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Absolute Intensity Measurement of Infrared Absorption by the Use of CO_2 Laser Source

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The absolute infrared absorption intensities have been measured for the $^{Q}R_0(0)$ line (ν_3 fundamental) of methyl fluoride and the $^{R}R_8(9)$ line (ν_6 fundamental) of methyl iodide by the use of CO_2 laser lines of P(16) and P(8), respectively. The observed intensities, Γ, were: 12500 ± 4300 $cm^2 \cdot mol^{-1}$ for the ν_3 band of methyl fluoride and 1040 ± 40 $cm^2 \cdot mol^{-1}$ for the ν_6 band of methyl iodide.

The absorption intensity of vibration spectrum has been discussed as an intensity integrated over the whole absorption band.[1] This has been largely due to the limited resolution that the dispersion type spectrometers have which is insufficient to observe individual vibration-rotation lines. As the absorption intensities of vibration-rotation lines in the gas phase are often influenced by intramolecular interactions like Coriolis interaction, it is very important to observe intensities of individual vibration-rotation lines separately. Moreover, there are many problems to be examined in conventional intensity measurement of infrared absorptions, the most fundamental arising from the lack of resolution.[1]

From these respects, attention has been focussed on the highly monochromatic property of the laser radiation and an attempt has been made to measure the absorption intensity of a single vibration-rotation line by the use of a laser source. The CO_2 laser was used in this work, because of its ease of construction and handling. Although the output frequencies are not tunable, it is possible to measure absorption intensities by the use of pressure broadening of an absorption line at a relatively high sample gas pressure. The principles of the present work are based upon the ideas proposed by Shimizu *et al.*[2]

The ν_3 band of methyl fluoride and the ν_6 band of methyl iodide have been chosen because their vibration-rotation spectra have been fully analyzed[3–5] and their vibrational intensities have been reported by the use of conventional methods.[6,7]

Experimental

The experimental arrangement is shown in Fig. 1. The instrument was composed of an infrared laser source, a sample cell with Stark plates, and a detecting system. The CO_2 laser used in this experiment as an infrared radiation source was composed of a 2 m water-cooled discharge tube sealed with NaCl Brewster windows, a concave mirror (radius of 5 m), and a plane grating blazed at 10.6 μm (Photo Technical Research, Inc.). The concave mirror and the plane grating made up a laser cavity which was about 2.5 m in length. First order light of the grating was used for the resonant cavity and zero order light was obtained as the output power. The concave mirror was attached on a voice coil in order to finely adjust the cavity length by changing the direct electric current of the voice coil. The laser components were mounted on a steel H-beam.

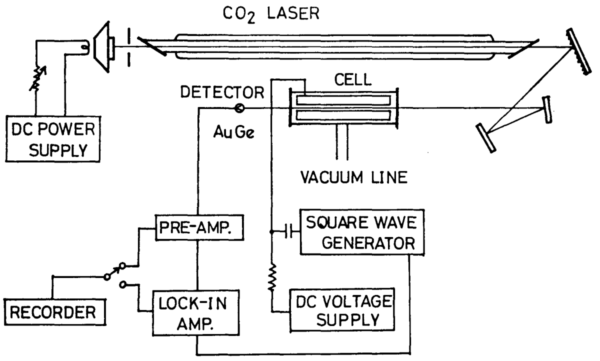

Fig. 1. Block diagram of the experimental arrangement.

The absorption cell was made of Pyrex galss 52.5 cm in length. Parallel aluminum electrodes were installed in the cell for observation of the Stark effect. The electrode glass spacers were 1.31 mm in thickness. In the case of a strong absorption intensity, an absorption cell 10 cm in length was used.

The detecting system consisted of a gold doped germanium detector (Barnes Engineering, A-200), a hand-made preamplifier, a lock-in amplifier (NF Circuit Design Block, LI-573), and a pen recorder (Yokogawa Electric Works, Ltd., 3051). After passing through the absorption cell, the laser beam was detected by the gold doped germanium detector cooled by liquid nitrogen. The output signal from the detector was amplified and recorded by the pen recorder. In the case of the observation of Stark effect of an absorption line, the signal was detected by the standard phase sensitive detection method with square wave modulation of the Stark field. Potential across the electrodes was measured by a voltage divider and a potentiometer. The accuracy and the precision of the voltage measurement were 0.25 and 0.1%, respectively.

An absorption coefficient was determined by the intenstiy ratio of the light passing through an empty cell to that passing through a cell filled with sample gas. Pressure of the sample gas was measured by the use of an oil or mercury manometer, the precision of which was ascertained to be about 5%.

Results and Discussion

Generally, frequency of a laser line does not coincide with that of a molecular absorption line, so the absorption of laser radiation by molecules cannot usually be observed. In the case where the frequency difference between an absorption line and a laser line is small, however, we may observe the absorption of light by increasing the sample pressure and, therefore, by broadening the width of the absorption line. In the case where a line-width is mainly determined by collision broadening, the shape of a molecular absorption line may be approximated by a Lorentzian function. Then, the absorption coefficient, $\alpha(\nu_l)$, of the molecular line at the frequency, ν_l, of laser light is given by the formula

$$\alpha(\nu_l) = \frac{\alpha_0(\gamma_p \cdot P)^2}{(\gamma_p \cdot P)^2 + (\nu_l - \nu_m)^2}, \tag{1}$$

where ν_m is the center frequency of the molecular absorption line, P the sample pressure, γ_p the pressure broadening parameter, and α_0 the constant independent of pressure. α_0 should be equal to the absorption coefficient at the center frequency of the absorption line. Equation 1 is reduced to a more convenient relation as[2)]

$$\frac{1}{\alpha(\nu_l)} = \frac{1}{\alpha_0}\left(1 + \gamma^2 \frac{1}{P^2}\right), \tag{2}$$

where

$$\gamma = \frac{|\nu_l - \nu_m|}{\gamma_p}.$$

Equation 2 shows that the inverse of $\alpha(\nu_l)$ linearly depends on the inverse of P^2. If we measure the absorption coefficients at various pressures and plot $1/\alpha(\nu_l)$ against $1/P^2$, a straight line with a slope of γ^2/α_0 should be generated. The extrapolated $1/\alpha(\nu_l)$ value at $1/P^2 \to 0$ corresponds to the $1/\alpha_0$ value. If a $|\nu_l - \nu_m|$ value is known, the γ_p value may be determined and the value of the transition moment calcualted with α_0 and γ_p values. In the present work, the $|\nu_l - \nu_m|$ value was determined by observing the Stark effect.

TABLE 1. OBSERVED VALUES OF α_0, γ^2, $|\nu_l - \nu_m|$, γ_p, AND $|(\partial\mu/\partial Q)\langle 0|Q|1\rangle|$ FOR ν_3 BAND OF CH$_3$F

	CH$_3$F ν_3	
	P (16)	P (18)
α_0/cm^{-1}	0.072(0.022)	0.47(0.18)
γ^2/Torr^2	7200(2500)	7200(2800)
$\lvert\nu_l - \nu_m\rvert$/MHz	4497	2133
γ_p/MHz Torr^{-1}	53(9)	25(5)
$\lvert(\partial\mu/\partial Q)\langle 0\vert Q\vert 1\rangle\rvert$/Debye	0.224(0.038)	0.329(0.059)

Numbers in parenthesis indicate standard deviations.

ν_3 Band of CH$_3$F. It has been known that the vibration-rotation spectrum of methyl fluoride ν_3 band appears in the 9.4 μm region of the CO$_2$ laser.[3)] This band has been previously studied by Stark spectroscopy using a CO$_2$ laser.[4)] By the aid of these results, the absorption lines of $^{Q}Q_1(1)$ and $^{Q}R_0(0)$ were easily found near the CO$_2$ laser lines of P(18) and P(16), respectively. The absorption coefficients were measured at these two laser lines for various pressures. The measured $\alpha(\nu_l)^{-1}$ values were plotted againts P^{-2} values, the results of which are shown in Fig. 2. The values of α_0 and γ were determined by means of the least-squares method. The $|\nu_l - \nu_m|$ values obtained by Stark spectroscopy were used for the determination of the γ_p values. The resultant values of α_0, γ^2, $|\nu_l - \nu_m|$ and γ_p are shown in Table 1.

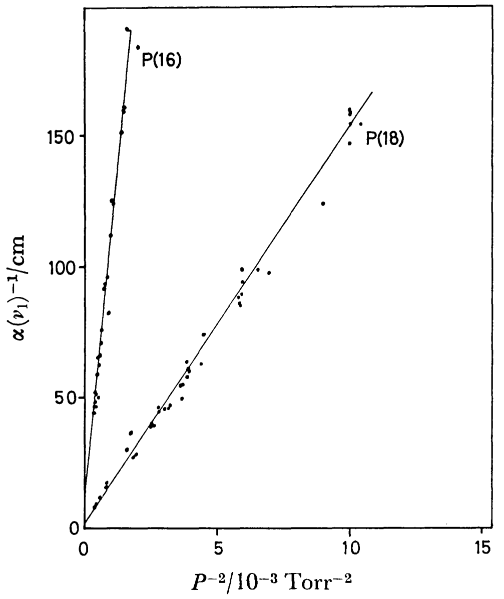

Fig. 2. Plots of measured $\alpha(\nu_l)^{-1}$ against P^{-2} for ν_3 band of CH$_3$F.

The transition dipole moment of ν_3 fundamental, $(\partial\mu/\partial Q)\langle 0|Q|1\rangle$, was calculated from the observed α_0 and γ_p values for the convenience of comparing the present result with the integrated intensity previously observed by conventional infrared techniques. For a symmetric top molecule an absorption coefficient, α_0, is related to a transition dipole moment as[8)]

$$\alpha_0 = \frac{8\pi^2 N_0 \nu_m d g_K g_I}{3ch\gamma_p Z_{R,V}} \exp\left(-\frac{E''}{kT}\right) \times \left\{1 - \exp\left(-\frac{h\nu_m}{kT}\right)\right\} |\Phi_{JK}^{J'K'}|^2 \left|\left(\frac{\partial\mu}{\partial Q}\right)\langle 0|Q|1\rangle\right|^2, \tag{3}$$

where N_0 is the number density of molecules at unit pressure, d the degree of vibrational degeneracy, g_I the nuclear statistical weight, $Z_{R,V}$ the vibrational and rotational partition function, E'' the energy of the initial state, $\Phi_{JK}^{J'K'}$ a matrix element of a direction cosine, and $g_K=1$ for $K=0$ and $g_K=2$ for $K>0$. The value of the transition moment calculated from Eq. 3 is given in the last row of Table 1.

As seen from Table 1, the two values of the transition moments obtained at the laser lines, P(16) and P(18), do not agree with each other . The detailed spectral features of the ν_3 band in the neighborhood of two

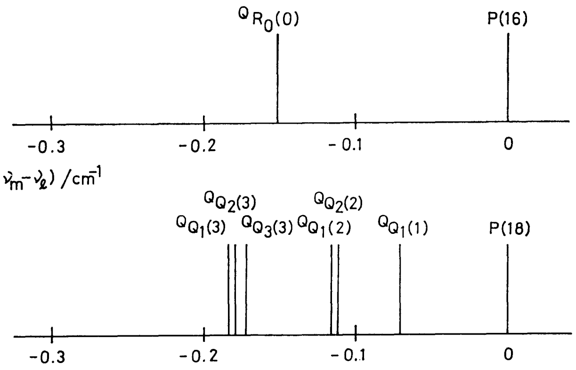

Fig. 3. Detailed spectral features of ν_3 band of CH$_3$F in the neighborhood of P(16) and P(18) laser lines.

laser lines are illustrated in Fig. 3. It is seen from the figure that there is only one absorption line, ${}^{Q}R_0(0)$, in the neighborhood of the P(16) line. In the neighborhood of the P(18) laser line, on the other hand, there are several Q-branch lines ${}^{Q}Q_2(2)$, ${}^{Q}Q_1(2)$, *etc.* in addition to the ${}^{Q}Q_1(1)$ line. Therefore the apparent value of the transition moment obtained from P(18) is expected to be larger than that from P(16), because of the contribution of the neighboring lines to the absorption of the P(18) laser radiation. In order to see the reliability of the observed transition moment value, the magnitude of the absorption of P(18) laser line due to these three absorption lines, ${}^{Q}Q_1(1)$, ${}^{Q}Q_2(2)$, and ${}^{Q}Q_1(2)$, was estimated by the use of the trasition dipole moment value of 0.224 Debye which was observed at the P(16) laser line. The $|\nu_l-\nu_m|$ values of these absorption lines were observed by Stark spectroscopy or calculated from the observed molecular constants.[4] The γ_p values of 25 MHz·Torr^{-1} were assumed for these absorption lines. The estimated pressure dependence of the absorption coefficient is shown in Fig. 4. The pressure dependence of the absorption estimated by taking into account only the ${}^{Q}Q_1(1)$ line is illustrated by the dash-dot line. This accounts for only half of the observed absorption. The absorption coefficient estimated by considering these three lines, ${}^{Q}Q_1(1)$, ${}^{Q}Q_2(2)$, and ${}^{Q}Q_1(2)$, is illustrated by the dashed line in Fig. 4. This explains the observed absorption coefficients very well. The solid line of Fig. 4 expresses the pressure dependence of the absorption coefficient calculated from the parameters given in Table 1. Thus it may be concluded that the transition moment value obtained at P(18) laser line is larger than that obtained at P(16) line because the absorption at P(18) laser line is not originating from a single absorption line, ${}^{Q}Q_1(1)$, but from a number of absorption lines. Consequently, the transition moment value obtained at the P(16) laser line has been adopted as the transition moment of the ν_3 fundamental of methyl fluoride.

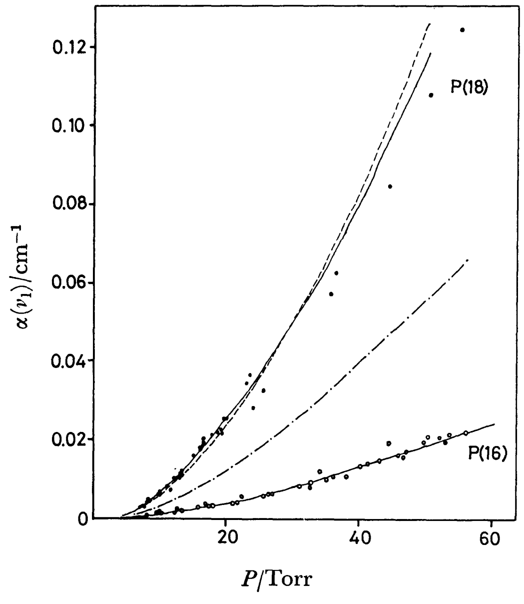

Fig. 4. Observed and estimated pressure dependence of absorption coeficients for CH_3F.

ν_6 Band of CH_3I. The band origin of the ν_6 band of methyl iodide is 882.7 cm^{-1} and a little far apart from the CO_2 laser region. However, the rotational structure spreads over a wide frequency range and, therefore, some of the absorption lines of this band may coincide with the 10.6 μm CO_2 laser lines. From the analysis of the conventional high resolution infrared spectrum[5] and the laser Stark spectroscopy, the ${}^{R}R_8(9)$ lines occurs near the P(8) line of the CO_2 laser. The observed values of $1/\alpha(\nu_l)$ at various pressures are shown in Fig. 5. The values of α_0, γ^2, $|\nu_l-\nu_m|$, and γ_p are calculated by the same way applied for the ν_3 band of methyl fluoride. The $1/\alpha(\nu_l)$ values observed at the pressure higher than 33 Torr were excluded from the least-squares fitting, because the $1/\alpha(\nu_l)$ values observed in this high pressure range were considered to be affected by the absorption of the neighboring lines. As the rotational energy levels of methyl iodide are expected to have hyperfine structures due to the nuclear quadrupole moment of the iodine atom, the ν_m value has been regarded as the center of the

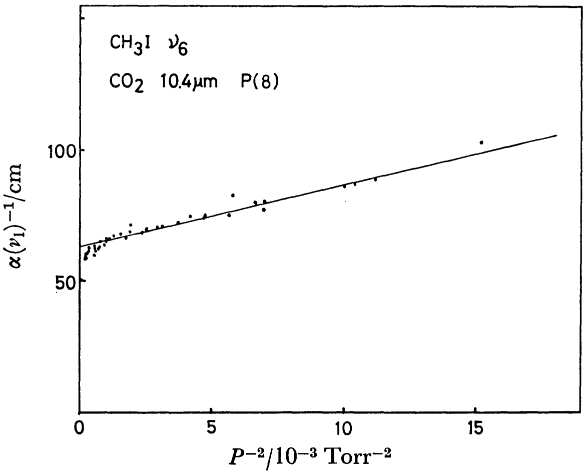

Fig. 5. Plots of measured $\alpha(\nu_l)^{-1}$ against P^{-2} for ν_6 band of CH_3I.

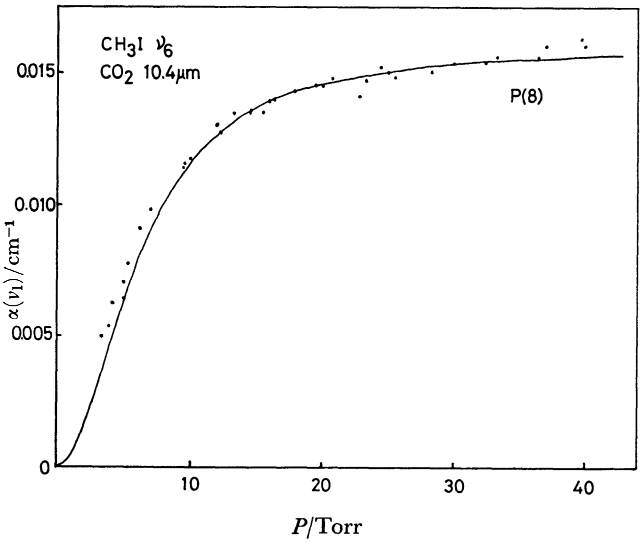

Fig. 6. Observed and estimated pressure dependence of absorption coefficient for CH_3I.

TABLE 2. OBSERVED VALUES OF α_0, γ^2, $|\nu_l-\nu_m|$, γ_p, AND $|(\partial\mu/\partial Q)\langle 0|Q|1\rangle|$ FOR ν_6 BAND OF CH_3I

	CH_3I ν_6
α_0/cm^{-1}	0.0159(0.0002)
γ^2/Torr^2	37.1(2.1)
$\|\nu_l-\nu_m\|$/MHz	55
γ_p/MHz Torr^{-1}	9.03(0.25)
$\|(\partial\mu/\partial Q)\langle 0\|Q\|1\rangle\|$/Debye	0.0455(0.0005)

Numbers in parenthesis indicate standard deviations.

unresolved hyperfine structures. In Fig. 6 the pressure dependence of the absorption coefficient reproduced from the parameters of Table 2 is expressed by the solid line and the observed values by the closed circles.

The uncertainty expected for the observed $1/\alpha(\nu_l)$ value is samll relative to that for methyl fluoride. In the plot of $1/\alpha(\nu_l)$ against $1/P^2$, the slope of the straight line decreases in magnitude as the $|\nu_l-\nu_m|$ values decreases. On the other hand, the dispersion of the resultant $1/\alpha(\nu_l)$ value due to the uncertainty of the pressure measurement is smaller, if the slope of the straight line is small. Therefore, the standard deviation of the resultant $1/\alpha(\nu_l)$ for methyl iodide is much smaller than that for methyl fluoride, because the $|\nu_l-\nu_m|$ value for methyl fluoride is much larger than that for methyl iodide.

Comparison with the Result from Conventioanl Methods. The obtained transition moment value was converted into the absolute absorption intensity value in order to compare the present results with the absorption intensities obtained by conventional methods. The absolute absorption intensity, Γ, which is integrated over the whole absorption band, is defined as

$$\Gamma = \frac{1}{c_B l}\int_{\mathrm{band}} \ln\left(\frac{I_0}{I}\right) d(\ln \nu), \qquad (\mathrm{cm^2\cdot mol^{-1}}), \qquad (4)$$

where c_B is the molecular density in mol·cm^{-3}, l the path length in cm, and the integration covers the whole absorption band. The relation between the absolute absorption intensity, Γ, and the trnasition moment, $(\partial\mu/\partial Q)\langle 0|Q|1\rangle$, is expressed as[1]

$$\Gamma = \frac{4\pi^2 N_A d}{3c\hbar}\left|\left(\frac{\partial\mu}{\partial Q}\right)\langle 0|Q|1\rangle\right|^2, \qquad (5)$$

where N_A is the Avogadro constant, and d the degree of vibrational degeneracy. In Table 3 the Γ values calculated from Eqs. 3 and 5, and the observed α_0 are compared with the Γ values obtained by conventional methods.

For the ν_3 band of methyl fluoride, the Γ value obtained in this work is somewhat larger than those obtained by conventional methods. This might be due to the weak Coriolis interaction between the ν_3 and ν_6 bands.[3] However, since the standard error is considerably large this will not be explored further.

For the methyl iodide ν_6 band, the present result agrees well with that obtained by conventional methods. This indicates that there is no intramolecular perturbaion which influences the absorption intensity in the $|v_6=1>$ state.

TABLE 3. ABSOLUTE INTENSITIES Γ/cm^2·mol^{-1}

	CH_3F ν_3	CH_3I ν_6
This work	12500(4300)	1040(40)
References	9108(260)[6] 9056(906)[7]	1012(26)[7]

Numbers in parenthesis indicate experimental errors.

Conclusive Discussion. This work has shown that the absorption intensity of a single vibration-rotation line of a molecule may be meaured by this method if the frequency of the laser line nearly coincides with that of the molecular absorption line, although the frequency of the laser radiation is not tunable. An accurate intensity value cannot be obtained, in the case that the absorption of the laser line due to plural number of lines occures simultaneously. The accuracy of the observed intenstiy value is governed mainly by the magnitude of the γ-value. For an absorption line with small γ, the intensity may be obtained with high accuracy. On the other hand, the γ-value is determined by the magnitudes of $|\nu_l-\nu_m|$ and γ_p. The γ_p-values are almost 10—50 MHz·Torr^{-1} for usual simple molecules, we can safely conclude that the experimental criterion for the accurate intensity measurement is $|\nu_l-\nu_m|\leq 4$ GHz. It is often difficult to observe the absorption intensities of a series of vibration-rotation lines in a certain vibration band by means of a frequency fixed laser. This method does not appear to be appropriate form obtaining detailed knowledge about the intensity distribution in a vibration band.

Incidentally, a rigorous assignment of rotation-vibration lines is required to apply the present technique to the observation of their intensities.

References

1) M. Davies, Ed, "Infrared Spectroscopy and Molecular Structure," Elsevier Publishing Co., New York (1963), Chap. X.

2) T. Shimizu, F. O. Shimizu, R. Turner, and T. Oka, *J. Chem. Phys.*, **55**, 2822 (1971).

3) W. L. Smith and I. M. Mills, *J. Mol. Spectrosc.*, **11**, 11 (1963).

4) S. M. Freund, G. Duxbury, M. Romheld, J. T. Tiedje, and T. Oka, *J. Mol. Spectrosc.*, **52**, 38 (1974).

5) H. Matsuura and J. Overend, *Spectrochim. Acta, Part A*, **27**, 2169 (1971).

6) S. Saeki, M. Mizuno, and S. Kondo, *Spectrochim. Acta, Part. A*, **32**, 403 (1976). In this report, the integrated intensity is expressed in the unit of A/cm^{-2}·mol^{-1} l. For convenience, we converted the value of A in the unit of Γ/cm^2 mol^{-1} by the use of the relation, $\Gamma=1000\nu_0^{-1}\cdot A$, where ν_0 is the wave number of the band origin.

7) J. W. Russell, C. D. Needham, and J. Overend, *J. Chem. Phys.*, **45**, 3383 (1966).

8) H. C. Allen, Jr., and P. C. Cross, "Molecular Vib-Rotors," John Wiley & Sons, Inc., New York (1963), Chap. 5.