonance structure, and can therefore be neglected.

Applying the Bohr–Sommerfeld quantization condition to the motion in the X–Y plane leads to

$$\int_{\rho_1}^{\rho_2} \left[ E - V(\rho, 0) \right]^{1/2} d\rho = (n_r + 1/2) \pi,$$

where $E$ is the energy of the electron, $n_r$ is a reduced quantum number given by $n_r = (n - \delta) - m - 1$, and $\rho_1$ and $\rho_2$ are limits of the integral.

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Fig. 6. Two-color REMPI spectra of NO measured via the $v = 1, J = 2.5, M = -1.5$ level in the A state for $0 \leq H \leq 10$ T. The broken line at 77069 cm$^{-1}$ shows the ionization potential, IP.($v = 1$).

Fig. 7. Comparisons between calculated energy levels and spectra. Solid curves show calculated energy as a function of continuous $n$. Vertical lines show the energy at integral values of $n$. 

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Thus, the spacing, 1/\(v\c\) and the resonance is dominated by a magnetic field. Coulomb potential to the resonance structure decreases Lorenz forces. As energy increases, contribution of with increasing energy and converges to 1/\(v\c\). As previously discussed, the rate of the processes strongly depends on \(n\) and \(l\). However, it is difficult to evaluate the rate of those processes from the spectra measured in this work. To evaluate the autoionization rate, the signal due to collisional ionization must be subtracted. This means that measurements must be done on molecules under collision-free conditions to avoid collisional ionization. To evaluate the predissociation rate, the fragment species must be detected, which for NO are N and O. The detection of the fragment species was successfully achieved in NO by using a third laser beam to ionize and detect the fragment atoms [14,15]. In this fragment-detection technique, the combination of a molecular beam apparatus and a mass analyzer is necessary to identify the fragment species from their mass number.

After the first observation in Ba atoms by Garton and Tomkins [13], a resonance spacing between energy peaks of 1.5/\(v\c\) at the IP has been observed in other atoms, such as Na and Rb [4]. The resonance is known as quasi-Landau resonance, and can be explained semi-classically as periodic, two-dimensional motion of the Rydberg electron in the \(X-Y\) plane driven by both Coulomb and Lorenz forces. As energy increases, contribution of Coulomb potential to the resonance structure decreases and the resonance is dominated by a magnetic field. Thus, the spacing, 1.5/\(v\c\) at \(E = 0\) (IP), gradually decreases with increasing energy and converges to \(v\c\), which is a spacing of the cyclotron motion of a free electron. Therefore, the resonance observed above the IP is assigned to the quasi-Landau resonance of NO, which was observed in molecules for the first time.

Although the calculation reproduced the locations of the quasi-Landau resonance, the agreement with the levels below the IP was not good. For \(H \leq 6\) T, calculated locations of lines qualitatively agree with the dominant lines in the spectra. However, the spectra show complicated, fine structures, which were not reproduced by the calculation. Moreover, for \(H \geq 8\) T, calculated line positions do not agree even with dominant lines in the spectra. This indicates that strong \(n\) - and \(l\)-mixing occur in Rydberg states, and a quantum mechanical calculation is necessary to reproduce the spectra. On the other hand, the fact that strong \(n\) - and \(l\)-mixing occurs in the states below the IP suggests that the rates of predissociation and autoionization in those states significantly differ from those for \(H = 0\). As previously discussed, the rate of the processes strongly depends on \(n\) and \(l\). However, it is difficult to evaluate the rate of those processes from the spectra measured in this work. To evaluate the autoionization rate, the signal due to collisional ionization must be subtracted. This means that measurements must be done on molecules under collision-free conditions to avoid collisional ionization. To evaluate the predissociation rate, the fragment species must be detected, which for NO are N and O. The detection of the fragment species was successfully achieved in NO by using a third laser beam to ionize and detect the fragment atoms [14,15]. In this fragment-detection technique, the combination of a molecular beam apparatus and a mass analyzer is necessary to identify the fragment species from their mass number.

To study the magnetic field effects on the rates of these processes, a molecular beam setup with a time-of-flight mass analyzer is under construction in our laboratory. Because molecules in a molecular beam are under collision-free conditions, ion signals generated from collisional ionization is eliminated. Therefore, ions produced only from the autoionization process are detected. Moreover, the time-of-flight mass analyzer provides information on the mass of fragment species by using a third laser beam for ionization, allowing identification of the fragment produced by predissociation. Results of the measurements using this setup will be reported in a future paper.

![Fig. 8. Observed spacing between peaks above the ionization potential (dots), and calculated spacing (solid curve) for \(H = 10\) T.](image-url)

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