

## PRECISE MEASUREMENT OF FREQUENCY SHIFT OF AMMONIA INVERSION SPECTRUM

BY

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### ABSTRACT

The shift of the center frequency of an ammonia inversion spectrum ( $J=K=3$ ) was accurately measured, when the gas was pure ammonia and when some foreign gas was mixed, respectively. The value of  $a$  which is the ratio of frequency shift to  $\Delta\nu_p$  (pressure broadening) was determined to be  $(2.8 \pm 0.1) \times 10^{-2}$ , the ratio of frequency shift to gas pressure to be  $(0.77 \pm 0.02)$  Mc/mmHg, and the collision broadening parameter  $\kappa$  to be  $(27.5 \pm 0.1)$  Mc/mmHg, when the ammonia purity is about 94% and the half-half width,  $\Delta\nu = 350$  kc/s.

### 1. Introduction

Atomic clocks (1~5) of different types based on the constancy of the spectral frequency have been studied and constructed. Thus, the center frequency of the ammonia inversion spectrum had been considered to be accurately constant at sufficiently low pressures. It was, however, found in the course of research on the Stark modulation atomic clock (5) by the author and his coworkers, that the frequency given by this atomic clock does shift downward with the decrease in the ammonia gas pressure (6~8).

Then, the frequency given by the atomic clock was plotted *versus* the square of Stark electric field for various pressures of the ammonia gas, and the curves thus obtained all became very nearly parallel straight lines (Fig. 1). From this, the above frequency shift

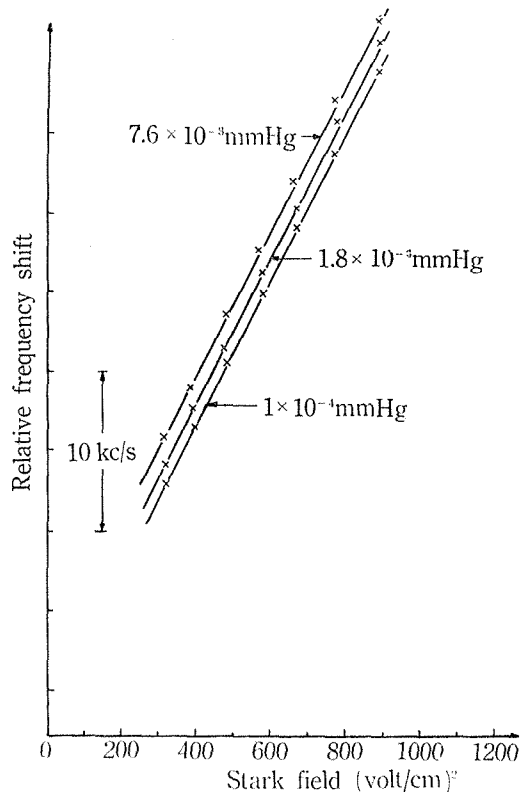


Fig. 1. Frequency *versus* square of Stark field intensity for various pressures.

can be ascribed to the shift of the center frequency of the used inversion spectrum. The measurement of the frequency shift was done about the pure ammonia and about the gas mixed with some foreign gas, respectively.

## 2. Experimental apparatus

For the measurement of the frequency shift and the half-half width  $\Delta\nu$ , a frequency comparator and a quartz chronometer (100 kc/s) were used. The former is a component of the atomic clock (Fig. 2) and illustrated in Fig. 3, and the latter has a stability better than  $1 \times 10^{-7}$ /day and an accuracy almost the same as the original accuracy ( $2 \times 10^{-8}$ ) of the JJY signal. In fact, the above quartz chronometer was calibrated by using the standard waves of 5 Mc/s from JJY. Though the radio waves reflected by the ionosphere are accompanied by the frequency shift (Doppler effect) caused by the movement of the ionosphere, the author has ascertained from his long time observation (9) that during daytime there occurs ordinarily no Doppler shift as large as  $1 \times 10^{-8}$  in the 5 Mc/s waves received in Kyoto.

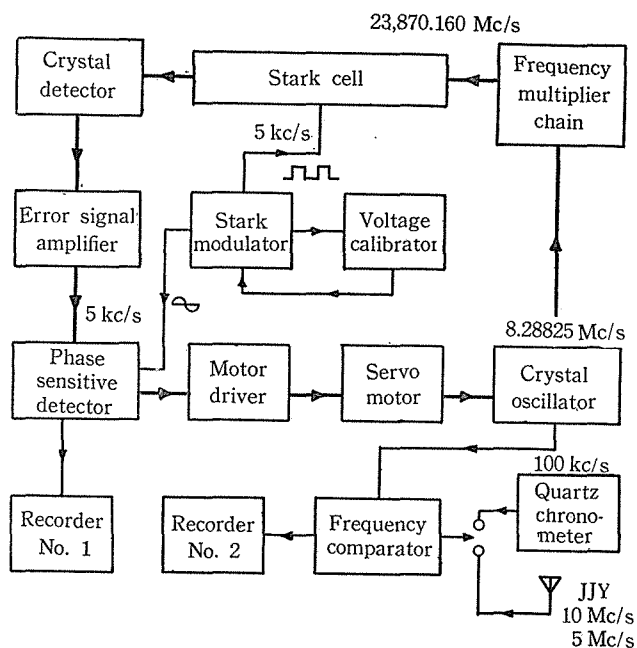


Fig. 2. Construction of the atomic clock.

The Stark cell consists of a brass X-band wave guide section 2 meter long and the absorption coefficient of the cell is about 1 db per foot. The Stark electrode is made of copper plate 0.5 mm thick and supported by teflon spacers (Fig. 4). Each end of the Stark cell is connected with a tapered section 20 cm long followed by a matching section and then by a ferrite uniguide, with a phase shifter between the

uniguide and the matching section on the output side of the cell. The phase shifter is used to test the matching of the microwave circuit. It has a voltage standing wave ratio within 1.11 at about 23,870 Mc/s and can shift the phase of the input microwave signal by more than  $3/4 \lambda_g$  ( $\lambda_g$ : guide wavelength).

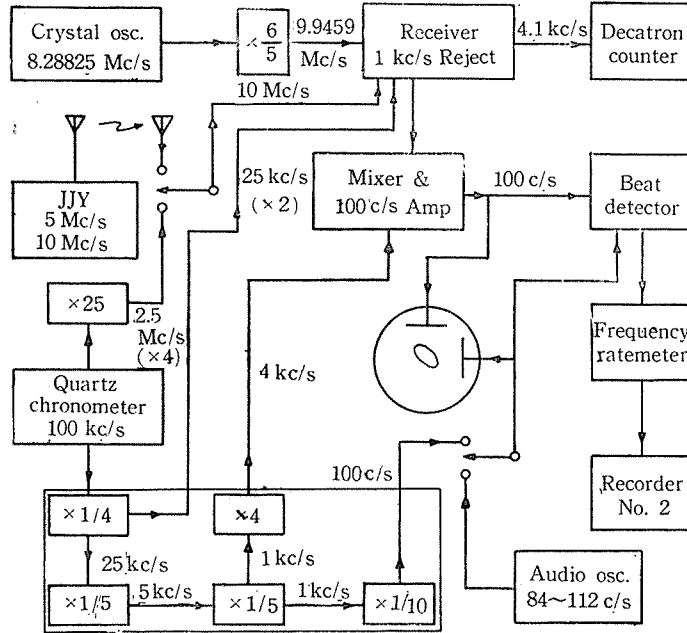


Fig. 3. Block diagram of the frequency comparator.

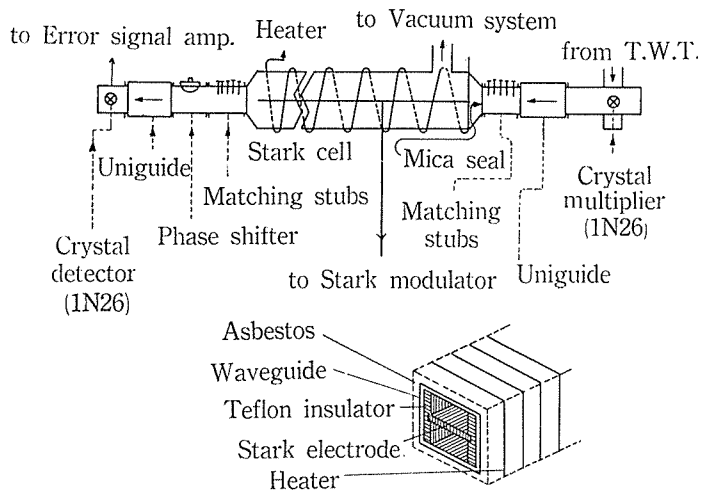


Fig. 4. Microwave circuit and cross section of Stark cell.

The input microwave to the Stark cell of the frequency 23,870 Mc/s is about  $6 \mu\text{W}$  in power, too weak to cause saturation broadening (11) and is produced by frequency multipliers of various types from the crystal oscillator of the frequency 8.28825 Mc/s and has an enough signal to noise ratio, since it was ascertained by a beat measurement at 8,000 Mc/s with another crystal controlled frequency standard.

In order to keep the wall temperature of the Stark cell constant, a heating wire was wound on the outside of the cell through the whole length with asbestos sheets as separator, and a mercury thermostat was set at the center so as to contact tightly with the wider face. This is absolutely necessary :

- (a) to be used when eliminating the substitution effect which is to be later described,
- (b) to keep the pressure of ammonia constant because it changes due to the variation in the adsorption by the wall with the wall temperature even if the cell is completely outgased,
- (c) to keep  $\Delta\nu$  constant, since it may change with the gas temperature.

In the experiment, the cell wall was kept at the temperatures: 44.4, 40.8, 36.8,  $31.9 \pm 0.3^\circ\text{C}$ .

The pressure measurement of the gas was done by using both Pirany gauge and vibration type quartz fiber pressure meter (14). The former is suitable for fast and continuous measurement but has zero point drift, while the latter takes more time for measurement (about 30 seconds at  $4.2 \times 10^{-3}$  mmHg) but has an absolute accuracy better than  $5 \times 10^{-2}$  in the pressure region about from  $1 \times 10^{-4}$  mmHg to  $2 \times 10^{-2}$  mmHg.

### 3. Experimental procedure

Before the measurement of the frequency shift, the calibration of the quartz chronometer has to be finished. Then, the ammonia gas is introduced into the Stark cell and set at the working pressure of about  $2 \times 10^{-3}$  mmHg and the matching of the microwave circuit is completed by means of two matching sections which have each five matching stubs. The five stubs on each side of the cell are adjusted to ensure that the frequency of the atomic clock does not vary with the phase change of the microwave. This is necessary to eliminate errors due to gas dispersion (5). The final accuracy of the atomic clock depends on this adjustment. When adjusting, the frequency is counted by the frequency comparator against the phase change artificially caused by the phase shifter.

The measurement of  $\Delta\nu$  was carried out with the frequency control loop open, by changing manually the frequency of the crystal oscillator within 100 c/s at 8.28825 Mc/s to trace the two absorption curves (with and without Stark field).

By detecting the maximum points of the 5 kc/s error signal, the frequencies  $\nu_m$

and  $\nu'_m$  of the maximum gradient of the curves can be determined.

$\Delta\nu$  is calculated from  $\nu'_m - \nu_m$  (6) in this case when the modulation frequency is 5 kc/s and the sweep width is about 60 kc/s. The stability of the crystal oscillator of the atomic clock with the servo-loop open is better than  $2 \times 10^{-8}$  during one measurement which takes about 30 seconds. But the final accuracy of  $\Delta\nu$  is limited by the signal to noise ratio of the frequency comparator and estimated to be  $1 \times 10^{-7}$  or 2.5 kc/s at 23,870 Mc/s.

The measurement of the shift of the center frequency was carried out by measuring the frequency  $\nu_s$  (the frequency of the cross point of the two curves) by the frequency rate meter of the frequency comparator with the servo-loop closed.

#### 4. Substitution of ammonia molecules

As reported before (7, 8, 9), the center frequency shifts downward for a few days after the introduction of the gas into the Stark cell. So the sample gas contained in the cell for 7 days was analyzed by means of mass-spectrometer and the result showed the remarkable decrease in the partial pressure of the ammonia gas (in an extreme case, from 94% to 20%). This fact corresponds to the substitution of ammonia molecules by foreign gas molecules contained in the cell wall and the frequency shift downward can partially be explained by the decrease in the partial pressure of ammonia gas.

The substitution, on the other hand, seems to occur connected with the adsorption (11) by, and the evaporation from, the cell wall at different temperatures.

In turn, the measurement of the frequency shift of ammonia spectrum is expected to give a means to investigate the adsorption character of a wall.

#### 5. Frequency shift by self-broadening

To eliminate the substitution effect, the Stark cell was treated in the following way, before it was used. The cell was kept at the pressure of about  $2 \times 10^{-5}$  mmHg and at the temperature of about 45°C during daytime and left off pumping and heating in the night for 3 weeks and then it was filled with dense fresh ammonia gas (of purity of about 94%) for a full week.

The above gas and cell were used, with the pressure reduced to the working value (about  $2 \times 10^{-3}$  mmHg). The measured values of the center frequency and  $\Delta\nu$  using the above gas and cell completely coincided with those using ammonia gas of purity of 94% which value was checked by mass-spectrometer analysis. Thus, it is certain that the cell treated in the above-mentioned way is completely free from the substitution effect.

Fig. 5 shows the frequency shift *versus* the pressure of ammonia gas,  $p$ . The

upper part of the curve (in the pressure region above some  $3 \times 10^{-3}$  mmHg) is quite straight and the lower part makes downward deviation from the straight line. The latter might be less reliable since the measurement of the partial pressure in the lower pressure region is far more difficult than in the larger.

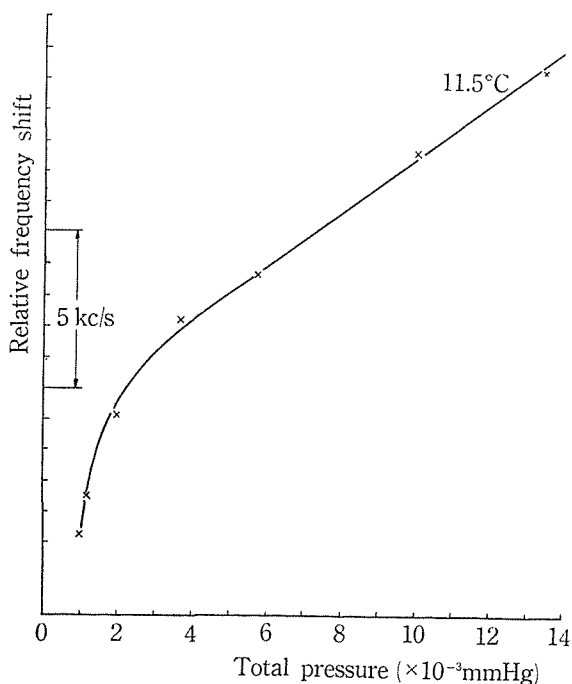


Fig. 5. Frequency shift *versus* pressure of ammonia gas. The cell wall temperature is indicated.

The frequency shift relative to the ammonia pressure was determined to be  $0.77 \pm 0.02$  Mc/s/mmHg at  $\Delta\nu = 350$  kc/s. Therefore, in order to realize a precise frequency standard of an accuracy better than  $5 \times 10^{-9}$  using the ammonia spectrum ( $\nu_0 = 23,870$  Mc/s) at the gas pressure of about  $2 \times 10^{-3}$  mmHg, the fluctuation of the partial pressure of ammonia gas should be kept within 14% or  $2.8 \times 10^{-4}$  mmHg.

Fig. 6 shows  $\Delta\nu$  *versus*  $p$ . Since the wall collision broadening  $\Delta\nu_w$  and the Doppler broadening  $\Delta\nu_d$  are considered constant, so that the result can be represented, if it is assumed that  $\Delta\nu_p/p = \kappa$  is constant (12), by the expressions (2, 18):

$$\begin{aligned} \Delta\nu &= \Delta\nu_p + \Delta\nu_w + \Delta\nu_d && \text{below some } 4 \times 10^{-3} \text{ mmHg,} \\ \Delta\nu &= \{(\Delta\nu_p + \Delta\nu_w)^2 + (\Delta\nu_d)^2\}^{1/2} && \text{between some } 4 \times 10^{-3} \text{ and } 1.6 \times 10^{-2} \text{ mmHg,} \\ \Delta\nu &= \{(\Delta\nu_p)^2 + (\Delta\nu_w)^2 + (\Delta\nu_d)^2\}^{1/2} && \text{above some } 1.6 \times 10^{-2} \text{ mmHg,} \end{aligned}$$

where  $\Delta\nu_w$  and  $\Delta\nu_d$  are assigned respectively the values 52.6 kc/s and 34.9 kc/s which are calculated from

$$\Delta\nu_w = 5 \left( \frac{a+b}{ab} \right) \left( \frac{T}{M} \right)^{1/2} \text{ kc/s (14),}$$

$$\Delta\nu_d = 3.58 \times 10^{-7} \left( \frac{T}{M} \right)^{1/2} \nu_0 \text{ kc/s (15),}$$

when  $T=274^\circ\text{K}$  and X-band wave guide is used.

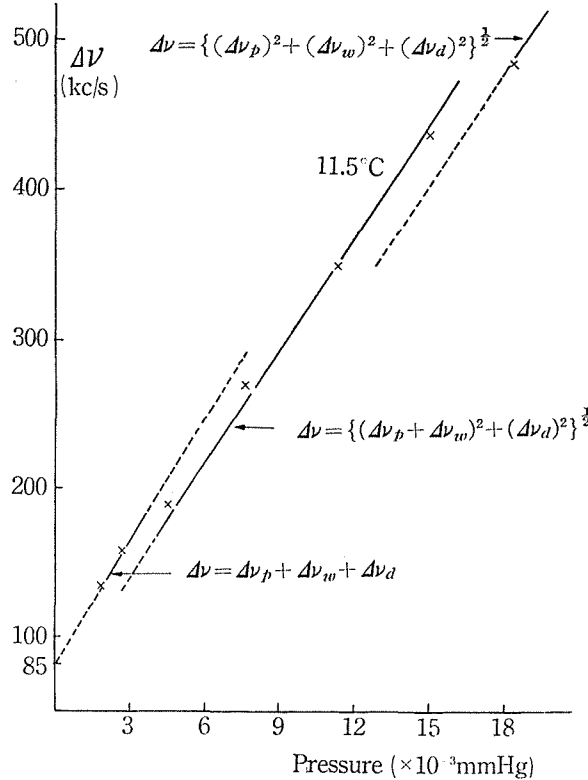


Fig. 6.  $\Delta\nu$  versus pressure of ammonia gas. The cell wall temperature is indicated.

The value of  $\Delta\nu_w + \Delta\nu_d$  at  $p=0$  obtained by extrapolation from the curve  $\Delta\nu = \Delta\nu_p + \Delta\nu_w + \Delta\nu_d$  becomes  $85 \pm 2$  kc/s, which agrees well with the value 87.5 kc/s resulting from the values  $\Delta\nu_w = 52.6$  kc/s and  $\Delta\nu_d = 34.9$  kc/s in the above.

Thus, the relation  $\Delta\nu_p = \kappa p$  and the expressions for  $\Delta\nu$  might be demonstrated to hold in the pressure region  $1 \times 10^{-2}$  to  $2 \times 10^{-2}$  mmHg, and collision broadening parameter  $\kappa$  was determined to be  $27.5 \pm 0.1$  Mc/s/mmHg. Fig. 7 shows the frequency shift versus  $\Delta\nu_p$  which was derived from Fig. 5 by using the relation  $\Delta\nu_p = \kappa p$ . The absorption coefficient  $\alpha$  is given by the expression (17):

$$\alpha = \frac{\alpha_0 (\Delta\nu_p)^2}{(\nu - \nu_0 \pm a \Delta\nu_p)^2 + (\Delta\nu_p)^2},$$

where  $\nu_0$  is the center frequency of the absorption curve and  $\alpha_0$  is the absorption coefficient at  $\nu=\nu_0$ . The value of  $\alpha$  was determined to be  $(2.8 \pm 0.1) \times 10^{-2}$  at  $\Delta\nu=350$  kc/s which is selected since it is situated on the linear part and when the ammonia purity is about 94%. At lower pressures, the larger values are obtained. Tomita\* gave the value 0.18 theoretically.

The temperature dependence of frequency shift (19) and  $\Delta\nu$  had been one of the research items, but the author was unable to finish it because of the following circumstances. To obtain a measurable change in  $\Delta\nu$ , it is necessary to make a considerable change in the temperature as large as  $100^\circ\text{C}$  at least. It is, however, connected with some difficulties, since a large temperature variation causes partial pressure change due to both or either of the selective adsorption and the substitution effect excited in the cell and further in the present case, teflon spacers cannot stand such a large temperature variation.

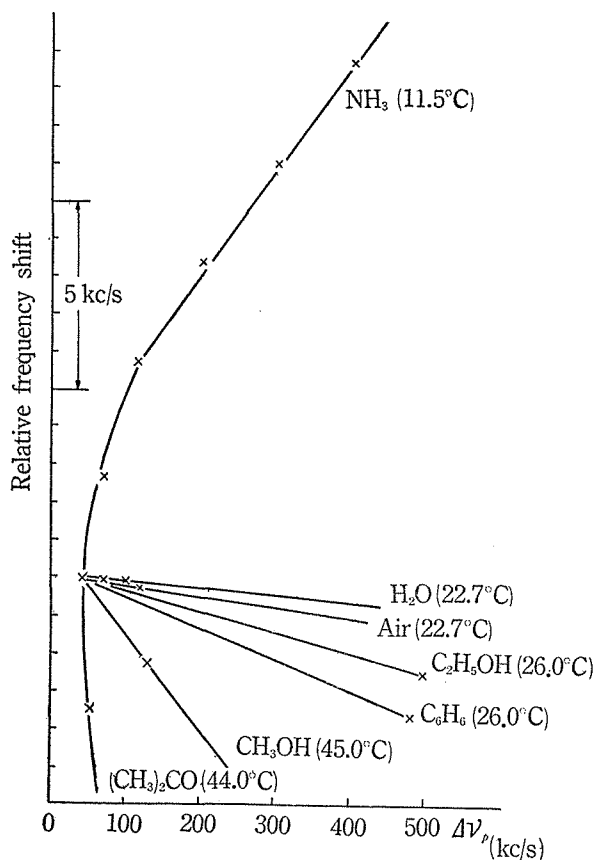


Fig. 7. Frequency shift *versus* pressure broadening. The cell wall temperature is indicated for each curve.

\* Reported before the meeting of Physical Society of Japan, April, 1957. See also Reference (22).



### 6. Frequency shift when foreign gas is mixed

The frequency shift of ammonia inversion spectrum was also measured when some foreign gas was leaked into the cell containing the ammonia gas at the pressure of about  $2 \times 10^{-3}$  mmHg and  $\Delta\nu = 140$  kc/s. Fig. 8 shows the frequency shift *versus*  $\Delta\nu_p$  of ammonia gas, each line being specified by the name of leaked foreign gas. All values of  $a$  have become negative, as shown in Table I and the author is sure of this result, though it is inexplicable for the present. Fig. 8 shows also the frequency shift of ammonia gas when the foreign gas was mixed at equal pressures before the introduction of the gas into the Stark cell. The measurement gives also the negative

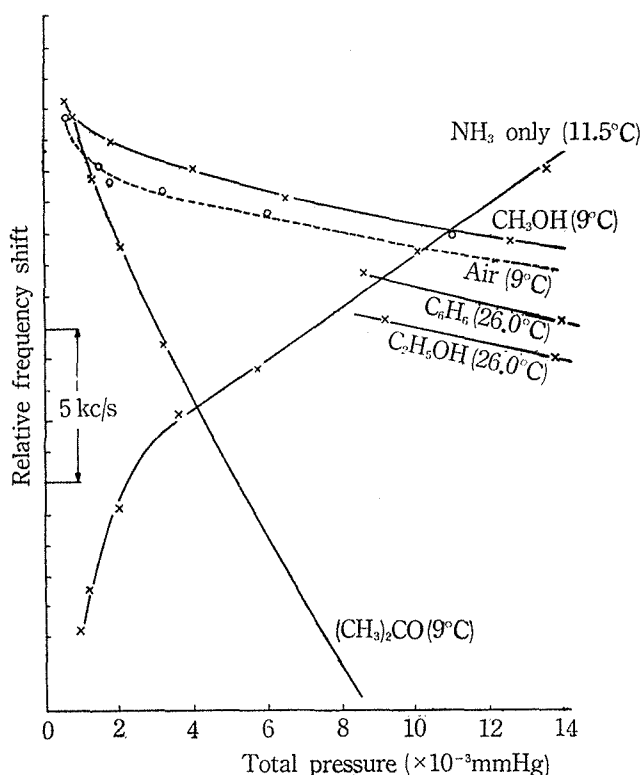


Fig. 8. Frequency shift *versus* total gas pressure. The cell wall temperature is indicated for each curve.

value of  $a$  for all the foreign gases. The large shift when acetone was mixed might be considered to be connected with the absorption by acetone at frequencies very near 23,870 Mc/s (20). The author, however, cannot come to any definite conclusion, considering that the absorption lines of acetone at those frequencies are very weak (21), while the used ammonia line is very strong. Either or both of the measurements of frequency shift and  $\Delta\nu$  might be useful for investigation of reaction rate of a gas reacting on ammonia gas.

Table I.

Gas	Molecular dipole moment (in Debye)	Value of $a$
NH <sub>3</sub>	1.47	$(2.8 \pm 0.1) \times 10^{-2}$
Air	0	$-(0.27 \pm 0.05) \times 10^{-2}$
H <sub>2</sub> O	1.8	$-(0.19 \pm 0.05) \times 10^{-2}$
C <sub>6</sub> H <sub>6</sub>	0	$-(0.82 \pm 0.05) \times 10^{-2}$
C <sub>2</sub> H <sub>5</sub> OH	1.7	$-(0.56 \pm 0.05) \times 10^{-2}$
CH <sub>3</sub> OH	1.7	$-(2.5 \pm 0.5) \times 10^{-2}$
(CH <sub>3</sub> ) <sub>2</sub> CO	2.7	$-(36 \pm 10) \times 10^{-2}$

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