

THE EFFECT OF PRESSURE AND TEMPERATURE ON THE HALF-WIDTH OF THE METHANE ABSORPTION AT 3.39μ

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Abstract—A determination of the self-broadened linewidth of methane at 2947.88 cm^{-1} has been made using a stabilized, single-mode helium-neon laser. The width at half-maximum has been found to be $0.16 \pm 0.01\text{ cm}^{-1}$ at atmospheric pressure. By taking into account neighbouring methane components, the variation of the absorption coefficient in the high-pressure region can also be accounted for. The variation of the linewidth with temperature T has also been determined and was found to be close to T^{-1} . The strength of the methane line nearest the laser emission is $1.76 \pm 0.04\text{ atm}^{-1}\text{ cm}^{-2}$; this line was found to be located $0.002 \pm 0.001\text{ cm}^{-1}$ from the laser emission.

1. INTRODUCTION

THE HELIUM-NEON laser emission at 2947.903 cm^{-1} ⁽¹⁾ almost coincides with the absorption line of methane at 2947.900 cm^{-1} . Hence useful information about the line shape and the absorption constants of methane can be obtained. The laser emission is due to the $3s_2-3p_4$ transition in neon.⁽²⁾ Since the methane molecule has tetrahedral symmetry, the splitting of the lines is complex and the number of split components increases as the rotational quantum number (J) increases. Examination of a high-resolution spectrum of methane published by PLYLER *et al.*⁽³⁾ shows that the ν_3 band of methane has a cluster of components which overlies the position of the helium-neon laser emission. The strongest of these belong to the $J = 7$ part of the P -branch. The strengths and energies of the components of this band of methane have been calculated by KYLE.⁽⁴⁾ The overall theoretical absorption agrees with the experimentally determined absorption to 10 per cent. The narrow bandwidth of the laser emission allows accurate measurements of absorption by methane at the laser-emission frequency. At low pressures, this absorption is mainly due to the 2947.900 cm^{-1} component but, as the pressure increases, the adjacent components have an increasing effect.

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EDWARDS and BURCH⁽⁵⁾ studied foreign-gas-pressure-broadening of the methane line at 2947.900 cm^{-1} and fitted a Lorentzian line shape to the absorption profile. They found the collision-broadened width at half maximum of the absorption line to be $0.13 \pm 0.04 \text{ cm}^{-1}$ at atmospheric pressure, and found the separation of the emission line and the nearest absorption line to be $0.003 \pm 0.002 \text{ cm}^{-1}$. HUBBERT *et al.*⁽⁶⁾ introduced a line profile which included the Doppler-broadening effect. They found the self-broadened linewidth at atmospheric pressure to be $0.15 \pm 0.03 \text{ cm}^{-1}$ and the frequency difference between the line centres of the laser emission and the nearest component of the ν_3 absorption band of methane to be $0.003 \pm 0.001 \text{ cm}^{-1}$.

The aim of this work was to improve the experimental accuracy and hence obtain more precise values of the linewidth at half-maximum and of the line strength. Once these are obtained, the complete pressure dependence of the linewidth can be evaluated. Then, by considering the absorption of the laser emission at various densities and temperatures, the temperature dependence of the linewidth will be found.

2. THEORY

If parallel light from a source emitting a continuous spectrum is sent through an absorption cell, the transmittance $T(\nu)$ is given by Lamberts' Law:

$$T(\nu) = \exp(-k(\nu)x); \quad (1)$$

$k(\nu)$ is the absorption coefficient of the gas at frequency ν , $x = pX$, p being the pressure and X the geometrical path length. This law may break down at large intensities because of saturation effects.

For combined Doppler and collision broadening, it is well known that $k(\nu)$ is given by the Voigt function:⁽⁷⁾

$$k(\nu) = \frac{S(\ln 2)\alpha_0 p}{\Delta\nu_D^2 \pi^{3/2}} \int_{-\infty}^{\infty} \frac{\exp(-x^2) dx}{\left(\frac{\alpha_0 p}{\Delta\nu_D}\right)^2 \ln 2 + \left[\frac{(\nu - \nu_0)(\ln 2)^{0.5}}{\Delta\nu_D} - x\right]^2}. \quad (2)$$

Here S is the line strength, α_0 is the half width due to pressure broadening at 1 atmosphere pressure, p is again the pressure, and $\Delta\nu_D$ is the Doppler half-width. For the contribution of n lines, assuming that α_0 and $\Delta\nu_D$ are the same for each line,

$$k(\nu) = \sum_n \frac{(\ln 2)S'_n \alpha_0 p}{\Delta\nu_D^2 \pi^{3/2}} \int_{-\infty}^{\infty} \frac{\exp(-x^2) dx}{\left(\frac{\alpha_0 p}{\Delta\nu_D}\right)^2 \ln 2 + \left[\frac{(\nu - \nu_0)_n (\ln 2)^{0.5}}{\Delta\nu_D} - x\right]^2}. \quad (3)$$

Temperature dependence of the strength and half width

The line strength and Doppler width will vary only with temperature, whereas the half width will vary both with temperature and with pressure. The primary effect of temperature on the line strength appears in the change in the number of molecules in the lower state of the transition. The full expression of the line strength has the form⁽⁸⁾

$$S = \frac{8\pi N_T}{3hcQ} \nu_0 |R|^2 \exp\left\{-\frac{E}{kT}\right\} \left[1 - \exp\left\{-\frac{h\nu_0}{kT}\right\}\right], \quad (4)$$

where N_T is the total number of absorbing molecules per unit volume and per unit pressure at S.T.P., Q is the internal partition function, E is the energy of the lower level, $|R|^2$ is the absolute value of the square of the matrix element for the transition under study, and h , c , k and T denote, respectively, Planck's constant, the velocity of light, Boltzmann's constant, and the absolute temperature.

The factor $[1 - \exp\{-hcv_0/kT\}]$ is practically equal to unity in the region being studied. Equation (4) can then be expressed in the form

$$S(T) = S(T_0) \frac{Q(T_0)}{Q(T)} \exp \left\{ -1.43877E \left[\frac{1}{T} - \frac{1}{T_0} \right] \right\}, \quad (5)$$

relating the strengths at the two temperatures, where $S(T_0)$ is the strength at temperature T_0 , Q is the partition function, and E is expressed in wave-numbers. If we assume a rigid-rotator temperature dependence,

$$\frac{Q(T_0)}{Q(T)} = \left(\frac{T_0}{T} \right)^{3/2} \quad (6)$$

and we then get from equation (5)

$$S(T) = S(T_0) \left(\frac{T_0}{T} \right)^{3/2} \exp \left\{ -1.43877E \left[\frac{1}{T} - \frac{1}{T_0} \right] \right\}. \quad (7)$$

The effect of temperature on the Doppler width is given by

$$\Delta v_D = \Delta v_{D_0} \left(\frac{T}{T_0} \right)^{0.5}. \quad (8)$$

We assume that the effect of pressure and temperature on the half-width can be expressed as

$$\alpha(pT) \propto f(p)f(T) \quad \text{or} \quad \alpha(pT) = \alpha_0 f(p)/f(p_0)/f(T)/f(T_0).$$

If we consider only the region where pressure broadening is dominant, $f(p)/f(p_0) = p/p_0$ and

$$\alpha(pT) = \alpha_0 \frac{p}{p_0} \left(\frac{T_0}{T} \right)^y \quad (9)$$

where y is the temperature-dependence parameter to be determined.

If experimental measurements are taken in a sealed absorption cell, the density ρ must be included in equation (9) instead of the pressure. The pressure in a sealed cell will vary in proportion to the temperature, but the density will remain constant. If the initial pressure is p_1 and, initially, $T = T_0$, we have $p_1/p_0 = \rho/\rho_0$; using the ideal gas law, we get $p/p_0 = p_1/p_0/T/T_0$ and, hence, from equation (9)

$$\alpha(pT) = \alpha_0 \left(\frac{p_1}{p_0} \frac{T}{T_0} \right) \left(\frac{T_0}{T} \right)^y. \quad (10)$$

According to the classical interpretation of the half-width being proportional to the collision frequency, the value of y would be 0.5. That is, the collision frequency is proportional to the square root of the temperature and to the density, $\rho T^{0.5}$, or $pT^{-0.5}$. The

quantum-mechanical treatment of Anderson alters the expected temperature dependence⁽⁹⁾ to approximately $T^{-(n+4)/2n}$. For methane, n has the value⁽¹⁰⁾ 12, and so one expects y to have the value 2/3.

We now reconsider the Voigt profile. Substituting into equation (3) with the three expressions for the temperature dependence of the line strength and the two half-widths, we get

$$k(\nu) = \sum_n \frac{(\ln 2)}{\pi^{3/2}} \frac{S(T_0)_n \alpha_0}{(\Delta \nu_{D_0})^2} \frac{p_1}{p_0} \left(\frac{T_0}{T}\right)^{y+3/2} \exp \left\{ -1.43877E \left[\frac{1}{T} - \frac{1}{T_0} \right] \right\} \\ \times \int_{-\infty}^{\infty} \frac{\exp[-x^2] dx}{\ln 2 \left(\frac{\alpha_0}{\Delta \nu_{D_0}}\right)^2 \left(\frac{p_1}{p_0}\right)^2 \left(\frac{T_0}{T}\right)^{2y-1} + \left[\frac{(\nu - \nu_0)_n (\ln 2)^{0.5} \left(\frac{T_0}{T}\right)^{0.5}}{\Delta \nu_{D_0}} - x \right]^2}. \quad (11)$$

When $k(\nu)$ is evaluated experimentally, the only unknown parameter in this expression is y and hence the temperature dependence of the half-width can be found.

Note that equation (11) is accurate only in the region where the assumption $[f(p)/f(p_0)] = (p/p_0)$ is valid; i.e. when the Lorentz shape (pressure broadening) is dominant.

3. APPARATUS AND EXPERIMENT

A stabilized version of the single axial mode 3.39 μ He-Ne laser described previously⁽⁶⁾ was used. The mirrors were separated by invar rods, around which heating coils were wound. The temperature of the rods could be controlled to within 0.1°C, which proved adequate to stabilize the laser within 2 per cent at its maximum output (close to line centre) for hours at a time. The output power was in the region of 4 mW, and was monitored at both ends of the laser, using indium arsenide photo-voltaic cells. Measurements of almost complete extinction by the methane indicated that the 2947.903 cm^{-1} transition is the only frequency which needs to be considered.

A very accurate and rapid data-logging system was used. The signals from the infrared detectors were measured by a Doric digital voltmeter, capable of measuring voltages as low as 10^{-5} V. The results were printed out by an electric typewriter. Five channels were employed, so that other data could be recorded simultaneously (see below).

The gas cell was cylindrical, with 2 quartz windows separated by 0.64 cm. The cylinder axis was horizontal, and the cell was attached to the bottom of a liquid nitrogen container by means of a variable heat leak; an evacuated enclosure, with two further quartz windows, surrounded the cell and liquid nitrogen container. The cell temperature was monitored by two thermocouples, one at the top and the other at the bottom of the cell. Density gradients or instability were not detected when the thermocouples registered temperatures within 1°C of each other. Instability set in at a temperature difference of $\sim 3^\circ\text{C}$. The voltages from these thermocouples were logged together with the infrared detector voltages.

A diffusion pump was used to evacuate the cell. A mercury manometer was used for pressures from 50 to 760 torr, and a silicon oil manometer for pressures below 50 torr. Extremely low pressures were measured by a Pirani gauge, which was also useful for checking leaks at low methane pressures.

The variation of absorption with temperature was measured at constant density, i.e. the cell was filled with an initial pressure of methane and closed off. The temperature was then varied. The variation of the quartz window losses with temperature was also determined and taken into account. In absorption determinations, the cell assembly remained fixed, and the output from one end of the laser provided a reference level. The output from the other end was passed through the cell. Laser, cell assembly and detectors were mounted on a 150 kg slab of granite, floating on four rubber inner tubes inflated to a pressure of 2 lb in^{-2} , in order to avoid vibrational troubles.

4. RESULTS AND DISCUSSIONS

Previous work^(5,8) had shown that the experimental curve departed from the theoretical Voigt curve determined by variation of the parameters $\alpha/\Delta v_D$ and $(\nu - \nu_0)/\Delta v_D$ (equation 2) at pressures above 300 torr. The present results were used to compute theoretical curves from the variation of parameters for the following cases: (1) single Lorentz line, (2) single Voigt line, (3) superpositions of neighbouring lines, using Voigt functions, assuming that they have the same value of α_0 as the main line, and using the strengths as calculated by KYLE.⁽⁴⁾ The single Lorentz line study was undertaken to determine the region in which pressure broadening ceased to become dominant, and hence the assumptions used in deriving equation (9) became invalid. The results for (1) and (2) above are displayed in Fig. 1. It is seen that the Lorentz line fails at pressures below 35 torr since no account is taken of Doppler broadening, and that both shapes fail above 300 torr because of line overlap. The region enclosed in the box in Fig. 1 is enlarged in Fig. 2, which gives the effect of adding

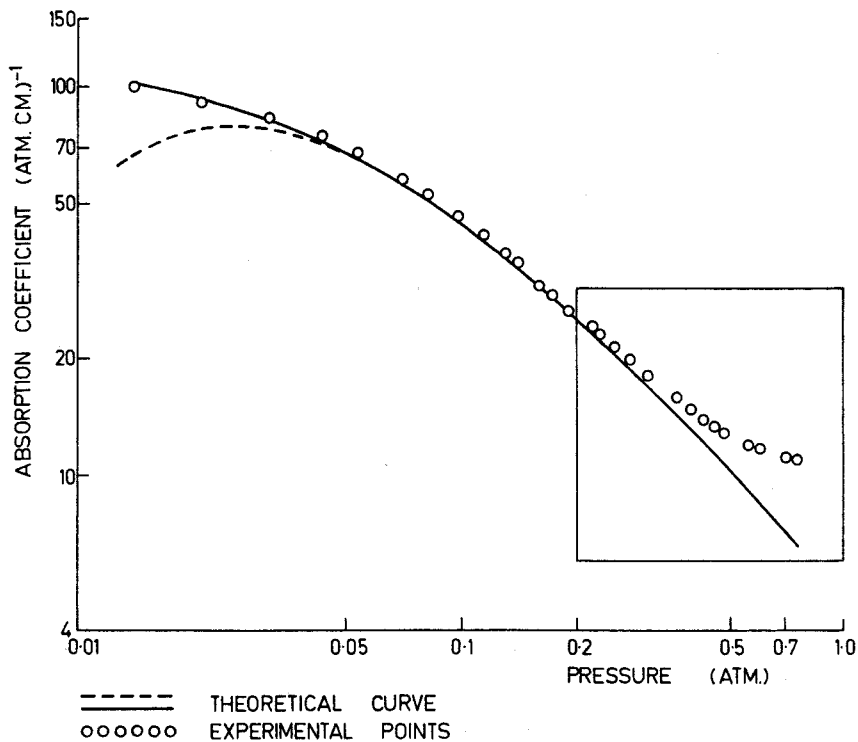


FIG. 1. Pressure dependence of the absorption coefficient. The solid curve is for a single Voigt line, and the dashed curve is for a single Lorentz line. \circ experimental points.

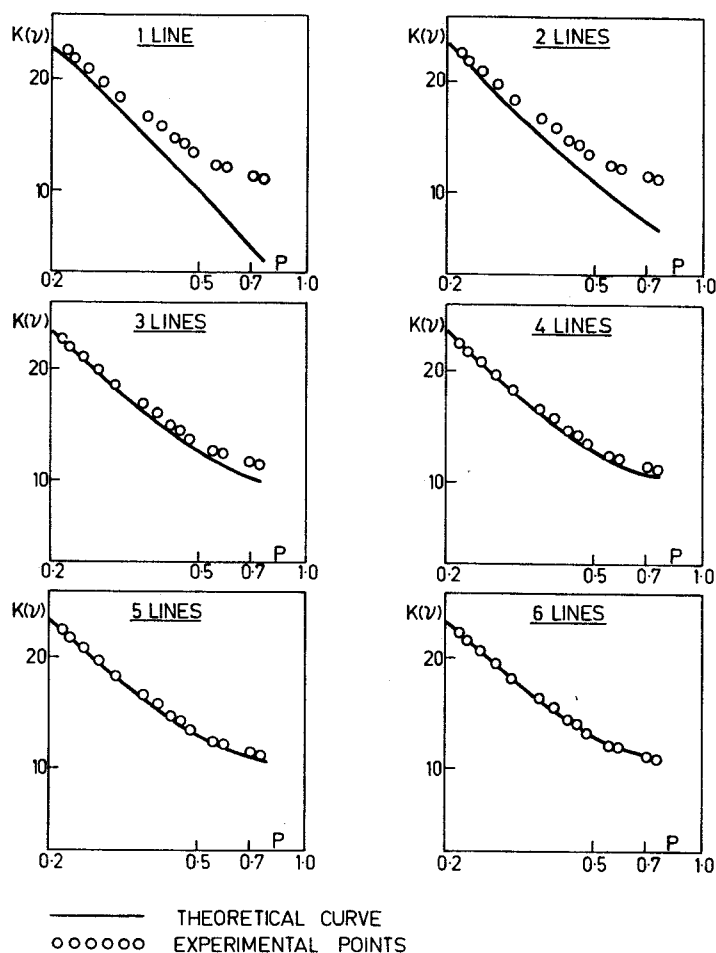


FIG. 2. Enlargement of high-pressure portion of Fig. 1, showing effect of adding successive neighbouring lines. ○ experimental points.

successively the neighbouring five $J = 7$ lines. If the six neighbouring $J = 6$ lines are added, although their effect is small, agreement between theory and experiment is even closer.

The constant-temperature, variable-pressure results shown in the first two figures were used to determine the line strength and half-width at room temperature. The previously reported method⁽⁶⁾ was used to fit equation (3) to the data. A total of six lines was used but the relative strengths were not allowed to vary from the reported⁽⁴⁾ ratios. The fitting of the strengths was therefore handled as if the total band strength was being adjusted, not the independent adjustment of each line.

The results of three separate constant-density runs are shown in Figs. 3–5. The curves were computer-calculated for values of the parameter γ (equation 11) differing by 0.1, and ranging from 0.5 to 1.5. By the variation of the sums of the squares of the differences for values of the parameter γ close to that displayed in the figures, it is concluded that the temperature dependence of the linewidth is close to, if not equal to, T^{-1} . The reason for the greater scatter of results at higher temperatures and pressures with the initial pressure of 403 torr (Fig. 3) is not understood, although a number of investigations was carried out. The scatter in results at the lowest initial pressure (Fig. 5) is to be expected since the transmission is small. Note that this pressure is in the region where Lorentz broadening ceases to become the dominant mechanism (Fig. 1).

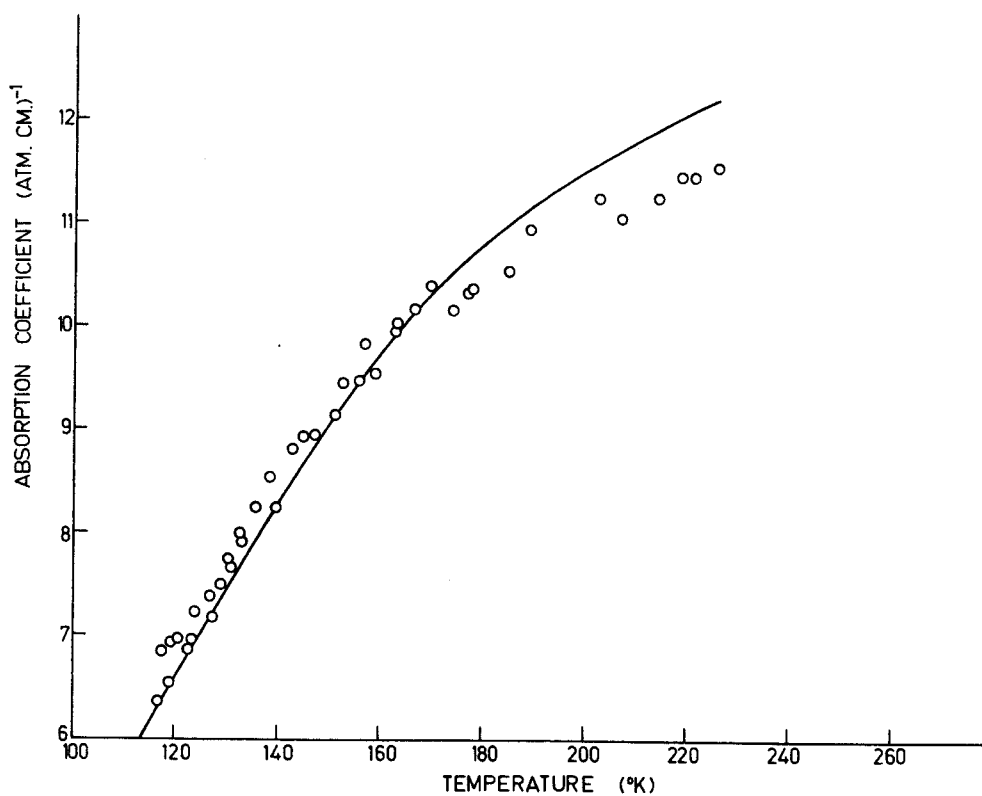


FIG. 3. Variation of absorption coefficient with temperature at constant density. Initial pressure 403 torr. \circ experimental points. Full curve is for $y = 1.0$.

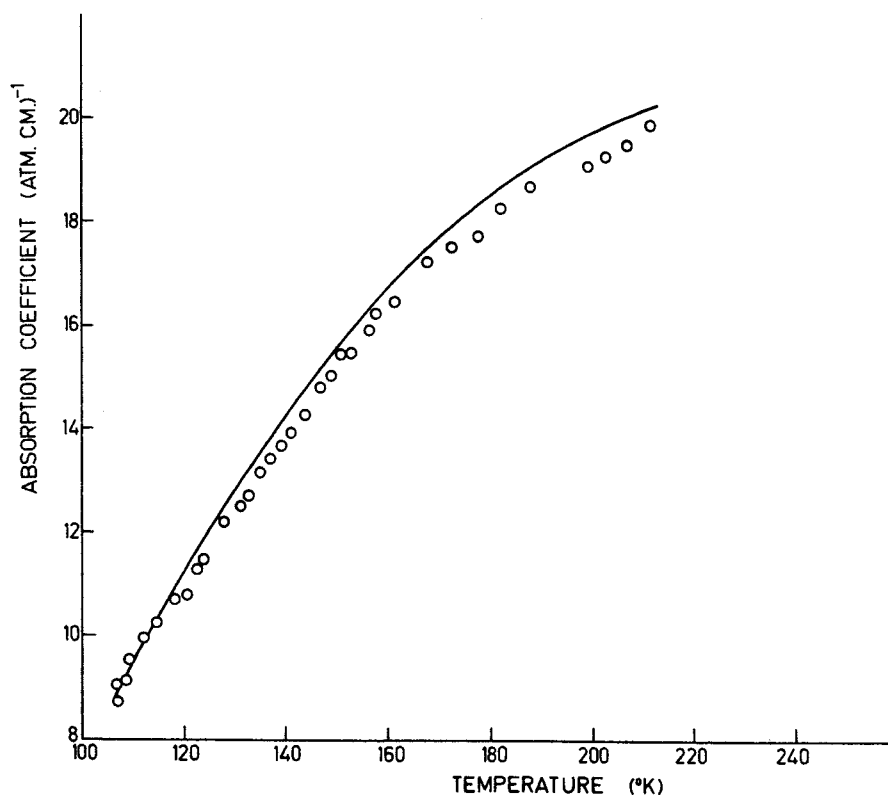


FIG. 4. Absorption coefficient vs. temperature at constant density; initial pressure 200 torr. \circ experimental points. Full curve for $y = 1.0$.

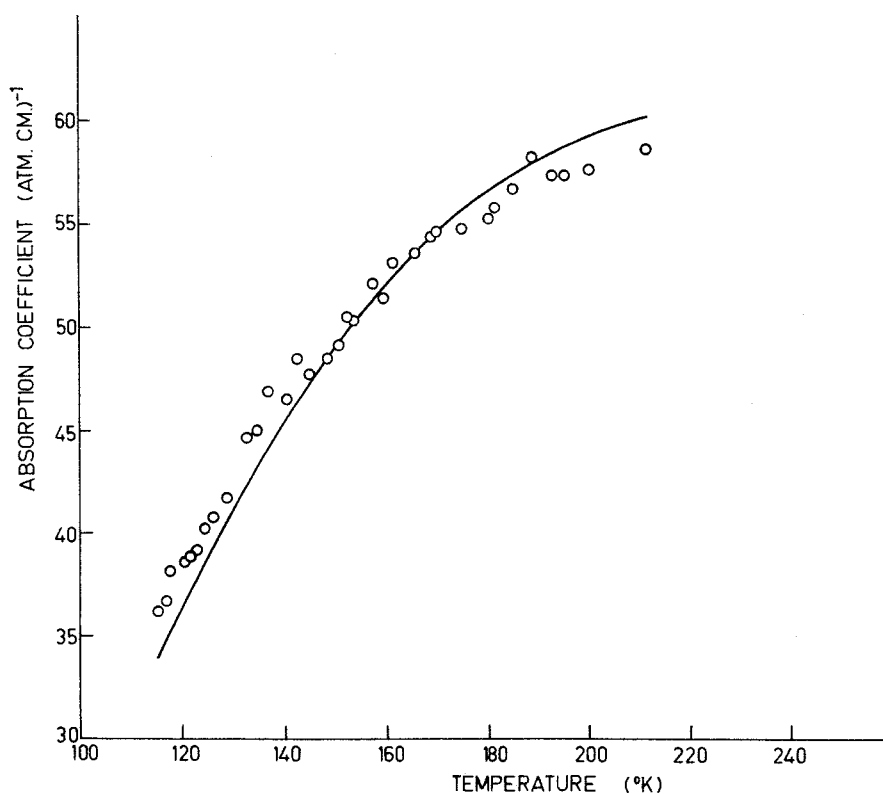


FIG. 5. Absorption coefficient vs. temperature at constant density; initial pressure 50 torr. \circ experimental points. Full curve for $y = 0.9$.

The temperature dependence of the $P(7)$ line of methane is considerably greater than the classical or Anderson's theory would predict. There has been little work reported concerning the effects of temperature on half-width in the infrared spectral regions, but other cases of a stronger than predicted temperature dependence have been found for both CO_2 and CO .

The measurements of the effect of temperature on the half-width of the $P(20)$ line of the 100-001 band of CO_2 ⁽¹¹⁾ generally fall between a T^{-1} and a $T^{-3/2}$ curve, with the $T^{-3/2}$ curve seeming to have the better slope for temperatures between 300 and 370°K. At higher temperatures, the experimental points have more nearly a T^{-1} slope.

A more complicated result has been found in the case of CO .⁽¹²⁾ The half-width has a $T^{-1/2}$ dependence at temperatures down to 193°K. At lower temperatures, the high J lines have less than $T^{-1/2}$ dependence, while the low J lines have a greater than $T^{-1/2}$ dependence.

The CO , CO_2 and CH_4 molecules have different moments which are responsible for the line broadening. The self-broadened widths are due to a quadrupole interaction in the case of CO and CO_2 , and an octupole as well as second-order dispersion interaction for CH_4 . The type of interaction gives no indication of the reason that the theory does not give correct result. The present results, taken in conjunction with those mentioned above, indicate that the theoretical dependence of linewidth on temperature should be used with caution.

5. CONCLUSION

The pressure-broadened linewidth at half amplitude (2α) of the methane absorption line nearest the laser line is $0.16 \pm 0.01 \text{ cm}^{-1}$. The line strength is $1.76 \pm 0.04 \text{ atm}^{-1} \text{ cm}^{-2}$ which is about 0.04 above the figure calculated by Kyle. The pressure-broadened linewidths of the neighbouring five $J = 7$ components are close to the value for the line nearest the laser, and the strengths are in the ratios as calculated by Kyle. The temperature dependence of the half-width is close to T^{-1} .

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