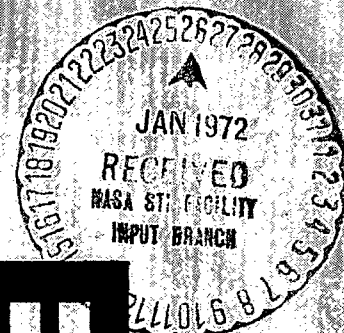


SEMI-ANNUAL STATUS REPORT

Infrared Laboratory Studies of
Synthetic Planetary Atmospheres

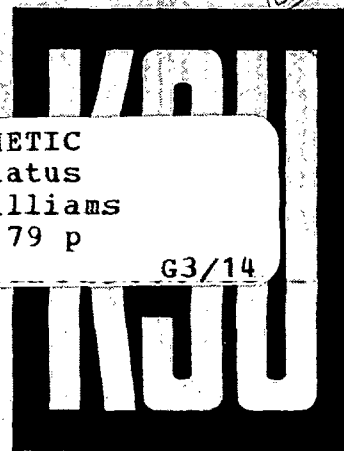
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Report, 1 Jun. - 30 Nov. 1971 D. Williams
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KANSAS STATE UNIVERSITY - MANHATTAN, KANSAS

SEMI-ANNUAL STATUS REPORT

Infrared Laboratory Studies of
Synthetic Planetary Atmospheres

Grant NGR 17-001-026

This report covers work for the period

1 June 1971 to 30 November 1971

It was prepared by

Prof. Dudley Williams, Department of Physics

Kansas State University, Manhattan, Kansas

Date: 15 December 1971

I. ABSTRACT OF RESEARCH TO DATE

The general program represents an extension and generalization of an earlier program dealing chiefly with telluric gases. The basic instrumentation includes three Perkin-Elmer Model 112 spectrometers equipped with prisms to cover the range between the visible and 40 microns, one Perkin-Elmer Model 421 grating instrument for the 2- to 18 micron region, and a Perkin-Elmer Model far-infrared spectrograph for the region 12 to 330 microns; this basic instrumentation was supplied by Kansas State University.

The initial stages of the research were involved with a test of Burch's law of multiplicative transmittance for mixed absorbing gases when their lines are broadened by H_2 and He, which are constituents of the atmospheres of the major planets. The results, which have resulted in journal publication, indicate that the multiplicative law as originally formulated can be applied with confidence.

The broadening of individual lines in the CO fundamental by various gases has been investigated. The results indicate that the ratio of the "self-broadening ability" of CO to the "line-broadening ability" of foreign gases is greater for lines in the band wings than for lines near the band center when the molecular mass of the broadener is less than that of CO. The results have been interpreted in terms of a phenomenological theory. Studies of the relative line broadening abilities of foreign gases have provided information that can be used to provide optical collision cross sections for individual lines in the CO fundamental.

Other work has been done on the determination of line strength S and half-width for individual CO lines as a function of temperature.

The results at reduced temperatures indicate (1) that line strengths S can be satisfactorily predicted by the Herman-Wallis expression but (2) that at very low temperatures the line half-widths differ markedly from values calculated by applying the "hard-sphere" approximations of kinetic theory to values of $\bar{\nu}^0$ measured at NPT. This work is being continued.

Measurements of total band absorptance $\int A(\nu) d\nu$ as a function of absorber thickness w and total effective pressure P_e have been made at various temperatures T for bands of CO and N₂O. This work is being extended to various other planetary gases.

Attempts have been made to develop a phenomenological theory of line broadening that will adequately account for the phenomena we have observed for the CO fundamental and those reported for more highly polar gases. This theory has been successful in accounting for the variation of line half-width with line number observed in our work on CO and in the studies of HCl-line broadening conducted in other laboratories. The results have been summarized in a journal article.

Laboratory measurements of nitric-acid vapor absorptance have been compared with balloon measurements at the University of Denver in arriving at an estimate of the quantity of nitric acid vapor present in the earth's atmosphere in the region of the ozone layer.

Funds from university sources have been used to purchase a partially completed high resolution spectrograph for use in the region between 2 microns and 5 microns. The instrument has now been completed at Kansas State University. Preliminary tests show that resolution has been reached nearing 50 percent of the Rayleigh limit at amplifier gains and spectrograph slitwidths that can be employed in routine operation.

The high-resolution spectrograph has been used to measure the line strengths and self-broadening parameters in the ν_3 fundamental of CO_2 at laboratory temperature and at a reduced temperature approximating that of the Martian atmosphere. Similar studies have been made for the lines in the CO fundamental for self-broadening and for broadening by CO_2 under conditions similar to those encountered on Mars.

Cumulative List of Publications*

1. "Further Studies of Overlapping Absorption Bands," Tubbs, Hathaway and Williams, J. Opt. Soc. Amer. 57, 570 (1967) P.
2. "Foreign-Gas Broadening of Absorption Lines in the CO Fundamental," Draegert, Chai, and Williams, J. Opt. Soc. Amer. 57, 570 (1967) P.
3. "Broadening of Absorption Lines in the CO Fundamental," Chai, Draegert, Williams; Bull. Am. Phys. Soc. 12, 542 (1967) P.
4. "Further Studies of Overlapping Absorption Bands," Tubbs, Hathaway, and Williams, App. Opt. 6, 1422 (1967).
5. "Strengths and Half Widths of CO Lines at Reduced Temperatures," Hoover, Hathaway, and Williams, J. Opt. Soc. Amer. 58, 739 (1968) P.
7. "Line Widths in Vibration-Rotation Bands," Williams, Bull. Am. Phys. Soc. II 13, 569 (1968) P.
8. "Comparison for Collision Cross Sections for Line Broadening in the CO fundamental," Chai and Williams, J. Opt. Soc. Amer. 58, 1395 (1968).
9. "Collisional Broadening of CO Absorption Lines by Foreign Gases," Draegert and Williams, J. Opt. Soc. Amer. 58, 1399 (1968).
10. "Absorption in the Wings of Rotational Lines in the CO Fundamental", Chai and Williams, Bull. Am. Phys. Soc. II 13, 906 (1968).
11. "Foreign-Gas Broadening of Lines in the CO Fundamental," Williams, Proceedings 23rd Symposium on Molecular Structure, Ohio State University, p. 89 (1968), P.
12. "Infrared Absorptance of Carbon Monoxide at Low Temperatures," Hoover and Williams, J. Opt. Soc. Amer. 59, 28 (1969).

* P denotes papers presented at scientific meetings.

13. "Nitric-Acid Vapor in the Earth's Atmosphere," Rhine, Tubbs, and Williams, J. Opt. Soc. Amer. 59, 483 (1969) P.
 14. "Nitric-Acid Vapor above 19 km in the Earth's Atmosphere," Rhine, Tubbs, and Williams. Applied Optics 8, 1500 (1969).
 15. "Half Widths of Collision-Broadened Lines of CO and HCl", Williams, Wenstrand, and Brockman, J. Opt. Soc. Amer. 59, 1526 (1969). P
 16. "A Czerny-Turner Spectrograph for the Infrared", Tubbs and Williams J. Opt. Soc. Amer. 60, 726 (1970). P.
 17. "Collisional Broadening of Infrared Absorption Lines," Williams, Wenstrand, Brockman, and Curnutte, Molecular Physics 20, 769 (1971).
 18. "Collisional Broadening of CO Absorption Lines by CO₂", Tubbs and Williams, J. Opt. Soc. Amer. 61, 673 (1971). P.
 19. "Line Strengths and Half-Widths in the ν_3 Fundamental of CO₂", Tubbs and Williams, J. Opt. Soc. Amer. 61, 1587 (1971). P.
 20. "Broadening of Infrared Absorption Lines at Reduced Temperatures: CO₂", Tubbs and Williams, J. Opt. Soc. Amer. (Accepted for publication).
 21. "Broadening of Infrared Absorption Lines at Reduced Temperatures: CO", Tubbs and Williams, J. Opt. Soc. Amer. (Accepted for publication).
 22. "Foreign-Gas Broadening of Nitrous-Oxide Absorption Lines", Appl. Opt. (Accepted for publication).
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II. PROGRESS DURING THIS REPORT PERIOD

A. Absorption-Line Broadening

The experimental results for CO and CO₂ line broadening at laboratory and Martian temperatures have been summarized in articles, which have been accepted for publication in the Journal of the Optical Society of America. Copies of these papers are appended to this report. Also appended is a reprint of our Molecular Physics article on a semi-empirical theory of line broadening.

It should be noted that our value of the band strength of the ν_3 fundamental band of CO₂ based on the sum of the measured line strengths differs by nearly 30 percent from the band strength as determined recently by others, who have made measurements at low resolution and high pressure. If this difference proves to be real, we shall have made an important contribution to telluric atmospheric studies; if the difference is merely an artifact based on differences in instrumental methods, we may add to present knowledge of applications of instrumentation to basic molecular problems.

During the present period we have also summarized some of our earlier results on the relative broadening abilities for lines in the ν_3 fundamental of N₂O. This work has been accepted for publication as an article in Applied Optics. A pre-print of the article is appended to this report.

New high-resolution work on the strengths and half-widths of lines in the ν_3 fundamental of N₂O has been initiated. This work will serve to clear up some of the questions raised in our earlier work on CO₂.

B. Studies of Particulate Constituents of Planetary Atmospheres

We have made measurements of the normal-incidence reflection spectrum of liquid ammonia in the spectral range 2-30 micrometers. The absorption spectrum of liquid ammonia has been mapped in the range 2 to 7 micrometers. The two sets of measurements can yield values of the real and imaginary parts of the refractive index of ammonia; these quantities needed for the application of Mie theory to the scattering of radiation in the cloud decks of Jupiter in layers where the clouds are predominantly liquid-ammonia droplets.

III. PERSONNEL

Dr. Dudley Williams, Regents' Professor of Physics:

Chief Investigator (WOC)

Dr. Basil Curnutte, Professor of Physics:

Senior Associate (WOC)

Dr. Charles W. Robertson, Research Associate:

(Part Time)

Lloyd Tubbs, B.S.: Graduate Research Fellow

Graduate Degrees Granted under the Grant

An-Ti Chai - Ph.D.

Gary M. Hoover - Ph.D.

David Schmieder - M.S.

IV. PLANS FOR THE NEXT REPORT PERIOD

- A. The work on N_2O will be continued.
- B. The studies of liquid ammonia will be completed and summarized.
- C. The conference with members of Dr. Farmer's group at JPL, proposed in the preceding report, will actually be held in January 1972.

Submitted: 15 December 1971

Signed: *Dudley Williams*
Dudley Williams

- Appendices: (1) Reprint: "Collisional Broadening of Infrared Absorption Lines"
- (2) - (3) "Broadening of Infrared Absorption Lines at Reduced Temperatures: I. CO_2 , II. CO "
- (4) "Foreign-Gas Broadening of Nitrous Oxide Absorption Lines."
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Collisional broadening of infra-red absorption lines

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(Received 20 March 1970)

The Lorentz half-widths of collision-broadened lines in the rotation-vibration bands of diatomic molecules vary with line number $|m|$ in the P and R branches. The observed variation of half-width for lines in the $0 \rightarrow 1$ and $0 \rightarrow 2$ bands of CO and HCl are interpreted in terms of a simple fitting procedure. One dominant source of line broadening is assumed to consist of diabatic hard collisions involving transitions from each rotational level to all higher rotational levels; the effectiveness of this process, which varies from line to line, is described in terms of an empirically adjusted collision cross section, a maximum collision parameter related to independently measured molecular properties, and upon the availability of the required energy and angular momentum in molecular collisions. The second source of line broadening, assumed to be the same for all lines, includes all other types of collisions and is represented by a single empirically adjusted cross section. The simple fitting procedure is applied successfully to self-broadening of CO lines and to foreign-gas broadening of CO and HCl; for HCl self-broadening an additional cross section for resonant-dipole processes must be included. Possible applications of the fitting procedure to HBr, HF, and CO₂ are discussed. The simple procedure presented represents an approximation that may prove useful pending the development of readily applicable complete theories based on first principles.

1. INTRODUCTION

After appropriate corrections have been made for instrumental effects, the finite widths of absorption lines in gas samples at extremely low pressure can, in the absence of wall collisions, be attributed to the limited radiative lifetimes of molecules in initial and final states and to Doppler broadening. At higher sample pressures the greater observed widths of infra-red absorption lines can be attributed to the effects of molecular collisions. In the present paper we present a simple phenomenological model that seems to account satisfactorily for certain aspects of the observed collisional broadening of lines in the fundamental and first overtone vibration-rotation bands of CO and HCl.

The spectral transmittance $T(\nu)$ of a gas sample is given by the relation: $T(\nu) = \exp[-k(\nu)w]$, where $k(\nu)$ is the Lambert spectral absorption coefficient and w is the absorber thickness or optical density of the sample. At pressures of one atmosphere or less, the shape of a collisionally broadened absorption line in the vicinity of ν_0 is described in good approximation by the Lorentz expression

$$k(\nu) = \frac{S}{\pi} \frac{\gamma}{(\nu_0 - \nu)^2 + \gamma^2} \quad (1)$$

where the line strength $S = \int k(\nu) d\nu$ depends on the quantum mechanical

probabilities for radiative transitions between the initial and final states and on the populations of these states; γ represents the half-width of the line between frequencies at which $k(\nu) = k(\nu_0)/2$.

In terms of simple theory $\gamma = 1/2\pi\tau_c = f_c/2\pi$, where τ_c is the mean time between collisions and f_c is the corresponding mean collision frequency. The mean collision frequency is given by the relation

$$f_c = N\bar{V}\sigma, \quad (2)$$

where N is the number of molecules per unit volume and is thus proportional to the sample pressure, σ is the collision cross section, and \bar{V} is the most probable relative speed $\bar{V} = \sqrt{(2kT/\mu)}$, where k is Boltzmann's constant and μ is the reduced mass of the collision pair.

Extensive experimental studies of the half-widths of lines in the rotation-vibration bands of CO have been made in several laboratories [1-8]. Although there are some relatively minor disagreements between the absolute values of the half-widths as measured in different laboratories, nearly all investigators report a gradual decrease of γ for self-broadening with increasing line number $|m|$ in both *P* and *R* branches; $m = J + 1$ in the *R* branch and $m = -J$ in the *P* branch, where J is the rotational quantum number of the initial level involved in the radiative transition. The values of γ for foreign-gas broadening show a somewhat similar variation with line number $|m|$ for most foreign gases studied, but γ values for H₂, D₂ and He show little variation with $|m|$.

Extensive experimental work has also been done on the determination of the half-widths of lines in the spectrum of HCl [9-13]. The results obtained indicate that the value of γ for self-broadening first increases with increasing $|m|$ to a maximum at $|m| = 3$ for samples at room temperature and thereafter decreases with increasing $|m|$; the value of $|m|$ at which γ is a maximum is a function of temperature. The values of γ for foreign-gas broadening of HCl lines vary with line number $|m|$ in a manner roughly similar to the corresponding variations noted above for foreign gas broadening of CO.

Impact theories [14-16, 19, 20] of spectral line broadening treat the observed half-width γ as the sum of two parts. One part γ_A is associated with adiabatic or elastic collisions in which the absorber remains in its original energy level following collision; such collisions lead to a broadening of the level by an amount $\Delta E_A = h/2\pi\tau_A$ where τ_A is the mean time between adiabatic collisions and is therefore the time in which the energy levels of the isolated molecule can be specified. The other part γ_D is associated with diabatic or inelastic collisions which remove the absorbing molecule from its original level; the level broadening in this case is given by the relation $\Delta E_D = h/2\pi\tau_D$ where τ_D is the average lifetime of the absorbing molecule in its original energy level.

The first detailed impact theory of line broadening was developed by Anderson [19] and its application to the broadening of molecular absorption lines has been discussed in considerable detail by Tsao and Curnutte [20]. This theory implies definite selection rules for diabatic collisions in which the distances between the centres of colliding molecules are sufficiently great to permit valid description of the collision in terms of specific electric multipole interactions; however, several types of interactions may, of course, be involved simultaneously. For closer collisions involving strong forces there are no definite selection rules. One of the difficulties in applying the Anderson theory results from the fact that many

of the numerous specific interaction parameters are not precisely known and must be simultaneously adjusted when experimental results are compared with the theoretical treatment.

Similar difficulties are encountered in employing the statistical theories [17, 18, 21, 22] which attempt to account for line broadening in terms of the perturbations of the energy levels of the isolated absorbing molecule by the average values of the fields of neighbouring molecules. After valiant but largely unsuccessful attempts to account for their experimental results on broadening of CO lines in terms of statistical theories involving dispersion forces, dipole-dipole forces, and dipole-induced dipole forces, Crane-Robinson and Thompson [4] suggested that the observed variation with line number $|m|$ might be interpreted on more general considerations of the dominant broadening processes involved rather than on the detailed nature of the forces during collision. Some progress in this direction has been made by Benedict *et al.* [9] in their moderately successful attempt to account for the observed self-broadening of the lines of the HCl fundamental in terms of the so-called resonant-dipole-billiards-ball (RDBB) approximation. In this approximation, $\gamma = \gamma_{BB} + \gamma_{RD}$ where the billiards-ball half-width γ_{BB} is the same for all lines and results from adiabatic collisions and all types of diabatic collisions except for those involving resonant-dipole interactions, in which lifetimes of molecules in a given rotational level are limited by the direct exchange of quanta between molecules in adjacent rotational levels. Because of resonant-dipole interactions the lifetimes of molecules in the most highly populated rotational states are shorter than those of molecules in other states. Benedict was able to account for the maximum value of γ in the vicinity of $|m| = 3$. The agreement between observed half-widths and those calculated on the RDBB approximation is poorer in other parts of the HCl band.

2. PRESENT MODEL

The model proposed in the present paper was adopted after detailed examination of the experimental results for self-broadening of CO and foreign-gas broadening of both CO and HCl. We noted that the general variation of γ with $|m|$ is strongly influenced by the mass of the molecule responsible for the broadening process. Thus, the ratio of the self-broadening γ for CO to γ for N₂ broadening of CO is the same for all values of $|m|$; the molecular masses of CO and N₂ are equal. Similarly, in the CO spectrum the ratio of γ for CO₂ ($M = 44$) broadening to γ for Ar ($M = 40$) is approximately the same for all values of $|m|$, even though the molecular structures of CO₂ and Ar are greatly different. A similar relationship exists for γ due to He and D₂ in spite of their quite different structures. Crane-Robinson and Thompson investigated broadening of CO lines by a series of polyatomic hydrocarbon gases; although they differ in magnitude from gas to gas, the values of γ for all these polyatomic gases vary with $|m|$ in strikingly similar fashion.

In view of these observations, we have, for purposes of calculation, adopted a model involving a broadening half-width γ_A which is tentatively assumed to be constant for *all* lines in the absorption band and is thus somewhat similar to the constant γ_{BB} broadening half-width proposed by Benedict [9]. The variation of total γ with $|m|$ is attributed to variations in a *dominant* diabatic half-width $\gamma_{D, |m|}$. We have assumed that the dominant $|m|$ -dependent process consists of diabatic collisions in which translational kinetic energy is transformed into

increased rotational energy of the absorbing molecule and that the net effect of all other collisions is to maintain the equilibrium population of each rotational energy level in a manner consistent with our assumptions. In view of the similarities of the γ versus $|m|$ dependence for such different broadeners as CO_2 and Ar, we have assumed that all collisions contributing to γ_D are close encounters in which no selection rules are involved; i.e. that collision-induced transitions from an initial energy level to all higher levels are caused by strong forces and are equally probable provided sufficient energy and angular momentum are available.

The kinetic energy in a binary collision available for conversion to rotational energy of the absorber is $(1/2)\mu V^2$, where μ is the reduced mass of the collision pair and V is the relative velocity. In view of the high vibrational energies of CO and HCl, few collisions in samples at 300 K involve sufficient energy to produce vibrational energy transitions; however, nearly every collision involves sufficient translational kinetic energy to cause transitions between the more closely spaced lower rotational levels in both ground and excited vibrational states. The minimum relative velocity V_E required to produce a rotational transition from level rotational $E(J)$ to a higher level $E(J')$ is given by the expression

$$V_E = \sqrt{\{2[E(J') - E(J)]/\mu\}} = \sqrt{(2hcB/\mu)}\sqrt{[J'(J'+1) - J(J+1)]}, \quad (3)$$

where B is the rotational constant of the absorbing diatomic molecule and centrifugal distortion effects are neglected.

If the transformation of translational kinetic energy to rotational energy were the only consideration, the variation of γ_D , $|m|$ with $|m|$ at a given sample temperature would be the same for all broadening gases, since the maxwellian translational kinetic energy distribution is independent of molecular mass. However, the conservation of angular momentum must also be considered. When the absorbing molecule is in the rotational state J prior to collision and higher state J' after collision, its angular momentum has increased by $(J' - J)h/2\pi$. The total angular momentum involved in a collision is μVb ; where μ is again the reduced mass of the collision pair, V the relative velocity of the colliding molecules, and b is the impact parameter. By considering the absorbing molecule in rotational state J and spatial quantum number $M=J$ in a weak field parallel to the Z axis, we note that molecules with components of relative velocity parallel to the XY plane can produce transitions $J \rightarrow J'$ with $M \rightarrow M'$ provided sufficient angular momentum is available. Thus, the minimum velocity V_P required to provide the angular momentum required for a transition $J \rightarrow J'$ is

$$V_P = (J' - J)h/2\pi\mu b. \quad (4)$$

By comparison of (3) and (4), we note that $V_P > V_E$ for small values of the impact parameter b but that $V_E > V_P$ for larger values of this parameter.

Thus, for small values of b , dynamical limitations involving conservation of angular momentum are of dominant importance; these dynamical limitations are greatest for the small values of μ involved in collisions of the absorbing molecule with light molecules such as H_2 , D_2 and He. For larger values of b , mass-independent energy limitations become dominant. We note, however, that the dominance of energy limitation occurs at a smaller value of b for large values of μ ; thus, energy limitations become dominant at small values of b in collisions between an absorbing molecule and heavy molecules such as Xe,

Kr, or the large polyatomic hydrocarbons studied by Crane-Robinson and Thompson [4]. These differences between the effects of heavy broadeners and light broadeners are qualitatively in accord with the experimental results discussed above.

In order to make a quantitative comparison with experiment, we have assumed that the dominant diabatic half-width $\gamma_{D, |m|}$ for lines involving transitions from initial level J can be written $\gamma_{D, |m|} = \phi(|m|)\gamma_D$, where γ_D is a constant for a given absorber and broadener and $\phi(|m|)$ is a factor that depends on the availability of the energy and angular momentum for collision-induced transitions from level J to higher levels J' . Since we have assumed that all dominant collisions involve strong forces, no selection rules are involved, and all collisions $J \rightarrow J'$ are equally probable provided sufficient energy and angular momentum are available. Another assumption is that there is a maximum value b_0 for a given collision pair; since only close collisions are involved, b_0 is related to the size for the electron clouds of the colliding molecules.

Under these assumptions, we make use of the normalized maxwellian distribution of relative velocities

$$\left. \begin{aligned} dP &= 4\pi \left[\frac{\mu}{2\pi kT} \right]^{3/2} V^2 \exp(-\mu V^2/2kT) dV, \\ dP &= 4\pi \left[\frac{1}{\pi \bar{V}^2} \right]^{3/2} V^2 \exp-(V/\bar{V})^2 dV, \end{aligned} \right\} \quad (5)$$

where dP is the probability that the relative velocity of the colliding molecules is between V and $V+dV$. The probability P that the relative velocity $V \geq V_{\min}$ is given by the expression

$$P = 4\pi \left[\frac{1}{\pi \bar{V}^2} \right]^{3/2} \int_{V_{\min}}^{\infty} V^2 \exp-(V/\bar{V})^2 dV. \quad (6)$$

Thus, for a given value of b , we may determine the probability $P_{J \rightarrow J'}(b)$, of a collision in the range b to $b+db$ involving sufficient relative velocity to produce transition $J \rightarrow J'$ by using as the lower limit V_{\min} the larger of the velocities V_E or V_P given in (3) and (4), respectively. The sum $P_J(b)$ of the probabilities

$$P_J(b) = \sum_{j'=j+1}^{\infty} P_{J \rightarrow J'}(b), \quad (7)$$

where the sum involves all values of $J' > J$, can be taken as a measure of the effectiveness of collisions in the conversion of translational energy to the rotational energy of the absorbing molecule. A plot of $P_J(b)$ versus b for collisions of CO with D₂ and He is given in figure 1 (A); the initial J value is indicated at the end of each curve. As expected, all curves start from zero at $b=0$, since for this value $V_{\min} = \infty$. With increasing b , the curve for an initial value J increases as long as the value of $P_J(b)$ is influenced by values of V_{\min} imposed by the angular-momentum limitation (4). For sufficiently large values of b , the values of V_{\min} are determined completely by the energy limitation (3); at these large values of b , each curve in figure 1 becomes horizontal at a value of $P_J(b)$ characteristic of J . As indicated in figure 1 (B) the energy limitation becomes dominant at a smaller value of b for Xe broadening.

The effectiveness P_J of a given broadener in causing collision-induced transitions from a given rotational level J to upper levels is proportional to the

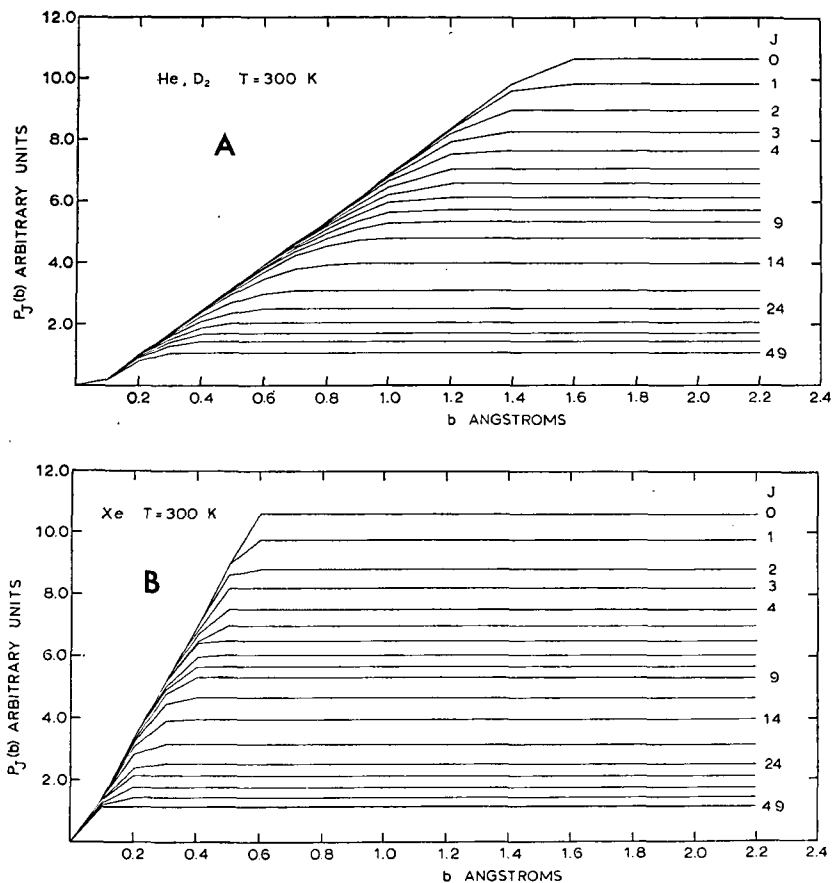


Figure 1. The function $P_J(b)$ expressed in arbitrary units for various rotational energy levels J as a function of impact parameter b in Ångström units. Panel A applies to CO collisions with He and D_2 ; panel B applies to CO collisions with Xe.

integral

$$P_J = \int_0^{b_0} P_J(b) db, \quad (8)$$

where the upper integration limit is related to the actual molecular dimensions but is to be determined ultimately by comparison with experimental data. The influence of the choice of b_0 on the value of P_J is illustrated in figure 2, where the curves have been normalized to unity for P_0 . Plots of P_J for CO collisions with H_2 are shown in figure 2 (A) and with D_2 and He in figure 2 (B) for three different choices of b_0 ; for these collisions, in which angular-momentum limitations are largely dominant, the choice of b_0 strongly influences the shape of the P_J versus J plot. Figure 2 (C) gives a similar plot for CO-Xe collisions, in which energy limitations are largely dominant; in this case, the P_J versus J plots are indistinguishable for b_0 values of 2.0, 2.5, and 3.0 Å. Thus, for heavy broadeners the choice of b_0 is relatively unimportant.

With the proper choice of b_0 , curves of the type shown in figure 2 give the assumed dominant diabatic collision broadening of the initial levels of the radiative

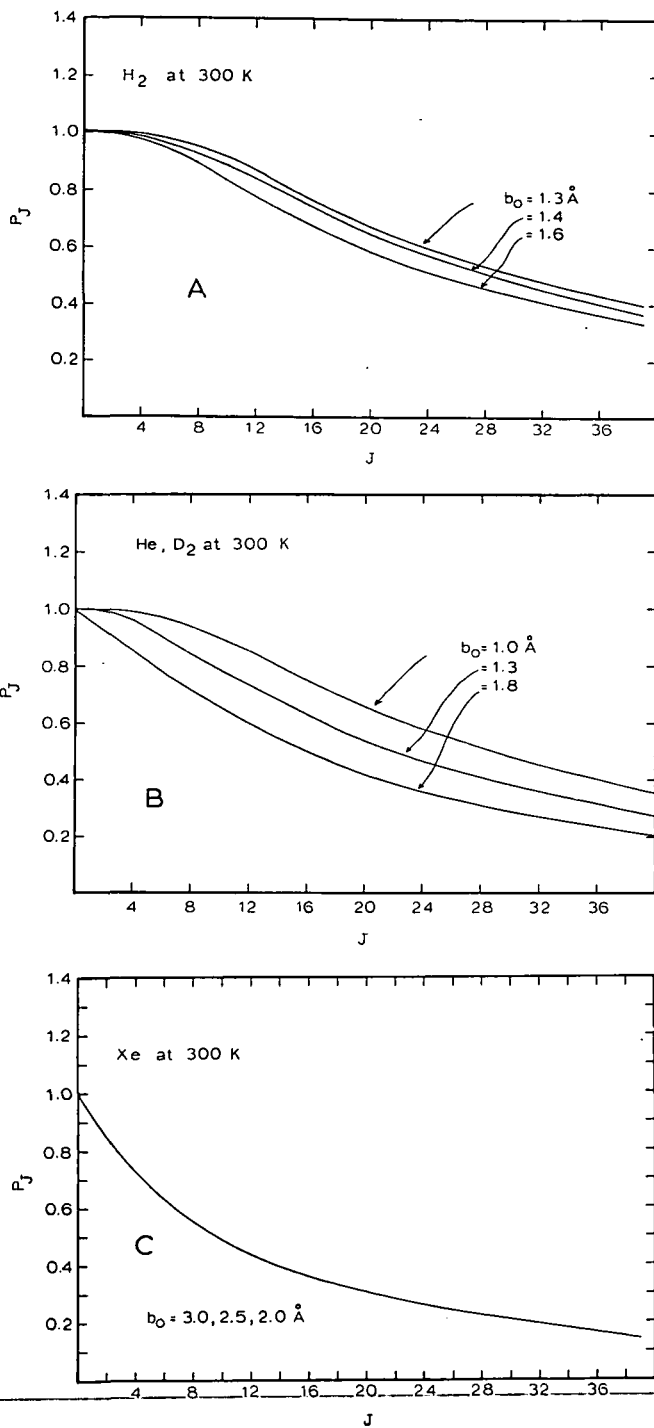


Figure 2. The function

$$P_J = \int_0^{b_0} P_J(b) db$$

normalized to unity at $J=0$ for various values of b_0 as a function of rotational quantum number J . Panel A applies to CO-H₂ collisions; panel B applies to collisions of CO with D₂ or He; panel C applies to CO-Xe collisions.

transitions involved in the vibration-rotation absorption bands. However, the observed absorption lines will also be broadened as a result of the broadening of the upper energy levels involved in the radiative transitions. We have ignored the influence of collision-induced vibrational transitions and have assumed that the collision processes involved in broadening the rotational levels in the upper vibrational states are the same as those involved in broadening the rotational levels of molecules in the ground vibrational state. In arriving at the value of $\phi(|m|)$ to be used in the relation $\gamma_{D, |m|} = \phi(|m|)\gamma_D$, we have assumed that $\phi(|m|) = [P_J + P_{J'}]/2$; where J' is the quantum number $J+1$ or $J-1$ of the final rotational state in the upper vibrational state. We thus assume the same collision processes for molecules in the ground and excited vibrational states and recall that the values of rotational numbers are the same in the $+m$ lines ($J \rightarrow J+1$) and $-m$ lines ($J+1 \rightarrow J$) in the absorption band.

3. COMPARISON WITH CARBON-MONOXIDE MEASUREMENTS

On the basis of the model described above we have applied the relation

$$\gamma_{|m|} = \gamma_A + \phi(|m|)\gamma_D \quad (9)$$

to the experimental results obtained by Hunt *et al.* [6] for the self-broadening of CO lines in the first overtone and by Draeger and Williams [7] for foreign-gas broadening of CO lines in the fundamental by monatomic and diatomic gases. In fitting the data we regard γ_A and γ_D as directly adjustable parameters but note that the function $\phi(|m|)$ is based on an adjustable impact parameter b_0 directly related to molecular sizes. We found that satisfactory fits to experimental data for noble-gas broadening could be obtained by setting b_0 approximately equal to one-half the CO internuclear distance plus the covalent radius of the monatomic broadeners; for broadening by diatomic broadeners, satisfactory fits to experimental results can be obtained with b_0 approximately equal to one-half the CO internuclear distance plus one-half the internuclear distance of the diatomic broadener. Thus, although the value of b_0 is essentially an adjustable parameter, b_0 can be related to molecular data obtained from other sources.

A comparison of the results calculated on the basis of the present model with the results of Plyler is given in figure 3. The ordinate in the figure gives a

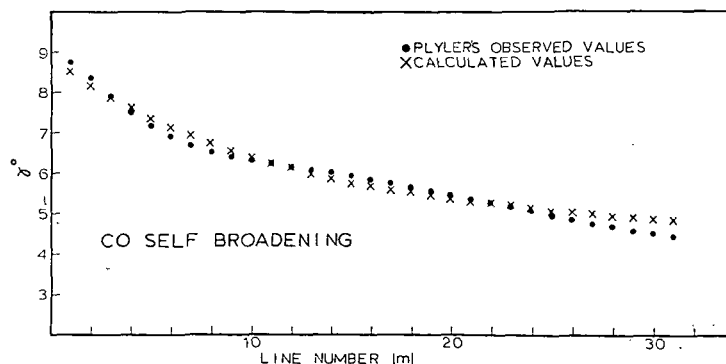


Figure 3. Line half-width parameter γ^0 in $0.01 \text{ cm}^{-1}/\text{atm}$ as a function of line number $|m|$ in the CO fundamental vibration-rotation band. Observed values are shown as filled circles; calculated values are shown by crosses and were computed from relation (9) on the basis of fitted parameters $\gamma_A^0 = 3.8 \text{ cm}^{-1}/\text{atm}$, $\gamma_D^0 = 4.7 \text{ cm}^{-1}/\text{atm}$ and $b_0 = 1.8 \text{ \AA}$.

parameter γ^0 numerically equal to γ for a sample pressure of 1 atm; in view of the relation between γ and collision frequency f_c , we note that in samples at other pressures γ can be obtained by multiplying γ^0 by the sample pressure in atmospheres. The agreement between calculated and observed values can be regarded as reasonably satisfactory for all 30 lines covered in the experimental study. However, we note that a somewhat improved fit to lines near $|m|=0$, where calculated values are low, and near $|m|=30$, where calculated values are high, could have been achieved at the expense of a somewhat poorer fit in the range $|m|=6$ to 20, where experimental measurements are somewhat more reliable.

A comparison of observed and calculated values of γ^0 for foreign-gas broadening of carbon monoxide is given in table 1 along with the parameters γ_A^0 , γ_B^0 and b_0 employed in each calculation. We note that with the adjustment of only these three parameters we are able to fit the observed data of Draeger and Williams [7] to within approximately ± 10 per cent for most of the 19 rotational lines for which experimental data are available. This agreement is remarkable in view of the fact that estimates of the uncertainties in the experimental values for foreign-gas broadening are at least ± 5 per cent and may be somewhat larger for weak lines nearest the band centre and in the far wings of the band. The corresponding experimental results of Crane-Robinson and Thompson [4] could easily have been employed in table 1; with slightly different values of γ_A , γ_D and b_0 , the agreement between observed and calculated values would have been satisfactory. In order to give a graphical comparison between the observed and calculated values for foreign-gas broadening of CO lines, we have plotted in figure 4 the optical collision cross sections σ given by the relation

$$\sigma = f_c / N\bar{V} = 2\pi\gamma^0 / N_0\bar{V},$$

where N_0 is the number of molecules per unit volume at a pressure of 1 atm. The values of σ for monatomic broadeners are plotted in figure 4 (A); we note that the observed and calculated values agree to within less than ± 10 per cent for nearly all monatomic broadeners. An equally satisfactory or even better agreement for diatomic broadeners can be noted in figure 4 (B). Thus, we conclude that our suggested model gives a fairly satisfactory account of the Draeger-Williams study of CO line broadening.

In table 2 we also present our analysis of Crane-Robinson and Thompson's results for molecules not covered in the Draeger-Williams study. The agreement between calculated and observed values of γ^0 for the diatomic broadeners can be regarded as satisfactory. Satisfactory analyses have also been achieved for the broadening of CO lines by polyatomic molecules, for which the impact parameter is large and the limiting value V_P is small; under these circumstances the energy limitations become dominant and the γ versus $|m|$ variations are similar for all hydrocarbons studied. The poorest agreement between calculated results and those obtained by Crane-Robinson and Thompson involve the polar broadeners HCl, NH₃ and SO₂, for which dipole-dipole or dipole-induced dipole interactions with CO are probably important.

4. COMPARISON WITH HYDROGEN CHLORIDE MEASUREMENTS

In applying the proposed scheme to the self-broadening of HCl lines, it is necessary to include an additional parameter to take account of the resonant-dipole

Line number [<i>m</i>]	He		Ne		Ar		Kr		Xe		H ₂		D ₂		N ₂	
	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C
1	4.79	4.75	3.91	3.89	7.04	6.48	7.48	7.22	8.93	8.35	7.49	7.12	6.45	6.27	8.12	8.00
2	4.68	4.75	3.85	3.80	6.65	6.19	6.94	6.80	8.00	7.91	7.15	7.12	6.34	6.27	7.76	7.69
3	4.66	4.75	3.74	3.76	6.14	5.94	6.46	6.43	7.30	7.39	7.00	7.12	6.30	6.26	7.21	7.40
4	4.64	4.75	3.58	3.70	5.69	5.70	5.92	6.13	6.80	7.06	6.93	7.12	6.15	6.24	6.84	7.13
5	4.60	4.75	3.54	3.63	5.34	5.51	5.56	5.84	6.39	6.68	7.00	7.11	6.10	6.21	6.55	6.90
6	4.58	4.74	3.49	3.59	5.08	5.31	5.20	5.60	6.00	6.36	6.95	7.09	6.05	6.17	6.32	6.66
7	4.55	4.74	3.44	3.55	4.85	5.14	4.91	5.36	5.66	6.08	6.92	7.06	6.00	6.13	6.12	6.45
8	4.55	4.73	3.44	3.49	4.72	4.98	4.72	5.12	5.47	5.82	6.90	7.01	5.95	6.09	6.02	6.25
9	4.55	4.73	3.46	3.44	4.63	4.84	4.56	4.92	5.29	5.61	6.90	6.99	5.92	6.04	5.94	6.07
10	4.61	4.72	3.45	3.44	4.56	4.72	4.50	4.73	5.13	5.40	6.87	6.99	5.90	6.00	5.84	5.93
11	4.67	4.72	3.45	3.35	4.46	4.61	4.43	4.60	4.98	5.19	6.86	6.94	5.87	5.95	5.76	5.75
12	4.68	4.72	3.42	3.32	4.44	4.50	4.34	4.45	4.85	5.01	6.90	6.90	6.85	5.92	5.72	5.66
13	4.66	4.72	3.39	3.30	4.38	4.39	4.25	4.30	4.73	4.84	6.95	6.85	5.84	5.88	5.66	5.49
14	4.71	4.71	3.33	3.28	4.35	4.30	4.19	4.19	4.65	4.69	6.90	6.81	5.83	5.86	5.60	5.39
15	4.70	4.71	3.26	3.26	4.31	4.22	4.14	4.04	4.57	4.57	6.78	6.78	5.83	5.82	5.51	5.29
16	4.69	4.70	3.22	3.23	4.23	4.13	4.07	3.93	4.52	4.45	6.82	6.72	5.78	5.80	5.45	5.21
17	4.67	4.70	3.18	3.21	4.14	4.06	4.00	3.82	4.50	4.36	6.84	6.69	5.74	5.76	5.38	5.11
18	4.68	4.69	3.20	3.19	4.07	3.98	3.90	3.71	4.37	4.25	6.81	6.64	5.76	5.71	5.24	5.02
19	4.69	4.69	3.13	3.18	4.00	3.93	3.79	3.66	4.24	4.17	6.74	6.61	5.75	5.68	5.10	4.94
20	4.69	4.69			3.89				4.08		6.58		5.63		4.86	
γ_A^0	4.61		2.76		2.64		1.91		2.05		5.46		4.83		3.15	
γ_D^0	0.142		1.13		3.84		5.31		6.30		1.66		1.44		4.85	
<i>b</i> ₀	1.3 Å		1.8 Å		2.5 Å		2.8 Å		3.0 Å		1.4 Å		1.3 Å		1.5 Å	

Table 1. Observed (O) and calculated (C) values of γ^0 for CO lines broadened by various gases in units of $0.01 \text{ cm}^{-1}/\text{atm}$.

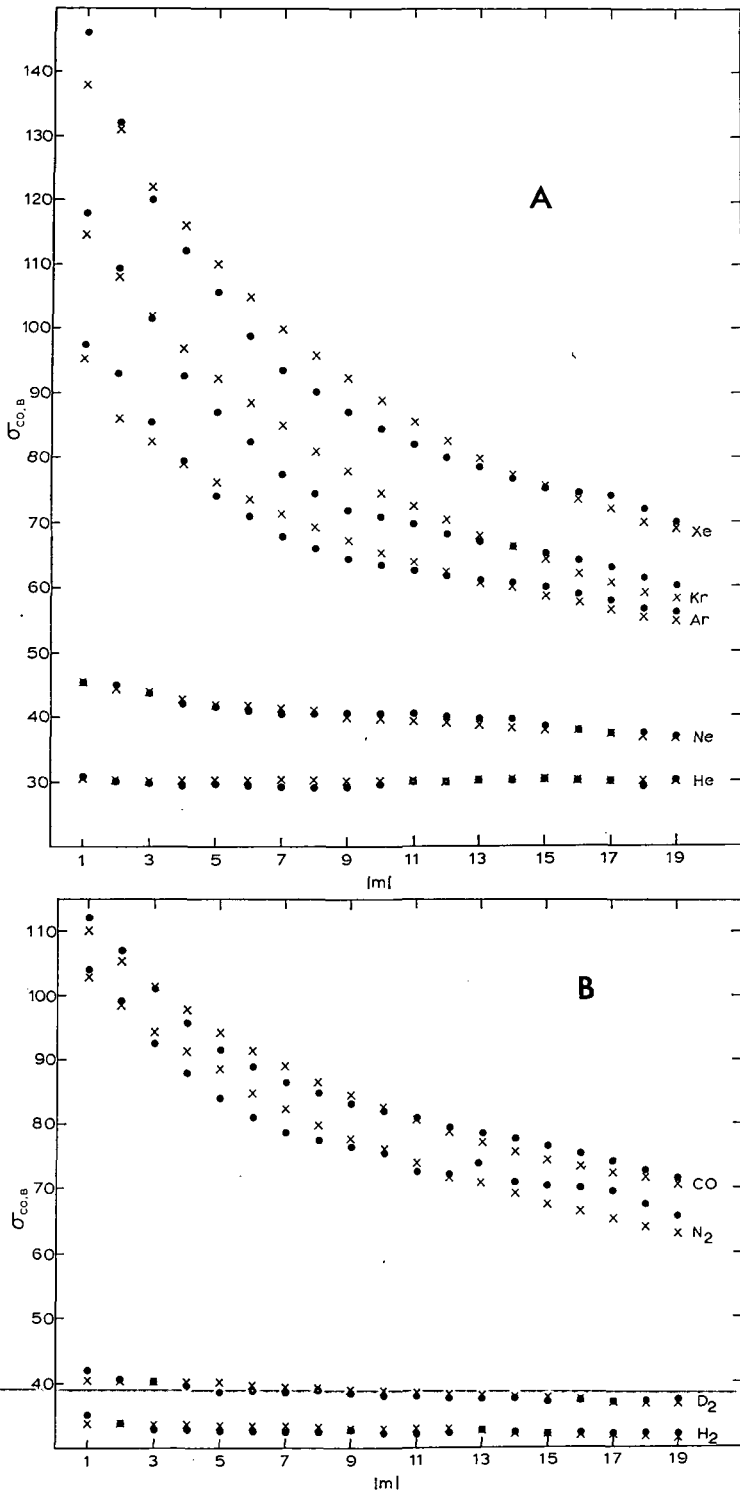


Figure 4. Collision cross sections for broadening of CO absorption lines by monatomic gases in panel A and by diatomic gases in panel B. The cross sections $\sigma_{CO,B}$ for various broadening gases are expressed in 10^{-16} cm^2 and are plotted as a function of line number $|m|$ in the CO fundamental. Observed values are given by filled circles; computed values by crosses.

Line number [m]	CO ₂		CH ₄		n-pentane		n-hexane		CF ₄		SF ₆		NO		HCl		SO ₂		NH ₃	
	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C
1	8.47	8.29	7.82	8.02	11.45	11.80	12.36	12.70	7.10	7.29	7.42	7.34	6.12	6.41	8.33	8.04	10.6	10.80	11.00	10.50
2	7.75	7.90	7.80	7.72	11.49	11.35	11.78	12.19	6.67	6.98	7.15	7.05	6.15	6.19	7.46	7.85	10.5	10.26	9.70	10.14
3	7.35	7.54	7.68	7.40	11.13	10.88	11.82	11.67	6.44	6.68	6.84	6.72	6.13	5.99	7.25	7.67	9.89	9.60	8.84	9.80
4	7.11	7.22	7.30	7.11	10.90	10.49	11.73	11.23	6.30	6.42	6.41	6.51	6.00	5.82	7.10	7.51	9.47	9.10	8.38	9.44
5	7.01	6.94	7.11	6.86	10.44	10.14	—	10.82	6.07	6.18	6.35	6.26	5.78	5.67	7.24	7.37	9.18	8.60	8.30	9.10
6	6.44	6.65	6.70	6.64	9.90	9.80	11.02	10.44	6.09	5.96	5.94	6.07	5.44	5.52	6.96	7.23	8.51	8.16	7.62	8.83
7	6.09	6.41	6.54	6.40	9.65	9.53	10.96	10.14	5.99	5.78	5.77	5.89	5.50	5.39	6.90	7.12	7.79	7.81	7.38	8.55
8	6.10	6.18	6.24	6.24	9.33	9.27	10.97	9.84	5.61	5.60	5.50	5.72	5.41	5.27	6.80	7.00	7.44	7.41	7.26	8.36
9	5.81	5.99	6.10	6.04	9.32	9.02	10.75	9.57	5.40	5.44	5.38	5.60	5.29	5.16	6.88	6.91	7.15	7.06	7.38	8.11
10	5.64	5.81	5.97	5.88	9.18	8.83	9.65	9.35	5.49	5.31	5.33	5.46	5.16	5.07	6.90	6.82	7.00	6.77	7.23	7.91
11	5.36	5.65	5.87	5.71	8.91	8.65	9.80	9.10	5.50	5.19	5.31	5.35	5.14	4.97	6.98	6.75	6.35	6.48	7.27	7.71
12	5.22	5.49	5.66	5.57	8.79	8.55	9.71	8.92	4.92	5.05	5.15	5.22	5.21	4.90	6.84	6.66	6.38	6.25	7.31	7.53
13	5.10	5.34	5.63	5.45	8.93	8.35	9.38	8.72	—	4.94	5.16	5.12	5.09	4.81	7.00	6.60	6.20	6.00	7.42	7.39
14	5.32	5.20	5.53	5.32	8.27	8.21	9.06	8.55	4.71	4.82	5.19	5.03	5.04	4.75	6.87	6.53	5.64	5.81	7.29	7.24
15	5.20	5.08	5.42	5.21	8.29	8.00	8.66	8.39	4.82	4.74	5.07	4.94	4.79	4.68	6.71	6.46	5.67	5.60	7.09	7.09
16	4.95	4.95	5.36	5.11	8.29	7.84	8.56	8.25	4.84	4.68	5.30	4.90	4.81	4.63	6.90	6.41	5.86	5.41	7.57	6.99
17	4.92	4.84	4.87	5.02	7.82	7.72	7.44	8.10	4.47	4.59	5.03	4.83	4.57	4.57	6.49	6.39	4.92	5.23	7.62	6.87
18	4.61	4.71	4.53	4.96	7.20	7.98	7.20	7.98	4.32	4.50	4.99	4.78	4.38	4.52	5.16	6.34	4.68	5.09	7.27	6.74
19	4.48	4.64	4.41	4.89	7.39	7.50	6.86	7.85	4.22	4.42	4.92	4.71	4.04	4.48	5.89	6.29	4.64	4.91	6.85	6.66
20	4.73	4.60	4.57	4.79	7.05	7.41	6.93	7.75	4.10	4.36	4.68	4.64	4.11	4.44	5.85	6.23	4.65	4.78	6.76	6.57
γ_A^0	2.74		3.10		5.40		5.48		3.02		3.38		3.48		5.31		1.87		4.43	
γ_D^0	5.55		4.92		6.40		7.22		4.27		3.96		2.93		2.73		8.93		6.07	
b_0	2.0 Å		2.0 Å		2.8 Å		2.8 Å		2.8 Å		3.0 Å		2.5 Å		2.0 Å		2.0 Å		1.8 Å	

Table 2. Observed (O) and calculated (C) values of γ^0 of CO lines broadened by various gases in units of $0.01 \text{ cm}^{-1}/\text{atm}$.

interactions that lead to a maximum in the γ^0 versus $|m|$ plots based on experiment. We have therefore assumed that

$$\gamma = \gamma_A + \phi(|m|)\gamma_D + f\gamma_{RD}, \quad (10)$$

where f is the fraction of the molecules in the adjacent rotational states involved in rotational resonance [9]; thus, we make use of four adjustable parameters: γ_A , γ_D , b_0 and γ_{RD} . A comparison of our calculated values of the half-widths of self-broadened HCl lines with observed values for the fundamental [9] and first-overtone [11] bands are given in figure 5. The agreement between calculated

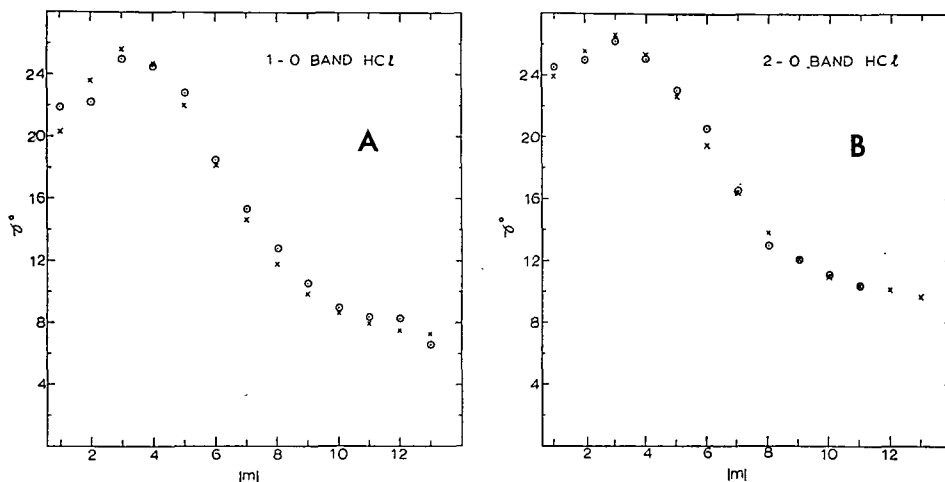


Figure 5. Observed and calculated half-width parameters γ^0 in $0.01 \text{ cm}^{-1}/\text{atm}$ for HCl self-broadening as a function of line number $|m|$; observed values are shown as circles and calculated values based on relation (10) as crosses. Panel A gives results for the HCl fundamental; calculated values are based on the following fitted parameters expressed in $0.01 \text{ cm}^{-1}/\text{atm}$: $\gamma_A^0 = 6.27$, $\gamma_D^0 = 5.74$ and $\gamma_{RD}^0 = 77.4$. Panel B gives results for the first overtone; calculated values are based on the following fitted parameters expressed in $0.01 \text{ cm}^{-1}/\text{atm}$: $\gamma_A^0 = 8.23$, $\gamma_D^0 = 9.06$, and $\gamma_{RD}^0 = 61.1$.

and observed values is excellent in all parts of the band and is better than that obtained with Benedict's RDBB approximation in which only two fitted parameters are employed; a comparison of the two sets of values with the observed values is given in table 3.

In the case of foreign-gas broadening of HCl lines, we have been able to fit the experimental results of Babrov *et al.* [11] for lines by means of relation (9) involving three adjustable parameters. Comparison of calculated and observed values of γ^0 is given in figure 6, in which the adopted values of b_0 , γ_A^0 , and γ_D^0 are listed for each broadener. We note that agreement is excellent for Ne and CO_2 , satisfactory for He, Ar, CO, O_2 , N_2 and H_2 , and poorest for D_2 . In view of the satisfactory agreement obtained for H_2 and He, the poor agreement for D_2 is difficult to understand; in the case of broadening of HCl lines by HBr there is no agreement at all between the observed values of γ^0 and values of γ^0 calculated from our model; however, since HCl and HBr both have large dipole moments, the lack of agreement with our fitting procedure is not at all surprising in view of selection rules associated with dipole-dipole interactions.

5. FURTHER APPLICATIONS.

In view of the influence of temperature on the maxwellian distribution of relative velocities, our model predicts that the half-widths of lines of small number $|m|$ relative to those of large $|m|$ should be enhanced as the sample temperature is reduced; this prediction has been verified by the work of Hoover and Williams [23]. At high temperatures the γ versus $|m|$ plot becomes flatter in accord with expectations. However, it is possibly disappointing, though not surprising, that different values of the adjustable parameters, γ_A and γ_D , must be employed at different temperatures; this result implies that the collision cross sections σ_A and σ_D are temperature dependent and therefore velocity dependent. In their studies of HCl at various temperatures, Goldring and Benesch [13] note that the successful use of the RDBB approximation also requires a variation of σ_{BB} with temperature; this result is in accord with our results for CO.

Although we have applied our model in detail only to existing data for CO and HCl, we have also considered Madden's quantitative study of CO₂ absorption in the vicinity of the ν_2 fundamental [24]. He has reported values of γ^0 ranging from 0.126 cm⁻¹ at $|m|=4$ to 0.06 cm⁻¹ at $|m|=56$. The observed gradual decrease of γ^0 with increasing $|m|$ can readily be described in terms of the present model. Similarly, for HBr and DCl the observed variations of γ^0 with $|m|$ for various foreign-gas broadeners show a gradual decrease that could be fitted by the present scheme; for lines of these absorbing gases broadened by H₂ the decrease in γ^0 with increasing $|m|$ is much larger than that for CO and HCl.

In view of the extremely wide spacing of its rotational levels, HF presents a case of special interest. Our present model, with the addition of a resonant-dipole parameter can provide agreement with observed γ^0 values for self-broadening; the agreement is comparable with that obtained by Mason and Nielsen [25] in their application of the RDBB model. The studies of Smith [26] and Wiggins [27] have covered the line-broadening effects of 24 foreign gases. For 20 of these gases the results are in accord with expectations based on our fitting procedure; however, the exceptions are rather interesting. Hydrogen-broadening values [26] of γ^0 show an unexpectedly large decrease with increasing $|m|$; this result is similar to that for HBr and DCl and, with proper choices of γ_A and γ_D , can be described in terms of our model. However, for HF broadening by the polyatomic gases UF₆ and MoF₆, Smith [26] finds that γ^0 shows an initial decrease with $|m|$ followed by an increase for large $|m|$ values; this unusual result cannot be accounted for by our model.

Wiggins' work [27] on HF broadening by Ar, Kr, and Xe in the fundamental (0→1) and overtone (0→2) bands has yielded some interesting and unusual results; in each case γ^0 for lines in 0→2 band is much larger than for lines in the 0→1 band. In the case of Ar, γ^0 decreases with increasing $|m|$ in both bands in a manner consistent with our present model, but we are unable to account for the differences in the magnitudes of γ^0 observed in the two bands. In the case of Kr, variation of γ^0 with $|m|$ in the 0→1 band is what would be anticipated, but in the 0→2 band, γ^0 shows an initial decrease between $|m|=1$ and $|m|=5$ and an increase in the range $|m|=5$ to $|m|=8$. For Xe broadening of HF, γ^0 is nearly constant for all lines observed in the 0→1 band but increases monotonically with increasing $|m|$ in the 0→2 band. These unusual effects cannot be interpreted in terms of our simple model.

6. CRITICISM OF THE PRESENT SCHEME

The fitting procedure that we have employed cannot in any sense be regarded as a complete theory but is rather an approximation comparable with the RDBB approximation. We have applied energy and angular-momentum conservation principles to a single class of hard collisions. We have assumed (1) that these collisions provide the only $|m|$ -dependent contribution $\phi(|m|)\gamma_D$ to line broadening and (2) that, except for resonant dipole effects, all other types of collisions combine to provide an $|m|$ -independent contribution γ_A to line broadening. The success of the present procedure, which neglects all details of the intermolecular potentials and concentrates on the statistical factors involving collisions of a certain kind, is rather surprising.

Although the ultimate theoretical treatment of collisional line broadening in terms of parameters calculated from first principles appears difficult to attain, considerable progress is being made in the treatment of collisions in terms of parameters based on independent experimental measurements of molecular parameters [28]; Galatry and his colleagues have successfully applied these newer theoretical techniques to the broadening of HCl lines by monatomic foreign gases [29]. Pending the development of more readily applicable general theories, data fitting procedures of the type presented here may be of use in the comparison and correlation of existing data on line widths and in the estimation of as yet unmeasured line widths.

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Broadening of Infrared Absorption Lines at Reduced Temperatures I:
Carbon Dioxide*

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ABSTRACT

An evacuated high-resolution Czerny-Turner spectrograph, which is described in this paper, has been used to determine the strengths S and self-broadening parameters γ^0 for lines in the R branch of the ν_3 fundamental of $C^{12}O_2^{16}$ at 298°K and at 207°K. The values of γ^0 at 207°K are greater than those to be expected on the basis of a fixed collision cross section σ . The approximate ratio of the measured cross sections for a given line is given by the relation: $\sigma(T_1)/\sigma(T_2) = T_2/T_1$; although this relation holds for the average of all lines measured, the cross-section ratio is greater than the temperature ratio for lines near the band center and less than the temperature ratio for lines in the wings of the band.

INTRODUCTION

Carbon dioxide is an important constituent of the atmospheres of Venus, the earth, and Mars. A knowledge of the strengths and widths of its collisionally broadened absorption lines in the infrared is important in gaining understanding of the heat balances of the earth and Venus and in making valid estimates of the composition of the extremely thin Martian atmosphere. In earlier studies at ambient laboratory temperatures Madden¹ has determined the strengths and the self-broadening parameters for selected lines in the ν_2 fundamental and Burch, Gryvnak, and Patty² have determined these quantities for the 02^0_3 combination band. If the line strengths at one temperature are known, the line strengths at other temperatures can be calculated.³ However, for the variation of collisional line broadening with temperature no satisfactory and readily applicable theories have been developed; Goldring and Benesch,⁴ Hoover,⁵ and Ely and McCubbin⁶ have demonstrated the failure of the hard-sphere approximation based on simple kinetic theory. The purpose of the present study was to determine the line strengths and self-broadening parameters for lines in the ν_3 fundamental at ambient laboratory temperature and at a reduced temperature comparable with that of the Martian atmosphere.

GENERAL METHOD

The true spectral transmittance of an absorbing gas is given by Lambert's law $T'(\nu) = \exp(-k(\nu)w^0)$, where $k(\nu)$ is the absorption coefficient and w^0 is the absorber thickness

$$w^0 = p_a z(273/T) \quad (1)$$

where p_a is the partial pressure of the absorbing gas in atm, z is the path length in cm, and T is the Kelvin temperature of the gas. For a collision-broadened line the absorption coefficient can be approximated⁷ by the Lorentz expression,

$$k(\nu) = S\gamma / [(\nu - \nu_0)^2 + \gamma^2], \quad (2)$$

where ν_0 is the central frequency of the line, γ is the half-width of the line between frequencies at which $k(\nu) = k(\nu_0)/2$, and the line strength $S = \int k(\nu)d\nu$ depends upon the transition probabilities between the initial and final states and upon the populations of these states.

The half-widths of rotational lines under atmospheric conditions are smaller than the spectral slit widths of most ir spectrometers; therefore, the true spectral absorptance $A'(\nu) = 1 - T'(\nu)$ is not equal to the measured spectral absorptance $A(\nu)$. However, it has been shown theoretically^{8,9} and experimentally^{7,10} that the equivalent width $W = \int A'(\nu)d\nu$ of an isolated line is, within certain limits, independent of spectral slit width. Utilizing this result, we can write

$$W = \int A'(\nu)d\nu = \int \{1 - \exp[-k(\nu)w_0]\} d\nu = \int A(\nu)d\nu \quad (3)$$

where the limits of integration include the entire range of measurable absorptance associated with the line. For a Lorentzian line, the value of W is given by

$$W = 2\pi\gamma L(x) \quad (4)$$

where $L(x)$ is the Ladenberg-Reiche function¹¹ with argument $x = Sw^0/2\pi\gamma$. Values

of $L(x)$ have been tabulated by Kaplan and Eggers¹² for values of x between 0 and 50. However, for certain regions of line growth, W can be approximated by

$$W = Sw^0 \quad \text{for } x \ll 1 \quad \text{(Linear Region)} \quad (5)$$

$$W = 2(Sw^0\gamma)^{\frac{1}{2}} \quad \text{for } x \gg 1 \quad \text{(Square-root Region).} \quad (6)$$

In the present study we have determined line strengths S from measurements in the linear region, in which we used a short absorption cell, small absorber thicknesses w^0 , and large total pressures obtained by the addition of N_2 . The product $S\gamma$ was obtained from measurements in the square root region, in which we used pure CO_2 in a longer cell at pressures sufficiently low to avoid serious overlap of adjacent lines. From the two sets of measurements we can determine both S and γ ; in the tables presented later we summarize our γ -measurements for each line in terms of a single parameter γ^0 , which is equal to the value of γ to be expected for a pure CO_2 sample at a pressure of 1 atm = $1.05 \times 10^5 \text{ N/m}^2$.

EXPERIMENTAL WORK

In order to determine S and γ^0 by the method just described it is necessary to use a spectrograph with a sufficiently high resolving power to separate rotational lines, a stable source of radiant flux, and a detector-amplifier system whose output is strictly proportional to the flux reaching the detector and which is capable of providing a high signal-to-noise ratio. Commercially available spectrographs equipped with thermocouple detectors are suitable for studies of HCl and CO spectra, in which the rotational lines are widely spaced, but are usually not suitable for larger molecules like CO_2 .

The specially constructed evacuated Czerny-Turner spectrograph used in the present study is shown schematically in Fig. 1. Radiant flux from the

Nernst glower NS passes through the sample SA to mirrors M_1 , M_2 , M_3 , and M_4 , which produces an image of the source at the entrance slit S_1 of the spectrograph. From S_1 the flux passes to collimating mirror M_5 , which directs a collimated beam of radiation to the grating G. The dispersed radiation proceeds to condensing mirror M_6 , which forms an image of the entrance slit at intermediate slit S_2 after reflection by M_7 . From S_2 the flux is directed by M_8 for a second pass at the grating and eventual focus at exit slit S_3 . The desired flux emerging from S_3 passes through filter F and is directed by an off-axis ellipsoidal mirror, not shown in the figure, to detector D.

System components NS and SA are located in a 'source tank', which is evacuated by a separate vacuum pump and can be opened without breaking the vacuum in the main tank. After trying out various source control circuits, we ended by operating the Nernst glower in series with a tungsten ballast lamp and utilizing the output of a constant-voltage transformer; the resulting source stability is comparable with that attained by means of more sophisticated techniques. The sample space SA is sufficiently large to accommodate absorption cells 30 cm long.

The construction of the absorption cells is shown schematically in Fig. 2. The cell windows, circular plates B of sapphire 3.8 cm in diameter, were bonded to kovar sleeves A by the Varian's Eimac Division; the kovar sleeves were in turn silver-soldered to heavy copper plates D. The central portions of the absorption cells consist of heavy tubular copper inserts, one of which is shown in Fig. 2. These inserts are equipped with recessed grooves C for use with teflon-coated cryogenic O-rings supplied by Tec. Seal Corporation. The window assemblies are attached to the central portions by means of threaded tie rods passing through holes near the periphery as suggested in Fig. 2. The

central inserts are also equipped with copper tubes through which sample gases can be introduced and with small wells into which thermocouples can be inserted for temperature measurements. Thermocouples are also attached to the end plates of the cell.

After the cells had been assembled they were inserted into close-fitting copper cooling jackets. Cooling was accomplished by circulating cold dry nitrogen through copper tubes which are soft-soldered to the outer surface of the cooling jackets. Cell temperatures were monitored by means of copper-constantan thermocouples attached to the insert portions and end plates of the absorption cells. Temperature gradients in the absorption cells were minimized by proper distribution of cooling tubes on the copper jackets; the jackets extend well beyond the ends of the absorption cells. Cell temperatures were controlled by adjustment of the flow of the cold nitrogen through the coils attached to the cooling jacket.

In passing from SA to M_7 in Fig. 1, the radiant flux passes through a CaF_2 window in the wall of the main vacuum tank and is periodically interrupted at a frequency of 1000 Hz by a tuning-fork-controlled radiation chopper C. Spherical mirrors M_5 and M_6 are 32 cm in diameter and have a focal length of 215 cm. Grating G is an aluminized 15.4 cm by 20.6 cm Bausch and Lomb replica having 3000 lines/cm with a blaze angle of $35^\circ 52'$ and is used in first order. The grating is rotated by a tangent drive operated by a 5-cm precision micrometer screw supplied by Boeckler Instruments; this relatively short screw can be positioned at different suitable locations by means of a kinematic mounting when different spectral regions are being scanned. The precision screw is advanced by a gear assembly operated by a stepping motor turning at rates as slow as one step in 20 sec and as high as 400 steps/sec; one step corresponds

to a grating rotation of $2\mu\text{rad}$. For each location of the precision-screw mounting, the grating orientation is indicated by a Veeder counter mounted on a shaft in the gear train operated by the stepping motor. Calibration was accomplished by noting the positions of absorption lines of known frequency on a recorder chart turned by a stepping motor operated from the master control circuit used to rotate the grating; the spectrograph held its calibration for prolonged periods and the grating-rotation mechanism proved to be highly satisfactory.

The main vacuum tank is evacuated by a mechanical pump with a molecular-sieve filter in the pumping line between the pump and the tank; after evacuation to 10^{-2} Torr the pressure inside the isolated tank rose by approximately 0.3 Torr in one week. After two years of operation there has been no apparent deterioration of the optical components.

Radiant flux emerging from the spectrograph exit slit, S_3 in Fig. 1 is incident on an interference filter supplied by the Optical Coating Laboratory, Inc.; the filter rejected radiation with frequencies higher than 3100 cm^{-1} . The off-axis paraboloid brings flux passed by the filter to a focus on a liquid-nitrogen-cooled indium antimonide photovoltaic detector operating with a matched preamplifier supplied by Texas Instruments; the Dewar vessel in which the detector element is mounted can be filled with liquid nitrogen through a copper tube passing through a port in the vacuum tank. The preamplifier output signal is further amplified by a Princeton Applied Research narrow band amplifier, whose output is displayed on a recorder chart.

The theoretical resolving power $R = \nu/\Delta\nu$ of the spectrograph is 120,000, where $\Delta\nu$ is the frequency difference corresponding to the diffraction limit at frequency ν . By introducing small quantities of gas at extremely low

pressure into the main tank of the spectrograph, we have made experimental tests of resolving power by observing closely spaced lines in the spectra of CH_4 , CO_2 , and CO . The measured value of resolving power is 60,000 to 80,000 when the signal-to-noise ratio is acceptable for use in scanning.

In the present study we used sufficiently large spectral slit widths to ensure large signal-to-noise ratios and confined our attention to the R-branch of the ν_3 fundamental, since the P branch is badly 'contaminated' by weak lines associated with isotopic molecules and hot bands. Typical transmittance curves are shown in Fig. 3, in which Panel A shows lines near the center of the band with pure CO_2 at a pressure of 0.18 Torr and an effective path length of 2000 cm in the spectrograph tank; the labels on the lines give line numbers $m = J + 1$ for lines in the spectrum of the abundant $\text{C}^{12}\text{O}_2^{16}$ molecule, where J is the initial rotational level involved in the transition. Panel B represents the spectral absorptance in the same spectral region for CO_2 at a pressure of 3.27 Torr in a cell 0.446 cm long when the lines have been pressure-broadened by the addition of N_2 to give a total pressure of 1 atm; we note that, although the weaker lines have disappeared as resolved lines, they contribute to the general background absorption and thus add to some extent to the uncertainties in S and γ^0 values for lines near the band center. Panel C shows spectral transmittance in the remote wing of the band for a pure CO_2 sample in a 10 cm cell at a pressure of only 20 Torr; in this region weak lines make little contribution to the absorptance.

An all-glass manifold was used in handling the samples used in the present work; pressures were measured by means of oil and mercury manometers. The gas leads to the sample cells were kept as short as possible.

RESULTS

The results obtained for line strengths $S_J(298^\circ)$ at room temperature $T_R=298^\circ\text{K}$ are plotted as a function of line number in Fig. 4 and are listed in Table I. The results are based on measurements with samples for which the Ladenberg-Reiche argument $x < 0.2$. The uncertainties indicated by the error bars in the figure are greatest in the vicinity of the strongest lines and are too small to be plotted for $m > 41$. Line strengths $S_J(207^\circ)$ for the low temperature $T = 207^\circ\text{K}$ were computed from the room-temperature values by the relation

$$S_J(207^\circ) = S_J(298^\circ) \times \frac{Q(298^\circ)}{Q(207^\circ)} \times \frac{\exp(-E_J/k \times 207^\circ)}{\exp(-E_J/k \times 298^\circ)} \quad (7)$$

where Q represents the rotation-vibration partition function at the indicated temperatures and J is the rotational quantum number for the initial rotational level with energy E_J . In using Eq.(7) we assume that the line strengths are directly proportional to the populations of the lower states involved in the transitions and that vibration-rotation interactions are the same at the two temperatures.

The values of the half-width parameters γ^0 obtained at 298°K and 207°K are plotted as a function of line number in Fig. 5 and are listed in Table I; the values of γ^0 are based on the $S_J(298^\circ)$ values listed in the table together with $S(207^\circ)$ computed from Eq.(7) along with measurements of equivalent width in the vicinity of the square root region with values of $x > 7$. The uncertainty bars in Fig. 5 represent the probable errors in numerous measurements; they are considerably larger for the low-temperature measurements than for the measurements at room temperature.

The chief factors contributing to the uncertainties in S and γ^0 are sampling errors in pressure measurements, errors in planimetry in obtaining equivalent

widths from the recorder charts, errors in temperature measurements, and possible non-linearities in detector-amplifier response. In the present study uncertainties in γ^0 as high as 30 percent are noted for some lines. These uncertainties are to be compared with estimated uncertainties as high as 26 percent reported by Madden¹ for some lines in the ν_2 fundamental and with estimated uncertainties as high as 11 percent listed by Burch et al.² for 02^0_3 combination band. Possible non-linearities in the response of the InSb detector used in the present work cannot be entirely eliminated; Madden employed a Golay cell and Burch used a PbS detector.

We note that for all lines shown in Fig. 5 γ^0 is greater for samples at 207°K than for samples at 298°K. For lines with $m > 5$, there appears to be a gradual decrease of γ^0 with increasing m at both temperatures. In Fig. 6 we give a comparison of the γ^0 values obtained at room temperature by Madden¹ and Burch et al.² with those obtained in the present study; in view of the uncertainties involved in the different studies, there seems to be fair agreement. For the three bands studied, the values of γ^0 decrease from approximately $0.10 \text{ cm}^{-1}/\text{atm cm}$ for lines near the band centers to approximately $0.06 \text{ cm}^{-1}/\text{atm cm}$ in the band wings.

DISCUSSION OF RESULTS

On the basis of simple theory, the parameter γ^0 is proportional to the mean collision frequency f_c of a molecule in a sample at atmospheric pressure; thus

$$\gamma^0 = f_c/2\pi = (n\bar{v}\sigma)/2\pi = [n(2kT/\mu)^{1/2}\sigma]/2\pi \quad (8)$$

where n is the number of molecules per unit volume, $\bar{v} = (2kT/\mu)^{1/2}$ is the mean

relative speed of colliding molecules and μ is the reduced mass of the collision pair, and σ is the collision cross section. Since, from the general gas law, $P = nkT$, we note that for the constant-cross-section approximation in which σ is a constant for each line:

$$\gamma^0(T_1) \cdot T_1^{\frac{1}{2}} = \gamma^0(T_2) \cdot T_2^{\frac{1}{2}} \quad (\text{Constant-Cross-Section Approximation}) \quad (9)$$

where $\gamma^0(T)$ is the half-width parameter for a sample at Kelvin temperature T . Goldring and Benesch⁴ in their studies of HCl and Hoover and Williams⁵ in studies of CO have noted the failure of the constant-cross-section approximation.

In the present study, Eq. (9) predicts that $\gamma^0(207^\circ)/\gamma^0(298^\circ) = (298/207)^{\frac{1}{2}} = 1.2$. Comparison of the measured values of $\gamma^0(207^\circ)$ and $\gamma^0(298^\circ)$ listed in Table I shows that $\gamma^0(207^\circ)/\gamma^0(298^\circ) > 1.2$ for nearly every absorption line; thus we conclude that the constant-cross-section approximation also fails for CO₂.

We have used Eq. (8) to compute the collision cross sections $\sigma(298^\circ)$ and $\sigma(207^\circ)$ from the measured values of the half-width parameters. The values for these cross sections are listed in Table I along with the ratio $\sigma(207^\circ)/\sigma(298^\circ)$. We note that the mean value of the ratio $\sigma(207^\circ)/\sigma(298^\circ) = 1.44$, which is just the temperature ratio $(298^\circ/207^\circ)$ and the standard deviation of ratios for individual lines from the mean is only 0.18. Thus, we might conclude that the collision cross-sections are inversely proportional to the absolute temperature; i.e.,

$$\sigma(T_1) \cdot T_1 = \sigma(T_2) \cdot T_2 \quad (10)$$

However, we note that, despite the small standard deviation, the ratios $\sigma(207^\circ)/\sigma(298^\circ)$ in Table I do not have truly random variations from the mean ratio. For lines with $m < 19$ near the band center, the ratios are generally higher than the mean while the reverse is true for lines with $m > 31$ in the

wing of the band. Thus, we must regard Eq. (9) as only a rough approximation. We note further that the ratios $\sigma(207^\circ)/\sigma(298^\circ)$ are based on the mean values of measurements involving large probable errors.

It is interesting to compare the present results with Ely and McCubbin's beautiful study of the P-21 line of 001 - 100 band of CO_2 in which they used laser radiation tuned to the central frequency of the line and measured absorption coefficients at numerous temperatures in the range $300^\circ - 420^\circ\text{K}$. Within their stated limits of uncertainty, their results are in clear agreement with Eq. (10) in the range $300 - 380^\circ\text{K}$ but come into some disagreement at higher temperatures. Thus, we must at best regard Eq. (10) as a rough approximation, which depends on the rotational states involved in the transitions.

LEGENDS FOR FIGURES

- Fig. 1 Schematic diagram of the source assembly and the Czerny-Turner spectrograph.
- Fig. 2 The components of the absorption cell designed for work at reduced temperatures.
- Fig. 3 Typical spectral transmittance curves. Panel A: Transmittance of a pure CO_2 sample for a total pressure of 0.18 Torr and an effective path length of 2000 cm. Panel B: Transmittance of CO_2 at a partial pressure of 3.27 Torr in a 0.5 cm cell with N_2 added to give a total pressure of 1 atm. Panel C: Transmittance of pure CO_2 at a pressure of 20 Torr in a 10 cm absorption cell.
- Fig. 4 Measured line strengths S for lines in the R branch of the ν_3 fundamental of CO_2 .
- Fig. 5 Measured values of half-width parameter γ^0 for lines in the R branch of the ν_3 fundamental of CO_2 for temperatures of 207°K and 298°K.
- Fig. 6 Self-broadening parameters γ^0 for various rotational lines in CO_2 samples at laboratory temperatures. Present results are given by circles. Madden's results for the ν_2 fundamentals are given by triangles. The results of Burch et al. for a combination band are given by the squares.

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*Supported in part by a grant from the National Aeronautics and Space Administration.

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TABLE I

Line Strengths S , Self-Broadening Parameters γ^0 , and Collision Cross Sections σ
for CO_2 at 298°K and 207°K

Line Number m	$S(298^\circ)$	$\gamma^0(298^\circ)$	$\sigma(298^\circ)$	$\gamma^0(207^\circ)$	$\sigma(207^\circ)$	$\sigma(207^\circ)/\sigma(298^\circ)$
1	15.5	92	148	158	213	1.43
3	29.3	91	147	173	233	1.58
5	42.6	102	165	207	279	1.70
7	52.3	92	148	202	272	1.84
9	62.1	103	166	190	255	1.54
11	71.2	115	186	198	266	1.43
13	75.7	87	140	179	241	1.73
15	78.0	92	148	172	232	1.57
17	77.7	85	137	157	211	1.54
19	73.1	97	156	181	243	1.55
21	71.3	86	139	143	192	1.38
23	63.8	97	156	172	231	1.47
25	60.0	82	132	149	200	1.51
27	52.6	78	126	155	209	1.65
29	47.1	89	144	167	227	1.57
31	41.4	87	140	130	175	1.25
33	34.2	87	140	143	192	1.37
35	29.8	83	134	119	160	1.19
37	24.8	77	124	119	160	1.29
39	19.7	80	129	138	186	1.44
41	15.8	74	119	129	173	1.45
43	12.5	70	113	109	147	1.30
45	10.2	67	108	98	132	1.22
47	7.56	63	102	88	118	1.15
49	5.80	60	97	83	112	1.15
51	4.60	56	90	86	116	1.29
53	3.25	53	86	81	109	1.27
55	2.24	55	89	91	122	1.37

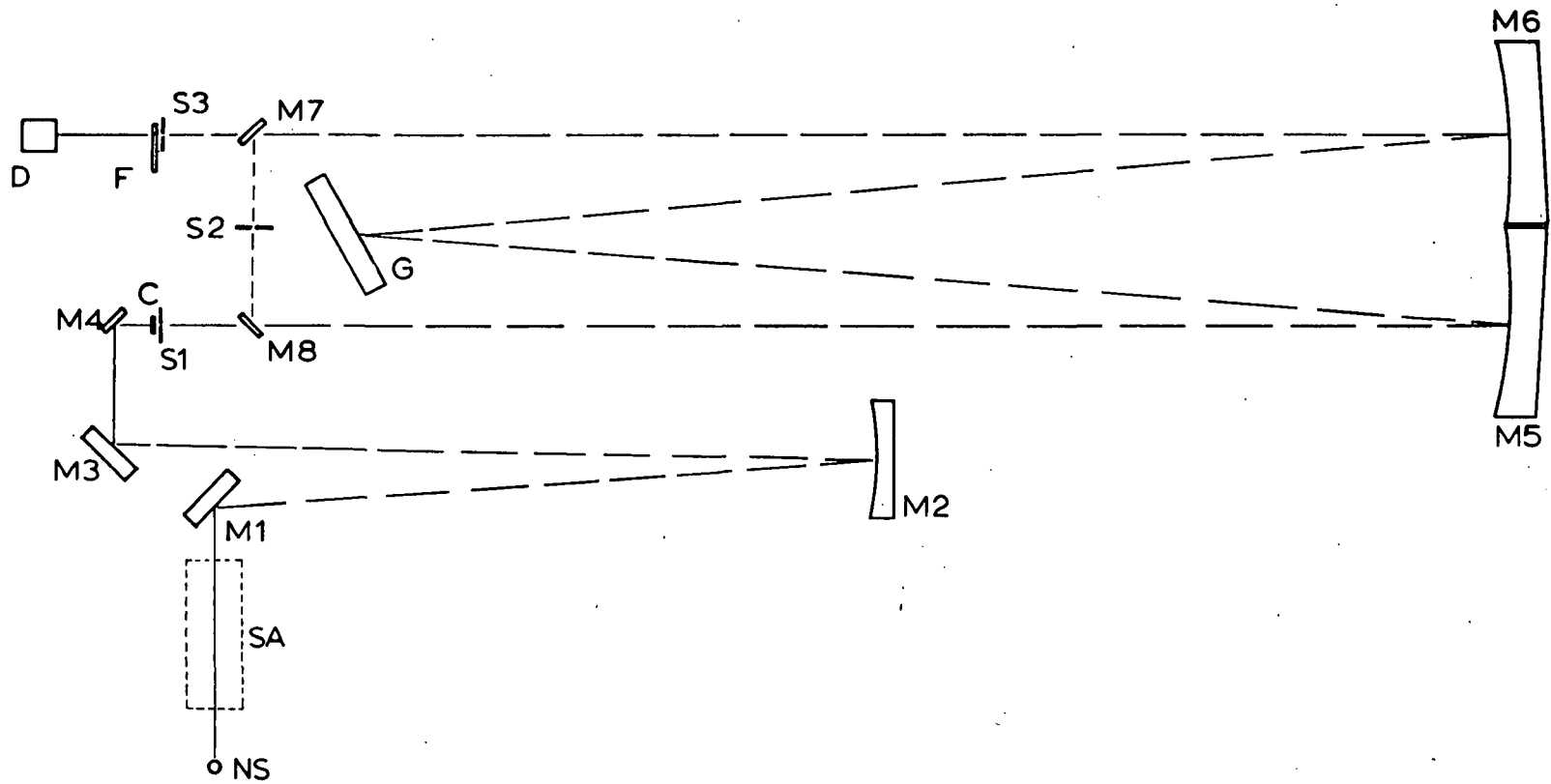


Fig. 1

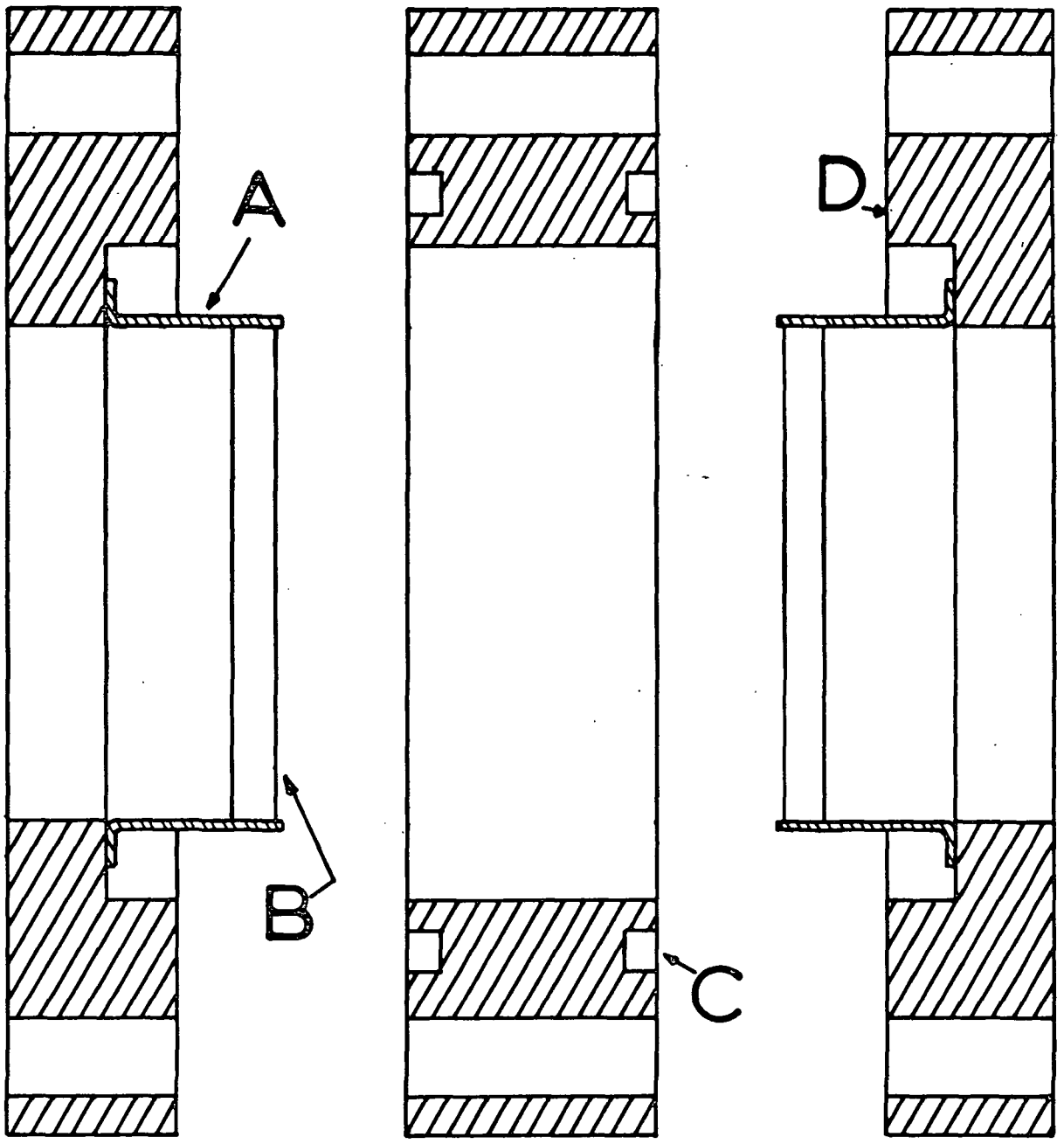


Fig. 2

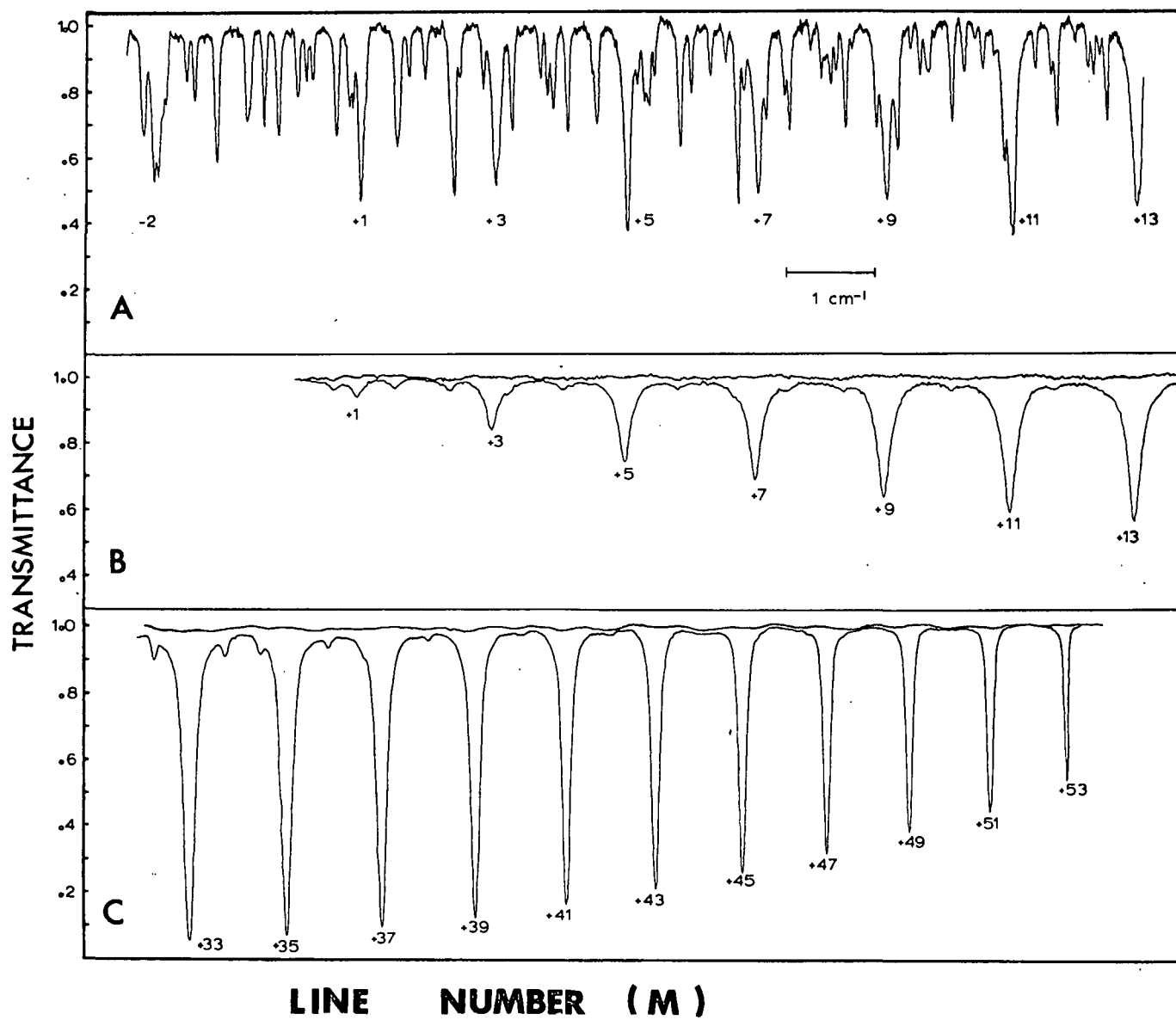


Fig. 3

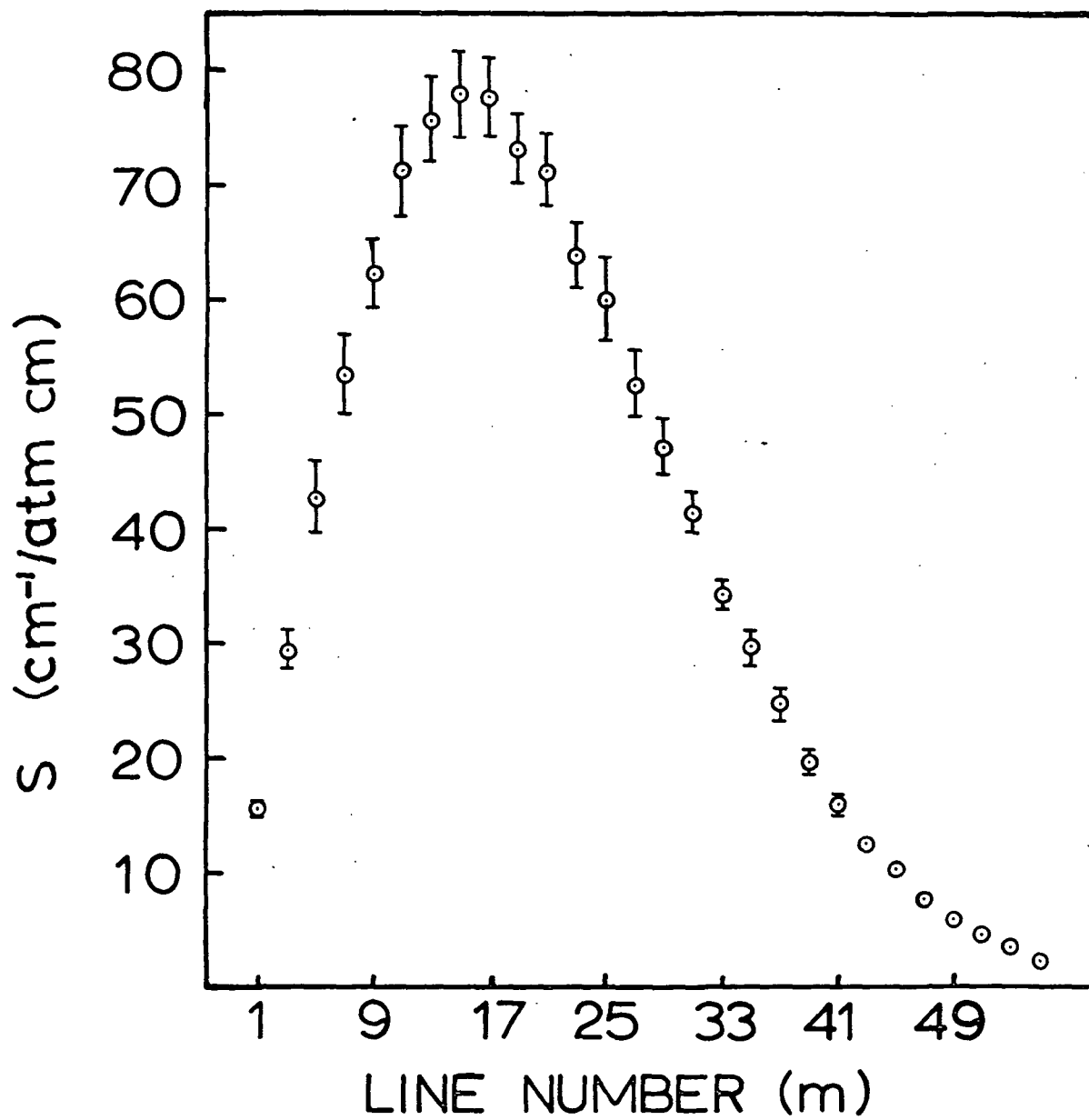


Fig. 4

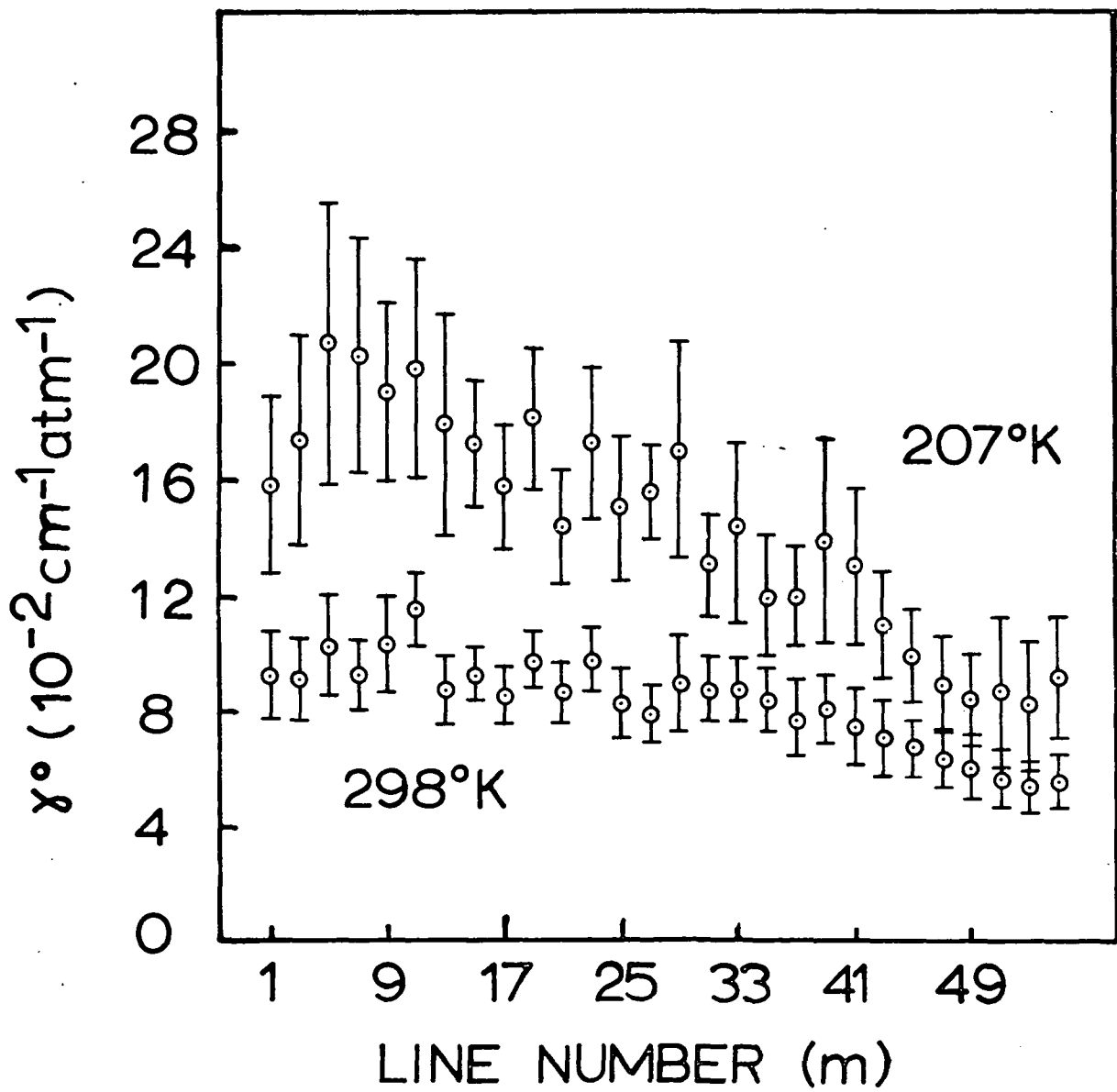


Fig. 5

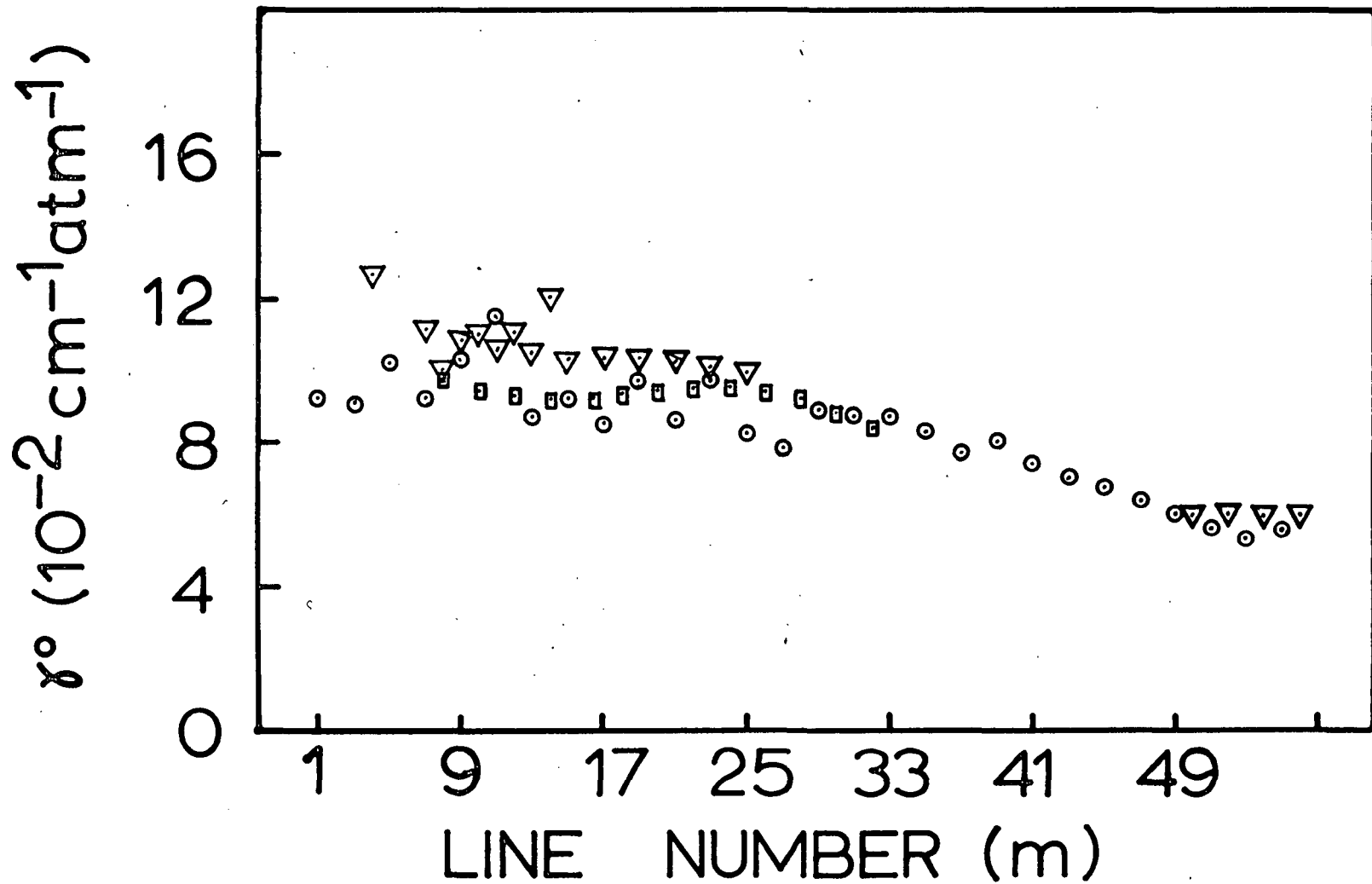


Fig. 6

BROADENING OF INFRARED ABSORPTION LINES AT REDUCED TEMPERATURES II:

CARBON MONOXIDE IN AN ATMOSPHERE OF CARBON DIOXIDE*

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ABSTRACT

The strengths of the rotational lines in the R branch of the CO fundamental have been determined at temperatures of 298^o, 202^o, and 132^o K by means of a high-resolution spectrograph. The results can be used to determine line strengths at other temperatures by means of the Herman-Wallis relation or by considerations of the populations of the rotational levels in the ground vibrational state. Parameters describing the self broadening and carbon-dioxide broadening of CO lines have been determined at 298^o K and 202^o K. The results are compared with other recent experimental and theoretical studies.

INTRODUCTION

Recent spectroscopic studies show that the thin Martian atmosphere consists chiefly of carbon dioxide along with a small quantity of carbon monoxide. In order to make realistic estimates of the amount of CO present from the observed infrared spectra, it is necessary to know the line strengths of CO at Martian temperatures and the broadening of the absorption lines caused by collisions with the more abundant gas CO₂. Although it is possible to make valid computations of line strengths S at reduced temperatures from measurements of line strengths at ambient laboratory temperatures, corresponding

computations of the widths of absorption lines at reduced temperatures in terms of ambient laboratory temperature measurements cannot be made at present, because the molecular optical collision cross sections are not the same at all temperatures and cannot be calculated in any simple way.^{1,2,3,4} This variation of collision cross section with temperature presents a currently important problem in molecular physics.

The purpose of the present work was to measure (1) the strengths of lines in the CO fundamental at room temperature and at a Martian temperature with the purpose of obtaining a set of 'best values' for use in calculations, (2) the corresponding line broadening parameters γ_{aa}^0 for CO self broadening, and (3) the corresponding line-broadening parameters γ_{ab}^0 for CO₂ as a foreign-gas broadener. The line-broadening parameter γ^0 is numerically equal to the half width of the applicable Lorentz line at a pressure of 1 atm; the half width at other pressures is thus $\gamma = \gamma^0 p$.

The experimental techniques used in the present work are essentially the same as those employed in our recent study⁴ of CO₂; we shall employ the same terminology in presenting the results of the present study. In the present study we measured CO line strengths S at 298° K, 202° K and 132° K and we determined line-broadening parameters at γ_{aa}^0 and γ_{ab}^0 298° K and 202° K. The gases employed were of reagent grade and were supplied by the Matheson Company.

LINE STRENGTHS

The measured line strengths S for lines in the R branch of CO at a temperature of 298° K are given by the circled points in Fig. 1, which is a plot of S as a function of line number $m = J+1$ where J is the rotational quantum number for the initial level. In this plot S rises to a maximum in the vicinity

of $m = 7$ and thereafter decreases with increasing m . The points for $m > 21$ are replotted on an expanded ordinate scale in the figure.

The points shown as triangles in Fig. 1 represent line strengths calculated from the simplified Herman-Wallis expression

$$S_m = S_V v_m |m| \exp [-E_R(m)/kT] / Q_R(T) \cdot \bar{v} \quad (1)$$

where S_V is the total band strength, $E_R(m)$ is the energy of the initial rotational state, Q_R is the rotational partition function for temperature T , and

$$\bar{v} = \sum_{m=-\infty}^{m=+\infty} v_m |m| \exp(-E_R(m)/kT) / Q_R(T) \text{ with } m \neq 0.$$

In this study we have regarded the band strength S_V as a fitted parameter and have used a computer program to determine the value of S_V that gives the best agreement between the measured and calculated values for the individual line strengths S_m . The value of S_V that gives the best fit for our 298° K data is $242 \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$; this value is to be compared with the value $236 \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$ used by Benedict et al.⁶ We note that all values of S_m calculated from Eq.(1) agree with the corresponding measured values within the limits of experimental uncertainty.

Figure 2 shows line strengths as a function of line number for CO samples at 202° K with measured values shown as circles and calculated values as triangles. Because of the low values of S_m for large m we have used two ordinate-scale expansions as indicated in the figure. The band strength $S_V = 233 \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$ gives the best fit between measured and calculated line strengths.

The line strengths as a function of line number for gas samples at 132° K are plotted in Fig. 3. For 132° K the best fit between measured and calculated values is obtained with band strength $S_V = 210 \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$. The mean value of S_V for the three temperatures is $228 \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$; the largest

value S_V is 6 percent above and the smallest value is 8 percent below the mean value.

We note that the present best-fit values of S_V decrease monotonically with decreasing temperature. In order to test the possible significance of this, we subjected the earlier data of Hoover and Williams⁴ to a best fit analysis and obtained S_V values of 213, 225, and 236 $\text{cm}^{-1}/(\text{atm cm})_{\text{NTP}}$ at temperatures of 300°, 193°, and 153°K, respectively. Since this variation with temperature is just the reverse of that obtained in the present study, we can report no significant systematic change of S_V with temperature.

The purpose of the present line-strength measurements was to provide data from which line strengths at reduced temperatures can be calculated. We have used the present measurements along with those of Hoover and Williams² and Benedict et al.⁶ as basic data for two sets of calculations; these data are supported by some 740 individual line measurements in the present study, 414 measurements in the Hoover-Williams study, and a comparably large number of measurements in the Benedict study.

One method of calculation is based on the simplified Herman-Wallis relation given in Eq. (1), in which vibration-rotation interactions are omitted. With the use of a nominal band strength $S_V=228 \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$, we find that the rms deviation of the observed line strengths S_m from the calculated line strengths is 8.4 percent. Thus, for the existing data we find that Eq. (1) can be used in good approximation in calculating S_m . The poorest agreement between observed and calculated values was noted at 132°K. Equation (1) with $S_V=228 \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$ should be used with caution in computing line strengths at elevated temperatures because rotation-vibration interactions may be appreciable for large values of m .

A second scheme for determining line strengths at various reduced temperatures can be based on the fact that the strength of a rotational line in the CO fundamental is directly proportional to the population of the initial rotational level. Thus, if line strength S_m is known at 298°K , the strength of the same line at temperature T can be determined from the relation

$$S_m(T)/S_m(298^\circ) = [\exp(-E_J/kT)/Q_R(T)] / [\exp(-E_J/k \cdot 298^\circ)/Q_R(298^\circ)]$$

where E_J is the energy of the initial rotational state and Q_R is the rotational partition function at the indicated temperatures. We have used the existing data to obtain a set of nominal values of $S_m(298^\circ)$ for use in Eq. (2) for prediction of S_m at other temperatures. With the use of the nominal S_m values listed in Table I, we find that the rms deviation of measured values from the predicted values is 7.3 percent. Thus, Eq. (2) provides a slightly better fit to the existing data than Eq. (1) with a single value for S_v .

We note that Eq. (2) can also be used to predict S_m values at elevated temperatures for the lines listed in Table I provided the vibrational partition function is introduced; it gives no information for lines for $m > 25$, for which we have not determined nominal S_m values at 298°K .

COLLISIONAL BROADENING

The measured values of line-broadening parameters are shown graphically as a function of line number in Figs. 4-8. Each point in these plots is based on eleven independent determinations. Although the experimental uncertainties indicated in the figures are somewhat larger than the uncertainty estimates in some earlier lower-resolution work summarized by Hoover,² the use of a high-resolution spectrograph has resolved certain paradoxes involving the widely differing values reported earlier for the γ^0 values at 300°K for line $m = 1$.

This line is actually a blend with the $m = 15$ absorption line of the isotopic molecule $C^{13}O$; although the $C^{13}O$ line contributes little to the measured line strength, its contribution to the measured γ^0 values can be important.** After correction for the blended line, our present results for $m = 1$ at $298^\circ K$ give a value $\gamma_{aa}^0 = 0.101 \text{ cm}^{-1}/\text{atm}$ instead of the value $0.124 \text{ cm}^{-1}/\text{atm}$ shown in Fig. 4 and our results at $202^\circ K$ give a value $\gamma_{aa}^0 = 0.154 \text{ cm}^{-1}/\text{atm}$ instead of $0.194 \text{ cm}^{-1}/\text{atm}$ shown in Fig. 5.

The present results for the influence of temperature on the self-broadening parameter γ_{aa}^0 are in general agreement with the earlier results of Hoover,² which covered the range $m = 1$ to 21. In both investigations it was found that the ratio of γ_{aa}^0 at approximately $200^\circ K$ to γ_{aa}^0 at approximately $300^\circ K$ decreases from approximately 1.6 for low m -values to nearly unity in the vicinity of $m = 20$. In the present work we find that the ratio is less than unity for $m > 22$; this result is consistent with Hoover's results at $T = 124^\circ K$, at which temperature the parameters γ_{aa}^0 for $m > 14$ are smaller than the corresponding parameters at $300^\circ K$. For the temperatures of $202^\circ K$ and $298^\circ K$ used in the present study, the ratio $\gamma_{aa}^0(202^\circ)/\gamma_{aa}^0(298^\circ) = 1.2$ is predicted on the basis of the constant-collision-cross-section approximation; the failure of this approximation is obvious.

Our results for the parameter γ_{ab}^0 for broadening of CO lines by CO_2 at $298^\circ K$ and $202^\circ K$ are plotted in Figs. 6 and 7, respectively. After corrections for the $C^{13}O$ blended line, the values $\gamma_{ab}^0 = 0.136 \text{ cm}^{-1}/\text{atm}$ at $298^\circ K$ and $\gamma_{ab}^0 = 0.186 \text{ cm}^{-1}/\text{atm}$ at $202^\circ K$ are obtained for $m=1$. The $298^\circ K$ results in Fig. 6 indicate a gradual decrease of γ_{ab}^0 with increasing line number m ; the ratio of γ_{ab}^0 for the lowest m -values to γ_{ab}^0 for the highest m -values is approximately 2. The values of γ_{ab}^0 at $202^\circ K$ plotted in Fig. 7 show a much more rapid decrease with increasing

m; the ratio of γ_{ab}^0 for the lowest m-values to γ_{ab}^0 for the highest m-values is approximately 3. The plotted values of γ_{ab}^0 in Fig. 7 actually show a slight increase as m increases from 12 to 16; however, in view of the large experimental uncertainties, no significance can be attached to the apparent 'hump' in the plot near m=16. We note that the ratio $\gamma_{ab}^0(202^\circ)/\gamma_{ab}^0(298^\circ)$ ranges from nearly 2 for some m values to slightly more than unity at m=22 and averages approximately 1.5; the constant collision-cross-section approximation again predicts a ratio of 1.2 for all lines.

It is perhaps of interest to compare the parameters for CO₂ broadening with those for CO self-broadening at the two temperatures covered in the present work. At 298° K, the ratio $\gamma_{ab}^0/\gamma_{aa}^0$ ranges from approximately 1.3 for m=1 to 5 to approximately unity for m>20. At 202° K, the ratio also ranges from approximately 1.3 for m=1 to 5 to approximately unity near line m=21.

DISCUSSION OF RESULTS

As we have indicated earlier, our results for CO self broadening are in general agreement with those obtained by Hoover and Williams,² who have given a detailed comparison of their values of γ_{aa}^0 at 300° K with the results of earlier investigations. Our present values of γ_{aa}^0 at 298° K are in somewhat closer agreement with the more recent values of Burch and Gryvnak⁷ and Kostkovski and Bass⁸ than with those reported by earlier investigators.^{9,10}

A comparison of our present values of γ_{ab}^0 for broadening by CO₂ at ambient laboratory temperature with those of other investigators is given in Panel A of Fig. 8. For the range m=1 to 8, the present values are in excellent agreement with recent experimental results reported by Varanasi;¹¹ for the range m=9 to 18, the present values of γ_{ab}^0 are higher than those reported by Varanasi.

There is fair agreement between the present results and those of Draegert and Williams¹² over most of the range of m ; the present values of γ_{ab}^0 are consistently higher than those reported by Crane-Robinson and Thompson.⁹

Although no values of γ_{ab}^0 at 200° K are available for comparison with our present results, we can make a comparison with a set of calculated values. Varanasi and Tejwani¹³ have applied the Anderson-Tsao-Curnutte (ATC) theory to the problem of the broadening of CO lines by CO₂. For a temperature of 295° K, their computed values of γ_{ab}^0 are in excellent agreement with Varanasi's experimental values¹¹ over the entire range $m=1$ to 18. These authors have also attempted to use the ATC theory in calculating γ_{ab}^0 at reduced temperatures.

Panel B of Fig. 8 shows a comparison of our present experimental values of γ_{ab}^0 with the calculated values of Varanasi and Tejwani. The calculated values are in general lower than our measured values but fall within our limits of experimental uncertainty for lines $m=1,3,4,5,6,19,20,21$, and 22. The differences between the observed and calculated values is greatest in the intermediate region $m=7$ to 18.

We recognize that the present work represents merely a first step in an understanding of the broadening of CO by CO₂ at Martian temperatures and have given conservatively large estimates of uncertainty; in view of the disagreements between earlier independent investigations of CO self broadening at 300° K we hope that other investigators will check our present measurements in the near future.

In order to provide data for comparison with ATC calculations it is desirable to undertake measurements of γ_{ab}^0 for broadening of CO by various simple gases as a function of temperature. Although the results of such studies would not have direct planetary applications, they might prove highly useful in the

development of readily and widely applicable theories. We point out that even relative measurements of line broadening as a function of temperature, which can usually be made more precisely than absolute measurements, could prove useful in providing tests of the validity of the ATC theory.

LEGENDS FOR FIGURES

Fig. 1 CO line strengths at 298° K in units of $10^{-2} \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$ as a function line number m . Measured values are shown as circles; values calculated from the Herman-Wallis expression with band strength $S_V=242 \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$ are shown as triangles.

Fig. 2 CO line strengths at 202° K in units of $10^{-2} \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$ as a function line number m . Measured values are shown as circles; values calculated for band strength $S_V=233 \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$ are shown as triangles.

Fig. 3 CO line strengths at 132° K in units of $10^{-2} \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$ as a function line number m . Measured values are shown as circles; values calculated for band strength $S_V=210 \text{ cm}^{-1}/(\text{atm cm})_{\text{STP}}$ are shown as triangles.

Fig. 4 Measured self-broadening parameters for CO at 298° K in units of $\text{cm}^{-1}/\text{atm}$ as a function line number. Note that the measured value for line $m=1$ should be reduced to $0.101 \text{ cm}^{-1}/\text{atm}$.

Fig. 5 Measured self-broadening parameters for CO at 202° K in units of $\text{cm}^{-1}/\text{atm}$ as a function line number. Note that the measured value for line $m=1$ should be reduced to $0.154 \text{ cm}^{-1}/\text{atm}$.

Fig. 6 Parameters for broadening of CO lines by CO_2 at 298° K in units of $\text{cm}^{-1}/\text{atm}$ as a function of line number. Note that the parameter for line $m=1$ should be reduced to $0.136 \text{ cm}^{-1}/\text{atm}$.

Fig. 7 Parameters for broadening of CO lines by CO_2 at 202° K in units of $\text{cm}^{-1}/\text{atm}$

as a function of line number. Note that the parameter for line $m=1$ should be reduced to $0.186 \text{ cm}^{-1}/\text{atm}$.

Fig. 8 Comparison of present values of parameters for CO_2 -broadening of CO absorption lines with those obtained in earlier studies. Panel A gives the parameters for broadening at approximately 300°K ; present results are given by circled points, those of Varanasi by diamonds, those of Draegert and Williams by triangles, and those of Crane-Robinson and Thompson by squares. Panel B gives the parameters for broadening at approximately 200°K . The present results are given by circled points; the values computed by Varanasi and Tejwani on the basis of the Anderson-Tsao-Curnutte theory are given by diamonds.

FOOTNOTES AND REFERENCES

*Supported in part by the National Aeronautics and Space Administration.

** In the S-determinations, measurements are made in the linear region of line growth; if the $C^{12}O$ line is in the linear region, the $C^{13}O$ line is also in the linear region. The γ^0 determination is made in the square-root region of line growth; even if the $C^{12}O$ line is in the square-root region, the $C^{13}O$ line may not be in this region. In correcting for the $C^{13}O$ line we have made use of tabulated values of the Ladenberg-Reiche function and have assumed no overlapping.

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TABLE I. Nominal Line Strengths at 298°K

m^a	S^b	m	S	m	S
1	2.02	10	9.08	18	2.36
2	4.26	11	8.23	19	1.76
3	5.92	12	7.22	20	1.31
4	7.47	13	6.55	21	0.973
5	8.82	14	5.34	22	0.716
6	9.73	15	4.49	23	0.500
7	10.17	16	3.77	24	0.350
8	10.30	17	3.09	25	0.240
9	9.21				

a. Line number $m=J+1$ in the R branch.

b. Line strengths S are in units of $\text{cm}^{-1}/(\text{atm cm})_{\text{STP}}$

Fig. 1

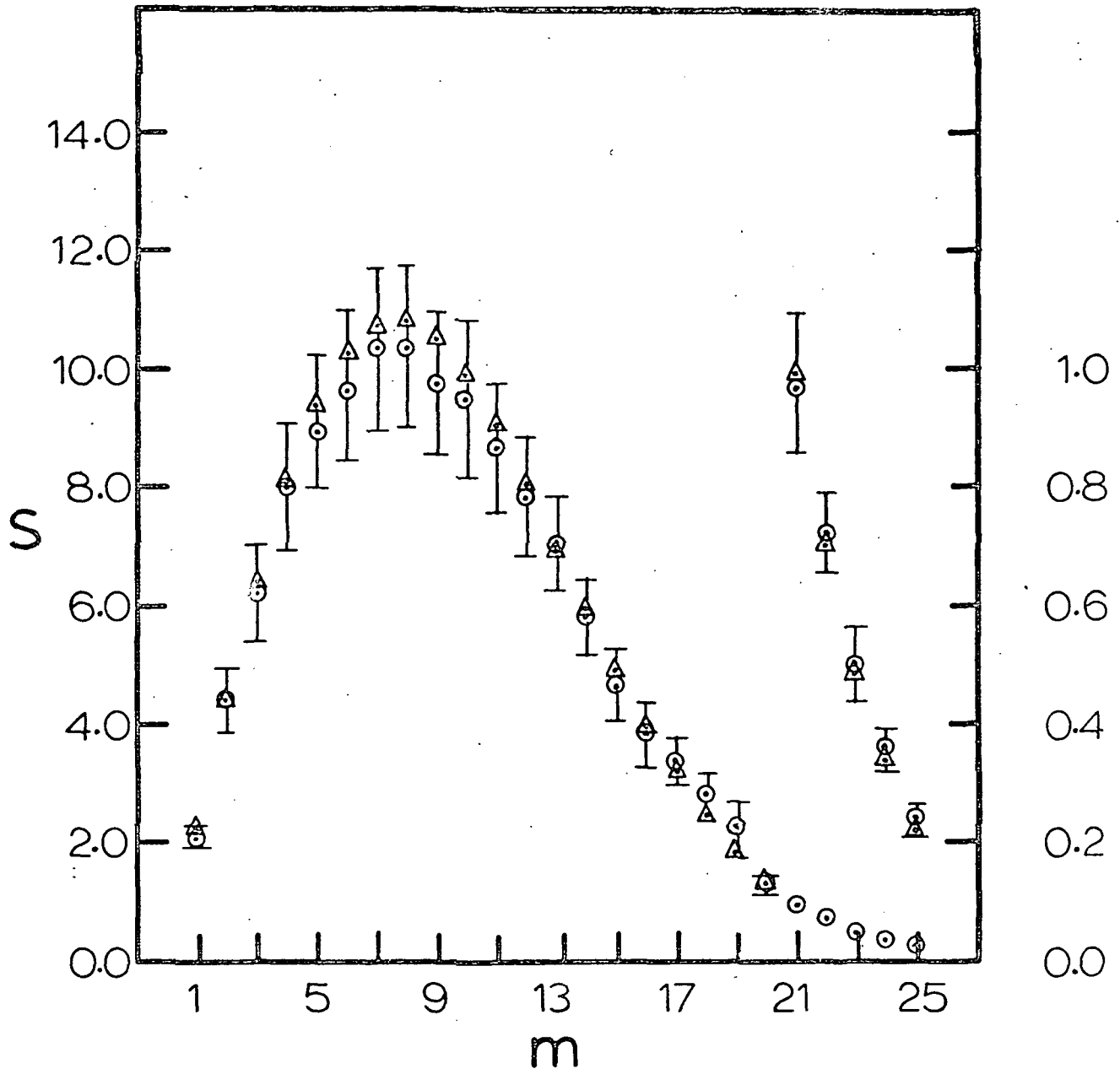


Fig. 2

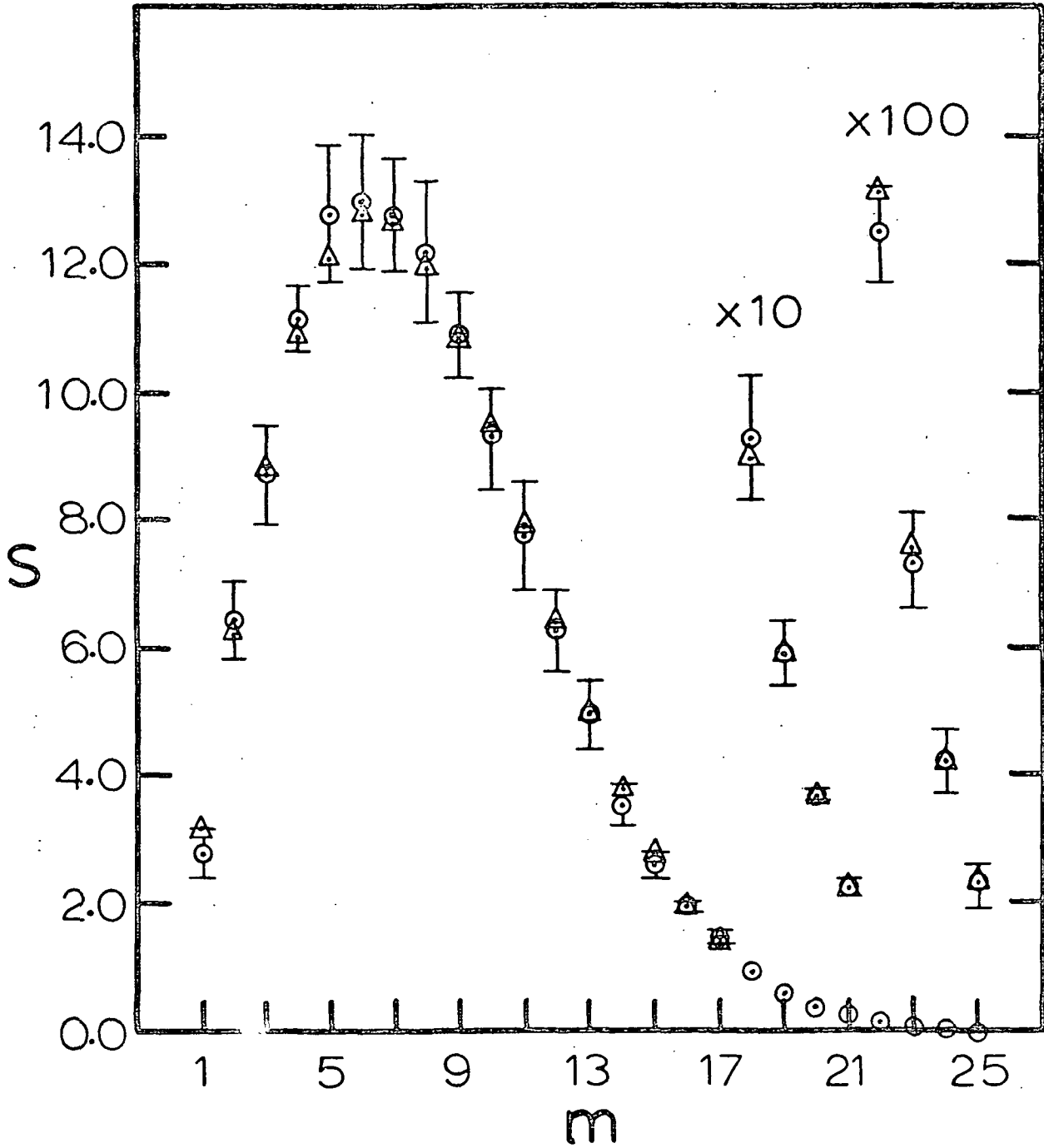


Fig. 3

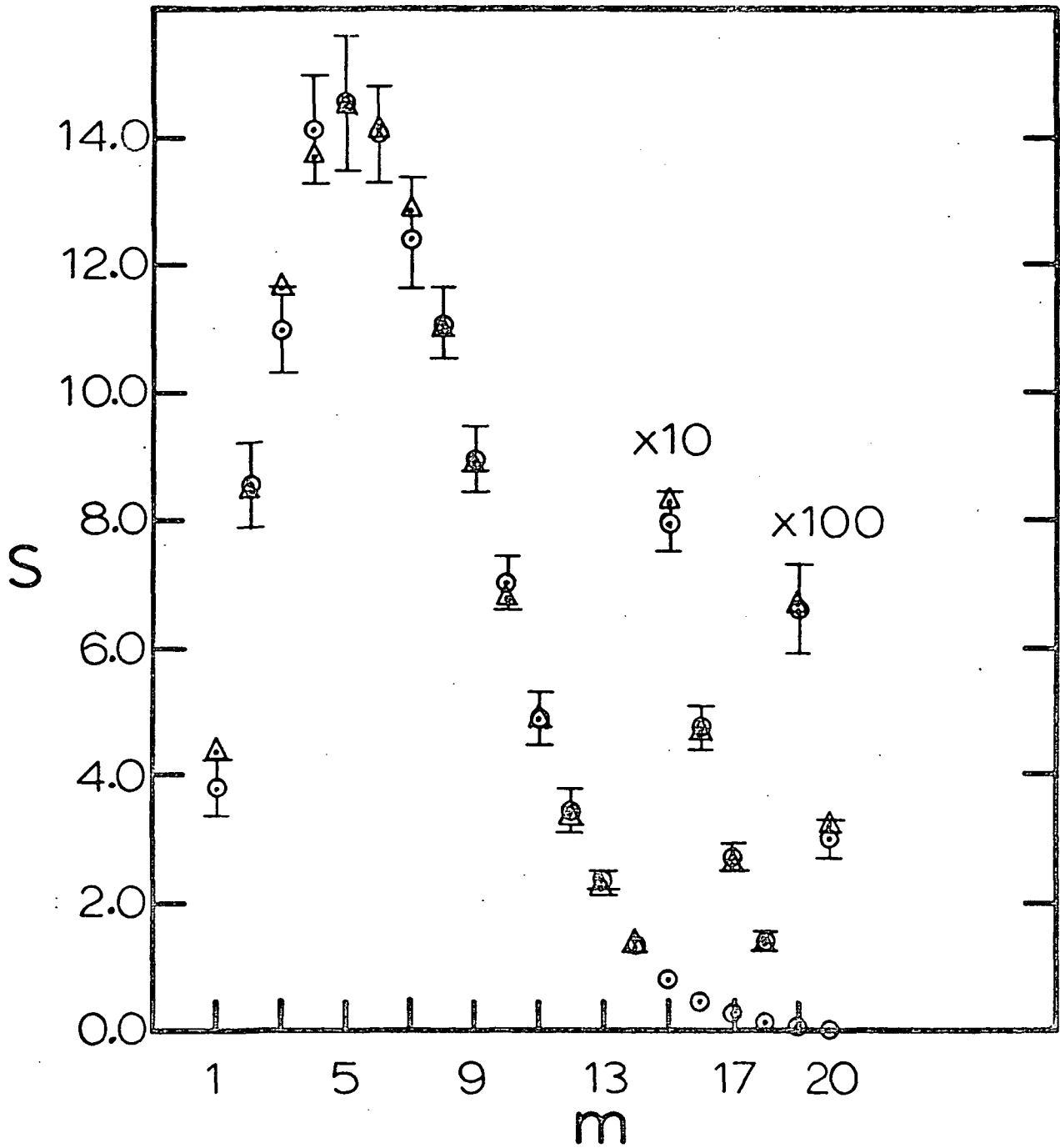


Fig. 4

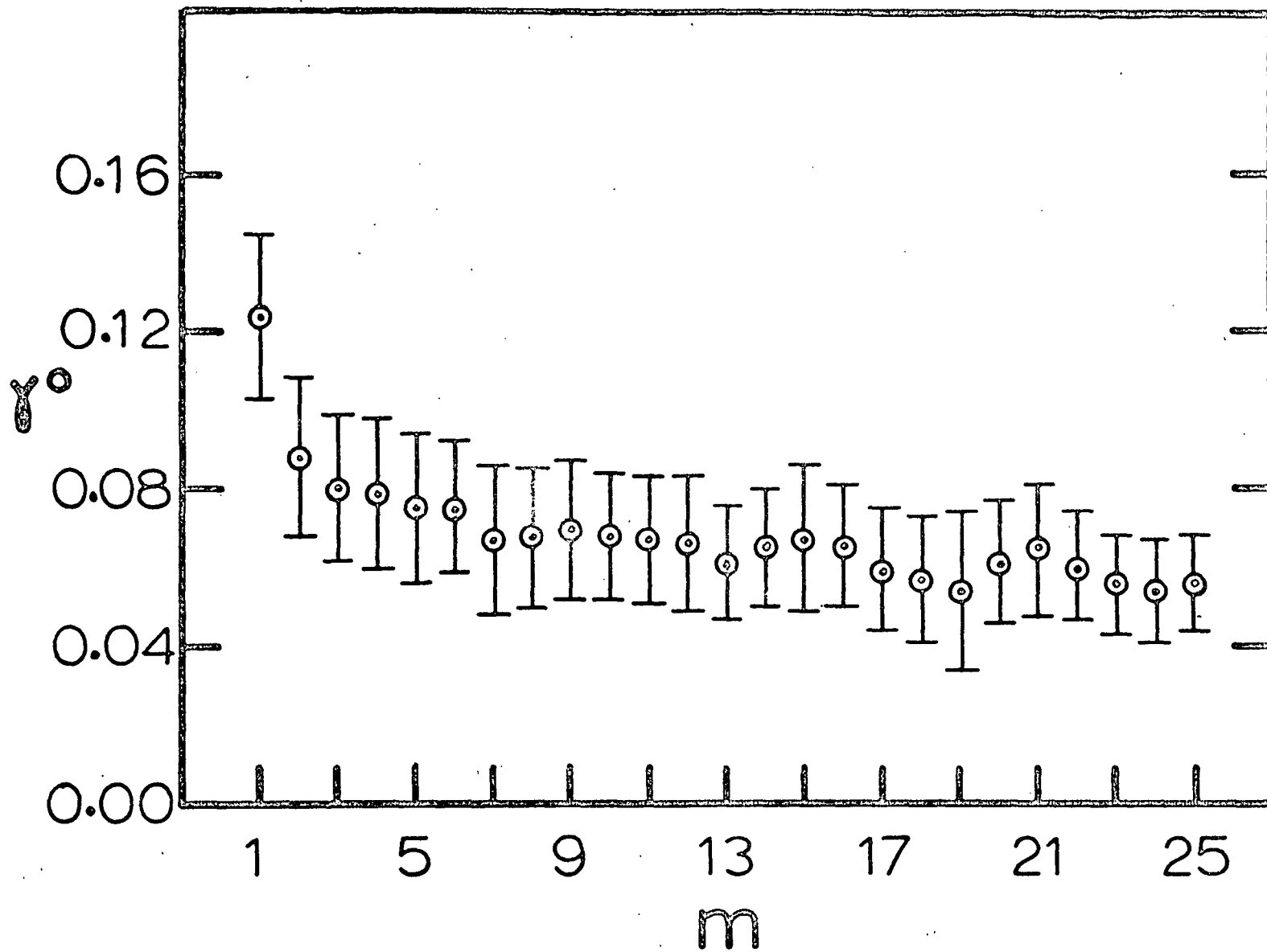


Fig. 5

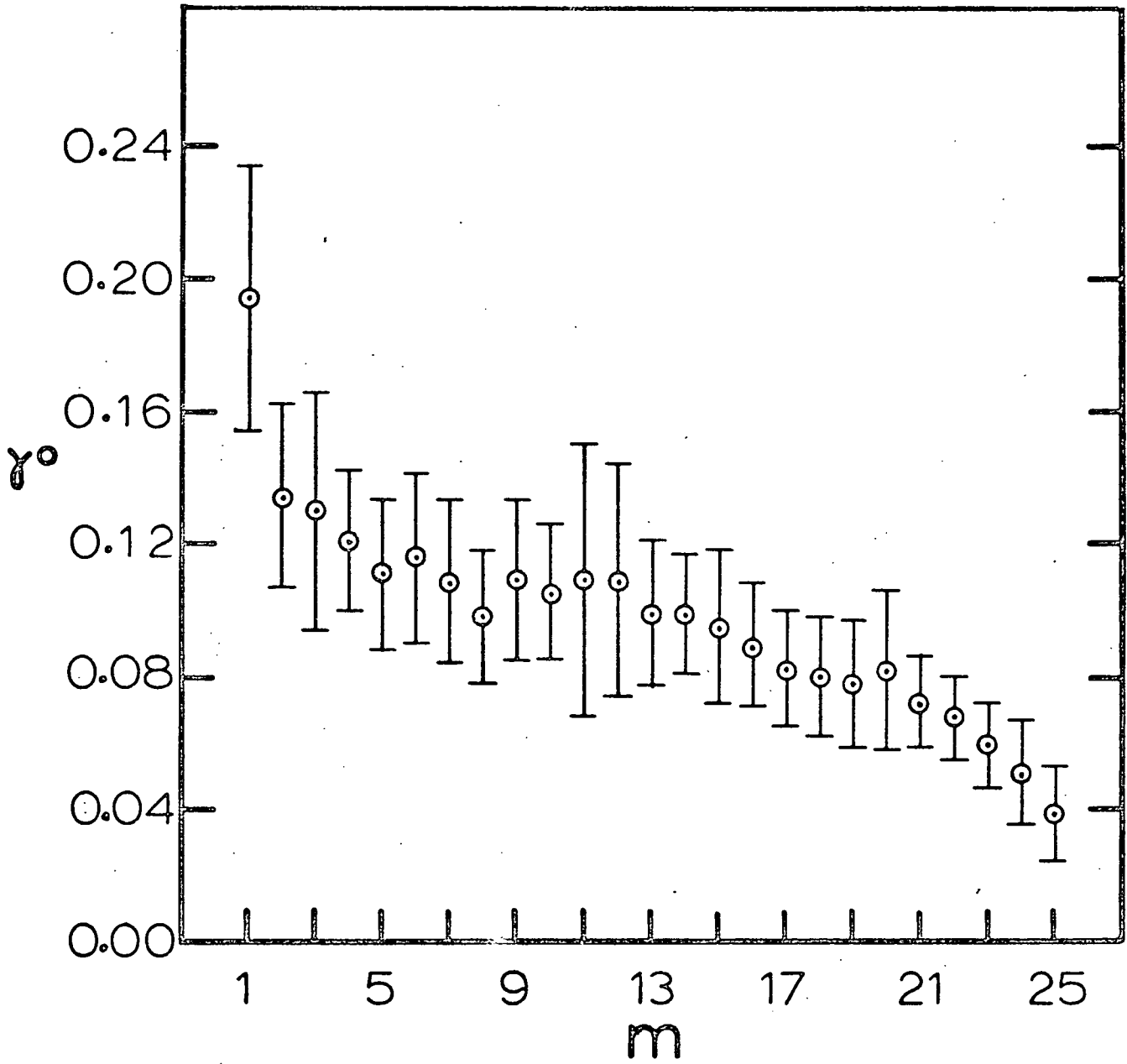


Fig. 6

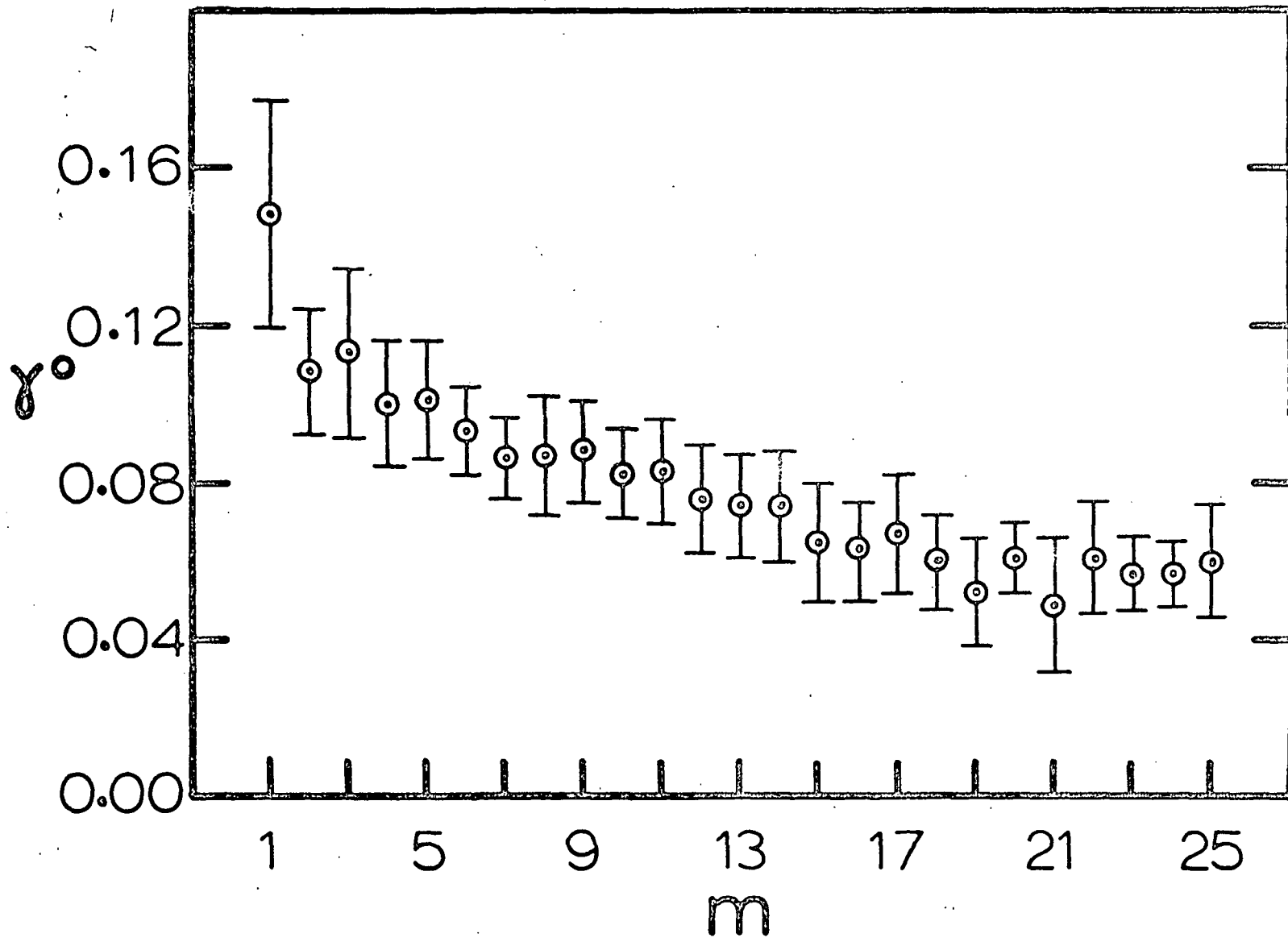


Fig. 7

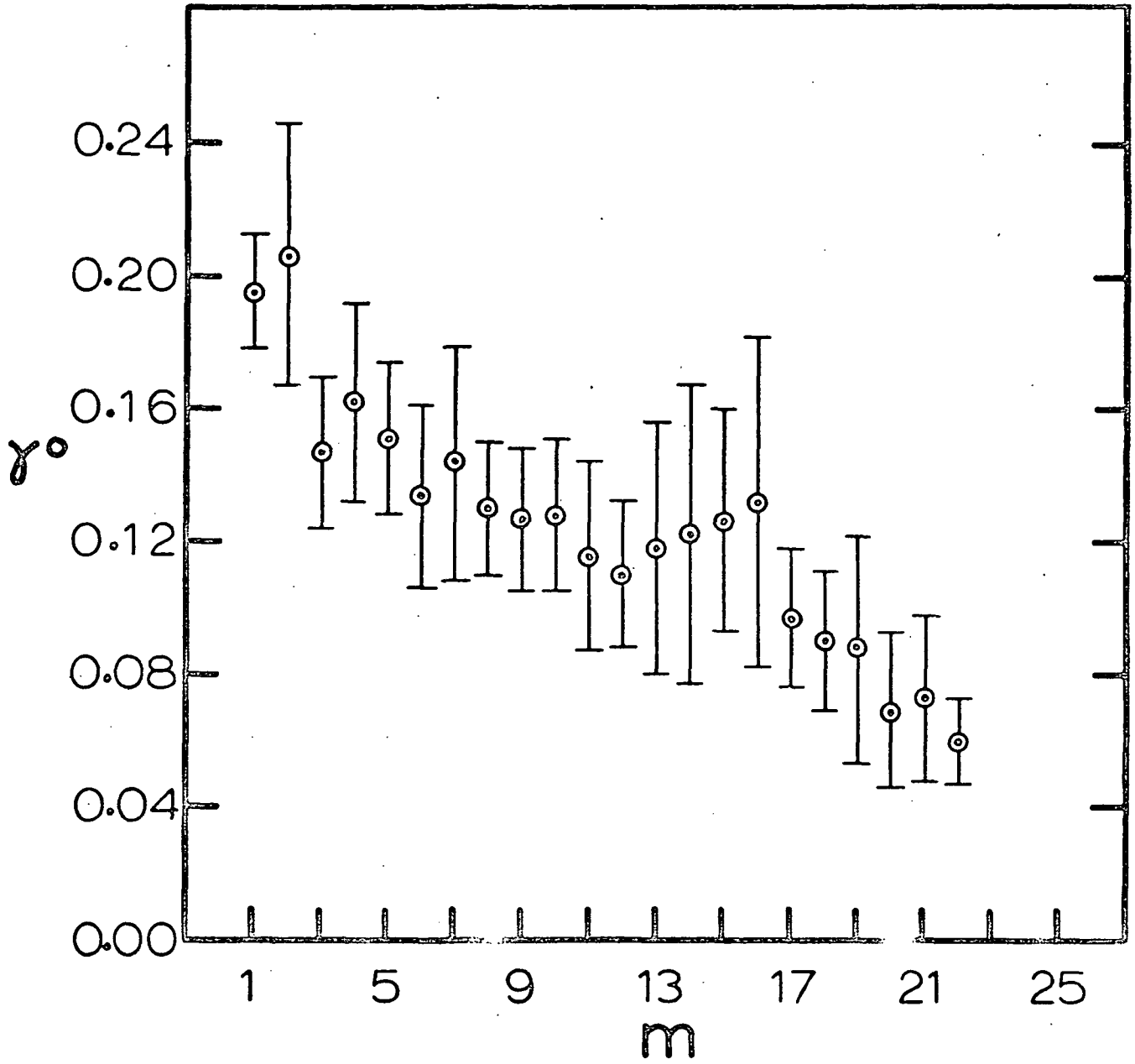
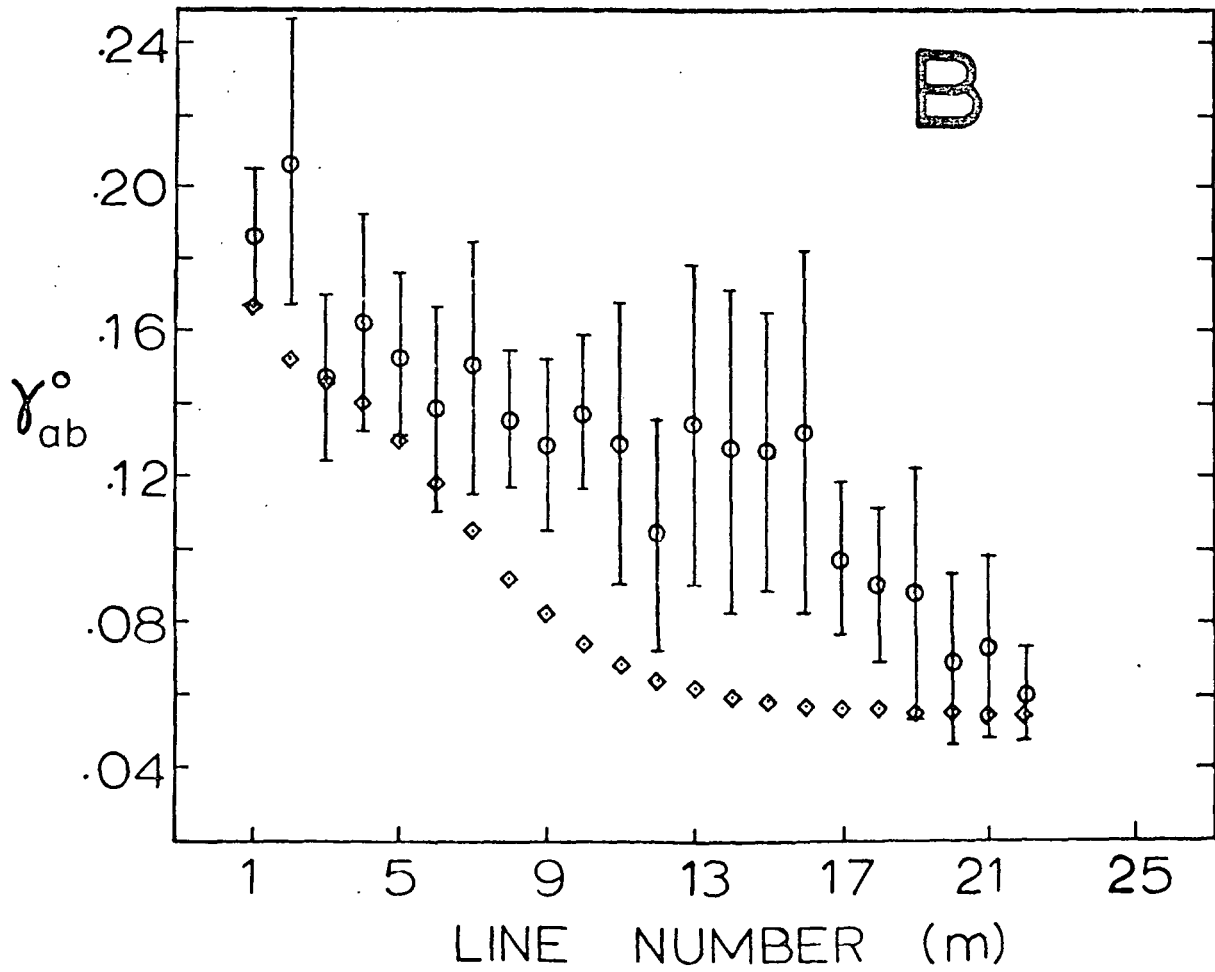
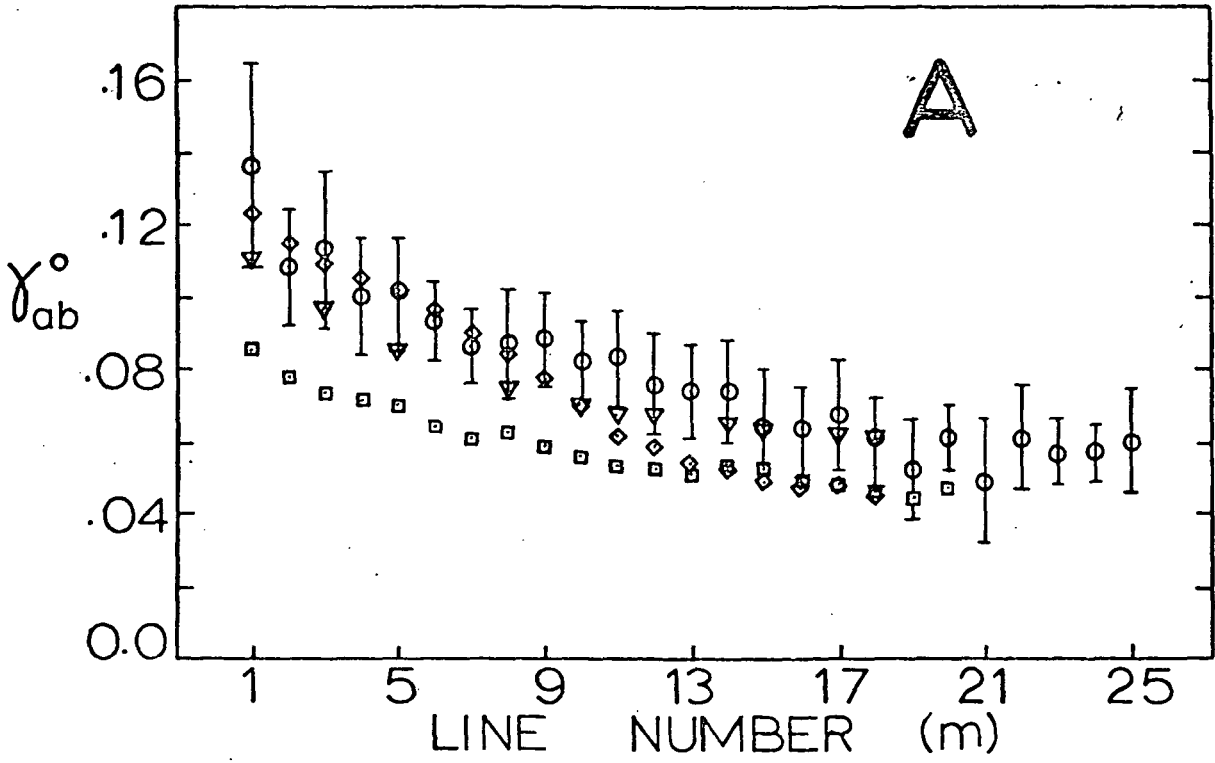


Fig. 8



Foreign-Gas Broadening of Nitrous Oxide Absorption Lines*

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ABSTRACT

We have measured the foreign-gas broadening coefficients for collisional broadening of lines in the ν_3 fundamental of N_2O by He, Ne, Ar, Kr, Xe, H_2 , D_2 and CH_4 . These coefficients, which give the ratio of the line broadening ability of these gases to the line broadening ability of N_2 , can be used with recent measurements and calculations of N_2 broadening to obtain optical collision cross sections.

Earlier studies¹ of the total band absorptance of telluric gases whose absorption lines are collisionally broadened by nitrogen have shown that the equivalent width of a band can be expressed in terms of absorber thickness w and an effective pressure:

$$P_e = B p_a + p_N \quad (1)$$

where p_N is the partial pressure of nitrogen, p_a is the partial pressure of the absorbing gas, and the self-broadening coefficient B is the ratio of the line broadening ability of the absorbing gas to the line-broadening ability of nitrogen. If a gas other than nitrogen is used as a broadener, the effective or nitrogen-equivalent pressure can be written:

$$P_e = B p_a + F p_b \quad (2)$$

where p_b is the partial pressure of the broadening gas and the foreign-gas broadening coefficient F is the ratio of the line-broadening ability of the broadening gas to that of nitrogen. Values of F appropriate for use with entire bands have been reported by Burch, Singleton, and Williams.²

In more recent studies Anderson, Chai, and Williams³ have determined self-broadening coefficients $B(\nu)$ appropriate for various frequencies ν within the major absorption bands of various atmospheric gases. Chai and Williams⁴ have determined $B(\nu)$ for individual lines in the R branch of the CO fundamental, and Draegert and Williams⁵ have made corresponding measurements of $F(\nu)$ for various foreign gases.

PRESENT STUDY

The present study is concerned with the determination of $F(\nu)$ values for various foreign gases for lines in the ν_3 fundamental of N_2O . The

general procedure involves first the introduction of a small carefully measured quantity of N_2O into an absorption cell of length $l = 5\text{cm}$ to give a relatively small absorber thickness $w \sim p_a l$ and then mapping the absorption spectrum. Addition of a broadening gas to the original gas increases spectral absorption $A(\nu)$ as a result of line broadening. The lower curve in Fig. 1 shows the spectral absorption at a given frequency as a function of the partial pressure p_N of added nitrogen; the upper curve in Fig. 1 shows spectral absorption for the same absorber thickness of N_2O as deuterium gas is added. For any particular value of fractional spectral absorption given by the ordinate in Fig. 1 the F-value of the deuterium broadener is given by the ratio of pressures; i.e., $F = p_N/p_b$, where p_N and p_b are the corresponding partial pressures given by the abscissa in Fig. 1. We note that the best values of F are obtained from the ratios for which the pressures of the broadening gases are sufficiently large to provide reliable separations of the curves but sufficiently low to avoid saturation effects.

A Perkin Elmer Model 421 spectrograph was used with spectral slitwidths sufficiently wide to include several adjacent spectral lines. In his CO studies Draegert⁵ found that the F-values obtained with wide spectral slitwidths are essentially the same as those obtained with narrow slits in spectral regions where the spectral absorption is not changing rapidly; for most of the CO-fundamental, smooth curves drawn through F-values obtained for individual lines coincide with the curves through the points giving the F-values obtained with broader slits when both curves are plotted as a function of frequency. Exceptions to this result were noted at the

band center and in the remote wings of the band, where the spectral absorption is changing rapidly with frequency. We have used this spectral averaging property of the spectral slitwidth in the present study.

The gases used in the present work were of reagent grade and were supplied by the Matheson company. All pressures were measured by suitable manometers attached to a gas-handling manifold similar to those used in previous studies.

RESULTS

The experimental results obtained in the present investigation are summarized in Fig. 2. Panel A of this figure shows the spectral transmission of a sample of pure N_2O as observed with the broad spectral slits employed in the course of the work. We note that, although the dominant absorption in the indicated spectral region is associated with the ν_3 fundamental of $N_2^{14}O^{16}$, the actual absorption spectrum is not simple. Whereas the R-branch is relatively 'clean', the P-branch is badly 'contaminated' by weak lines associated with the ν_3 fundamental of various isotopic species and by the somewhat stronger lines of hot bands associated with molecules initially in the first excited state of ν_2 .

Plots of measured F-values as a function of frequency are given in Panels B, C, and D of Fig. 2. We note that the F-values for H_2 have their minimum values for lines near the center of the major ν_3 band and rise rapidly in the P and R branches; the sudden decrease in $F(\nu)$ suggested by the final points in the extreme wings is probably an artifact associated with the failure of our broad slitwidth technique. The $F(\nu)$ -vs- ν plots

for D_2 and H_e also show minima near the band center with generally increasing values in the P and R branches and attaining nearly constant or even slightly decreasing values in the remote wings.

For Ne the F-value remains nearly constant at the low value of 0.6 throughout the entire band. In contrast to Ne, the Ar, Kr, and Xe plots indicate a decrease in $F(\nu)$ as one proceeds from the band center through the P and R branches into the wings of the band. The decrease is least for Ar and greatest for Xe.

For the larger polyatomic molecule CH_4 , the $F(\nu)$ values fall in the range 1.2 to 1.3 throughout the entire band.

DISCUSSION OF RESULTS

If we assume that our measured values of $F(\nu)$ are indeed valid measures of F for individual rotational lines in the vicinity of ν , we note that $F(m)$ increases with increasing line number m for H_2 , D_2 , and He, where $m = J+1$ in the R-branch and $m = J$ in the P branch, and J is the rotational quantum number of the lower level involved in the transition. We note further that $F(m)$ does not vary appreciably with m for CH_4 or Ne and that $F(m)$ decreases with increasing m for Ar, Kr, and Xe. The present results for the monatomic and diatomic broadeners are similar to earlier results for CO ⁵ and to the results obtained by others in studies of the foreign-gas broadening of the rotational lines of CO and HCl; these earlier results have been summarized by Williams, Wenstrand, Brockman, and Curnutte,⁶ who note a connection between the $F(m)$ -vs- m variation and the reduced mass μ_{ab} of the absorbing and broadening molecules constituting

the collision pair; the $F(m)$ values increase with increasing m for $\mu_{ab} < \mu_{aN}$ but decrease with increasing m for $\mu_{ab} > \mu_{aN}$.

In order to use the measured F -values in making theoretical estimates of transmission it is convenient to make use of the Lorentz model of absorption lines and apply the Ladenberg-Reiche⁷ function $L(x)$, which provides a measure for the equivalent width $\int A(\nu) d\nu$ of a line; the argument $x = Sw^0/2\pi\gamma$ where w^0 is the absorber thickness, S is the line strength, and γ is the halfwidth of the collision-broadened line. Kaplan and Eggers⁸ have tabulated the values of $L(x)$ over wide ranges of the argument. The line strength depends on the quantum-mechanical transition probability for transitions between the initial and final states and upon the populations of these states; at a given sample temperature, S is independent of pressure for pressures as high as several atmospheres. The halfwidth γ depends upon the mean molecular-collision frequency and is therefore directly proportional to the pressure at a given temperature.

According to simple theory, $\gamma = f_c/2\pi$ where the mean collision frequency $f_c = n\bar{v}\sigma$, n is the number of molecules per unit volume, \bar{v} is the mean relative speed of the colliding molecules, and σ is the collision cross section. Making use of the general gas law $p = nkT$ and the expression $\bar{v} = (2kT/\mu)^{1/2}$, where μ is the reduced mass of the collision pair, we may write for gas samples at the same temperature:

$$\sigma_{ab} = F(\mu_{ab}/\mu_{aN})^{1/2} \mu_{aN} \quad (3)$$

where σ_{ab} is the cross section for collisions between the absorbing molecule and broadening molecule b and σ_{aN} is the cross section for collisions between the absorbing molecule and nitrogen molecules. Once the cross

sections are known, line halfwidths can be determined for any pressure at the temperature in question.

Thus far, σ_{aN} values for lines in the ν_3 fundamental have not been determined by direct curve-of-growth measurements for N_2O-N_2 collisions. However, Tejwani and Varanasi⁹ have used the Anderson-Tsao-Curnutte theory to compute γ_{aN} and hence σ_{aN} for N_2O-N_2 collisions at laboratory temperature and have compared their results with estimates based on earlier experiments as summarized by Goldman et al.¹⁰ The computed values of σ_{aN} agree best with values based on Goody's recent work¹¹ on N_2O bands near $3.9\mu m$. If the calculated values of σ_{aN} are accepted, the values of $F(m)$ obtained in the present work can be used to compute σ_{ab} for collisions between N_2O and the broadening gases covered in the present investigation.

Tejwani and Varanasi⁹ have pointed out that direct curve-of-growth measurements of line broadening for N_2O can be made with a spectrometer having a resolution of 0.05 cm^{-1} or less. Preliminary tests indicate that our recently constructed spectrograph may indeed prove satisfactory for the purpose; we have recently obtained reasonably satisfactory results for CO_2 lines,¹² which have twice the spacing of N_2O lines. It is also possible that deconvolution techniques for collisionally broadened lines can be developed to obtain line widths directly from spectral chart recordings.

Although we did not obtain $F(\nu)$ values for O_2 in the present study, an earlier study² of total band absorption gave an O_2 F -value of 0.83 for the ν_3 band 0.72 for the ν_1 band. These measured values are to be compared with the corresponding value of approximately 0.6 that is obtained by taking the ratio of the calculated line widths given by Tejwani and Varanasi.

LEGENDS FOR FIGURES

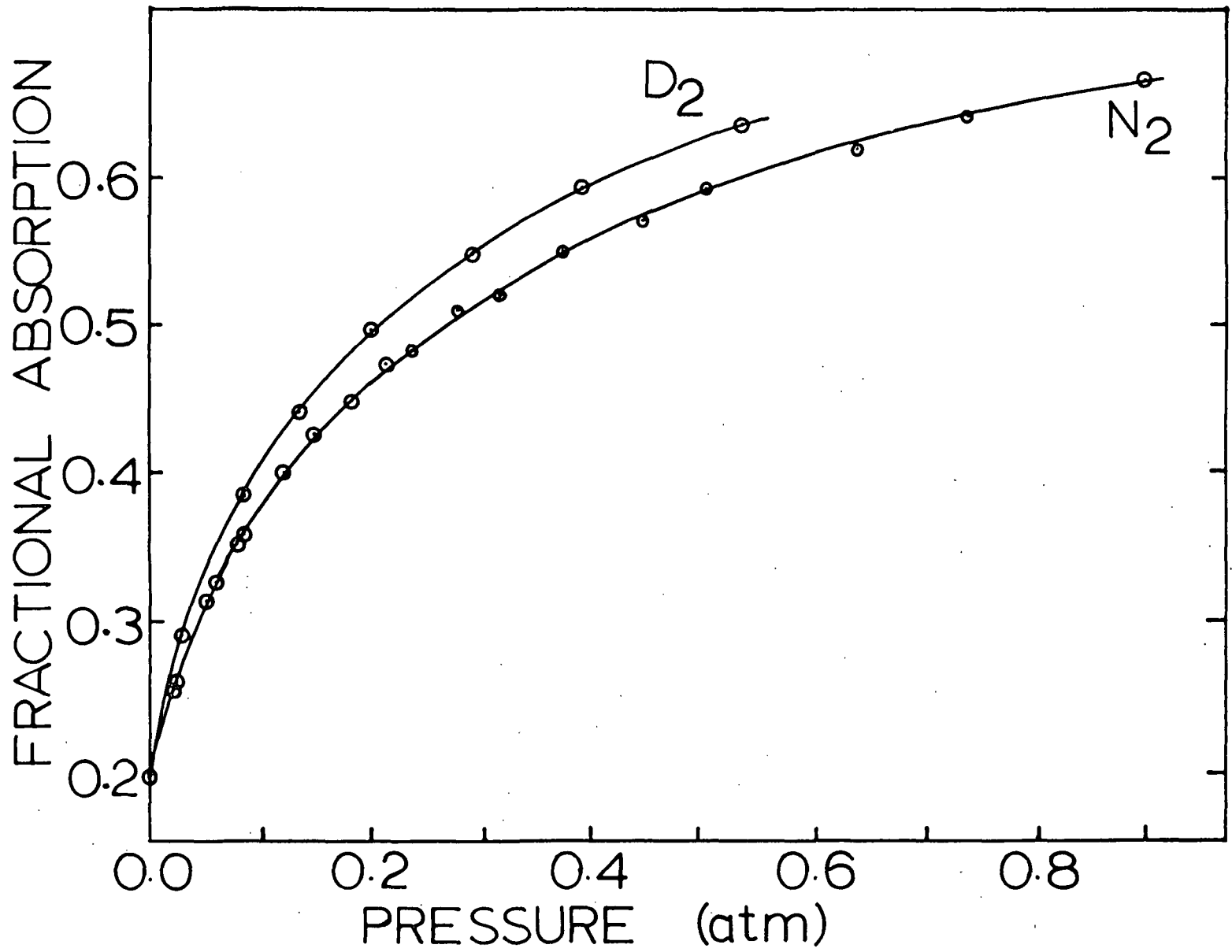
Fig. 1 Measured spectral absorption at a given frequency for a given absorber thickness of N_2O as a function of the partial pressure of the line-broadening gases D_2 and N_2 .

Fig. 2 Panel A shows spectral transmittance of a pure N_2O sample as observed with the broad spectral slit width employed in determining $F(\nu)$. Panels B, C, and D show measured values of $F(\nu)$ for various gases as a function of frequency; we estimate that, except for values in the extreme wings of the band, the values of $F(\nu)$ given by the points have an uncertainty of ± 5 percent.

FOOTNOTES AND REFERENCES

* Supported in part by the National Aeronautics and Space Administration.

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F₂ 1

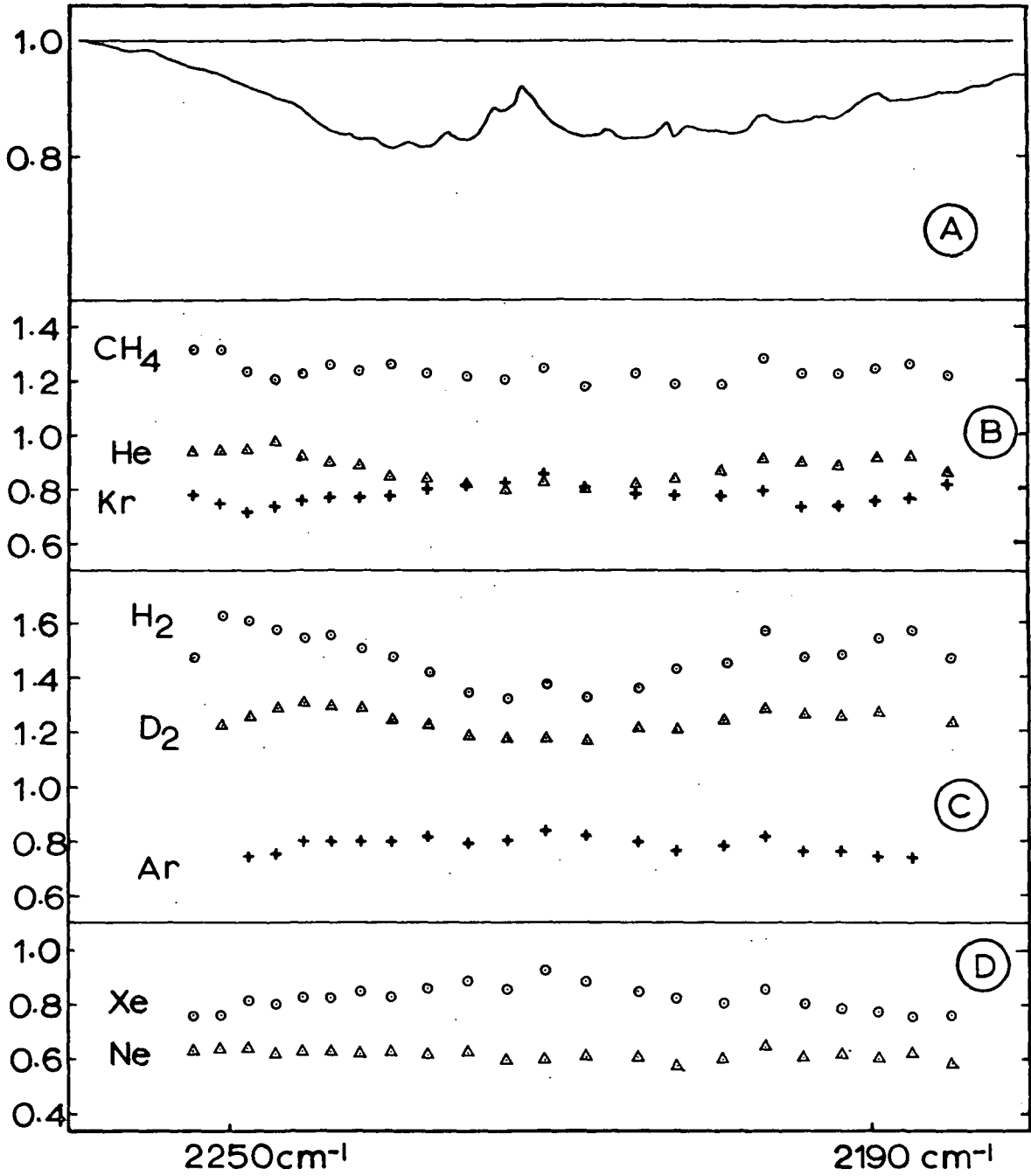


Fig. 2