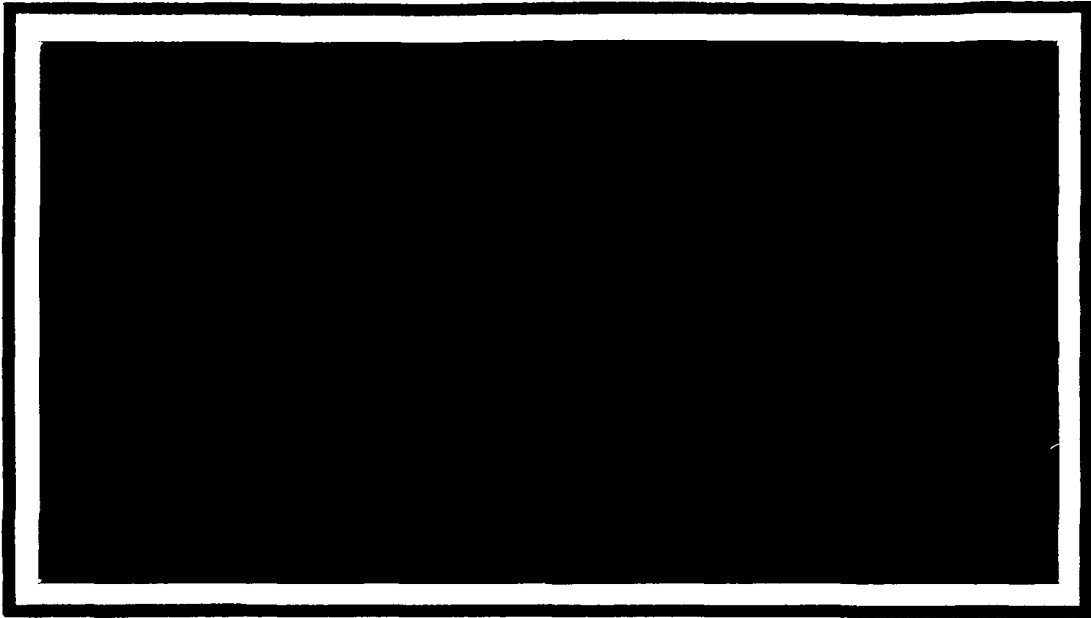
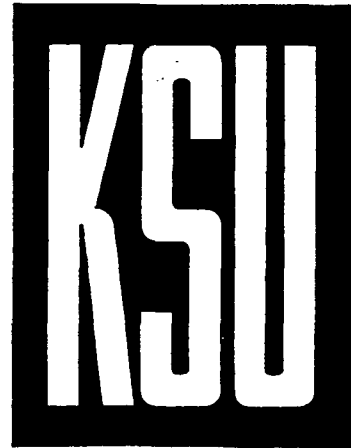


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SEMI-ANNUAL STATUS REPORT

Infrared Laboratory Studies of
Synthetic Planetary Atmospheres

Grant NGR 17-001-026

This report covers work for the period

1 December 1972 to 31 May 1973

It was prepared by

Prof. Dudley Williams, Department of Physics

Kansas State University, Manhattan, Kansas

Date: 14 June 1973

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 301 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 γ differ markedly from values calculated by applying the "hard-sphere" approximations of kinetic theory to values of γ^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.

The line strengths S and self-broadening parameters γ^0 of lines in the ν_3 fundamental of N_2O have been measured and compared with earlier values based on earlier S values based on measured band strength and the Herman-Wallis expression and values of γ^0 calculated on the basis of the Anderson theory of line broadening. The results of this study have been incorporated in a doctoral dissertation by L. D. Tubbs and presented in a subsequent journal article.

In view of the importance of ammonia in condensed states in the atmospheres of the Jovian planets, we have attempted to determine the optical constants n_r and n_i of liquid ammonia in the infrared. A paper on the subject has been accepted for journal publication. Subsequently, the work on liquid ammonia has been extended to the very near infrared, the visible, and the near ultraviolet; these are the regions in which the absorption of solar radiation would be most important.

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., 62, 285 (1972).
21. "Broadening of Infrared Absorption Lines at Reduced Temperatures: CO", Tubbs and Williams, J. Opt. Soc. Amer., 62, 423 (1972).
22. "Foreign-Gas Broadening of Nitrous-Oxide Absorption Lines", Appl. Opt., 11, 551 (1972).
23. "Reflection and Absorption Spectra of Liquid Ammonia in the Infrared", Charles W. Robertson, Proc. Twenty-Seventh Symposium on Molecular Structure and Spectroscopy (Ohio State University), p.110 (1972).P

24. "The Optical Constants of Liquid Ammonia in the Infrared",
Robertson and Williams, J. Opt. Soc. Am., 63, 188 (1973).
25. "Collisional Broadening of Nitrous Oxide Absorption Lines",
L. D. Tubbs and D. Williams, J. Opt. Soc. Am., 62, 1358 (1972). P.
26. "Absorption Coefficients of Liquid Ammonia in the Visible and
Near Infrared", C. W. Robertson, J. Opt. Soc. Am. 63, 475
(1973). P.
27. "Broadening of Infrared Absorption Lines at Reduced Temperatures
III Nitrous Oxide", L. D. Tubbs and D. Williams, J. Opt. Soc.
Am. (Accepted for publication.)
28. "Lambert Absorption Coefficient of Liquid Ammonia in the Visible
Region", C. W. Robertson and D. Williams, J. Opt. Soc. Am.
(Accepted for publication.)

II. PROGRESS DURING THIS REPORT PERIOD

A. Absorption-Line Broadening

The work on self-broadening of N_2O and CO_2 lines has been carefully rechecked in various ways. At present there is no real explanation of the differences between values of band strengths as obtained by our high-resolution techniques and those based on earlier low-resolution studies.

Our results for N_2O have been incorporated in a journal article that has been accepted for publication in the Journal of the Optical Society of America. A preprint of this work is appended to the present report.

Additional work has been done on foreign-gas broadening of the absorption lines of CO , CO_2 , and N_2O . Our high-resolution results on this subject are in reasonable agreement with earlier studies at lower resolution.

Dr. Lloyd D. Tubbs, who has been engaged in our studies of collisional broadening of absorption lines, left us at the end of March to accept a position at the Johns Hopkins University Applied Physics Laboratory at Silver Springs, Maryland.

B. Studies of Particulate Constituents of Planetary Atmospheres

1. Ammonia.

Our article on the optical constants of liquid ammonia in the $350 - 5100 \text{ cm}^{-1}$ range has been published; a reprint of the article is appended to the present report.

As pointed out in our previous semi-annual report, the absorption of liquid ammonia in the visible and near infrared is important to the heat balance of Jupiter. We have completed measurements of the Lambert absorption coefficients in this spectral region and have incorporated these results in a Letter to be published in the Journal of Optical Society of America. A copy of the manuscript is appended to this report.

Dr. Palmer has made quantitative measurements of the Lambert absorption coefficient of solid NH_3 in the range 2.5 to 10 μm . Thus far we have been unable to prepare solid surfaces of optical quality for use in reflection studies; after a smooth plane surface has been formed, it rapidly deteriorates as a result of sublimation. We are still working on the problem.

2. Sulphuric Acid.

Under other sponsorship we had begun a quantitative study of the optical properties of sulphuric acid. The original purpose was to account for the effect of H_2SO_4 as an aerosol in the earth's stratosphere. However, in view of the recent observations of Venus, which indicate that its cloud cover may, in large part, consist of H_2SO_4 droplets, we have decided to devote a large part of our effort under this grant to completion of our studies of this material. The work done to date involves measurements of the reflection spectrum in the region 0.3 to 10 μm . We have made plans to (1) map the reflection spectrum in the range 10 - 30 μm and (2) determine the Lambert

absorption coefficients from measurements in the range 0.3 to 3 μm . These measurements should provide values of the real and imaginary parts of the refractive index over most of the region of planetary interest.

C. Cooperation with NASA Research Centers

We have maintained close contact with Dr. James Pollack and his associates at the Ames Research Center. This group has special interests in the optical properties of H_2SO_4 . We have supplied Dr. Pollack with preliminary values of measured reflectivities; he is in the process of making a dispersion analysis to yield values of n and k for use in his Mie-theory calculations.

During late May I made a visit to JPL for conferences with Dr. Farmer and members of his group. Dr. L. G. Young and Dr. Andrew Young of this group are also very interested in our H_2SO_4 work.

Several times we have been in telephonic communication with Dr. Robert Curran of Hanel's group at Goddard. Dr. Curran has used some of our optical constants for ice to determine the ice content of the Martian atmosphere from the Mariner IX data.

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)

Dr. Lloyd D. Tubbs, Research Associate. (Resigned 31 March 1973)

Graduate Degrees Granted Under the Grant

An-Ti Chai - Ph.D.

Gary M. Hoover - Ph.D.

David Schmieder - M.S.

Lloyd Tubbs - Ph.D.

IV. PLANS FOR THE NEXT REPORT PERIOD

- A. Further work will be done on solid NH_3 .
- B. Work will be done on reflection of H_2SO_4 in the 10 - 30 μm region and on absorption of H_2SO_4 in the 0.3 - 2.5 μm region.
- C. Work on other stratospheric aerosols will be initiated.
- D. D. Williams will present a paper on "Optical Properties of Particles in Planetary Atmospheres" at the Copernicus IV Symposium in Poland in September.

Submitted: 12 June 1973

Signed:


Dudley Williams

Appendices:

- (1) "Optical Constants of Liquid Ammonia in the Infrared" by Robertson and Williams.

- (2) "Broadening of Infrared Absorption Lines at Reduced Temperatures III: Nitrous Oxide" by Tubbs and Williams.
- (3) "Lambert Absorption Coefficient of Liquid Ammonia in the Visible Region" by Robertson and Williams.

Optical constants of liquid ammonia in the infrared*

Charles W. Robertson and Dudley Williams

Department of Physics, Kansas State University, Manhattan, Kansas 66502

(Received 23 June 1972)

On the basis of quantitative studies of spectral reflectance in the range 350–5100 cm^{-1} and spectral transmittance between 875 and 7000 cm^{-1} , we have determined the real and imaginary parts of the refractive index of liquid ammonia in the spectral region in which the two sets of measurements overlap. We have also determined these optical constants in the range 5000–350 cm^{-1} from a Kramers–Kronig analysis of the reflectance measurements. The results of the investigation are presented in graphical and tabular form.

Index Headings: Spectra; Reflectance; Infrared; Transmittance.

In view of the presence of ammonia in the cloud cover of the Jovian planets, a detailed knowledge of the optical constants of ammonia in condensed states is important to studies of the radiative energy balances of these planets. Recent studies of liquid ammonia have included a precise determination of its refractive index in the spectral vicinity of the *D* lines of sodium¹ and two studies of its infrared absorption spectrum.^{2,3} In the present study we have determined the real n_r and imaginary n_i parts of its refractive index in the infrared.

REFLECTION MEASUREMENTS

Figure 1 gives a schematic diagram of the reflectometer employed. Radiant flux from the Nernst glower *N* is reflected by concave mirror *M*₁ and plane mirror *M*₂, which produce a magnified image of the glower at *I*₁. The flux is then reflected by plane mirror *M*₃ to concave mirror *M*₄, which produces a still-further-magnified image *I*₂ at the surface of the liquid-ammonia sample or the horizontal surface of a reference mirror. After reflection by the test surface, the flux reaches concave mirror *M*₅ and plane mirror *M*₆, which produce a final

image *I*₃ at the entrance slit of a Perkin–Elmer model No. 112 spectrometer; final image *I*₃ is twice the size of the Nernst glower. The reflectometer was designed to under fill the spectrometer's optical system.

The angle of incidence of the central ray at the sample surface was 5°; the angles of incidence for the extreme rays in the converging flux cone were 9° and 1°. Thus, conditions for near-normal incidence were closely approximated. Image *I*₂ at the sample surface had a linear magnification of 6, relative to the glower; the use of this enlarged image minimized difficulties due to localized heating at the sample surface. With *I*₂ at the sample surface, small surface waves can alter the fill of mirror *M*₅ but have negligible effect on the position of the final image *I*₃; by making mirror *M*₅ larger than needed to accept all flux reflected from a quiescent sample surface, we attempted to eliminate the effects of surface waves, which are produced by building vibrations even in our basement laboratory. Having distance *I*₂–*M*₅ greater than distance *M*₅–*I*₃ reduces defocusing effects due to changes of the liquid surface caused by evaporation.

The liquid-ammonia sample *S* in a shallow glass dish *D* and the reference mirror *M* were housed side by side

at the bottom of a pair of communicating stainless-steel wells *W* mounted inside a hollowed block *P* of polystyrene foam, in the manner suggested by Fig. 2. The sample and reference mirror were positioned in this way in an effort to equalize the amount of ammonia vapor in sample and reference paths and thus to compensate for absorption by ammonia vapor. The polystyrene-foam block was mounted on a cart providing lateral motion for positioning either the sample or the reference mirror at I_2 in Fig. 1. This cart was housed in a plywood box from which the ammonia was gently removed by an exhaust fan and vented outside the building.

The ammonia was Air Products' anhydrous grade and was taken directly from the tank without further purification. Ammonia in the dish *D* in Fig. 2 was cooled to $-45^\circ \pm 2^\circ \text{C}$ by rapid evaporation and remained at this low temperature while measurements were being made. While the sample dish was being filled, an aluminum baffle was inserted between the wells in order to protect the aluminized mirror surface. Although liquid condensates were formed on the cold-well walls, no identifiable spectroscopic difficulties were encountered as a result of contamination of the sample by condensation of atmospheric water vapor. In order to, inhibit condensation on the reference mirror, we kept the temperature of the mirror somewhat above the temperature of the surrounding walls; dissipation of only 3.5 W in resistors *H* was sufficient to prevent conden-

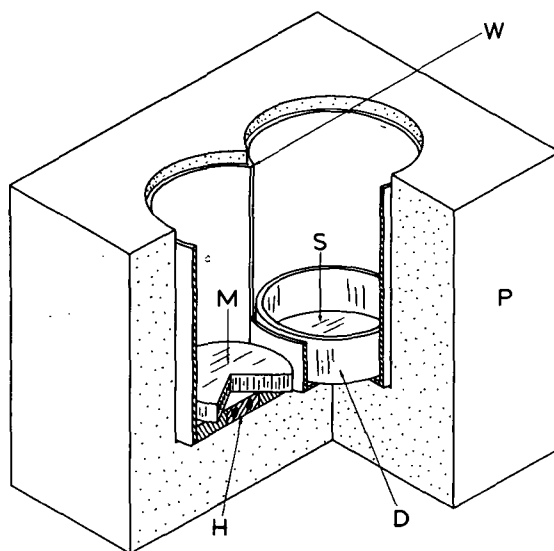


Fig. 2. The sample holder used for reflectance measurements. The liquid-ammonia sample *S* in a glass dish *D* and the reference mirror *M* were located at the bottom of a pair of connecting wells *W* of stainless steel, which were embedded in a block of polystyrene foam *P*; resistive heaters *H* below the mirror were used to inhibit condensation on the mirror surface.

sation. We detected no changes of the spectral reflectance of ammonia during the useful life of a sample.

The techniques used in mapping spectral reflectance were essentially the same as those used in our earlier study of water.⁴ Since the reflectance of ammonia is small compared with that of the reference mirror, we used a rapidly rotating calibrated sector wheel to attenuate the flux reflected by the mirror so that, without change of amplifier gain settings, we could compare sample and mirror reflectance from pen deflections on a recorder chart. An auxiliary He-Ne laser was used to advantage during leveling adjustments of the reference mirror to the horizontal. The absolute reflectance of the reference mirror was measured from time to time by means of an auxiliary Strong reflectometer.⁵

The spectral reflectance curve in Fig. 3 is the smoothed result of the average of 3–10 reflectance measurements taken at each of 220 different frequencies. The reflectance curve shows typical dispersion features in the vicinity of strong absorption bands near 3300, 1630, and 1058 cm^{-1} and appears to reach a maximum at 350 cm^{-1} , the lowest frequency for which we have plotted results in Fig. 3. The probable error of measured spectral reflectance is less than 0.001 except in the vicinity of the resonance features, where the probable error is 0.002.

TRANSMISSION MEASUREMENTS

In measuring transmittance, we employed techniques involving a wedge-shaped absorbing layer, which had been developed in our earlier work on water transmittance.⁶ A concave mirror produced an intermediate

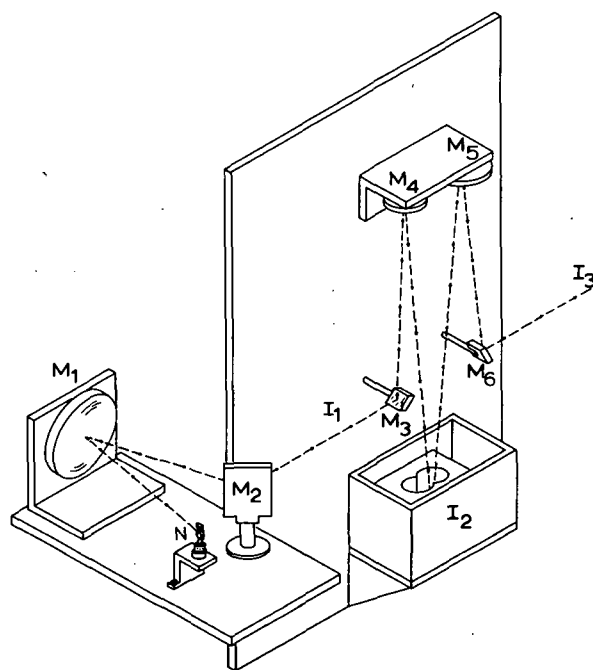


Fig. 1. The reflectometer used for near-normal-incidence reflectance measurements. The final image I_3 was located at the entrance slit of a Perkin-Elmer model No. 112 spectrometer equipped with a Reeder thermocouple; LiF, CaF_2 , NaCl, and CsBr prisms were used in appropriate spectral regions.

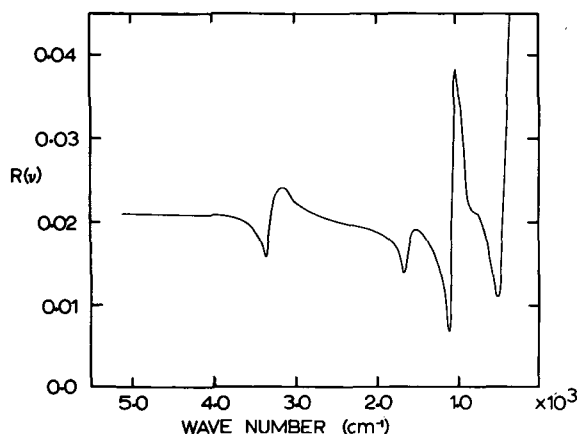


FIG. 3. Spectral reflectance $R(\nu)$ of liquid ammonia at near-normal incidence.

image of a Nernst glower inside the thin absorption cell; flux transmitted by the cell reached a second concave mirror which produced a final image of the glower at the entrance slit of a Perkin-Elmer model No. 112 spectrometer. By moving the wedge cell laterally through the beam, we could vary the thickness of the absorbing layer without altering reflection at the cell surfaces. The Lambert absorption coefficient α can be obtained from the ratio $I/I_1 = \exp[-\alpha(Z-Z_1)]$, where I and I_1 represent flux transmitted by film thicknesses Z and Z_1 , respectively. The cell windows used in the present work were polished rectangular CaF_2 crystals supplied by Harshaw Chemical Company; the windows were 38.5 mm long, 19.5 mm wide, and 5 mm thick. The windows were in close optical contact at one end and were separated by a 25- μm aluminum spacer at the other end.

The wedge cell C was mounted in a vacuum jacket, as shown in Fig. 4. The CaF_2 windows were sealed to the cell's aluminum end plates with General Electric RTV-108 silicone adhesive. These end plates were sealed to the body of the cell by TEC low-temperature ring seals; similar ring seals connected the assembled cell to the stainless-steel reservoir R, which was filled with liquid ammonia. The upper end of the reservoir was attached by neoprene O-rings to the heavy external body E of the vacuum chamber, the end plates of which were equipped with CaF_2 windows W sufficiently large to transmit the beam of radiant flux required to fill the optics of the spectrometer.

In order to minimize thermal shock to the cell windows, we pre-cooled the cell by filling the reservoir with liquid ammonia when the orifice between the reservoir and the cell was closed by Teflon plug P. The filled reservoir was allowed to stand for thirty minutes in order to bring the cell slowly into thermal equilibrium with the liquid ammonia at its equilibrium boiling point of -33.6°C . As in our earlier work, we measured the thickness profile of the absorption cell interferometrically; we made a thickness-profile measurement prior to

each set of transmission measurements with the cell pre-cooled but unfilled.

When the Teflon plug had been removed, the pre-cooled cell filled rapidly; provided that the cell windows were clean, the absorbing layer was free of bubbles. Admission of atmospheric water vapor to the reservoir was inhibited by means of a stopper in the top of the reservoir; ammonia vapor emerging from a small hole in the stopper was removed from the laboratory by an exhaust fan. Provided that the liquid-ammonia level in the reservoir was several centimeters above the orifice to the cell, there was no evidence of water-vapor contamination.

The whole assembly shown in Fig. 4 was suspended from a cart that moved on tracks parallel to the cell windows. The cart, driven by a synchronous motor, moved the cell 30 mm laterally in 12 min; this time provided a complete lateral scan of the absorbing layer and was long compared with the 1-s time constant employed in the amplifier-recorder system. With the spectrometer set for a given frequency ν , we obtained recorder traces giving measures of transmitted flux as a function of absorbing film thickness Z ; from these traces we determined the Lambert absorption coefficient $\alpha(\nu)$.

In spectral regions of weak absorption, where $\alpha(\nu) < 100\text{ cm}^{-1}$, it was necessary to use thicker absorbing layers to determine $\alpha(\nu)$. In such regions, cells of

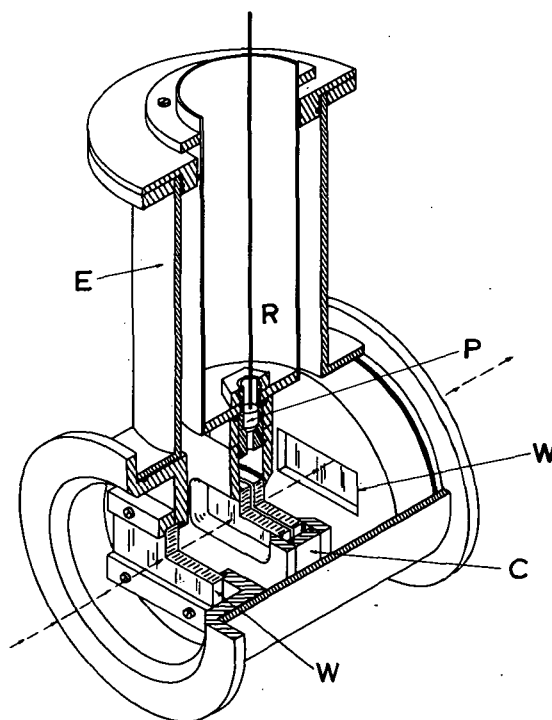


FIG. 4. The wedge cell used for measurements of the transmittance spectrum of liquid ammonia. The cell C was mounted below reservoir R; during pre-cooling procedures the orifice between R and C was closed by Teflon plug P. The end plates of the vacuum jacket E were equipped with CaF_2 windows W.

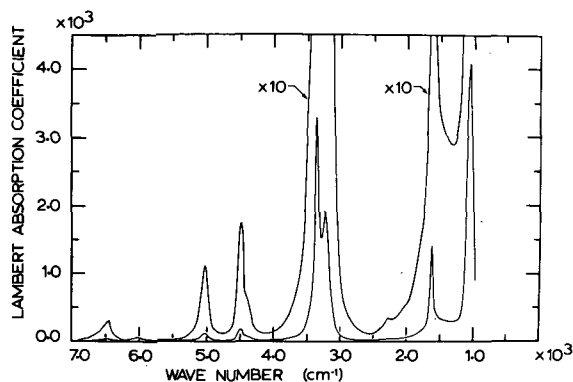


FIG. 5. The Lambert absorption coefficient of liquid ammonia in cm^{-1} .

uniform thickness can be employed; we used cells of thickness 16, 135, 300, and 855 μm . The thickness of the thinnest of these cells was measured interferometrically; the thicker cells were assembled with carefully measured lead spacers.

Figure 5 gives a plot of the measured values of the Lambert absorption coefficients; the curves represent the smoothed results of 3–10 independent measurements taken at each of 215 frequencies. The probable error in the values of $\alpha(\nu)$ given in the figure is less than 5% except at the peaks of the sharp absorption bands near 3300 cm^{-1} , where the probable error is 10%. In addition to the strong bands near 3300, 1630, and 1058 cm^{-1} , several minor absorption bands are visible in the upper trace of Fig. 5; these minor bands can be more clearly seen in the upper curve of the figure for which the ordinates have been expanded by a factor of 10.

OPTICAL CONSTANTS

The imaginary part of the refractive index at frequency ν can be expressed as $n_i = c\alpha/4\pi\nu = \lambda\alpha/4\pi$, where α is the Lambert coefficient. If n_i is known, the real part of the refractive index can be determined from the reflectance R at near-normal incidence from the Fresnel relation

$$n_r = \left\{ (1+R) + [(1+R)^2 - (1-R)^2(n_i^2 + 1)]^{1/2} \right\} / (1-R). \quad (1)$$

On the basis of our measurements of $\alpha(\nu)$ and $R(\nu)$, we have determined $n_r(\nu)$ and $n_i(\nu)$ in the range 5000–875 cm^{-1} .

We also used the Kramers–Kronig (K–K) relation for phase-shift dispersion analysis of reflectance data to obtain n_r and n_i from our reflectance data. This relation states that, if the modulus $\rho(\nu) = [R(\nu)]^{1/2}$ of the complex reflectivity $\rho(\nu)e^{i\phi(\nu)}$ is known for all frequencies, then

$$\phi(\nu_0) = \frac{2\nu_0}{\pi} \int_0^\infty \frac{\ln \rho(\nu)}{\nu_0^2 - \nu^2} d\nu. \quad (2)$$

Although the value $\phi(\nu_0)$ is most strongly influenced by

values of $\rho(\nu)$ in the immediate vicinity of ν_0 , values of $\rho(\nu)$ for all frequencies must be known if the K–K relation (2) is to be applied with rigor. Since our reflectance measurements were limited to the range 5100–350 cm^{-1} , we made assumptions regarding values outside this range. We assumed that the gentle slope of the $R(\nu)$ -vs- ν curve in Fig. 3 was maintained from 5100 to 10 000 cm^{-1} and that $R(\nu)$ was constant for $\nu > 10 000 \text{ cm}^{-1}$. For $\nu < 350 \text{ cm}^{-1}$, we assumed that $R(\nu)$ first decreased from its maximum value of 0.047 at 350 cm^{-1} to a minimum of 0.029 at 110 cm^{-1} and then rose to a value of 0.10 near 10 cm^{-1} . Provided that the assumed curve is smooth and is smoothly connected to the measured reflectance curve, the exact shape seems to have little influence on the values of the optical constants

$$n_r = (1-R)/(1+R-2R^{1/2} \cos \phi), \quad (3)$$

$$n_i = (-2R \sin \phi)/(1+R-2R^{1/2} \cos \phi) \quad (4)$$

in the 5000–350- cm^{-1} range. In making the K–K analysis, we used a computer program developed by Query and his associates.⁷

The values of $n_r(\nu)$ obtained by the two methods are in remarkably good agreement over the range 5000–875 cm^{-1} . The only serious disagreement is in the vicinity of the minimum near 1100 cm^{-1} , where the value of n_r obtained from Eq. (2) is slightly less than unity and the value given by the K–K analysis is 1.14. Figure 6 gives a plot of $n_r(\nu)$ -vs- ν ; values of $n_r(\nu)$ given by the K–K analysis are given by the dotted curve in the vicinity of 1100 cm^{-1} . All values of $n_r(\nu)$ for $\nu < 900 \text{ cm}^{-1}$ are supported by only K–K analysis. Linear extrapolation of the curve toward higher frequencies leads to the value 1.335 ± 0.005 obtained by Marcoux for the sodium D lines.¹ Table I lists values of $n_r(\nu)$ at closely spaced frequencies; the curve in Fig. 6 can be used in making interpolations. The uncertainty of the tabulated values of n_r is estimated as $\pm 2\%$ except in the vicinity of 1100 cm^{-1} .

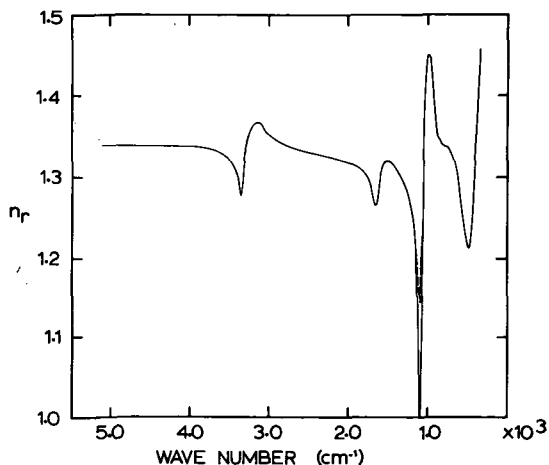


FIG. 6. The real part n_r of the refractive index of liquid ammonia.

TABLE I. Optical constants of liquid ammonia in the infrared.

ν in cm^{-1}	n_i	n_r	ν in cm^{-1}	n_i	n_r
7000	0.000 01		3450	0.012 71	1.312
6900	0.000 02		3400	0.031 99	1.300
6800	0.000 04		3380	0.067 45	1.286
6700	0.000 08		3360	0.075 31	1.275
6600	0.000 16		3340	0.052 18	1.289
6550	0.000 22		3320	0.040 75	1.312
6500	0.000 31		3300	0.036 36	1.331
6450	0.000 38		3280	0.038 26	1.343
6400	0.000 18		3260	0.042 30	1.351
6350	0.000 10		3240	0.046 79	1.356
6300	0.000 05		3220	0.042 56	1.360
6200	0.000 03		3200	0.035 61	1.363
6100	0.000 05		3150	0.018 67	1.367
6000	0.000 07		3100	0.008 78	1.365
5900	0.000 03		3050	0.004 12	1.357
5800	0.000 02		3000	0.002 27	1.351
5700	0.000 01		2900	0.001 13	1.344
5600	0.000 02		2800	0.000 74	1.339
5500	0.000 04		2700	0.000 47	1.335
5400	0.000 06		2600	0.000 35	1.332
5300	0.000 12		2500	0.000 38	1.329
5250	0.000 17		2400	0.000 64	1.327
5200	0.000 26		2350	0.000 84	1.325
5180	0.000 31		2300	0.001 12	1.324
5160	0.000 37		2280	0.001 20	1.324
5140	0.000 46		2260	0.001 17	1.323
5100	0.000 83	1.338	2240	0.001 14	1.323
5080	0.001 24	1.338	2220	0.001 13	1.322
5060	0.001 51	1.338	2200	0.001 16	1.322
5040	0.001 72	1.338	2150	0.001 34	1.321
5020	0.001 77	1.338	2100	0.001 61	1.320
5000	0.001 58	1.338	2050	0.001 91	1.318
4980	0.001 12	1.338	2000	0.002 21	1.317
4960	0.000 79	1.338	1950	0.002 65	1.315
4960	0.000 56	1.338	1900	0.003 56	1.312
4920	0.000 40	1.338	1850	0.004 82	1.309
4900	0.000 31	1.338	1800	0.006 54	1.304
4850	0.000 24	1.337	1750	0.008 78	1.296
4800	0.000 20	1.337	1700	0.012 97	1.277
4700	0.000 23	1.337	1680	0.018 00	1.267
4650	0.000 30	1.337	1660	0.029 00	1.264
4600	0.000 49	1.337	1640	0.061 87	1.266
4580	0.000 67	1.337	1620	0.058 46	1.279
4560	0.001 31	1.337	1600	0.031 33	1.298
4540	0.001 89	1.337	1550	0.020 13	1.316
4520	0.002 78	1.337	1500	0.017 56	1.318
4500	0.003 06	1.337	1450	0.017 07	1.315
4480	0.003 06	1.337	1400	0.017 05	1.309
4460	0.002 52	1.337	1300	0.017 75	1.291
4440	0.001 36	1.337	1250	0.019 35	1.277
4420	0.001 24	1.337	1200	0.024 67	1.256
4400	0.001 16	1.337	1150	0.050 10	1.213
4380	0.001 05	1.337	1100	0.204 73	1.000
4360	0.000 92	1.337	1080	0.269 09	1.059
4340	0.000 76	1.337	1060	0.306 52	1.206
4320	0.000 57	1.337	1040	0.272 55	1.374
4300	0.000 42	1.337	1020	0.205 97	1.430
4250	0.000 29	1.337	1000	0.130 43	1.450
4200	0.000 23	1.337	950	0.025 20	1.425
4100	0.000 21	1.337	900	0.000 90	1.365
4000	0.000 28	1.337	850	0.008 70	1.344
3900	0.000 41	1.336	800	0.013 20	1.337
3850	0.000 54	1.336	750	0.011 60	1.335
3800	0.000 73	1.335	700	0.006 40	1.326
3750	0.000 97	1.334	650	0.002 30	1.310
3700	0.001 26	1.332	600	0.006 10	1.276
3650	0.001 66	1.330	550	0.034 10	1.241
3600	0.002 32	1.328	500	0.090 10	1.211
3500	0.006 46	1.319	450	0.180 70	1.247
3550	0.003 47	1.324	400	0.236 10	1.348
			350	0.021 03	1.484

Our best values of $n_i(\nu)$ are plotted in Fig. 7 and listed in Table I. Throughout the range from 7000 cm^{-1} to the CaF_2 cutoff at 980 cm^{-1} , values of n_i based on the Lambert coefficient are given; as noted earlier, the uncertainties involved are $\pm 5\%$ except at the band peaks near 3300 cm^{-1} , where the uncertainty is $\pm 10\%$. The K-K values of $n_i(\nu)$ at the absorption maxima at 3300 and 1630 cm^{-1} are consistently lower than those based on transmission measurements, but agreement between the two sets of values improves at lower frequencies. In spectral regions between the strong bands, the K-K analysis gives small negative values of $n_i(\nu)$; in view of the large uncertainties in $R(\nu)$, these non-physical results are not altogether surprising. The values of $n_i(\nu)$ given in Table I and Fig. 7 for $\nu < 980\text{ cm}^{-1}$ are based on the K-K analysis and have an estimated uncertainty of $\pm 15\%$.

DISCUSSION OF RESULTS

The frequencies and shapes of the absorption bands as determined in the present work are in essential agreement with the results of earlier studies^{2,3} of liquid ammonia at ambient laboratory temperature and high pressure. By comparing the spectra of normal and deuterated ammonia with the vapor spectrum, earlier investigators have identified the band at 3366 cm^{-1} as the ν_3 fundamental and the 3262-cm^{-1} band as the overtone $2\nu_4$; the ν_1 fundamental lies between the two but cannot be resolved in the spectrum of the liquid. The ν_2 fundamental appears at 1058 cm^{-1} and the ν_4 fundamental appears at 1631 cm^{-1} in the liquid. The weaker bands that we have observed for $\nu > 3400\text{ cm}^{-1}$ also appear close to the frequencies at which combination and overtone bands appear in the vapor spectrum.⁸

The strong band at 385 cm^{-1} and the weaker band at 785 cm^{-1} are in a spectral region not covered in earlier studies of liquid ammonia; the very weak band at 2286 cm^{-1} has been hitherto undetected. The bands at $\nu < 1000\text{ cm}^{-1}$ are tentatively attributed to intermolecular motions. It is possible that the weak band at 2286 cm^{-1} is a combination of ν_4 with one or more intermolecular modes of vibration. It is highly desirable that the spectral region $\nu < 1000\text{ cm}^{-1}$ be studied by transmission methods, since bands in this region have been detected only by the K-K analysis of our reflection data. Although no suitable window materials are available for quantitative studies of transmission in most of this region, polyethylene windows might be suitable for survey work. Quartz windows could be used for $\nu < 200\text{ cm}^{-1}$ in the far infrared.

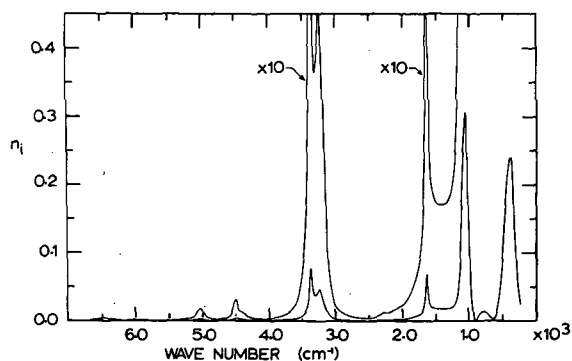


Fig. 7. The imaginary part n_i of the refractive index of liquid ammonia.

The general agreement between our present results and those obtained in the earlier transmission studies,^{2,3} which were conducted with the liquid ammonia in a closed system, gives added assurance that condensation of atmospheric water vapor did not lead to spurious results in the present study. Until more precise values of the optical constants become available, our values should prove useful in planetary studies. We are at present adapting our techniques to studies of solid ammonia, which is probably the major constituent in the cloud cover of the outer planets.

ACKNOWLEDGMENTS

We offer our thanks to Professor Marvin R. Querry and his associates at the University of Missouri, Kansas City, for valuable assistance in the K-K analysis of the reflectance data.

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Lambert Absorption Coefficient of Liquid Ammonia in the Visible Region*

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We have recently measured¹ the real n_r and imaginary n_i parts of the refractive index of liquid ammonia in the infrared region 350 - 5100 cm^{-1} and have obtained values of n_i in the 5100 - 7000 cm^{-1} range. A knowledge of these optical constants is important to studies of the heat balance of the Jovian planets because ammonia in condensed states is present in their cloud covers. Although the values of n_r and n_i in the infrared are the important factors involved in radiation from the Jovian planets to space, the corresponding values in the visible and near ultraviolet are the important parameters in the absorption and reflection of solar radiant flux by the planets.

We have therefore extended our measurements of absorption to the visible and near ultraviolet regions of the spectrum. In the present study we have measured the spectral transmittance of liquid ammonia at a temperature of -34°C in four different absorption cells equipped with CaF_2 windows; the cell thicknesses employed were 12, 27, 35, and 50 mm, respectively. As in the earlier work, we were able to determine Lambert absorption coefficients $\alpha(\nu)$ by taking ratios of transmittance and thus to avoid the necessity of measuring

reflection and absorption factors for the cell windows. We used a Perkin-Elmer model 112 spectrometer equipped with a glass prism; emission lines of Hg, He, and Ar were used for spectrometer calibration.

Figure 1 gives a plot of $\alpha(\nu)$ as a function of wave number in the range 7000 - 27,000 cm^{-1} . Throughout the entire region $\alpha(\nu)$ is small compared with its values in the intermediate infrared; however, there are observable absorption bands which can be identified as overtones and combinations of bands in the intermediate infrared. In Table I we give a tabulation of $\alpha(\nu)$ for selected frequencies; Fig. 1 provides a basis for interpolation between tabulated values. Values of $n_1 = c\alpha/4\pi\nu = \lambda\alpha/4\pi$ are readily obtainable from the measured values of α .

The absorption bands shown in Fig. 1 are so weak that they are not accompanied by observable dispersion features in reflectance $R(\nu)$ or in n_r . The value of $n_r(\nu)$ for the sodium D lines³ is 1.335 ± 0.005 ; this value agrees with an extrapolation of our infrared values and is probably sufficiently accurate for use in Mie-theory calculations throughout the visible region.

We should like to thank Dr. J. S. Margolis of the Jet Propulsion Laboratory for pointing out the importance of extending our earlier measurements to the visible region.

Table I
Lambert Absorption Coefficients

Wave Number cm ⁻¹	$\alpha(\nu)$ cm ⁻¹	Wavelength nm
7 650	1.53	1 310
7 900	1.03	1 265
8 150	1.70	1 226
9 000	0.064	1 110
9 600	1.03	1 040
10 700	0.085	935
11 100	0.147	901
11 800	0.027	847
12 500	0.178	800
14 000	0.034	714
15 300	0.054	654
22 000	0.139	455
25 000	0.212	400
27 000	0.285	370

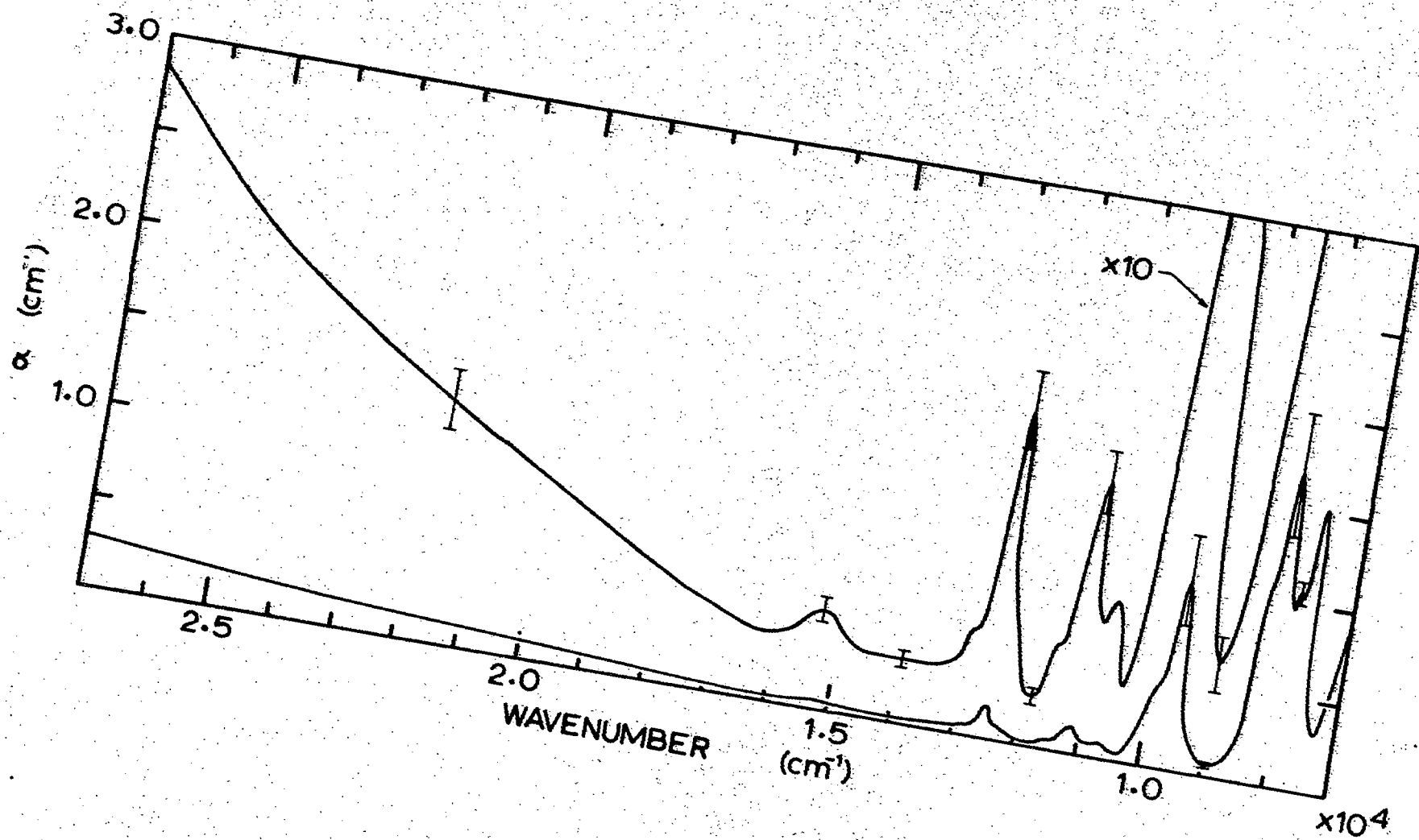
LEGEND FOR FIGURE

Fig. 1 Lambert absorption coefficient as a function of frequency in wave numbers.

FOOTNOTES AND REFERENCES

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

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Broadening of Infrared Absorption Lines at
Reduced Temperatures, III. Nitrous Oxide^{*}

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Abstract

The strengths and self-broadening parameters for lines in the R branch of the ν_3 fundamental of N_2O have been measured for gas samples at 300 and 204K. The results indicate that the collision cross sections at the two temperatures are nearly the same. Differences between values for total band strength of ν_3 based on the present high-resolution measurements and values based on earlier low resolution studies are discussed. The results obtained for self-broadening parameters are in excellent agreement with recent results of Toth and Margolis.

INDEX HEADINGS: Infrared; Absorption; Spectra.

In earlier studies^{1,2} we have determined line strengths S and self-broadening parameters γ^0 for lines in the vibration-rotation bands of CO and CO_2 in samples near 300K and at reduced temperatures. The present work is chiefly concerned with a similar investigation of lines in the ν_3 fundamental band of N_2O . Total N_2O band strengths for this region have been measured at ambient laboratory temperatures by numerous investigators who employed low-resolution techniques³; the strengths of individual lines in the ν_3 fundamental have recently been measured by Lowder⁴. The present investigation also covered the weaker $\nu_1 + \nu_3$ band, which has recently been studied under high resolution by Toth^{5,6}.

The experimental methods employed in the present work involved curve-of-growth techniques and are similar to those used in our earlier work¹ on CO_2 . The reagent-grade N_2O used was supplied by the Matheson Company.

LINE STRENGTHS

A recorder tracing of the absorptance in the $4.5\mu\text{m}$ region showing the nitrous oxide ν_3 fundamental band arising from the transition $00^0_0 - 00^0_1$ and a weaker overlapping hot band arising from the transition $01^1_0 - 01^1_1$ is shown in Fig. 1. The P branch, band center, and R branch of the fundamental band are indicated below the tracing by P, ν_0 , and R along with the rotational line numbers m for some of the fundamental band absorption lines. The band center and branches of the hot band are indicated by the labels ν'_0 , P' and R' along with rotational line numbers for $m = -43$ to $m = +45$ above the tracing.

Only a portion of the R branch of the fundamental band is free from absorption due to the hot band; the strengths of the hot band lines are less than one percent of the strength of the fundamental band lines for $m > +22$ of the fundamental band. The strengths of the lines from $m = -40$ to $m = +60$ of the fundamental band were measured by the curve of growth method, where the equivalent width of an absorption line is equal to the integrated absorbance due to the line. All of the absorption occurring in a frequency interval equal to the rotational line separation and centered on the absorption line was initially attributed to the absorption line; thus nearly all of the measured line strengths include some contribution due to the overlapping hot band. Averaged measured line strengths are represented by the circles in Fig. 2. Approximately eight determinations of the line strength were made for each rotational line and the error bars represent one standard deviation of the individual determinations from the mean. The measured values are close approximations to the true line strengths of the fundamental band for $m > 22$. We calculated the strengths of the lines in both the fundamental and the overlapping hot band by using the expression

$$S(m) = \frac{1}{(273K) \cdot k} \cdot \frac{8\pi^3}{3hcQ(T)} \nu_m |m| |R|^2 \exp[-E(m)/kT] \quad (1)$$

where ν_m is the frequency of the absorption line, $|R|^2$ is the square of the dipole-moment matrix element connecting the lower and upper state, $E(m)$ is the energy of the lower state of the transition giving rise to the absorption line and $Q(T)$ is the internal partition function as defined and tabulated for N_2O by Young⁷. This expression gives the line strengths in units of $\text{cm}^{-1}/(\text{atm}\cdot\text{cm})_{\text{STP}}$ and is similar to that used by Toth except

that no vibration-rotation interaction is included. We have omitted the vibration-rotation interaction term because our experimental measurements of line strength were representative of the true line strength only in the R branch so that insufficient experimental data were available to make a valid determination of the interaction constants.

The triangles in Fig. 2 represent calculated line strengths for the ν_3 fundamental band based on $|R| = 0.2320$ Debye units. This value of $|R|$ was determined by assuming that the transition moment for the fundamental band and the overlapping hot band were the same and requiring that the sum of the calculated line strengths due to both the fundamental and the overlapping hot band occurring in the region where measurements were made be equal to the total of the measured line strengths. The band strengths of the fundamental and the hot band satisfying this requirement were 1181 and $142 \text{ cm}^{-1}/(\text{atm}\cdot\text{cm})_{\text{STP}}$, respectively, where the strength of a band is the sum of all of the calculated line strengths for that band.

The total of the calculated line strengths in the spectral region 2230 to 2261.5 cm^{-1} , which contains a large part of the R branch of the fundamental band, is approximately 5 percent larger than the total of the measured line strengths; however, the total of the calculated strengths is about 5 percent less than the total of the measured values in the spectral region 2184 to 2215 cm^{-1} which contains a large portion of the P branch of the fundamental band. These results may suggest that a rotation-vibration interaction which enhances the strengths of the rotational lines in the P branch may be present.

An examination of the region very near the fundamental band center where the hot band contributes approximately fifty percent of the total strength indicates that the dipole-moment matrix element $|R|$ of the hot band must be very nearly equal to that of the fundamental band. This is in agreement with the measurements of Lowder⁴ who recently measured the strengths of 21 lines in the ν_3 fundamental band and 16 lines in the overlapping hot band.

The line strengths for lines $m = +6$ to $m = +54$ of the ν_3 fundamental were also measured at 204K. The results of these measurements are shown in Fig. 3 where measured values of line strength are indicated by circles. The error bars represent one standard deviation of individual measurements from the average value for each line. The triangles indicate values of line strength calculated by using equation (1) with a dipole-moment matrix element value of $|R| = 0.2320$ Debye units. The calculated values are in good agreement with most of the measured values; thus the value of $|R| = 0.2320$ Debye units seems to yield good agreement between measured and calculated values of line strength at both 204 and 302K. The strengths of lines in the wing of the band depend more strongly on the temperature than those nearer the band center; thus the increasing differences between the calculated and measured values in Fig. 3 for larger rotational line numbers m may be caused by cell windows that are not as cold as the cell body.

The sum of the calculated fundamental and hot band strength at 302K is $1323 \text{ cm}^{-1}/(\text{atm}\cdot\text{cm})_{\text{STP}}$ which can be compared with Lowder's recent measurement of $1608 \text{ cm}^{-1}/(\text{atm}\cdot\text{cm})_{\text{STP}}$. The results of earlier measurements by other investigators have been summarized by Lowder and most of them compare

favorably with his results.

Since our measured values of N_2O line strengths in the ν_3 fundamental were considerably smaller than those of earlier investigators, we decided that a measurement of the strengths of some lines in the $\nu_1 + \nu_3$ N_2O combination band near 3480 cm^{-1} should be made in order to compare our values with the recent results of Toth⁵, who has measured the strengths of most of the lines in this band by using a low-pressure technique.

The experimentally measured values of line strength for the N_2O $\nu_1 + \nu_3$ band at 296K for lines $m = +12$ to $m = +40$ are shown as circles in Fig. 4. Calculated values of line strength using equation (1) with $|R| = 0.0367$ Debye are represented by triangles; the rms percentage difference between calculated and measured values is 3.6 percent. The increasing difference between calculated and measured values near $m = +10$ is due in part to absorption by an overlapping hot band. The above value of the dipole-moment matrix element yields a band strength of $46.5\text{ cm}^{-1}/(\text{atm}\cdot\text{cm})_{\text{STP}}$ which is approximately 10 percent larger than the value of $41.9\text{ cm}^{-1}/(\text{atm}\cdot\text{cm})_{\text{STP}}$ reported by Toth.

LINE BROADENING PARAMETERS γ°

The Lorentz halfwidth γ of a collision broadened absorption line is related to the pressure P in atmospheres by $\gamma = \gamma^{\circ} P$ where γ° is expressed in units of $\text{cm}^{-1}/\text{atm}$ and is numerically equal to the halfwidth of the absorption line at a pressure of one atmosphere. Line-broadening parameters γ° were measured by the curve-of-growth method in a region where the equivalent width of an absorption line is related to both the line strength and the halfwidth. Absorption cells with lengths

in the range 0.5 to 10.2 cm were used to ensure that the pressure-broadening width was several times larger than the Doppler halfwidth and that the absorption lines were essentially black at the line centers.

The results of the present measurements for lines up to $m = +60$ in the R-branch of the ν_3 fundamental at a temperature of 302K are shown as circles in Fig. 5. The uncertainty bars represent one standard deviation of individual measurements from the average values for each line. The halfwidths of some lines near the band center could not be measured because of overlapping lines in the hot band; the equivalent widths of other lines in the fundamental were corrected by graphically subtracting contributions of the hot-band lines to the equivalent widths. Calculated values of line strength based on our measurements were used in the determination of the line-broadening parameters. The line-broadening parameters in Fig. 5 have values which are larger than those obtained for CO and CO₂ in our earlier studies but the values decrease as one proceeds from near the band center towards the wings of the band as has been observed in other gases.

Line-broadening parameters were also measured for 21 lines in the N₂O $\nu_1 + \nu_3$ band at a temperature of 296K; the results of the measurements are shown as open squares in Fig. 5. The values obtained in the two different vibrational bands are nearly the same. Calculated values of line strength represented by the triangles in Fig. 4 were used in the determination of the line-broadening parameters for the $\nu_1 + \nu_3$ band.

The values of line broadening parameters measured by other investigators at a temperature of 296K for different N₂O bands are shown in

Fig. 6. The values of Toth⁶ for the 02⁰₁ - 00⁰₀ band are represented by open circles and the values of Margolis⁸ for the 00⁰₂ - 00⁰₀ band are represented by open squares. Both Toth and Margolis used a so-called direct method of measuring line width in which observed widths are corrected for spectrometer-slit effects to determine true widths. Values obtained for the ν_3 fundamental band in the present study are shown as solid circles.

It has been shown experimentally for CO and CO₂ that the line-broadening parameters do not depend strongly upon the vibrational state of the molecule; the present results along with those of Toth and Margolis confirm that this is also true for N₂O. The shaded squares in Fig. 6 are line-broadening parameters for N₂O as calculated by Varanasi et al.⁹ The rather poor agreement between calculated and measured values serves to emphasize the inadequacies of existing theories; however, Toth⁶ and Hirono¹⁰ have both shown that calculated values can be made to agree with experimental values by proper choice of the N₂O quadrupole moment.

The measured values of line-broadening parameters for some lines in the R branch of the ν_3 fundamental at a temperature of 204K are shown in Fig. 7 along with the measured values at 302K for comparison. The values at 204K are larger than those at 302K, a result that is in agreement with the results of low temperature studies of CO and CO₂.

On the basis of simple theory, γ is proportional to the mean collision frequency f_c or

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

where n is the number of molecules per unit volume, $\bar{v} = (2kT/\mu)^{1/2}$ is the mean relative speed of the collision pairs, μ is the reduced mass of the collision pair and σ is the collision cross section. By using the general gas law $P = nkT$ we can express the collision cross section σ in terms of γ^0 as $\sigma = \gamma^0 \pi c (2kT\mu)^{1/2}$. We have used this relationship to calculate collision cross sections σ for 204 and 302K. The ratio $\sigma(204K)/\sigma(302K)$ has an average value of 1.01 for the 34 lines where collision cross sections were measured for both temperatures. Although there is some scatter in the value of the ratio, there are no definite trends; thus it would seem that the collision cross sections do not depend upon the temperature of the gas in this limited temperature range. This implies that the collision broadening parameters can be calculated for any temperature in this range by using the experimentally determined cross sections and the relationship between γ^0 and σ .

This result for N_2O is in sharp contrast to our earlier results for CO and CO_2 , for which the collision cross sections are temperature dependent.

DISCUSSION OF RESULTS

The excellent agreement of values of the self-broadening parameters obtained in the present work with those reported by Toth⁶ and Margolis⁸ is gratifying. The value we obtain for the band strength of the $\nu_1 + \nu_3$ band agrees with Toth's value within the limits of uncertainty of the two sets of measurements. There is, however, serious disagreement between the value we obtain for the total band strength of the ν_3 -fundamental region and the values obtained in other investigations. Our value of

$1323 \text{ cm}^{-1}/(\text{atm}\cdot\text{cm})_{\text{STP}}$ is approximately 20 percent lower than the value of $1608 \text{ cm}^{-1}/(\text{atm}\cdot\text{cm})_{\text{STP}}$ reported by Lowder⁴, where both values include contributions of both the fundamental and the overlapping hot band. Lowder has summarized the corresponding values based on earlier low-resolution studies; these values fall in the range 997 to $1920 \text{ cm}^{-1}/(\text{atm}\cdot\text{cm})_{\text{STP}}$. In view of the amount of work done on N_2O , the lack of agreement on values of band strength is surprising.

Our values of γ° are based on measurements in the vicinity of the square-root region of the curve of growth and thus involve our measurements of line strength obtained in the linear region. Any increase in our values for line strengths would result in a proportionate decrease in our values for γ° ; an increase of 20 percent in our line strengths would lead to disagreements with the values of γ° obtained by Toth and Margolis by direct methods.

We have devoted considerable effort to a search for possible non-linearities in our detector-amplifier system, for the influence of spectral slitwidths on our results, for possible systematic sampling errors, and for other instrumental problems. After this critical evaluation of our experimental techniques we find no reason to alter the best-values of line strengths given in Figs. 2, 3 and 4. Careful additional measurements on several clean lines in the R branch indicate an upper limit of S-values of 14 percent above those we show as best values.

Since most of our measurements have been restricted to lines in the R branch, we have been unable to obtain realistic estimates of vibration-rotation interactions. Therefore, we have neglected this type of

interaction in arriving at values for total band strength. Our assumption that vibration-rotation interactions are negligible could thus introduce an error in our estimates of band strength. Further work on the band strength of the ν_3 fundamental would seem highly desirable.

LEGENDS FOR FIGURES

- Fig. 1 Recorder tracing of the N_2O absorption lines in the vicinity of the ν_3 fundamental. Some rotational lines of the P and R-branches of the fundamental band are indicated below the tracing while some lines of the P and R-branches of the overlapping hot band $01^1_0 - 01^1_1$ are indicated above the tracing.
- Fig. 2 Measured values of line strength in units of $cm^{-1}/(atm \cdot cm)_{STP}$ as a function of rotational line number m for some lines in the ν_3 fundamental at 302K including contributions from the overlapping hot band are indicated by the circles. Calculated values of line strength for the ν_3 fundamental are indicated by triangles.
- Fig. 3 Measured values of line strength in units of $cm^{-1}/(atm \cdot cm)_{STP}$ as a function of rotational line number m for some lines of the ν_3 fundamental band of N_2O at 204K are indicated by circles. Calculated values of line strength for the same band are represented by triangles.
- Fig. 4 Measured values of line strength in units of $cm^{-1}/(atm \cdot cm)_{STP}$ as a function of rotational line number m for some lines in the R branch of the $\nu_1 + \nu_3$ combination band at 296K are indicated by circles. Calculated values of line strength for the same band are represented by triangles.
- Fig. 5 Measured values of collisional-broadening parameters γ^0 in units of cm^{-1}/atm as a function of rotational line number m

for some lines in the R branch of the ν_3 fundamental at 302K are indicated by circles. Some measured collision-broadening parameters for the $\nu_1 + \nu_3$ combination band at 296K are indicated by the squares.

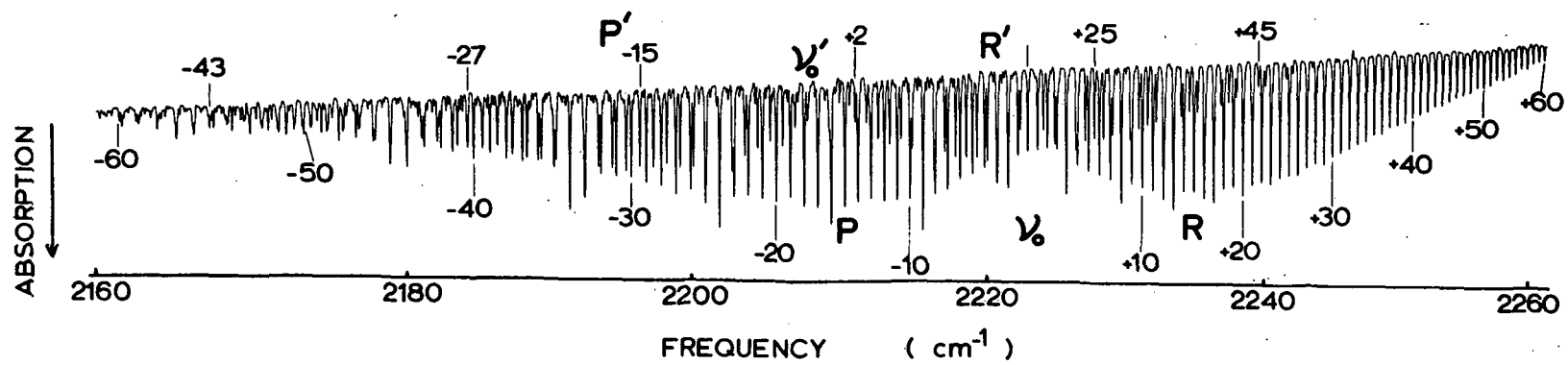
Fig. 6 Measured values of collision-broadening parameters γ^0 in units of $\text{cm}^{-1}/\text{atm}$ as a function of rotational line number m from the present investigation of the ν_3 fundamental are indicated by solid circles; values measured by Toth in the $2\nu_2 + \nu_3$ band by open circles; values measured by Margolis for the $2\nu_3$ overtone by open squares; and values calculated by Varanasi for N_2O rotational lines by solid squares.

Fig. 7 Measured values of collision-broadening parameters γ^0 in units of $\text{cm}^{-1}/\text{atm}$ as a function of rotational line number m for some lines in the ν_3 fundamental at temperatures of 204 and 302K.

FOOTNOTES AND REFERENCES

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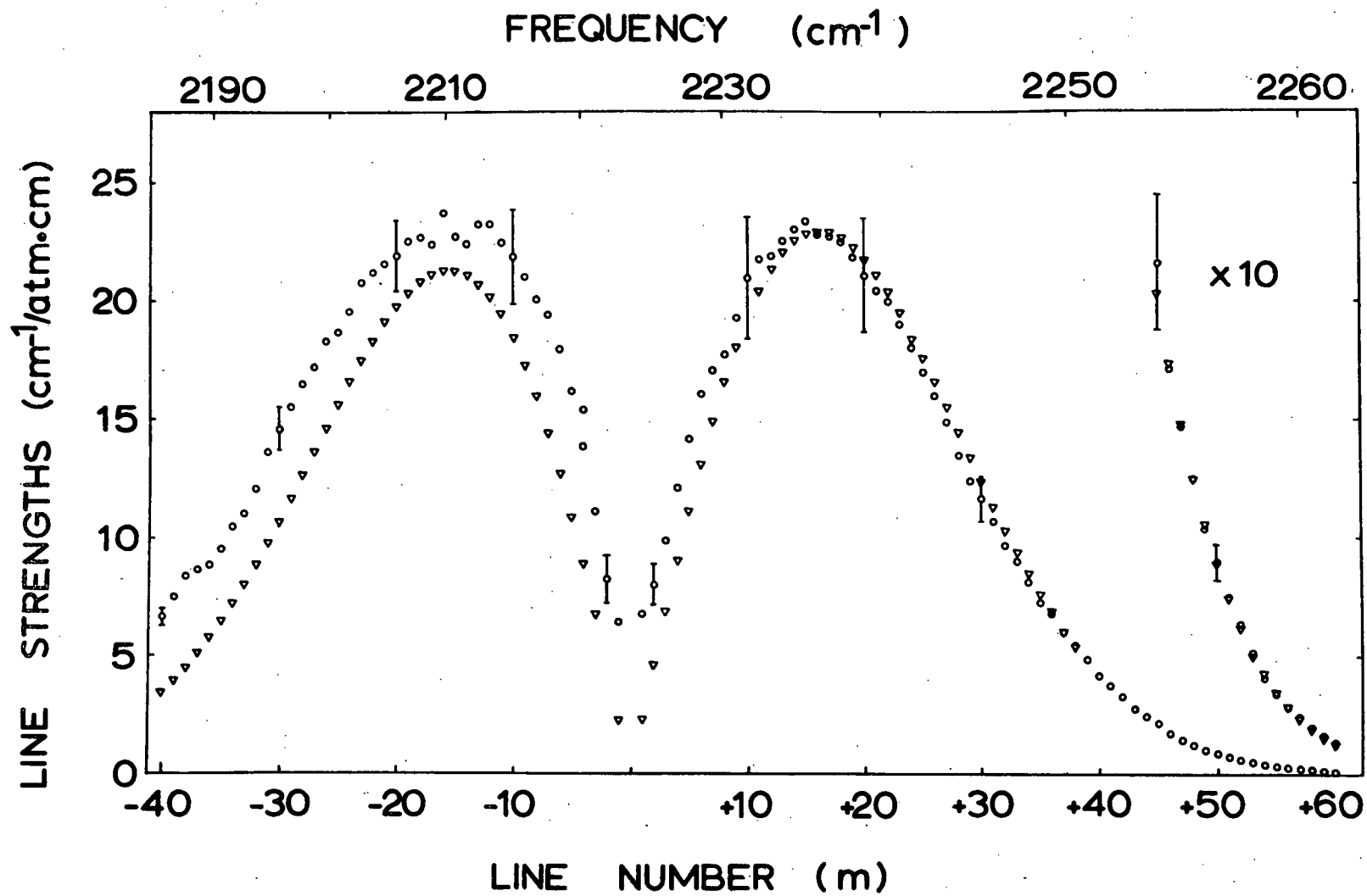


Fig 2

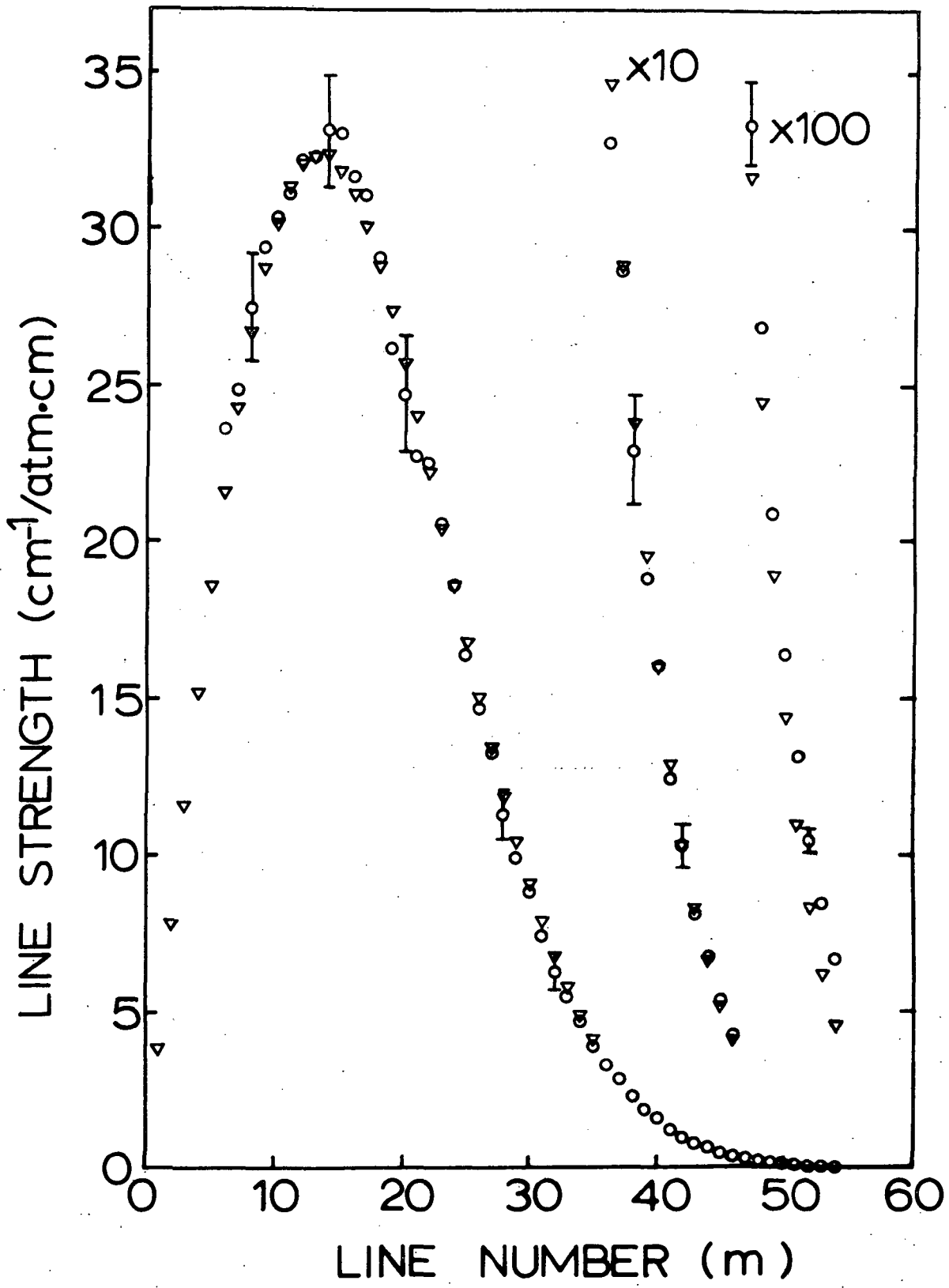


Fig 3

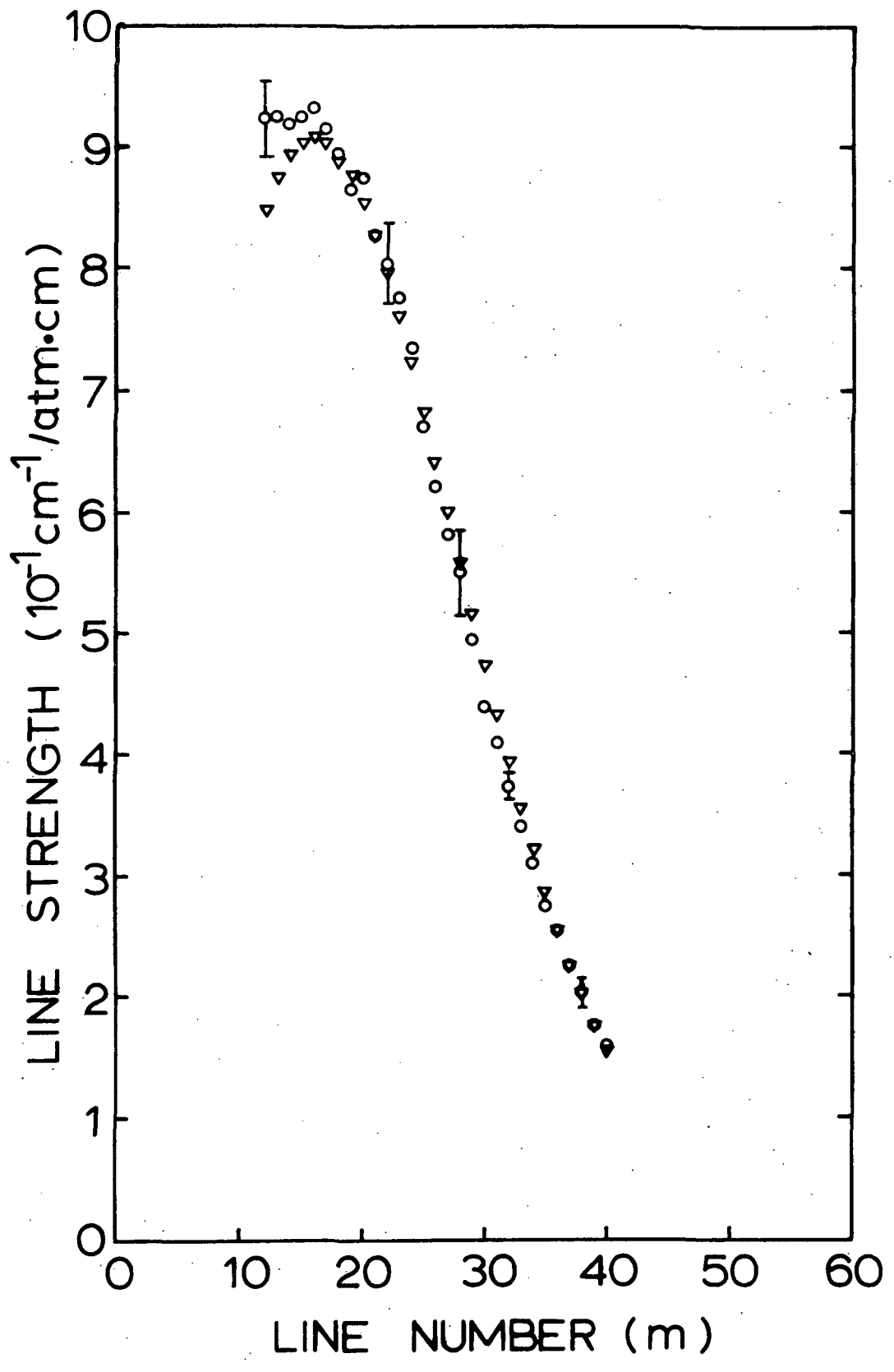


Fig 4

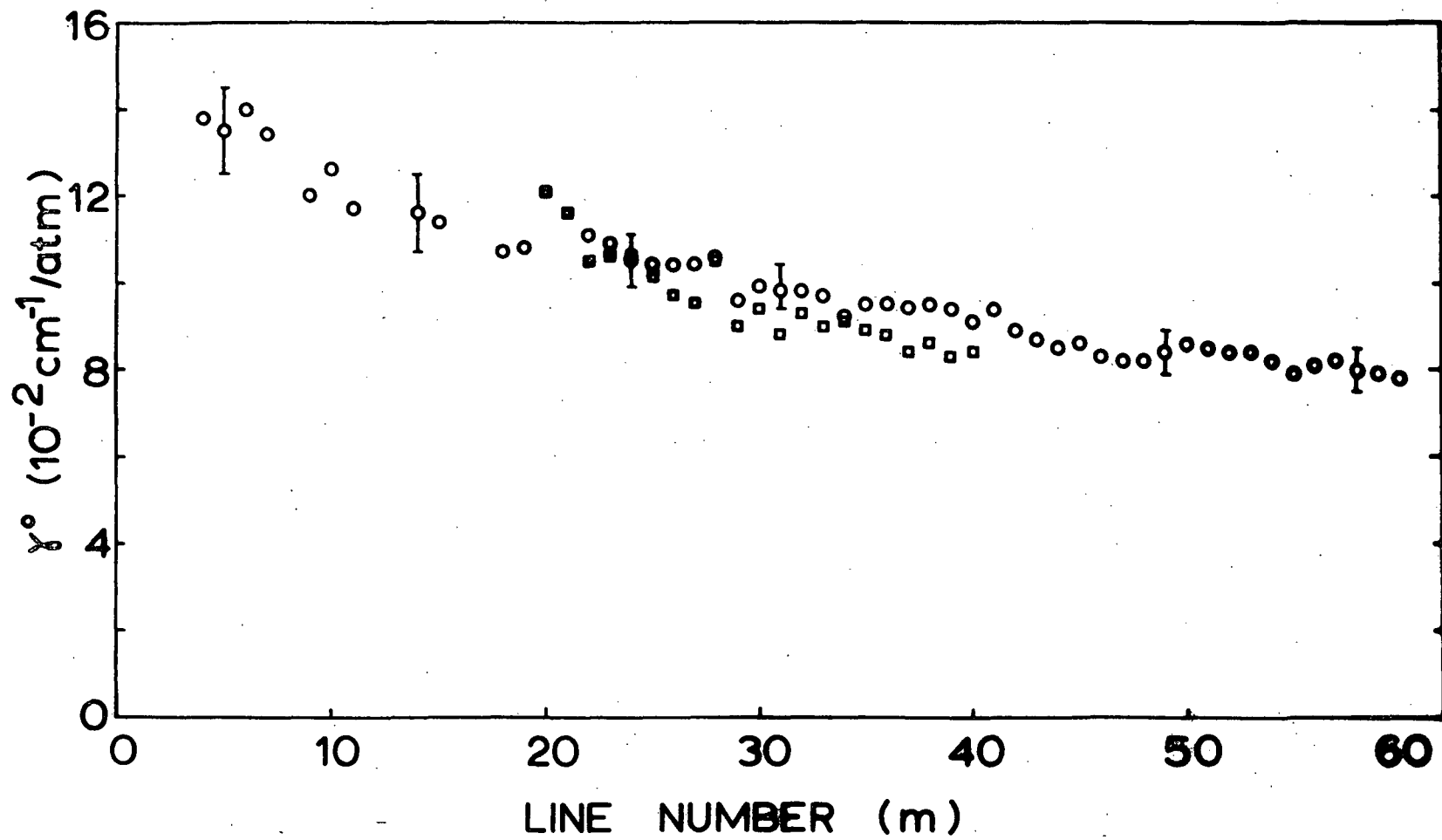
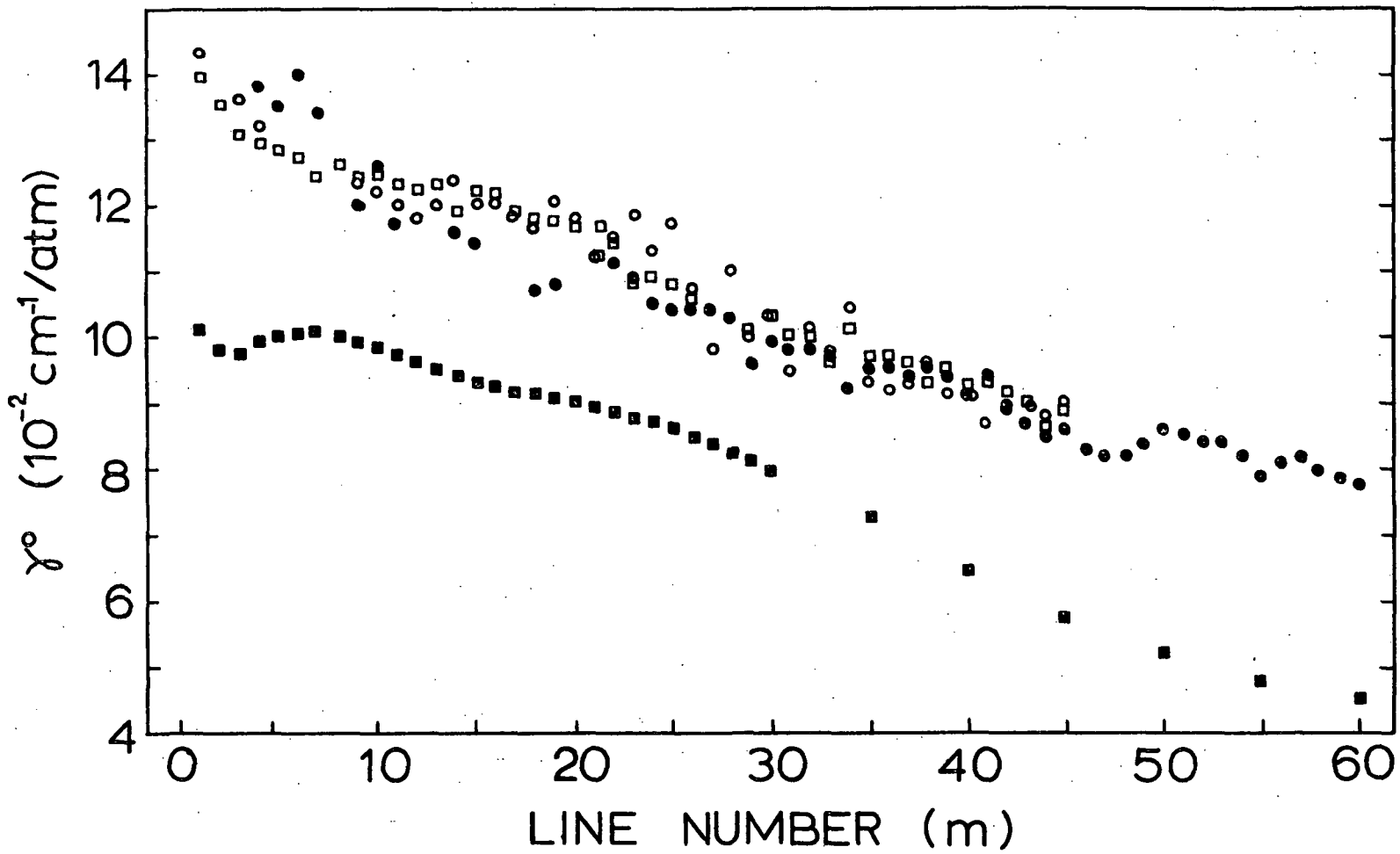


Fig 5



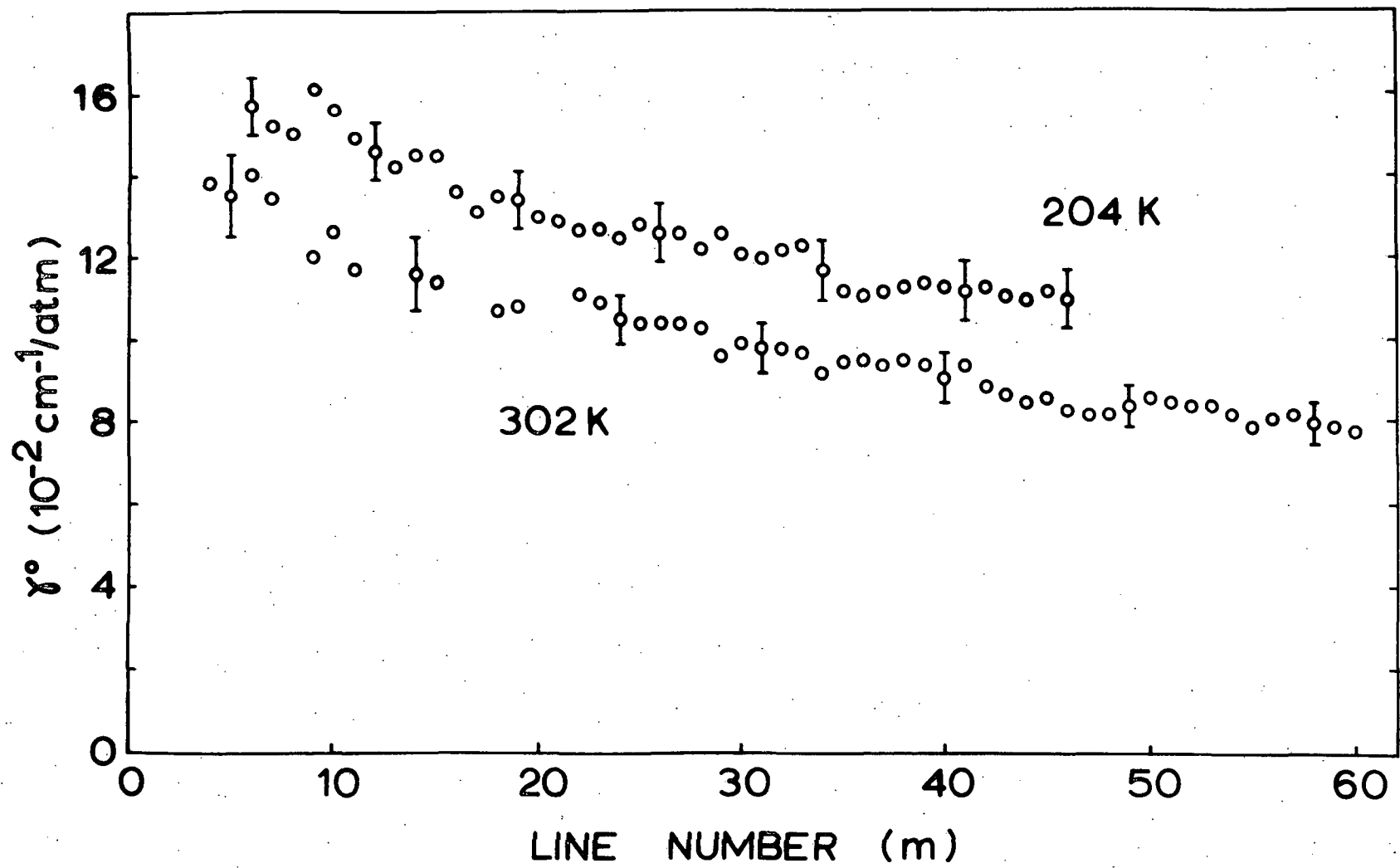


Fig. 7