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ROTATIONAL-VIBRATIONAL LINE PROFILES AND ISOTOPE SHIFT OF $^{14}N^{16}O$ AND $^{15}N^{16}O$ MEASURED BY ZEEMAN SHIFTING THE $^{114}Cd(II)$ LINE

Hideaki Koizumi, Tetsuo Hadeishi, and Ralph D. McLaughlin

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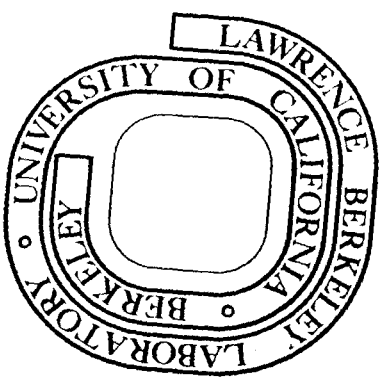

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Rotational-vibrational Line Profiles and Isotope Shift of $^{14}N^{16}O$ and $^{15}N^{16}O$ Measured by Zeeman Shifting the $^{114}Cd(II)$ Line

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The scanning of an emission line by Zeeman effect was originally used for the investigation of hyperfine structures in a mercury resonance line by Mrozowski in 1930.[1] This technique can be extended to high resolution molecular spectroscopy.[2,3] Because the zero field wavelength is accurately known and the Zeeman shifted wavelength is very stable (better than 0.1 GHz/hour), this technique brings more reliable results than tunable lasers at present, and also it can be used in far U.V and V.U.V regions. By using this technique, we measured the profiles of the absorption line of $^{14}N^{16}O$ [$A^2\Sigma$-$X^2\pi_{3/2}$, (1,0), $Q(10\frac{1}{2})$] and that of $^{15}N^{16}O$ [$Q(11\frac{1}{2})$] utilizing the ion line of $^{114}Cd(^2S_{1/2} - {}^2P_{1/2})$ at 2265.017 A. The energy diagram for the connecting transitions in NO γ bands are shown in Fig. 1. J and K are rotational quantum numbers with and without spin, and v is the vibrational quantum number.

Since the γ bands of NO exhibit very sharp rotational structure,[4] the ion lines of Cd at 2265 and 2144 A have been used for the monochromatic excitation of NO.[5~9] Naturally occurring Cd consists of several even and odd isotopes. This causes the line width due to the hyperfine structures to be very large, 15.6 GHz and 14.6 GHz for the lines at 2144 A and 2265 A, respectively.[10] Therefore, a single even isotope ^{114}Cd was used for a radiation source to avoid nuclear spin and isotope shift effects. ^{114}Cd O powder (98.55% ^{114}Cd) was packed in a cathode. The emission from a discharge plasma passed through a hole in an electromagnet in the direction parallel to the magnetic field. The σ^+ and σ^- components were separated by a $\frac{\lambda}{4}$- plate and a linear polarizer.

Both DC (125 V, 150 mA) and RF (70 MHz, 10 W) power were simultaneously supplied to the light source.[11,3] Argon gas was flowed through the source at a rate of 17.3 L/min at 5 Torr. The measured gas temperature of the discharge plasma was 198°C.

The self-reversal of the emission line would be very small because this line is an ion line. Since the pressure broadening at 5 Torr of Ar and the natural broadening are very small, the emission line width is determined by the Doppler broadening.[12] The calculated emission line width at this temperature is 1.92 GHz. Then the resolving power with this technique is 6.9×10^5.

Since L-S coupling is valid for the Cd 2265 A line,[13] and the Lande g values for $^2S_{1/2}$ and $^2P_{1/2}$ states are 2/3 and 2, respectively, then each of the σ^+ and σ^- components has only one line. The shift of these components is given by:

$$\Delta\nu_{\sigma^\pm}\ (\mathrm{GHz}) = 1.867\ H\ (\mathrm{kgauss}).$$

Here, H is the strength of the magnetic field applied to the radiation source.

Figure 2 shows obtained line profiles for the rotational-vibrational lines of $^{14}N^{16}O$ and $^{15}N^{16}O$. The pressure of NO in the absorption cell was 0.12 Torr/of each isotopic species and the temperature was 25°C. The observed line profiles were quasi-Gaussian type, because Lorentzian type broadening is much smaller than Doppler broadening under these conditions. Correcting the emission line width,[14] the width of the absorption line was 4.43 GHz for $^{15}N^{16}O$ and 4.36 GHz for $^{14}N^{16}O$. The calculated Doppler width at 25°C was 2.93 GHz for $^{15}N^{16}O$, 2.98 GHz for $^{14}N^{16}O$. The residual width of about 1.5 GHz might be attributed to unexpected broadening of the emission line or broadening due to the predissociation of NO.

The observed separation from the $^{14}N^{16}O$ line to the $^{114}Cd(II)$ line was -30.8 GHz. The observed separation from the $^{15}N^{16}O$ line to the $^{114}Cd(II)$ line was +19.0 GHz. The separation between the $^{14}N^{16}O$ levels with $J=10\frac{1}{2}$ and $J=11\frac{1}{2}$ has been reported as 7.658 cm^{-1} (229.7 GHz).[15] Then, the isotope shift between $^{15}N^{16}O$ and $^{14}N^{16}O$ becomes 180.1 GHz for the levels with $J=11\frac{1}{2}$. We calculated the isotope shift for this level according

to the theory by Mulliken.[16,17] The values of molecular constants were taken from Herzberg.[18] The calculated isotope shift was 169.7 GHz for this transition. The experimental value agrees with the calculated value within 6% error.

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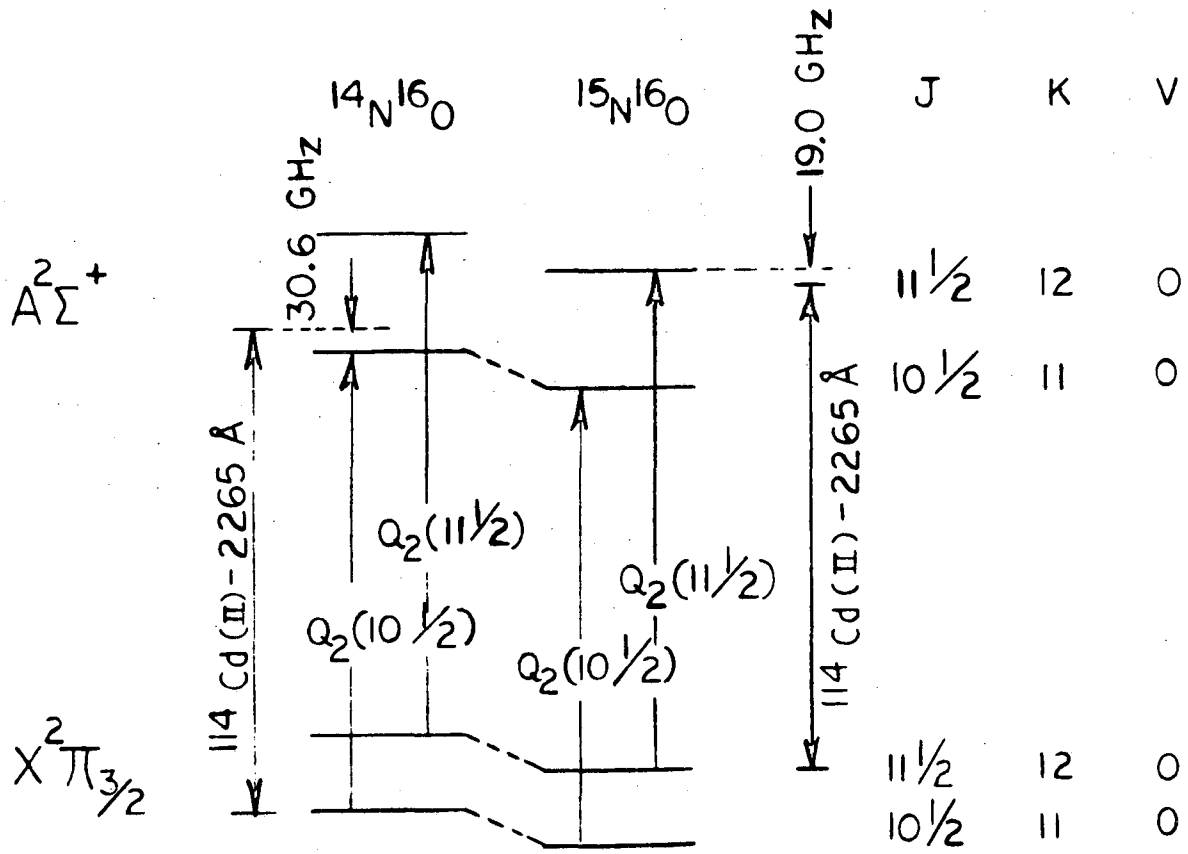
Figure Captions

Fig. 1. Energy levels of NO used in the determination of the isotope shift.

Fig. 2. Absorption line profiles of $^{14}N^{16}O$ and $^{15}N^{16}O$ observed by $^{114}Cd(II)$ line at 2144 A (0.12 Torr in 25 mm cell).



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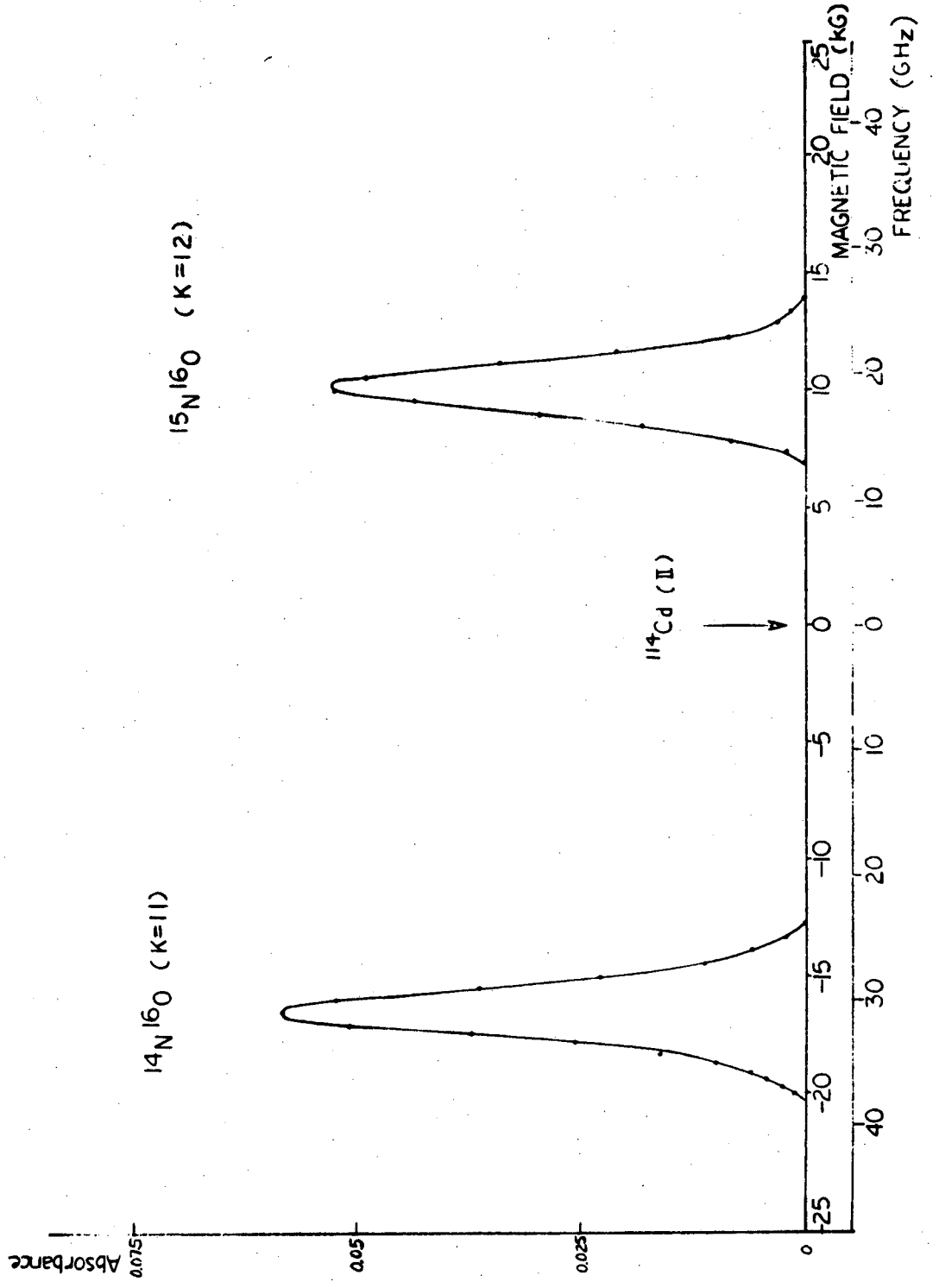

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