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USING ZEEMAN SCANNING OF AN ATOMIC LINE

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A new technique for the determination of isotopic species
using Zeeman scanning of an atomic line.

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Abstract

We measured the vibrational-rotational line profiles of $^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{16}\text{O}$ in the electronic transition spectrum by using the magnetically scanned ion line of $^{114}\text{Cd}(\text{II})$ at $2165.017\overset{\circ}{\text{A}}$. The observed separation between the line of $^{14}\text{N}^{16}\text{O}$, Q ($10\frac{1}{2}$) and the line of $^{15}\text{N}^{16}\text{O}$, Q ($11\frac{1}{2}$) was 49.6 GHz, and the half width of these lines was 4.4 GHz. We could observe the line profile of $^{15}\text{N}^{16}\text{O}$ in naturally occurring NO, even though its abundance is 0.37%. Also, the ratio of $^{15}\text{N}/^{14}\text{N}$ in nitric acid was determined with this technique. The lower detection limit was about 50 ppb.

Recently, we developed a sensitive and reliable technique for the determination of the isotopic species of small molecules. Small molecules exhibit discrete rotational lines in the electronic spectrum below a predissociation level.¹ Usually, the isotope shift for the rotational-vibronic line of a small molecule is much larger than the width of the rotational-vibrational lines. By scanning a suitable atomic line, by means of the Zeeman effect, we can observe the absorption line profile for each isotopic species in the gas mixture. Since the line absorption is measured for an electronic transition, the sensitivity is much higher than that of the I.R. technique. Also, the sensitivity can be easily changed by varying the absorption cell length; hence, this technique has a large dynamic range.

In the case of nitric oxide (NO), Cd(II) lines at $2144\overset{\circ}{\text{\AA}}$ and $2265\overset{\circ}{\text{\AA}}$ and Zn line at $2139\overset{\circ}{\text{\AA}}$ have been used to monochromatically excite a single level of natural NO.^{2,3} The Cd(II) line at $2265.017\overset{\circ}{\text{\AA}}$ is close to both the rotational-vibrational lines of $^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{16}\text{O}$ in the $A^2\Sigma^+ - X^2\Pi_{3/2}$ transition.

Naturally occurring Cd consists of several even and odd isotopes and also Cd(II) lines show large hyperfine structures.⁴ Hence, we used a single isotope of ^{114}Cd , without nuclear spin, for the emission source in order to obtain a sharp line over the magnetic field range of 0-15 kG. The lower and upper states of the Cd(II) line at $2265\overset{\circ}{\text{\AA}}$ are $^2S_{1/2}$ and $^2P_{1/2}$, respectively. This line has only one σ component with the same circular polarization. The shift of $\sigma^{\pm}$ components, ΔV_s , in a magnetic field, H, is expressed by $\Delta V_s (\text{GHz}) = 1.869 H (\text{kG})$ since L-S coupling is valid for this line.⁵

Therefore, we can determine the density of $^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{16}\text{O}$ in an absorption cell by scanning the $\sigma^{\pm}$ components of the $^{114}\text{Cd}(\text{II})$ emission line over the $^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{16}\text{O}$ lines with the field strength of 0~25 kG.

An optical system similar to one reported before was used in this experiment.⁶ Both DC (125 V, 150 mA) and R.F (70 MHz, 10W) power was simultaneously supplied to the MCL light source.⁷ ^{114}Cd O powder (^{114}Cd abundance : 99%) was packed into a cathode pipe of stainless steel. Argon gas was flowed through the light source at a flow rate of 17.3 L/min. and a pressure of 5 Torr. This source was placed between the pole pieces of an electromagnet (Varian Associates, Model V-400 4) which can produce 30 kG in a gap of 7 mm.

The measured temperature of the discharge plasma was 198°C. Thus, the Doppler width of the $^{114}\text{Cd}(\text{II})$ line is 2.0 GHz and the resolving power with this technique is 7×10^5 . A variable phase retarder that utilized the photo-elastic effect was used instead of the Babine Soleile compensator.⁸ $^{15}\text{N}^{16}\text{O}$ gas (98.55%) was prepared by the Oak Ridge National Laboratory.

Figure 1 shows the absorption line profiles of $^{14}\text{N}^{16}\text{O}$, $Q(10\frac{1}{2})$ and $^{15}\text{N}^{16}\text{O}$, $Q(11\frac{1}{2})$ measured using the $\sigma^{\pm}$ components of the Cd(II) line at 2165.017Å. The pressure of both isotopes of NO in the absorption cell was 0.12 Torr and the temperature was 25°C.

The observed line profile is close to a Gaussian type, because the Lorentz and the Holzmarm broadenings are much smaller than the Doppler broadening under these conditions. The relative absorption intensity of these lines is influenced by the Boltzman distribution in the ground state $X^2\Pi_{3/2}$. At this temperature, the calculated population of the molecules in the rotational level of $J = 10\frac{1}{2}$ is 1.107 times larger than

that of $J = 11\frac{1}{2}$. Then, as shown in Figure 1, the absorption intensity of the $^{14}\text{N}^{16}\text{O}$ line is 1.1 times larger than that of the $^{15}\text{N}^{16}\text{O}$ in this experiment. As shown in Figure 1, the observed separation of the $^{14}\text{N}^{16}\text{O}$, $Q(10\frac{1}{2})$ line and the no field $^{114}\text{Cd(II)}$ line was -30.6 GHz, and the observed separation of the $^{15}\text{N}^{16}\text{O}$, $Q(11\frac{1}{2})$ line and the $^{114}\text{Cd(II)}$ line was 19.0 GHz.

Figure 2 shows the relation between the NO lines and the $^{114}\text{Cd(II)}$ line on a frequency axis. The observed separation between the $^{14}\text{N}^{16}\text{O}$, $Q_2(10\frac{1}{2})$ line and $^{14}\text{N}^{16}\text{O}$, $Q_2(11\frac{1}{2})$ has been reported by several researchers as 229.7 GHz.^{9,10} Then, as shown in Figure 2, the observed isotope shift between $^{15}\text{N}^{16}\text{O}$, $Q_2(11\frac{1}{2})$ and $^{14}\text{N}^{16}\text{O}$, $Q_2(11\frac{1}{2})$ becomes 180.1 GHz.

The isotope shift of a rotational-vibrational line is calculated according to the following equation.^{11,12}

$$\begin{aligned} v_1 - v_2 = & (1-p) [We'(v' + \frac{1}{2}) - (We''(v'' + \frac{1}{2}))] \\ & - (1-p^2) [We'x'(v' + \frac{1}{2})^2 - We''x''(v'' + \frac{1}{2})^2] \\ & + (1-p^2) [Be'J'(J'+1) - Be''J''(J''+1)] \end{aligned} \quad (1)$$

where v_1 refers to the ordinary molecule and v_2 to the isotopic molecule, $p^2 = \frac{\mu_1}{\mu_2}$ where μ_1 and μ_2 are the reduced mass for ordinary and isotopic

species, and where We and We_x are the vibrational constants, v is the vibrational quantum number, Be is the rotational constant, J is the rotational quantum number, " and ' refer to the ground state and excited state, respectively.

The molecular parameters for NO are listed in Table 1.¹ The mass numbers used are 14.00307 for ^{14}N , 15.00011 for ^{15}N and 15.99491 for ^{16}O .¹³ The calculated isotope shift between $^{15}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{16}\text{O}$ for the lines of Qz($11\frac{1}{2}$) is 169.7 GHz. Thus, the experimental result of 180.1 GHz agrees with the calculated value within an error of 6%. Furthermore, even in the case of small molecules with sharp lines it would be very rare that a rotational line exactly coincides with these NO lines.

Even NO_2 did not show rotational structure around the $^{114}\text{Cd(II)}$ line because of predissociation. Therefore, in a vast majority of cases this technique does not suffer interference from the background caused by coexisting molecules. This results in a more accurate determination than is achieved by other techniques for isotopic species analysis.

Next, we put naturally occurring NO into the cell. Although the natural abundance of ^{15}N is only 0.37%, we could observe a clear absorption peak due to $^{15}\text{N}^{16}\text{O}$ on the wing absorption of $^{14}\text{N}^{16}\text{O}$ as shown in Figure 3. The signal from $^{14}\text{N}^{16}\text{O}$ was overscaled, but it can be easily measured by reducing the absorption with a shorter cell.

Even if the isotope ratio of $^{15}\text{N}^{16}\text{O}/^{14}\text{N}^{16}\text{O}$ is very small or there is background absorption caused by other molecules, only the additional absorption caused by $^{15}\text{N}^{16}\text{O}$ is measured. The peak height of $^{15}\text{N}^{16}\text{O}$ absorption above the background is not affected by other molecules because, in a vast majority of cases, large molecules do not exhibit rotational structure in the electronic transition region. This is true because the spacing of rotational lines is frequently smaller than the Doppler width and broadening due to predissociation is more likely than with small molecules.

We also determined ^{15}N and ^{14}N abundances in nitric acid.

Nitric acid easily produces NO by reaction with Cu^{14} . The NO produced was introduced into the absorption cell and the absorption by $^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{16}\text{O}$ of the σ^+ components of the $^{114}\text{Cd(II)}$ line was measured. We obtained a linear analytical curve for mixtures of H^{14}NO_3 and H^{15}NO_3 with various mixing ratio. The lower detection limit of the technique was about 50 ppb.

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Table 1. Molecular constants of NO (cm^{-1}).¹

	We	Wex	Be
Excited state ($A^2\Sigma^+$)	2371.3	14.48	1.9952
Ground state ($x^2\Pi_{3/2}$)	1903.68	13.97	1.7046

Figure Captions

- Fig. 1. Absorption line profiles of $^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{16}\text{O}$ observed by $^{114}\text{Cd(II)}$ line at $2265\overset{\circ}{\text{A}}$ (0.12 Torr in 25 mm cell).
- Fig. 2. Relation between NO lines and Cd(II) line at $2265\overset{\circ}{\text{A}}$.
- Fig. 3. Observed peak of $^{15}\text{N}^{16}\text{O}$ in naturally occurring NO (natural abundance of $^{15}\text{N}^{16}\text{O}$: 0.37%).

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APL FIG.3 OBSERVED PEAK OF $^{15}\text{N}^{16}\text{O}$ IN NATURALLY OCCURRING NO (NATURAL ABUNDANCE OF $^{15}\text{N}^{16}\text{O}$ 0.37%)

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