

CENTER FREQUENCY OF AMMONIA INVERSION SPECTRUM IN LOW PRESSURE REGION

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ABSTRACT

The center frequency of ammonia inversion spectrum ($J=K=3$) was measured in Kyoto by Stark modulation atomic clock of absorption type (1) with reference to Tokyo UT2. The measured value of the center frequency was corrected using the pressure dependence which was measured by the author (2). Stark coefficient was also determined to be 23.52 ± 0.04 c/(volt/cm)². Error due to Doppler shift in the frequency measurement was minimized by using 5 Mc/s JJY and by a long time comparison of the JJY signal with 100 kc crystal oscillator (3). The center frequency of the spectrum was determined from a long time comparison with the astronomical frequency standard (JJY) from February to October in 1957 to be

$$23,870,130.05 \pm 0.05^* \pm 0.1^{**} \pm 0.2^{***} (\pm 1.2) \text{ kc/s}$$

reduced to zero pressure on UT2 with ammonia of purity of 94%.

1. Introduction

The center frequency of the ammonia inversion spectrum ($J=K=3$) in low pressure region (below 10^{-2} mmHg) had been considered to be accurately constant until the frequency shift with gas pressure was found (4, 5, 6).

Therefore, the center frequency of the spectrum measured by atomic clock must be expressed, reduced to zero pressure, using the results of the frequency shift. Since the measurements of the frequency shift of the spectrum were performed using the Stark modulation system atomic clock of absorption type when the gas was pure ammonia and when some foreign gas was mixed respectively, the center frequency of the spectrum could be determined, based on Tokyo UT2 to the accuracy of the atomic clock, which corresponds to the comparison of the astronomical time with the atomic time. In the determination, the effect of the Doppler shift of JJY signal received in Kyoto was minimized, by a long time measurement of the center frequency of the spectrum utilizing the different frequencies (10 Mc/s and 5 Mc/s) of JJY.

* error of the atomic clock

** error of the reference (UT2)

*** error due to Doppler effect of JJY of 5 Mc/s (or 10 Mc/s).

Further, in the atomic clock, the cross point frequency, ν_s , (Fig. 1) was directly measured instead of the center frequency at the working pressure, ν_0 , but the latter was accurately determined by the extrapolation of the curve of ν_s versus the square of the Stark field.

2. The determination of the center frequency

The experiment was performed with the same apparatus as in I*, only improved in such a way that the input microwave power to the

cell is continuously changeable from $10 \mu\text{W}$ to $1 \times 10^{-3} \mu\text{W}$, in order that the experiment might be carried out without saturation broadening even below the gas pressure of about $1 \times 10^{-3} \text{mmHg}$. The value of ν_s was directly measured by using the atomic clock and the standard wave JJY (5 Mc/s), and the Stark shift determined by extrapolation from the curves of ν_s versus the square of the Stark field. Then ν_0 was obtained by subtracting the Stark shift from ν_s . Finally it was reduced to zero pressure by extrapolating the upper linear part of the curve in Fig. 5 in I.

(1) Measurement of ν_s

The final accuracy of measured ν_s is estimated to be 4.2×10^{-9} which is affected by the following errors.

a) The error due to random noise $\delta\nu_n$ (1) given by

$$\delta\nu_n = \frac{\pi}{M} (4kTB)^{\frac{1}{2}} \frac{1}{P_i} e^{\alpha_i} \frac{\{(\nu - \nu_0)^2 + (\Delta\nu)^2\}}{2l\alpha_m(\Delta\nu)^2(\nu - \nu_0)},$$

where

M : figure of merit,

B : Band width of detector amplifier,

k : Boltzmann constant,

α_m : maximum absorption coefficient of gas,

l : Stark cell length,

P_i : input microwave power,

$$\alpha = \alpha_c + \alpha_g \begin{cases} \alpha_c : \text{absorption coefficient of the cell,} \\ \alpha_g : \text{absorption coefficient of the gas.} \end{cases}$$

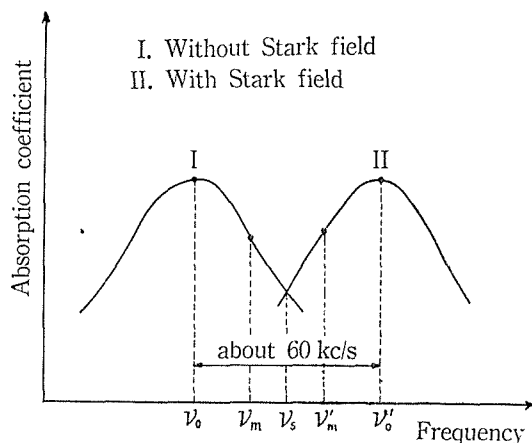


Fig. 1. Absorption curves with and without Stark electric field.

* The preceding paper: "Precise measurement of frequency shift of ammonia inversion spectrum" by the present author is referred to as I.

When the values (1) :

$$\begin{aligned} B &= 1 \text{ c/s}, & P_i &\leq 5 \mu\text{W}, \\ M &= 25, & \nu_s - \nu_0 &\approx 30 \text{ kc/s}, \\ l &= 3 \times 10^2 \text{ cm}, & \alpha_m &= 7 \times 10^{-4} \text{ cm}^{-1}, \\ \Delta\nu &\approx 100 \text{ kc/s}, & \alpha_c &= 7.5 \times 10^{-3} \text{ cm}^{-1} \end{aligned}$$

are used, we have $\delta\nu_n = 28 \text{ c/s}$. Therefore, the error due to random noise is less than 1×10^{-9} , but experimentally it was less than 2.0×10^{-9} .

b) The error due to gas dispersion, $\delta\nu_d$, given, after some calculations, by the following expression (1) :

$$\delta\nu_d \leq \frac{1}{2} e^{-\alpha l} |I'| \frac{\lambda_g}{\lambda_0} \Delta\nu,$$

if

$$(\nu_s - \nu_0)^2 \ll \Delta\nu^2,$$

where

$$\begin{aligned} l &= 3 \times 10^2 \text{ cm} : \text{ Stark cell length,} \\ \lambda_g &= 1.55 \text{ cm} : \text{ guide wavelength,} \\ \lambda_0 &= 1.25 \text{ cm} : \text{ wavelength in free space,} \\ \Delta\nu &\approx 10^9 \text{ c. p. s.,} \end{aligned}$$

$$|I'| = |I'_i \cdot I'_o|$$

with I'_i : input reflection coefficient,

I'_o : output reflection coefficient,

ν_s : frequency of the cross point of the two curves when Stark field is off and on.

ν_0 : center frequency of the absorption curve at working pressure of the atomic clock.

If $|I'| \leq 1 \times 10^{-2}$, $\delta\nu_d = 60 \text{ c/s}$. Therefore, the error due to gas dispersion is less than 2.5×10^{-9} . In the experiment, adjusting the microwave circuit, $|I'|$ could be made less than 1×10^{-2} and the measurement using a phase shifter gave the error less than 2.0×10^{-9} .

c) The error due to the uncertainty of the Stark field. It was experimentally less than 2.4×10^{-9} .

d) The error due to the frequency shift with pressure change (7). It was experimentally less than 2.0×10^{-9} , averaged over more than 5 measurements, with the pressure of the gas indirectly measured by measuring $\Delta\nu$ and the gas purity higher than 94%.

All the errors are considered to be independent of each other. Therefore, the final accuracy of measured ν_s is given by

$$(2.0^2 + 2.0^2 + 2.4^2 + 2.0^2)^{1/2} \times 10^{-9} = 4.2 \times 10^{-9}.$$

The frequency comparison of ν_s was chiefly done with 5 Mc/s JJY as mentioned before, at 9 a. m. and 3 p. m. every day through six days of each week. Then the

error due to Doppler shift could be reduced (3) within 1×10^{-8} . But during daytime, the field intensity of 5 Mc/s JJY is usually weak and when it was so weak that the frequency measurement was impossible, 10 Mc/s JJY was used which is usually strong in daytime, but then the error due to Doppler shift becomes larger up to 5×10^{-8} . Five values of ν_s obtained at each measurement were averaged. These measurements of ν_s on UT2 were performed from February to October, 1957, by 5 Mc/s and 10 Mc/s JJY.

(2) *Measurement of Stark shift ($\nu_s - \nu_0$)*

It is the most accurate and simple way of getting ν_0 from ν_s , to extrapolate to the zero Stark field the curves which show ν_s versus square of the Stark field for various pressures, because at the Stark field below 5 volt/cm, the loop gain of the frequency control loop was experimentally sufficient and the error of the measured ν_s was below 2×10^{-9} . Since the impedance matching of the Stark cell is more difficult

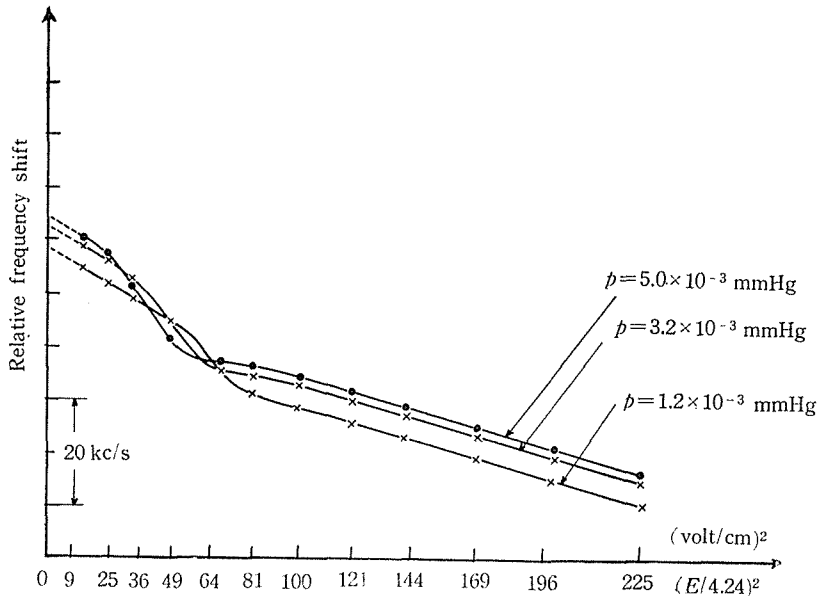


Fig. 2. ν_s versus square of Stark field at various pressures of ammonia of purity of 94%.

in the wide frequency range, the source modulation method of getting ν_0 is a simple way but may be less accurate than that of the extrapolation of the curves. Fig. 2 shows ν_s versus square of Stark field at various pressures of ammonia of purity of 94%. The kinks in the curves seem to be caused by the splitting-up of the spectral line into 23 components (8) in a weak field and the sudden change of the envelope

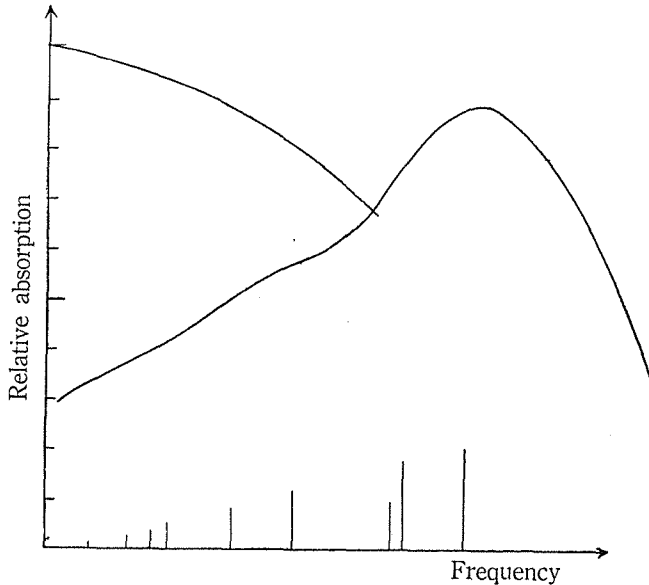


Fig. 3. Stark splitting of the spectrum and its envelope in the weak field, nine major components being plotted out of 23 altogether.

of the components near 9 volt/cm Stark field (Fig. 3). The Stark voltage was measured to the accuracy of 2×10^{-4} by using an amplifier with chopper and two standard cadmium cells (1). The precisely measured value of Stark field intensity can be used to determine the Stark coefficient of the spectrum so far as the absorption curve may be considered to shift with the shape unchanged in a weak Stark field. The value $23.52 \pm 0.04 \text{ c}/(\text{volt}/\text{cm})^2$ (at $E=61.98 \text{ volt}/\text{cm}$ and $\Delta\nu=150 \text{ kc}/\text{s}$) was obtained in this way.

(3) Frequency shift due to self-broadening

The frequency shift of the spectrum due to pressure change was found (4, 5, 6) and precisely measured (2) first when the gas was pure ammonia and when some foreign gas was mixed respectively. Figs. 5 and 7 in I show frequency shift *versus* p and frequency shift *versus* $\Delta\nu_p$ respectively. Fig. 8 in I also shows the frequency shift when some foreign gas is mixed. The value $(2.8 \pm 0.1) \times 10^{-2}$ of a , the ratio of frequency shift to $\Delta\nu_p$ (pressure broadening) and the value $(0.77 \pm 0.1) \times 10^{-2}$ of the ratio of frequency shift to pressure are used to calculate the center frequency at zero pressure from ν_0 at the working pressure of the atomic clock.

Finishing the above-mentioned processes, the center frequency of the spectrum at zero pressure was determined on UT2. Fig. 4 shows the center frequency *versus* time in month, which was obtained from ν_s . The center frequency of the ammonia 3,3 line was determined to be

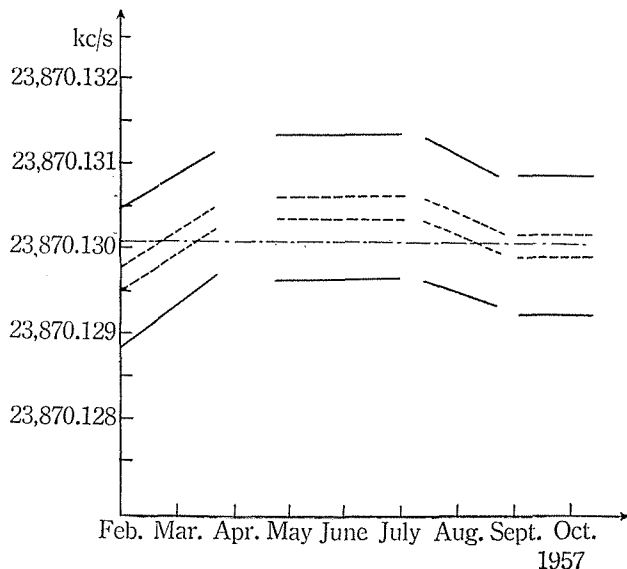


Fig. 4. Center frequency *versus* time in month. When compared with 5Mc/s JJY, it is limited between two dotted lines indicated whereas when with 10Mc/s JJY, it is limited between two solid lines.

$$23,870,130.05 \pm 0.05^* \pm 0.1^{**} \pm 0.2 \text{ kc}^{***} (1.2 \text{ kc/s})$$

from February to October in 1957 reduced to zero pressure on UT2, where * denotes the error of the atomic clock, ** the error of the reference (UT2) and *** the error due to Doppler shift of JJY of frequency 5 Mc/s (or 10 Mc/s). In the above determination, the shift due to $\Delta\nu_w$ (wall collision broadening) was neglected, though it was not certain whether it existed. The center frequency given above is lower than the value by K. Shimoda (9), namely :

$$23,870,131.05 \pm 0.05 \text{ kc/s,}$$

on UT2, reduced to zero pressure with $a = 0.4$, measured by Stark, source and Zeeman modulation atomic clock, with circular waveguide, but purity of ammonia unspecified, while it is larger than the value by Sugiura and Hatoyama *et al.* (10), namely :

$$23,870,129.31 \pm 0.05 \text{ kc/s,}$$

on UT2, reduced to zero pressure with $a = 0.18$, measured by source modulation atomic clock, with *K* band wave guide, but purity of ammonia unspecified.

These three values of the center frequency do not agree within the experimental error. This seems to be connected with the disagreement of the values of a which will be in part explained by the circumstance that the partial pressure of the ammonia was not measured in the experiments by the others than the present author.

3. Conclusion

The accuracy of the absorption type atomic clock which utilizes ammonia inversion spectrum as a frequency standard had been considered to be mainly limited by the errors due to the detection of the spectral line, neglecting the effect of a as being very small. On the contrary, the value of a is considerable and it affects the center very frequency through the gas pressure, as can be seen. The value of a was measured for three different types of atomic clock and the three values agreed with each other in the order of magnitude. So, to obtain the atomic clock of the final accuracy better than 1×10^{-9} , the gas pressure must be kept within the error of 1×10^{-2} in 10^{-3} mmHg region. It is almost impossible, however, by the present vacuum technique. To keep the constancy of the total gas pressure in the cell might be realized, for instance, by supplying fresh ammonia gas very slowly into the cell from a large gas container attached. However, to keep the constancy of the partial pressure of ammonia within the error of 1×10^{-2} in 10^{-3} mmHg is another difficulty. Even if it is possible, for obtaining the atomic clock of the accuracy better than 1×10^{-9} , the molecular beam method seems better than the absorption method. But the frequency shift connected with a may also happen in the molecular oscillator using ammonia gas (11), although the amount of the shift is far smaller than that in the absorption type atomic clock.

Theoretically, Tomita's theory (12), which is based upon Anderson's impact theory, is most accurate but does not agree so well with the experimental results. He ascribed the difference of the theory from the experiment to the rough assumption, since he assumed that the perturber should pass straightly with uniform velocity. But when foreign gas exists, his theory cannot explain the negative value of a .

According to the phase shift theory (13), if the potential of interaction of two molecules is assumed to be of the form

$$V = \frac{B}{r^n},$$

where B is a certain constant and r the intermolecular distance, the value of a vanishes and $n=3$ for the dipole-dipole interaction, and otherwise the higher n , the smaller a . But by this theory, the negative value of a when foreign gas is mixed cannot be explained either.

Further experiments of the frequency shift when foreign gas is mixed for various samples and by various mixing methods are now in progress. Table I in the preceding paper (I) shows no correlation existing between dipole-moment and a . For the purpose of measuring more precise partial pressure of ammonia under the working conditions, the mass-spectrometer or some other equipment working with the atomic clock may be necessary.

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