High-resolution laser spectroscopy and Zeeman effect of NO[3] radical

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論文内容の要旨

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専　攻　　化学

論文題目（外国語の場合は，その和訳を併記すること。）

High-resolution laser spectroscopy and Zeeman effect of NO_3 radical
（NO_3 ラジカルの高分解能レーザー分光とゼーマン効果）

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This doctoral dissertation, which consists of five chapters, reports high-resolution laser spectroscopic study of nitrate radical (NO_3) and observation of an external magnetic effect.

Chapter 1. Introduction

Under the Born-Oppenheimer (BO) approximation, three types of motion of molecule (electronic, vibrational and rotational) may be separated. The rotational constants and the vibrational frequencies of electronically excited molecules, which are related to the geometrical molecular structure and the rigidity of chemical bonding respectively in the excited electronic states, can be determined precisely by using high-resolution laser spectroscopic methods. Simultaneously, high-resolution laser spectroscopy is experimentally able to reveal the breakdown of the BO approximation which is important for chemistry and chemical reactions.

Free radicals, which are the molecules with unpaired electrons, are of importance in chemistry, because of their chemical instability promoting chemical reactions. Spectroscopically, free radicals are of interest because of the non-zero electronic spin angular momentum. The electronic spin couples with other degrees of freedom of molecular framework to provide us the information of radicals. The electronic spin also couples with external magnetic or electric field, leading to the noticeable Zeeman or Stark splitting of quantum levels.

NO_3 has two low-lying excited electronic states $\tilde{A}\,^2E''$ and $\tilde{B}\,^2E'$ within 2 eV above the ground electronic state $\tilde{X}\,^2A_2'$. The spectroscopic study of the $\tilde{X}$ state in NO_3 has been carried out for several decades; however, the $\tilde{X}$ state is still a challenging subject for both experimentalists and theoreticians, because it is fully beyond the BO approximation, and strongly interacts with the excited electronic states. The dark $\tilde{A}$ state also interacts with the $\tilde{B}$ state and appears by the intensity borrowing from an optically allowed $\tilde{B}-\tilde{X}$ transition. The detailed investigation of the $\tilde{B}$ state is thus desired for the understanding of the intra-molecular interactions of NO_3.

This study aimed at obtaining the detailed information of the $\tilde{B}$ state of NO_3 radical, and aimed at understanding the intra-molecular interactions including the $\tilde{B}$ state. In this study, the most intense vibronic bands located in 15100 cm^{-1} region assigned to the 0 – 0 band of the $\tilde{B}-\tilde{X}$ transition in $^{14}NO_3$ and $^{15}NO_3$ isotopologues were investigated by using high-resolution laser spectroscopy. The observed spectra were complicated; however, the rotational assignment was successfully carried out based on the detailed observation and analysis of the Zeeman splitting.

Chapter 2. Theoretical treatment

Ab initio calculation with the UCIS method and density functional theory calculation with the UB3LYP method were performed to estimate the energies of the excited electronic states. The results indicate the other states excluding the $\tilde{X}$ and $\tilde{A}$ states are far from the $\tilde{B}$ state. Thus we can focus only on the $\tilde{X}$, $\tilde{A}$ and $\tilde{B}$ states to treat the intra-molecular interactions of NO_3.

Various angular momenta were defined to describe the rovibronic states of NO_3. The $\tilde{B}\,^2E'$ state was considered to be described by Hund's coupling case (a). In this case the $\tilde{B}\,^2E'$ state splits into the $\tilde{B}\,^2E'_{3/2}$ and $\tilde{B}\,^2E'_{1/2}$ by the spin-orbit interaction. Then the symmetry-adapted linear combinations (SALCs) of these spin-orbit components were derived. The $\tilde{X}\,^2A_2'$ state is known to be described by Hund's coupling case (b), where each level with the quantum number N splits into two spin components by the spin-rotation interaction, because of the electronic spin of 1/2. The SALCs of the spin-rotation components and matrix elements were derived. Nuclear spin statistics of ^{16}O nuclei was considered under the D_{3h} structure assumption.

The Hamiltonian and matrix elements of the Zeeman interaction were introduced. It was demonstrated that the magnitude of the Zeeman splitting of rovibronic levels depends on the quantum numbers. The matrix elements of the electric dipole moment were introduced and the selection rules of the $\tilde{B}\,^2E' \leftarrow \tilde{X}\,^2A_2'$ transition were derived. The Hönl-London factors were calculated using the derived SALCs. The fundamental idea of the perturbation mechanism of a two-level system was introduced to demonstrate the intensity borrowing mechanism due to the coupling between a bright state and a dark state.

Several types of spectral linewidth were introduced. The Doppler broadening of the spectral lines of NO_3 located in 15100 cm^{-1} region in room temperature is estimated to be 700 MHz. Natural linewidth broadening of NO_3 is estimated to be the order of kilohertz. Transit time broadening is estimated to be 25 kHz. Power broadening of spectral lines is estimated to be a few megahertz. The natural linewidth broadening, the transit time broadening, and the power broadening may be neglected; however, the Doppler width has to be reduced to achieve the rotationally-resolved high-resolution laser spectroscopy.

Chapter 3. Experiment

In this study, dinitrogen pentoxide (N_2O_5) was used as a precursor of NO_3, and NO_3 was generated by using the N_2O_5 pyrolysis reaction: $N_2O_5 \rightarrow NO_3 + NO_2$. Considering the natural abundance of atomic isotopes of oxygen, $N^{16}O_3$ isotopologue is largely dominant. Thus it was considered that only $^{14}N^{16}O_3$ and $^{15}N^{16}O_3$ isotopologues were investigated in this study.

One of the fundamental ideas to reduce the Doppler width is we cross a molecular beam and an incident laser beam at the right angles to prevent molecules from having the velocity along the propagation vector of the laser beam. The molecular beam can be realized using a pulsed nozzle to eject gaseous sample into a vacuum chamber and mechanical apertures to collimate the supersonic molecular jet into a molecular beam. The supersonic molecular jet is also useful for the adiabatic cooling of gaseous sample rotationally and vibrationally which allows us to observe simpler spectra than those in the room temperature.

The experimental procedures are the following. N_2O_5 vapor was mixed with helium gas at −5°C and injected into a differentially-pumped vacuum chamber. The mixture gas was heated to about 300°C to generate NO_3 radical by the N_2O_5 pyrolysis reaction. Then, the molecular jet was collimated to a molecular beam. An output of a single-mode ring dye laser and the molecular beam was crossed at the right angles. High-resolution fluorescence excitation spectra were observed by detecting the fluorescence from excited molecules with a photomultiplier tube. A pair of solenoid was used to generate a homogeneous external magnetic field whose strength was up to 360 G, to observe the Zeeman splitting of the spectral lines of NO_3.

Doppler-free saturation spectrum of iodine molecule and fringe patterns of a stabilized étalon were simultaneously recorded with the NO_3 measurement for the absolute wavenumber calibration. Absolute wavenumber of each NO_3 signal was calibrated in the accuracy of 0.0001 cm^{-1} by using the Doppler-free iodine spectrum as the wavenumber standard and the fringe patterns of the étalon as the interpolation markers.

The N_2O_5 pyrolysis reaction generates not only NO_3 but also NO_2, and NO_2 also absorbs the visible light. Then high-resolution fluorescence excitation spectra of NO_2 were observed by using commercially available NO_2 gas to discriminate the NO_3 signals from the NO_2 signals.

Chapter 4. High-resolution laser spectroscopy of $^{14}NO_3$ radical

Rotationally-resolved high-resolution fluorescence excitation spectrum of $^{14}NO_3$ was observed in 15070 – 15145 cm^{-1} region assigned to the 0 – 0 band of the $\tilde{B}\,^2E' \leftarrow \tilde{X}\,^2A_2'$ transition. The NO_2 contamination to the NO_3 spectrum was confirmed to be negligible in the observed region. More than 3000 rotational lines of NO_3 were found in the observed region, and they seemed to have less the rotational branch structures. The rotational assignment was thus difficult.

In the observed region more than 20 intense rotational line pairs with 0.0246 cm^{-1} spacing were identified. This spacing is the same with the spin-rotation splitting of the $\tilde{X}\,^2A_2'$ ($v'' = 0$, $k'' = 0$, $N'' = 1$) level in magnitude. The candidates of the upper level of this line pairs are the $^2E'_{3/2}$ ($J' = 1.5$), $^2E'_{1/2}$ ($J' = 0.5$), and $^2E'_{1/2}$ ($J' = 1.5$) levels. The Zeeman splitting enabled us to discriminate from each other clearly. Seven line pairs were assigned to the transitions to the $^2E'_{3/2}$ ($J' = 1.5$), and 15 line pairs were assigned to those to the $^2E'_{1/2}$ ($J' = 0.5$), based on the observed Zeeman splitting and the ground state combination differences. This is the first study that the rotational assignment of the $\tilde{B} - \tilde{X}$ transition in NO_3 radical was successfully carried out. The effective rotational constants of the excited electronic states were estimated. The magnetic g-factors of the ground state and the excited states were determined.

In the 15070 – 15145 cm^{-1} region many vibronic bands were identified, while only one vibronic 0 – 0 band had been expected to appear. This result indicates that the $\tilde{B}\,^2E'$ ($v = 0$) state massively interacts with the surrounding dark vibronic states, and they appeared by the intensity borrowing from the optically allowed $\tilde{B}$ – $\tilde{X}$ electronic transition. From the density of the identified vibronic states, it was concluded that the complicated rotational structure of the observed region mainly owes to the vibronic coupling between the $\tilde{B}\,^2E'$ state and the $\tilde{A}\,^2E''$ state through the a_2'' symmetry vibrational modes. The effective spin-orbit interaction constant of the $\tilde{B}\,^2E'$ ($v = 0$) state was estimated to be –21 cm^{-1}. The Curl's relationship was confirmed to be verified in the ground state of NO_3 radical.

Chapter 5. High-resolution laser spectroscopy of $^{15}NO_3$ radical

Rotationally-resolved high-resolution fluorescence excitation spectrum of jet-cooled $^{15}NO_3$ radical was observed by using the $^{15}N_2O_5$ pyrolysis reaction. This is the first high-resolution spectroscopic study of the electronic transition of $^{15}NO_3$ isotopologue. The observed region was 15080 – 15103 cm^{-1}, which is assigned to the 0 – 0 band of the $\tilde{B}\,^2E' \leftarrow \tilde{X}\,^2A_2'$ transition. The $^{15}NO_2$ contamination to the $^{15}NO_3$ spectrum was assumed to be negligible in this region, referring to the $^{14}NO_3$ study in the previous chapter. About 200 strong lines and several thousand weak lines were found.

Many rotational line pairs with 0.0248 cm^{-1} spacing were recognized. Eighteen pairs of them were successfully assigned to the transitions from the $\tilde{X}\,^2A_2'$ ($v'' = 0, k'' = 0, N'' = 1, J'' = 0.5$ and 1.5) levels, based on the Zeeman splitting and the ground state combination differences. Starting from these line pairs, about 90 rotational lines were finally assigned. From this rotational assignment the molecular constants of the ground state were determined as $B = 0.458544(2)$ cm^{-1}, $D_N = 0.56(2) \times 10^{-6}$ cm^{-1}, and $\varepsilon_{bb} = -0.01670(4)$ cm^{-1}. The molecular constants of the $\tilde{B}\,^2E'_{1/2}$ state were estimated to be $T_0 = 15098.20(4)$ cm^{-1}, $B = 0.4282(7)$ cm^{-1}, and $D_J = 4 \times 10^{-4}$ cm^{-1}, under a perturbation-free assumption.

Eight vibronic bands were identified in 15080 – 15103 cm^{-1} region. This complicated structure was concluded to be due to the vibronic couplings between the $\tilde{B}\,^2E'$ ($v = 0$) state and the $\tilde{X}$ and $\tilde{A}$ electronic states. Both the two spin-orbit components $^2E'_{1/2}$ and $^2E'_{3/2}$ were identified, and the spin-orbit interaction constant of the $\tilde{B}\,^2E'$ ($v = 0$) state was estimated to be –12 cm^{-1} as the lower limit based on the energy separation of these spin-orbit components.

（別紙１）

論文審査の結果の要旨

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論文題目	High-resolution laser spectroscopy and Zeeman effect of NO_3 radical （NO_3ラジカルの高分解能レーザー分光とゼーマン効果）		
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要旨

レーザー光の単色性の良さと絶対波数精度の高さを活用した高分解能レーザー分光は、複雑な分子の励起状態を電子・振動・回転準位まで分離して観測することが可能であり、分子構造や電子状態における相互作用について、詳細で正確な研究を遂行することができる。従来の線幅の広いパルスレーザーを用いた励起準位の測定では多数の準位へ同時に励起するため、単一の励起準位を測定することができないのに対し、高分解能分光では単一の励起準位についての情報が高い精度で得られ、スペクトル線の線形、線幅、強度の微小な変化から励起状態間の相互作用等の励起状態ダイナミックスを発見・解明することが期待できる。

本研究では、硝酸ラジカル（NO_3）の可視光領域の電子遷移を研究対象として、狭線幅レーザー・分子線・外部磁場を利用した高分解能レーザー分光法を適用して高分解能かつ高精度なスペクトルの測定を行い、エネルギー準位構造と状態間相互作用に関する研究成果を報告している。

本論文は５章から構成されている。第１章では研究目的および研究の背景が述べられている。研究対象である NO_3 ラジカルは夜間の大気中に存在して大気中のラジカル反応において重要な役割を持つため、大気化学の視点から多くの研究がなされていると同時に、平面正三角形という基本的構造であることから、分子科学の観点から構造や相互作用を理解するためのモデル分子としても興味深く、理論と実験の両面から多くの研究が行われている。しかしながら、可視光領域の電子遷移：$B \leftarrow X$ 遷移についてはスペクトルの観測例はあるものの、複雑すぎて回転構造は解析できないと報告されていた。そこで、より高分解能かつ高精度な分光計測と磁場によるスペクトル変化の観測により明確な帰属を行うことで構造と状態間相互作用に関する新たな知見を得ることを目的としている。

第２章では対称コマ分子モデルを用いて NO_3 ラジカルの基底状態並びに電子励起状態の回転エネルギー準位の理論的記述を行い、観測される遷移エネルギー、遷移選択則ならびに遷移強度を説明し、次に外部磁場によって生じる Zeeman 効果による回転準位の分裂を理論的に導出している。また、スペクトル線幅についての理論的記述も行っている。第３章では個々の回転線を分離して観測・解析するために本研究で用いた手法である分子線と電磁石を利用した高分解能レーザー分光法を説明している。ここでは、最初に試料について N_2O_5 の熱分解による NO_3 ラジカルの生成法と条件について記述し、次に、分子線・単一モードレーザー直交法によるサブドップラー分光法の原理を述べている。さらに、本研究で必要不可欠な電磁石の作製とその性能評価について述べた後、本測定の特徴である絶対波数精度の高さについて説明している。第４、５章では以下に示すように、それぞれ $^{14}NO_3$ ラジカルおよび $^{15}NO_3$ ラジカルについての研究結果を報告している。

氏名	多田 康平

（第4章）High-resolution laser spectroscopy of $^{14}NO_3$ radical　（$^{14}NO_3$ ラジカルの高分解能レーザー分光）

NO_3 ラジカルは大気化学において重要な反応中間体である。昼間は太陽光によって分解するために大気中では確認されないが、夜間においては大気中で観測され、大気中のラジカル反応において重要な役割を果たしている。そのため、NO_3 については多くの研究が行われてきた。特に、電子遷移である $B\,^2E' \leftarrow X\,^2A_2'$ 遷移は光学許容遷移で、662 nm に強い吸収を持つことが知られており、これは 0−0 バンドと呼ばれる。本研究では $^{14}NO_3$ の $B \leftarrow X$ 遷移の 0−0 バンドについて高分解能蛍光励起スペクトルを観測した結果、3000 本以上の回転線を分離して観測することに成功している。これは理論的に予測されるスペクトル線よりもはるかに多い回転線である。試料は N_2O_5 の熱分解 [$N_2O_5 \rightarrow NO_3 + NO_2$] によって生成しており、同時に発生する NO_2 ラジカルのスペクトル線の可能性があったため、確認のために NO_2 のみの高分解能スペクトルも観測している。その結果、N_2O_5 の熱分解について 662 nm 付近で観測された回転線は NO_3 ラジカルに起因することを確実にしている。NO_3 のスペクトルは複雑で回転構造の解析は困難であったため、精度の高い測定値と磁場によるスペクトル変化（Zeeman 分裂）の観測を併用して回転量子数の帰属を確実に行った結果、基底状態 $X\,^2A_2'(J''=0.5$ および $1.5)$ 準位からの遷移を明確に帰属することに成功している。帰属された回転線は、理論的に予測される遷移よりも多く、一つの準位が状態間相互作用によって多くの準位に分裂し、それらのエネルギーシフトがスペクトル線を複雑にしていると考え、その機構を考察している。考えられる相互作用の相手として第一励起状態である $A\,^2E''$ 状態および基底状態の高振動励起状態を挙げて、それらの振電準位の対称性(選択則)と準位密度の考察から、相互作用を $A\,^2E''$ 状態の a_2'' 対称性を持つ振電準位との振電相互作用に起因すると結論している。

（第5章）High-resolution laser spectroscopy of $^{15}NO_3$ radical　（$^{15}NO_3$ ラジカルの高分解能レーザー分光）

最近、$^{14}NO_3$ と $^{15}NO_3$ の低分解能スペクトルの観測から、$B \leftarrow X$ 遷移 0 − 0 バンドのバンド構造が大きく異なることが報告されている。そこで、本研究では、$^{15}NO_3$ の $B \leftarrow X$ 遷移 0 − 0 バンドについても、同様に高分解能蛍光励起スペクトルと磁場によるスペクトル変化を観測している。結果として、$^{14}NO_3$ と同様に予測されるよりも多くの基底状態 $X\,^2A_2'(J''=0.5$ および $1.5)$ 準位からの遷移を帰属するとともに、回転構造を見出すことに成功している。このとき、複雑に分裂したスペクトル線のエネルギーシフトと遷移強度を利用して摂動を考慮した回転構造解析を行い、分子定数の見積りにも成功している。このとき、基底状態の分子定数についてもこれまでに報告されている定数よりも高い精度の分子定数を決定している。得られた分子定数から理論的に遷移強度とスペクトル線位置を計算して相互作用のない場合のスペクトルシミュレーションを行い、実測のスペクトルとよい一致を示すことを確認している。こうした回転構造は $^{14}NO_3$ では見られなかった構造であり、同位体の違いで相互作用する相手状態とのエネルギー的な関係の違いにより $^{15}NO_3$ ではより局所的な相互作用が顕著になっているため、狭い範囲でスペクトル線が密集して解析が可能となったと結論している。

本研究は、NO_3 ラジカルの可視光領域に観測される $B \leftarrow X$ 遷移について、高分解能分光の手法を用いて詳細かつ精密に観測した結果、励起状態の構造およびダイナミックスについて重要な知見を得たものとして価値ある集積であると認める。よって、学位申請者の 多田 康平 は、博士（理学）の学位を得る資格があると認める。