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 1977 to 30 November 1977

It was prepared by

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Date: 20 December 1977

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.

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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 <u>band</u> absorptance $\int A(\nu)d\nu$ as a function of absorber thickness $\underline{w}$ and total effective pressure P_e have been made at various temperatures T for bands of CO and N_2O. 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-wdith 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^o 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^o 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 and k of liquid ammonia in the infrared. A paper on the subject has been published as a journal article. 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; this work has been published as a scientific note in a journal.

Work has also been done on the optical properties of solid NH_3. This work has been incorporated in a journal article.

In view of the suggestion that H_2SO_4 droplets are the major component of the cloud cover of Venus, we have made extensive studies

of this material at various concentrations in water in the range

between the near ultraviolet and the far infrared. On the basis

of the results we have prepared a major article with extensive tables

listing the values of n and k for various concentrations. It appears

that the concentration of H_2SO_4 in the droplets of the Venus clouds

is greater than 70 percent. This work was followed by a study of

the optical properties of H_2SO_4 at a temperature of 250°K, which

approximates the temperature of the Venus clouds; a report of the

250°K study was published in the Journal of the Optical Socity of

America.

Recent work has included studies of ammonium sulphate, a major

aerosol in the earth's stratosphere, and methane and other hydro-

carbons possibly present in the cloud covers of the Jovian planets.

Cumulative List of Publications[*]

1. "Further Studies of Overlapping Absorption Bands," Tubbs, Hathaway and Williams, J. Opt. Soc. Amer. <u>57</u>, 570 (1967) P.

2. "Foreign-Gas Broadening of Absorption Lines in the CO Fundamental," Draegert, Chai, and Williams, J. Opt. Soc. Amer. <u>57</u>, 570 (1967) P.

3. "Broadening of Absorption Lines in the CO Fundamental," Chai, Draegert, Williams, Bull. Am. Phys. Soc. <u>12</u>, 542 (1967) P.

4. "Further Studies of Overlapping Abosrption Bands," Tubbs, Hathaway, and Williams, App. Opt. <u>6</u>, 1422 (1967).

5. "Strengths and Half Widths of CO Lines at Reduced Temperatures," Hoover, Hathaway, and Williams, J. Opt. Soc. Amer. <u>58</u>, 739 (1968) P.

7. "Line Widths in Vibration-Rotation Bands," Williams, Bull. Am. Phys. Soc. II <u>13</u>, 569 (1968) P.

8. "Comparison for Collision Cross Sections for Line Broadening in the CO fundamental," Chai and Williams, J. Opt. Soc. Amer. <u>58</u>, 1395 (1968).

9. "Collisional Broadening of CO Absorption Lines by Foreign Gases," Draegert and Williams, J. Opt. Soc. Amer. <u>58</u>, 1399 (1968).

10. "Absorption in the Wings of Rotational Lines in the CO Fundamental", Chai and Williams, Bull. Am. Phys. Soc. II <u>13</u>, 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. <u>59</u>, 28 (1969).

[*] P denotes papers presented at scientific meetings.

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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 CO_2", Tubbs and Williams, J. Opt. Soc. Amer. 61, 673 (1971). P.

19. "Line Strengths and Half-Widths in the ν_3 Fundamental of CO_2", Tubbs and Williams, J. Opt. Soc. Amer. 61, 1587 (1971). P.

20. "Broadening of Infrared Absorption Lines at Reduced Temperatures: CO_2", 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
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27. "Broadening of Infrared Absorption Lines at Reduced Temperatures
    III Nitrous Oxide", L. D. Tubbs and D. Williams, J. Opt. Soc.
    Am. 63, 859d (1973).

28. "Lambert Absorption Coefficient of Liquid Ammonia in the Visible
    Region", C. W. Robertson and D. Williams, J. Opt. Soc. Am.
    63, 763 (1973).

29. "Lambert Absorption Coefficient of Solid Ammonia in the Infrared",
    C. W. Robertson, Proceedings of 1973 Symposium on Molecular
    Spectroscopy, Ohio State University.

30. "Optical Properties of Particles in Planetary Atmospheres:
    Laboratory Studies", D. Williams Proceedings of the
    Copernicus Symposium IV in Torun, Poland, September, 1973.
    (In Press).

31. "The Clouds of Venus", K. F. Palmer and D. Williams, J. Opt. Soc.
    Am. 64, 530 (1974). P.

32. "Optical Constants of Sulphuric Acid", K. F. Palmer. Proceedings
    of 1974 Symposium on Molecular Spectroscopy, Ohio State University.

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33. "Sulphuric Acid and the Clouds of Venus," Kent F. Palmer and
    Dudley Williams, Bull. Am. Phys. Soc. 19, 1130 (1974).

34. "The Optical Properties of Sulfuric Acid in the Infrared:
    Application of the Venus Atmosphere?", K. F. Palmer and
    D. Williams, Appl. Opt. 14, 208 (1975).

35. "The Optical Constants of Solid Ammonia in the Infrared,"
    C. W. Robertson, H. D. Downing, B. Curnutte, and D. Williams,
    J. Opt. Soc. Am. 65, 432 (1975).

36. "The Infrared Reflectance of Aqueous Solutions of Sulfuric
    Acid at 250°K," L. W. Pinkley, OSU Molecular Spectroscopy
    Symposium 1975. P.

37. "Optical Constants of Ammonium Sulphate," H. D. Downing, OSU
    Molecular Spectroscopy Symposium 1975. P.

38. "Optical Properties of Matter in Condensed States," D. Williams,
    Proc. XII Conference of European Molecular Spectroscopists
    (Elsevier Publishing Co., Amsterdam, 1975) p. 765.

39. "Infrared Optical Constants of Sulphuric Acid at 250°K," L. W.
    Pinkley and D. Williams, J. Opt. Soc. Am. 66, 122 (1976).

40. "Optical Constants of Ammonium Sulfate in the Infrared,"
    H.D. Downing, L.W. Pinkley, P.P. Sethna, and D. Williams,
    J. Opt. Soc. Amer. 67, 186 (1977).

41. "Optical Constants of Cupric Sulfate in the Infrared,"
    P.P. Sethna, L.W. Pinkley, and D. Williams, J. Opt. Soc.
    Amer. 67, 499 (1977).

42. "Van Vleck's Principles of Spectroscopic Stability: Molecular
    Applications," D. Williams, L.W. Pinkley, and P.P. Sethna,
    J. Opt. Soc. Amer. 66, 1065 (1976). P.

43. "The Infrared Reflectances of Liquid Hydrocarbons", L. W. Pinkley,
    Molecular Spectroscopy Symposium, Ohio State Univ. 1977.   P.

44. "Optical Constants of Liquid Methane in the Infrared", L. W. Pinkley,
    P. P. Sethna, and D. Williams, J. Opt. Soc. Am. (Accepted for
    publication).

45. "Optical Constants of Liquid Hydrocarbons in the Infrared", L. W.
    Pinkley, P. P. Sethna, and D. Williams, J. Phys. Chem. (Submitted
    for publication).

46. "Optical Constants of Ammonium Hydroxide in the Infrared", P. P.
    Sethna, H. D. Downing, and D. Williams, J. Opt. Soc. Am. (Submitted
    for publication).

II. PROGRESS DURING THIS REPORT PERIOD

Studies of Particulate Constituents of Planetary Atmospheres

A. Methane in Condensed States

A paper summarizing our work on liquid methane has been submitted to the Journal of the Optical Society of America and has been accepted for publication. A pre-print of the paper is included as an appendix to this report.

B. · Hydrocarbons

A paper summarizing our work on saturated hydro-carbons has been submitted to the Journal of Physical Chemistry. A preprint of this article is included as an appendix to this report.

C. Ammonium Hydroxide

This material, which has been suggested as an aero-sol in the Jovian atmosphere, has been studied by re-flection methods. A paper summarizing our results has been submitted to the Journal of the Optical Society of America. A preprint of the article is included as an ap-pendix to this report.

Cooperation with NASA Research Centers

At the request of Dr. Pearl of Goddard I visited Dr. U. Fink and ·Dr. G. Sill at the University of Arizona for a critical review of their recent work on materials suggested as planetary aerosols. While in the Southwest I also visited Dr. B. Farmer and his asso-ciates at the Jet Propulsion Laboratory for a discussion of recent work.

We have delivered a computer program for the use of Dr. John Pearl at Goddard – along with a set of test data. Dr. Pearl plans to use the program in the analysis of the experimental work of Fink and Sill.

In November I spent a day in consultation with a group of research workers at Langley Research Center, who are beginng marine studies and are interested in the infrared properties of water.

III. PERSONNEL

Dr. Dudley Williams, Regents' Professor of Physics:

Chief Investigator (WOC)

Dr. Basil Curnutte, Professor of Physics:

Senior Associate (WOC)

Dr. Larry Pinkley (Part-Time): Research Associate (Resigned 1 July, 1977)

Dr. Prochy Sethna (Part-Time): Research Associate

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 consideration will be given to the application of
Van Vleck's Principle to molecules in condensed states.

    B. We shall investigate the optical constants of certain poly-
atomic groups that may be present in dust in the earth's atmo-
sphere.

    C. Our work on hydrocarbons has indicated that certain "group in-
tensities" can be associated with atomic groups in polyatomic
molecules. In order to pursue this subject we shall investi-
gate the spectral properties of certain classes of molecules.

Signed _____
Dudley Williams

Appendices:

Preprints of articles on liquid methane, hydrocarbons, and ammonium
hydroxide.

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OPTICAL CONSTANTS OF LIQUID METHANE IN THE INFRARED[*]

Lary W. Pinkley,[**] P.P. Sethna, and Dudley Williams

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The near-normal incidence spectral reflectance $R(\nu)$ of liquid methane at 98 K has been measured in the infrared in the spectral range $6700.\,cm^{-1}$ to $350\ cm^{-1}$. The resulting values of $R(\nu)$ have been subjected to Kramers-Kronig phase-shift analysis to provide values of the real $n(\nu)$ and imaginary $k(\nu)$ parts of the complex index of refraction $N(\nu) = n(\nu) + i\ k(\nu)$ in the range 4000 to $400\ cm^{-1}$. The results of the present study are presented in graphical form and in tabular form over this range. The strengths $S = \int k(\nu)d\nu$ of the absorption bands are compared with the corresponding bands in gaseous methane. Techniques for using the present results to obtain approximate values of the corresponding optical constants of solid methane are discussed.

Methane in condensed states is believed to be an important component of the cloud cover of the outer planets of the solar system. It is thus important to have a knowledge of the optical constants of this material in the infrared for use in the interpretation of proposed studies of these planets from space probes as well as for use in the interpretation of observations being conducted at ground-based observatories. The present work on liquid methane was undertaken as a first step in acquiring the needed information. We selected liquid methane for study because the reflection techniques developed in our recent studies[1] are more readily applied to liquids than to solids. In some of these earlier studies[2] we have shown that valid estimates of the optical properties of solids can be obtained from the measured properties of the corresponding liquids; it is therefore to be hoped that our present work will also provide approximate values of the optical constants of solid methane, which is probably more abundant than liquid methane in planetary cloud covers.

Methane is a very interesting material from many points of view. The methane molecule CH_4 is a spherically symmetric molecule that has certain spectroscopic properties that have long been of interest to theorists and experimentalists alike. The spectrum of gaseous methane is characterized by the following fundamental vibration-rotation bands[3]:

$\nu_1(a_1)$ at 2914 cm^{-1}, $\nu_2(e)$ at 1526 cm^{-1}, $\nu_3(f_2)$ at 3020 cm^{-1}, and $\nu_4(f_2)$ at 1306 cm^{-1}.

There are numerous much weaker overtone and combination bands in the spectrum of the gas.

The study of the finer details of these bands continues to be a topic of major interest to spectroscopists; with every improvement in the resolving

power of spectrographs, further information is obtained[4]. The intermolecular forces between methane molecules are very small, as evidenced by the low boiling point 109.1K and the low melting point 90.7K for the material; the vapor pressure of methane is high over most of its relatively narrow liquid range. Even solid methane at its melting point has a vapor pressure of 70 Torr.

EXPERIMENTAL WORK

Our experimental work involved the measurement of spectral reflectance $R(v)$ of methane at near-normal incidence. The liquid methane was obtained by the condensation of UHP 99.97 percent gaseous methane (Matheson) in a copper coil immersed in liquid nitrogen. Samples of the liquid were placed in a shallow glass beaker suspended inside a Dewar vessel containing liquid nitrogen. By adjustment of the height of the beaker above the liquid nitrogen surface, we were able to control the temperature of the liquid methane. The temperature of the liquid methane was monitored by means of a thermocouple; in the course of our study, measurements were made for samples at various temperatures over most of the liquid range. The results we report can be regarded as typical of liquid methane at a nominal temperature of 98K near the middle of the liquid range. Samples in the beaker were maintained at a depth of several centimeters; the level of the free surface of the liquid methane was monitored by means of a cathetometer with viewing through an un-silvered portion of the Dewar walls. Because of sample loss due to the high vapor pressure of the liquid, it was necessary at frequent intervals to refill the beaker with liquid methane. Probably as a result of the rapid evaporation of the liquid methane, we never encountered problems arising from the condensation of atmospheric water vapor on the cold sample surface.

In determining the radiant flux reflected by the free surface of the methane we were faced with a formidable problem associated with the absorption by gaseous methane above the surface of the liquid. This problem was minimized by the use of a system of exhaust pumps used to remove gaseous methane from the optical path and from the air of the laboratory. One of the intakes of the exhaust system was placed inside the Dewar vessel close to the surface of the liquid; others were placed close to the top of the Dewar vessel. The pumping system with its intake openings was arranged to remove the unwanted gaseous methane without producing waves on the surface of the liquid methane sample. The effectiveness of the system in removing methane gas was checked from time to time by a search for absorption associated with the strong Q-branches of the gas bands in the air just above the Dewar vessel; an auxilliary horizontal beam of infrared radiation was used in this monitoring process.

In arriving at values of $R(\nu)$ for liquid methane, we first measured the ratio $r(\nu)$ of the radiant flux reflected from the methane surface to the radiant flux reflected from a water surface when a water sample was placed at the sample position in the reflectometer. The spectral reflectance $R(\nu)$ of methane was then obtained from the relation $R(\nu) = r(\nu) \, R_w(\nu)$, where $R_w(\nu)$ is the reflectance of water based on the tables of optical constants of water given in a paper by Downing and Williams[5], which gives a critical summary of numerous earlier studies of water; in spectral regions where $R_w(\nu)$ is extremely small it was necessary to use a calibrated mirror in place of water as a reference. Reflectance $R(\nu)$ was determined in the spectral range 6700 cm^{-1} to 350 cm^{-1}.

RESULTS

Figure 1 gives a plot of our values of spectral reflectance $R(\nu)$ as a function of frequency expressed in cm^{-1}. The fractional reflectance over the entire range 4000 to 400 cm^{-1} is rather low. There are two observable dispersion features: the feature between 3200 and 2800 cm^{-1} in the figure is associated with the overlapping fundamental vibration bands ν_1 and ν_3: the second somewhat sharper feature between 1400 and 1200 cm^{-1} is associated with the overlapping fundamental bands ν_2 and ν_4. Over most of the range we believe that the uncertainties in the values of $R(\nu)$ amount to ± 2 percent of the plotted values. Incomplete removal of gaseous methane from the optical path could produce somewhat larger uncertainties in the vicinity of the two dispersion features.

In order to obtain values of the optical constants from our measured values of $R(\nu)$ we made use of the values of $R(\nu)$ over the entire range of measurement 6700 cm^{-1} to 350 cm^{-1}. We first made use of simple Kramers-Kronig phase shift analysis with linear high frequency and low frequency extrapolations to obtain values of $n(\nu)$ and $k(\nu)$; the resulting values were then compared with those obtained by subtractive Kramers-Kronig analysis, which leads to more reliable values of $n(\nu)$ and $k(\nu)$ in the vicinity of the highest and lowest frequencies in the range of actual measurement. We discarded values of the optical constants in the 6700-4000 cm^{-1} region and in the 400-350 cm^{-1} region in order to minimize the influence of extrapolations on the values of the optical constants plotted in subsequent figures.

The values of $n(\nu)$ as a function of wave number are plotted in Fig. 2 for the spectral region between 4000 and 400 cm^{-1}. The general features of the

curve in Fig. 2 are similar to the features in the reflectance curve in Fig. 1. The uncertainties in n(ν) amount to approximately ± 1 percent of the plotted values over most of the spectral range; the uncertainties in the vicinity of the two dispersion features may be somewhat larger in view of the possibly larger uncertainties in R(ν) in these regions.

The values of k(ν), sometimes called the spectral absorption index, are plotted as a function of wave number in Fig. 3 with one major peak at 3000 cm^{-1} and a second peak at 1300 cm^{-1}. Although it is difficult to estimate the uncertainties in k(ν) as obtained from the Kramers-Kronig analysis of reflectance data, we estimate that the uncertainties in the present work amount to ± 0.001 in spectral regions where k(ν) is small and somewhat less in the vicinity of absorption peaks. Thus, in the range 4000 to 3100 cm^{-1} our values of k(ν) are not significantly different from zero and have been omitted from the plot in Fig. 3. The uncertainty δk = ± 0.001 should be borne in mind when the low values of k(ν) between the major absorption peaks and in the 1200-400 cm^{-1} regions are considered. There is also some reason to believe that the values of k(ν) in the low-frequency tail of the absorption band centered at 3000 cm^{-1} are somewhat high and may be subject to a correction δk'(ν) of -0.001 in this region.

In Table 1 we give an abbreviated list of the optical constants of liquid methane. In the table we give values of n(ν) at widely spaced frequency intervals except in the vicinity of the regions of strong absorption; values of n(ν) between the listed frequencies can readily be obtained by using the curve in Fig. 2 as the basis for making interpolations between the values tabulated in Table 1. Values of k(ν) are stated in the table for frequencies in the vicinities of absorption bands. As indicated in Fig. 3 values of k(ν)

in other spectral regions are very small; they are, in fact, so small that they are negligible in the computation of particle scattering based on the Mie theory.

DISCUSSION OF RESULTS

We were interested in comparing the intensities of the overlapping ν_1 and ν_3 bands at 3000 cm^{-1} and the ν_2 and ν_4 bands at 1300 cm^{-1} with the intensities of the corresponding bands in the spectrum of methane gas. Spectroscopists usually compare band intensities by comparing the values of $\int \alpha(\nu)d\nu$ for the bands, where $\alpha(\nu)$ is the Lambert absorption coefficient and is related to $k(\nu)$ by the relation $\alpha(\nu) = 4\pi\nu \, k(\nu)$ with ν expressed in cm^{-1}. In a study of gaseous methane Burch and Williams[6] have reported values of $\int \alpha(\nu)d\nu = 320$ cm^{-2} for overlapping ν_1 and ν_3 bands and 185 cm^{-2} for the ν_2 and ν_4 bands for a pressure of one atmosphere and a temperature of 273K; these authors indicate that these values have an uncertainty of $\pm$ 15 percent and are in fair agreement with earlier studies, to which reference is made. The measured values of $\int k(\nu)d\nu$ obtained in the present study are 4.4 cm^{-1} for the ν_1 and ν_3 band with a peak at $\nu_p = 3000$ cm^{-1} and 5.7 cm^{-1} for the ν_2 and ν_4 band with its peak at $\nu_p = 1300$ cm^{-1}; these values also have an estimated uncertainty of approximately 15 percent. Our present results for $\int k(\nu)d\nu$ can be reliably converted to $\int \alpha(\nu)d\nu$ by the relation $\int \alpha(\nu)d\nu = 4\pi\nu_p \int k(\nu)d\nu$. The ratios of $\int \alpha(\nu)d\nu$ for the ν_1, ν_3 band to $\int \alpha(\nu)d\nu$ for the ν_2, ν_4 band are 1.73 for the gas and 1.78 for the liquid; in view of the estimated uncertainties, the agreement is nearly perfect.

A more important comparison involves the absorption per molecule in the two phases. Because $k(\nu)$ and $\alpha(\nu)$ are both proportional to the number N_1 of absorbing molecules per unit volume, we can compare absorption in the gaseous and liquid samples by comparing values of $\int \alpha(\nu)d\nu/N_1$. The results are listed

in Table 2 in terms of Avogadro's number N_A. The ratio of the absorption $\int \alpha(\nu)d\nu$ per molecule in the gas to the absorption per molecule in the liquid is 1.19 for the ν_1, ν_3 band and 1.22 for the ν_2, ν_4 band. Within the limits of uncertainty stated for the present study and for the Burch-Williams study, we can conclude that the integrated absorption per molecule in the two phases are not significantly different.

This result is in agreement with our earlier results for other materials, in which we have compared the intensities of corresponding bands in the solid and liquid states[2]; in those studies we have shown that $\int k(\nu)d\nu$ for a given band of a molecule or molecular group such as SO_4^{--} is directly proportional to the number density N_1 of the absorbers. These results suggest that the absorption spectrum $k(\nu)$-vs-ν for solid methane can be obtained in good approximation from the spectrum of liquid methane and from the known ratio of the densities of methane in the two phases. Although the details in the shape of a given band may be different, the value of $\int k(\nu)d\nu$ of a given band in the solid can be expressed as $\int k(\nu)d\nu$ for the liquid multiplied by the density ratio $\rho(\text{Solid})/\rho(\text{Liquid})$.

If we agree to ignore differences in characteristic band shapes between the solid and liquid, we can use subtractive Kramers-Kronig relations along with a knowledge of $n_D(\nu)$ for the solid at some single frequency to obtain a plot of $n(\nu)$-vs-ν for the solid. This plot can be checked in spectral regions remote from characteristic absorption bands by the use of the Lorentz-Lorenz relation to obtain $n(\nu)$ for the solid from the known values of $n(\nu)$ for the liquid. These methods can provide tentative approximate values of the optical constants for solid methane until it is possible to determine these constants from direct measurements on samples of solid methane.

LEGENDS FOR FIGURES

Fig. 1   Spectral reflectance $R(\nu)$ of liquid methane at 98 K as a function

of wave number cm^{-1}.

Fig. 2   Refractive index $n(\nu)$ of liquid methane at 98 K as a function of wave

number cm^{-1}.

Fig. 3   Absorption index $k(\nu)$ of liquid methane at 98 K as a function of

wave number cm^{-1}.

TABLE 1 Optical Constants of Liquid Methane in the Infrared

Wave Number (cm^{-1})	n(v)	k(v)	Wavelength µm
400	1.27	0.003	25.0
600	1.27	0.005	16.7
800	1.27	0.007	12.5
1000	1.27	0.008	10.0
1200	1.28	0.01	8.33
1220	1.29	0.02	8.20
1240	1.29	0.02	8.06
1250	1.29	0.03	8.00
1260	1.30	0.03	7.94
1270	1.31	0.04	7.87
1280	1.32	0.06	7.81
1290	1.33	0.12	7.75
1300	1.25	0.16	7.69
1310	1.18	0.11	7.63
1320	1.16	0.06	7.58
1330	1.17	0.03	7.52
1340	1.19	0.006	7.46
1350	1.20	—	7.41
1360	1.22	—	7.35
1370	1.23	—	7.30
1380	1.24	—	7.25
1390	1.25	—	7.19
1400	1.25	—	7.14
1500	1.26	0.002	6.67

TABLE 1 Continued

Wave Number (cm^{-1})	n(v)	k(v)	Wavelength µm
1600	1.26	0.005	6.25
1800	1.26	0.006	5.56
2000	1.26	0.006	5.00
2200	1.26	0.005	4.55
2400	1.26	0.005	4.17
2600	1.26	0.007	3.85
2700	1.26	0.01	3.70
2800	1.26	0.01	3.57
2900	1.27	0.02	3.45
2930	1.27	0.02	3.41
2960	1.27	0.03	3.38
2970	1.27	0.04	3.37
2980	1.27	0.05	3.36
2990	1.26	0.06	3.34
3000	1.24	0.07	3.33
3010	1.22	0.06	3.32
3020	1.21	0.05	3.31
3030	1.21	0.03	3.30
3040	1.21	0.03	3.29
3050	1.21	0.02	3.28
3060	1.22	0.01	3.27
3070	1.22	0.009	3.26
3080	1.22	0.005	3.25
3090	1.22	0.002	3.24

TABLE 1 Continued

Wave Number	n(v)	k(v)	Wavelength
3100	1.23	–	3.23
3150	1.24	–	3.17
3200	1.24	–	3.12
3250	1.25	–	3.08
3300	1.25	–	3.03
3400	1.25	–	2.94
3600	1.25	–	2.78
3800	1.25	–	2.63
4000	1.25	–	2.50

TABLE 2   Comparison of Absorption of Methane in the Gas and Liquid Phases a,b

Band	Gas	Liquid	Ratio: Gas to Liquid
	$\int \alpha(\nu)d\nu/N_1$	$\int \alpha(\nu)d\nu = 4\pi\nu_p \int k(\nu)d\nu/N_1$	
ν_1, ν_3	$7.2 \times 10^6/N_A$	$6.04 \times 10^6/N_A$	1:19
ν_2, ν_4	$4.14 \times 10^6/N_A$	$3.39 \times 10^6/N_A$	1.22

a) N_A represents Avogadro's number.

b)   Note that the values of $\int \alpha(\nu)d\nu$ have an uncertainty of $\pm$ 15 percent in both gas and liquid phases.

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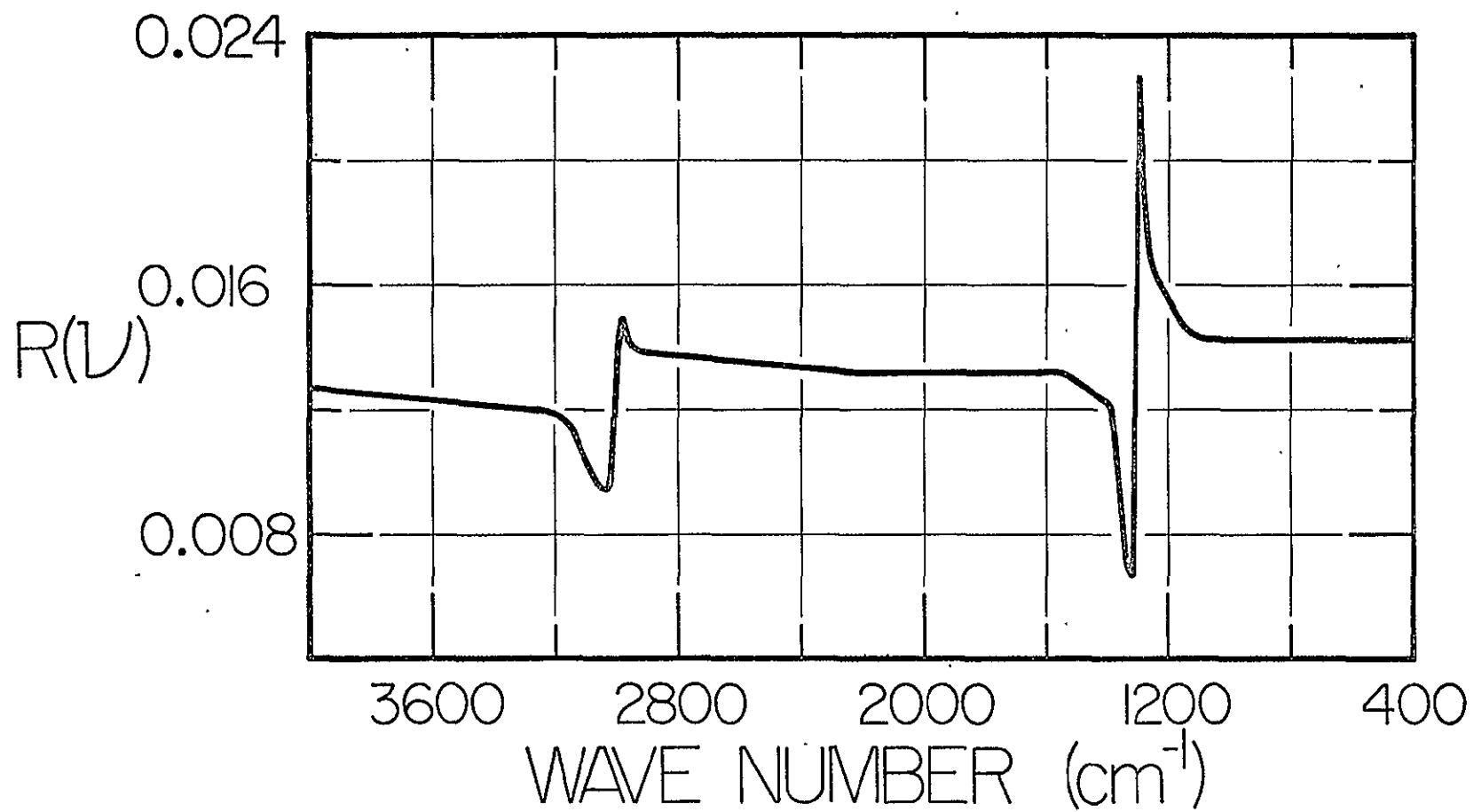
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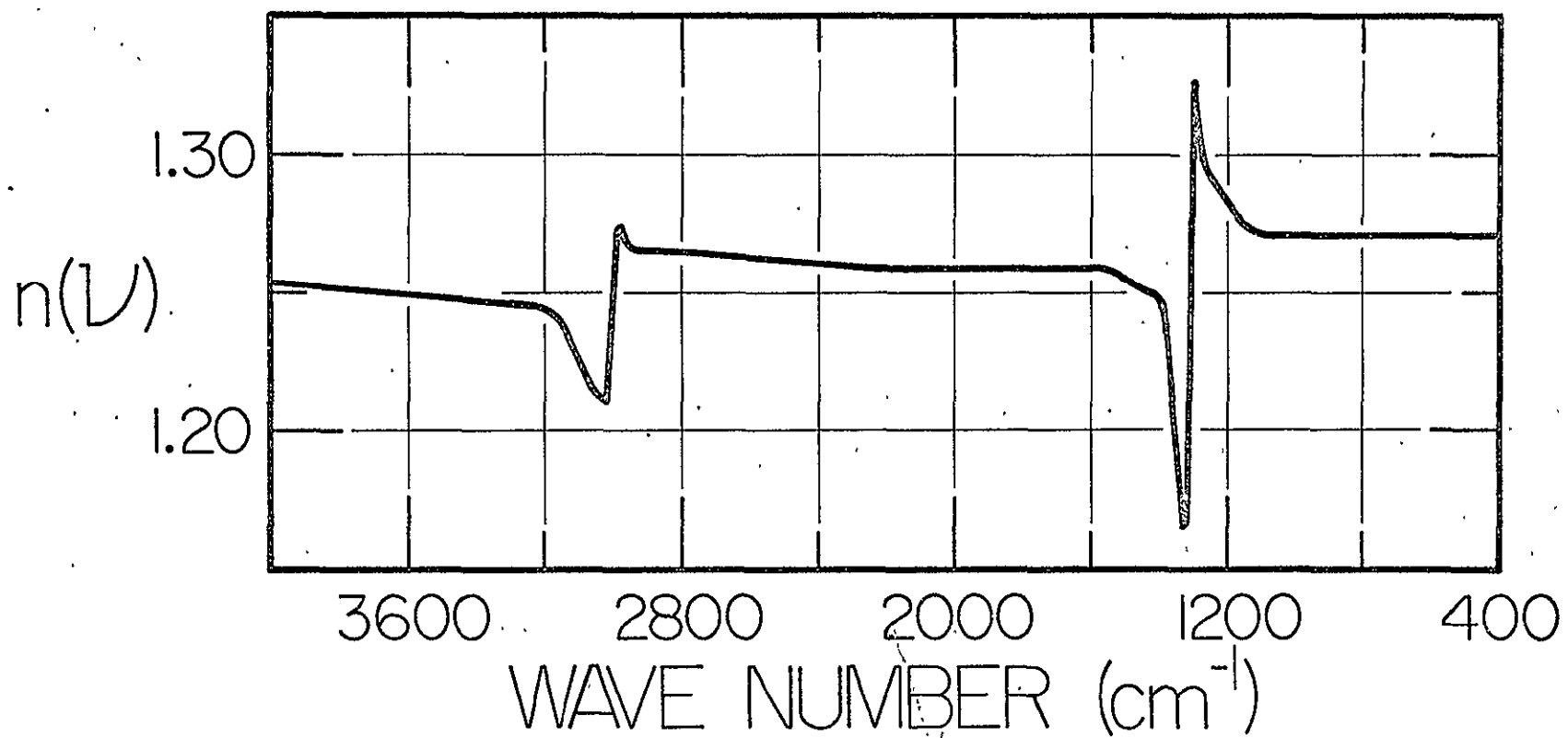
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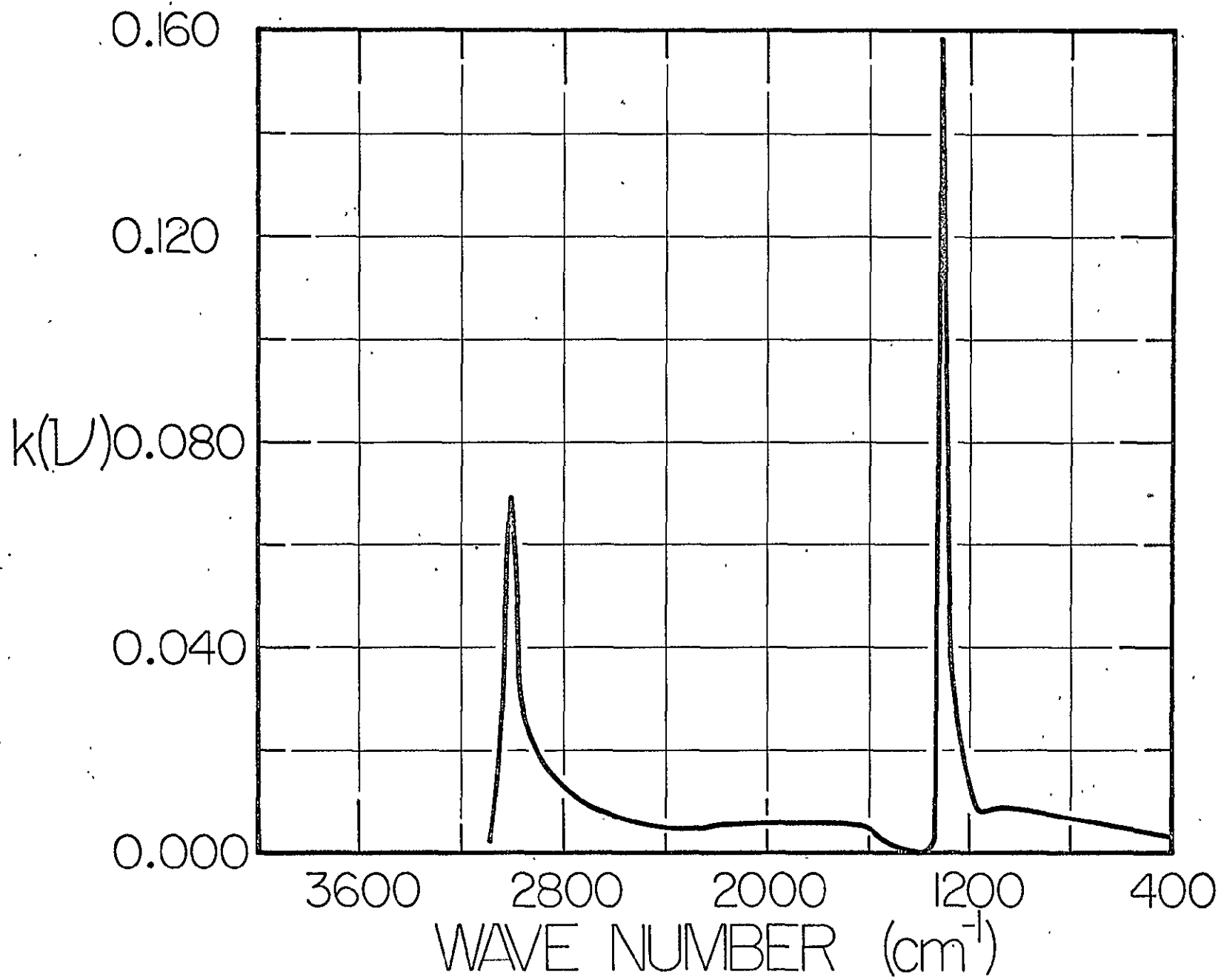
Fig. 3

Infrared Band Intensities of Saturated Hydrocarbons

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On the basis of measured values of spectral reflectance $R(\nu)$ at near-normal incidence, we have used Kramers-Kronig analysis to obtain the real $n(\nu)$ and the imaginary $k(\nu)$ parts of the complex index of refraction $\hat{N}(\nu) = n(\nu) + ik(\nu)$ for methane, ethane, propane, n-butane, n-hexane, n-heptane, and n-decane in the liquid state. Our results indicate that, with the exception of methane, the intensity $S = \int k(\nu)d\nu$ for the CH valence vibration bands in the spectra of these liquids is directly proportional to the number of CH groups per unit volume. Similar relations for the intensity of the bands due to CH_2 and CH_3 deformations have been established. We point out that characteristic group intensities like characteristic group frequencies may prove useful in molecular spectroscopy.

INTRODUCTION

The complete description of the spectroscopic properties of any
optical medium is given by the complex index of refraction of the medium:
$\hat{N}(\nu) = n(\nu) + ik(\nu)$.

Although it has long been recognized that any quantitative treatment of
the spectrum of a material requires a knowledge not only of its absorption
index $k(\nu)$ but also of its refractive index $n(\nu)$, most spectroscopic studies
in the infrared have been concerned with a mere mapping of the spectrum of
the material with the purpose of determining the frequencies at which character-
istic absorption bands occur.   Some practitioners of this type of frequency
spectroscopy content themselves with the publication of absorption or trans-
mission curves with no numbers at all on the ordinates.   Others present their
results with absorptance or absorbance plotted as a function of frequency
or wave number ν but make no serious attempt to make corrections for reflec-
tion at the inner and outer windows of their absorption cells and ignore the
effects of the nearly inevitable stray radiation in the vicinity of strong
absorption bands.   In spite of these semi-quantitative treatments of intens-
ities, frequency spectroscopy in the infrared has provided an important
method of investigating molecular structures, intermolecular forces, and
chemical reactions.

The present study of hydrocarbons is an example of another type of
investigation which might be termed intensity spectroscopy, in which we place
major emphasis on the quantitative determination of the strengths or intens-
ities $S = \int k(\nu)d\nu$ of absorption bands. As presently practiced, intensity
spectroscopy is usually conducted at lower spectral resolution than that
employed in conventional frequency spectroscopy; quantitative measurement of
band intensity is thus accomplished with a sacrifice of detailed information
regarding band shapes.

1

Experimental Methods

In order to determine both n(ν) and k(ν) from direct experimental measurements, it is usually necessary to make quantitative reflection measurements along with quantitative absorption measurements yielding values of the Lambert absorption coefficient $\alpha(\nu) = 4\pi k(\nu)/\lambda = 4\pi\nu k(\nu)$ with ν in wave numbers cm^{-1}.

A second method of determining the refractive and absorption indices is based on measurements of attenuated total reflectance (ATR). Another method involves the careful experimental determination of α(ν) or of spectral reflectance R(ν) at the free surface of the material and the subsequent use of Kramers-Kronig analysis to give both n(ν) and k(ν).

In the present work we employed the free-surface reflection technique. The methane, ethane, propane, and butane samples were obtained by condensation of high-purity gases supplied by the Matheson Company. The temperatures of the resulting liquids were controlled by supporting their shallow containers at adjustable heights above the surface of liquid nitrogen in a Dewar vessel; sample temperatures were monitored by thermocouples immersed in the liquids. In order to obtain a satisfactory measure of the surface reflectance of a volatile liquid it is necessary to remove vapor from the optical path above the liquid surface; we accomplished this by means of a set of exhaust pumps with intakes near the liquid surface inside the Dewar and at the top of the Dewar vessel. The most serious vapor problems were encountered in the study of methane, which has a high vapor pressure even at its melting point. The handling of the liquid hydrocarbons n-hexane and n-heptane, supplied by Fisher, and n-decane, supplied by Eastman, offered fewer experimental problems; a single exhaust pump with intake near the liquid surface served to remove vapor from the optical path.

In the present study we determined spectral free-surface reflectance at near-normal incidence by measuring the ratio $r(\nu) = R(\nu)/R_w(\nu)$, where $R(\nu)$ is the reflectance of the sample and $R_w(\nu)$ is the reflectance of water. Our values of $R(\nu) = r(\nu) \cdot R_w(\nu)$, where $R_w(\nu)$ is based on the tables in the summary article by Downing and Williams.[1] The resulting values of $R(\nu)$ were then employed in the determination of $n(\nu)$ and $k(\nu)$ by Kramers-Kronig (K-K) phase shift analysis by means of computing techniques described recently;[2] the resulting values of $n(\nu)$ and $k(\nu)$ were further verified by subtractive Kramers-Kronig relations,[3] which serve to minimize errors involving the extrapolation of $R(\nu)$ beyond the spectral range actually covered in the laboratory measurements.

We determined $R(\nu)$ over the spectral range 6700 cm^{-1} to 350 cm^{-1} but report values of $n(\nu)$ and $k(\nu)$ over the more limited range 4000 cm^{-1} to 400 cm^{-1}. The experimental uncertainties in $R(\nu)$ amount to $\pm$ 2 percent of the values plotted in the figures; the corresponding uncertainties in $n(\nu)$ are $\pm$ 1 percent. The fractional uncertainties in $k(\nu)$ are more difficult to state; they are large in regions where $k(\nu)$ is small but are fortunately much smaller in the vicinity of the absorption peaks. We estimate the uncertainties in $S = \int k(\nu)d\nu$ as $\pm$10 to 15 percent of their tabulated values.

Results

The values of spectral reflectance $R(\nu)$ at near-normal incidence are plotted as a function of wave number in Figs. 1 and 2. In each curve there are strong dispersion features in the ranges 3200-2800 cm^{-1} and 1600-1200 cm^{-1}. For every compound except methane greater excursions of $R(\nu)$ are noted in the first of these ranges than in the second. For all compounds except methane there are smaller dispersion features imposed on both of the major dispersion features. In the curves for n-heptane and n-decane there are readily obser-

able dispersion features in the 800-700 cm^{-1} region. The spectral reflectance in the high-frequency region shows a general increase with increasing chain-length of the hydrocarbon; for example, at 3600 cm^{-1} $R(\nu)$ for n-decane is nearly twice that of methane and the corresponding values of $R(\nu)$ for the other compounds have intermediate values.

The values of the refractive index $n(\nu)$ are plotted as a function of wave number in Figs. 3 and 4. The major features of these curves are strikingly similar to those in the reflectance curves Figs. 1 and 2. We note that $n(\nu)$ at 3600 cm^{-1} shows a gradual, nearly monotonic increase from 1.25 for methane to 1.40 for n-decane. For frequencies below 1200 cm^{-1} a gradual decrease of $n(\nu)$ with decreasing frequency is to be noted for all compounds except methane; this gradual decrease is probably associated with absorption bands in the far infrared, a region not covered in the present study.

Figures 5 and 6 give plots of the absorption index $k(\nu)$ as a function of wave number. In the spectrum of each hydrocarbon there are strong absorption features in the range 3000 to 2800 cm^{-1} and in the range 1600 to 1200 cm^{-1}; the positions of the major peaks within these ranges vary from compound to compound. With the exception of methane, all hydrocarbons studied have absorption bands with observable structure in the two major ranges. N-heptane and n-decane have small observable absorption bands in the 800-700 cm^{-1} region. The values of $k(\nu)$ in the spectral range 2800 to 1600 cm^{-1} are very small for all hydrocarbons studied; the values of $k(\nu)$ in this region for n-hexane and n-heptane are spurious but are included in Fig. 6 as an illustration of some of the shortcomings of K-K analyses for determining $k(\nu)$ in regions where $k(\nu)$ is actually small.

In Table 1 we give a list of the frequencies at which absorption peaks were observed in the liquid hydrocarbons at the indicated sample temperatures.

All the major absorption peaks listed are associated, in large part, with the fundamental vibration bands of the molecules. The peaks in the 3000 to 2850 cm^{-1} region correspond to bands in which vibrations involving CH stretch in CH_3 and CH_2 groups are important. The peaks in the 1460–1300 cm^{-1} regions are associated with fundamentals in which vibrations involving deformation of CH_3 and CH_2 groups are important.

The methane spectrum is a special case, in which the band observed at 3000 cm^{-1} is associated with the overlapping ν_1 and ν_3 fundamentals. Although we are giving a detailed account of the methane results elsewhere,[4] we point out here that the ratio of the strength $S = \int k(\nu)d\nu$ for the 3000 cm^{-1} band to the strength of the 1300 cm^{-1} band is very nearly the same as the ratio of the measured intensities of these bands in the spectrum of the gas. Within the limits of uncertainty in experimental measurements, the absolute value of the corresponding band strengths in the liquid and the gas are the same.

In Table 2 we present the results obtained for the strengths of the bands involving CH stretch and CH_2, CH_3 deformation. With the exception of methane, for every compound the strengths of bands associated with stretch are greater than the strengths of the bands involving deformation. The strength $S = \int k(\nu)d\nu$ of a simple absorption band is proportional to the number of absorbers per unit volume. Although the bands involving CH stretch are due to the normal vibrations of entire molecules, we found that the strengths of these bands are directly proportional to the number density of CH groups in the liquid rather than to the density of molecules. On the basis of the known densities of the liquids along with known molecular weights and structures we computed the molar concentration M_{CH} of CH groups in moles per liter. In Table 2 we list ratio $S_{CH}/M_{CH} = \int k(\nu)d\nu/M_{CH}$ for each compound; the mean value of this quantity for all compounds other than methane is 0.107 cm^{-1}/(mole/liter) and the mean deviation from the mean is 0.007 cm^{-1}/(mole/liter).

In the case of the bands involving deformation, the corresponding absorption involves both CH_2 and CH_3 groups; in view of the large uncertainties in our values of $\int k(\nu)d\nu$, we decided to disregard the differences in the contributions of CH_2 and CH_3 groups to the combined strengths of the overlapping bands with peaks in the 1370 to 1460 cm^{-1} region. On the crude assumption that individual CH_2 and CH_3 groups make equal contribution to the observed band strengths, the number density of absorbers is equal to the molar concentration M_C of carbon atoms in each liquid. In Table 2 we list the values of $S_C/M_C = \int k(\nu)d\nu/M_C$ for the deformation bands. Neglecting methane, we obtain a mean value of 0.066 $cm^{-1}/(mole/liter)$ for $\int k(\nu)d\nu/M_C$ with a mean deviation from the mean of 0.009 $cm^{-1}/(mole/liter)$.

We note that the values of $\int k(\nu)d\nu/M_{CH}$ for the CH-stretch bands and $\int k(\nu)d\nu/M_C$ for the deformation bands are much higher for n-hexane than for the other compounds studied. However, in view of the estimated uncertainty of $\pm$ 15 percent in measured values of $\int k(\nu)d\nu$, the values for these quantities for n-hexane do not constitute a real anomaly as in the case of methane.

DISCUSSION OF RESULTS

In earlier studies[5,6] we have shown that it is possible to obtain characteristic band strengths for NH_4^+ and SO_4^{--} ions in solution that can be used in making predictions of the gross features of the spectra of $(NH_4)_2SO_4$ and $CuSO_4 \cdot 5H_2O$ crystals on the assumption that the value of $\int k(\nu)d\nu$ is directly proportional to the number density of absorbers. The results of the present study indicate that the values of $\int k(\nu)d\nu$ for the CH stretch and the deformation bands in straight-chain hydrocarbons are also proportional to the number density of absorbers. It thus appears possible to attribute characteristic absorption strengths or absorption cross sections to atomic

groups in molecules in much the same way that characteristic group frequencies have been assigned on the basis of earlier work on frequency spectroscopy.

On the basis of the present results it should be possible to make quantitative predictions regarding the intensities of the bands near 2900 cm^{-1} and 1400 cm^{-1} in the spectra of n-pentane, n-octane, n-nonane, and the longer-chain normal hydrocarbons. We would expect our predictions to be valid providing the CH, CH_2, and CH_3 groups in the molecules are not subject to large perturbations like those encountered in methane, in which the CH_2 and CH_3 groups cannot even be distinguished and in which the immediate atomic environment of the CH groups is markedly different ~~for~~ *from* the atomic environment of CH groups in the other straight-chain hydrocarbons. We note that even the frequencies of the stretch and deformation bands in methane are somewhat different from the frequencies of these bands in the other hydrocarbons.

In addition to providing predictions regarding the spectra of materials not previously investigated, it is possible that characteristic group intensities can provide important theoretical insights into molecular structure and into the interactions between molecules and electromagnetic fields. Group intensities may also prove useful in infrared spectrochemical analysis.

We close by noting that the absorption bands of hydrocarbons are sufficiently weak to make it possible to use transmission techniques useful in the intensity spectroscopy of these materials provided suitable variable-thickness absorption cells are developed. Careful corrections for window reflection, for interference effects, and for stray radiation should be made. Strictly linear response of the detector-amplifier systems is necessary. Commercially available double-beam techniques should be employed with extreme caution because of their slightly incomplete beam balance.

<center>ACKNOWLEDGEMENT</center>

8

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TABLE 1

ABSORPTION PEAK POSITIONS IN HYDROCARBONS

			Absorption peaks	
Liquid	Sample Temperature (°C)	CH Stretch (cm^{-1})	CH_2, CH_3 Deformation (cm^{-1})	Other Bands (cm^{-1})
Methane	−175	3000	1300	
Ethane	−175	2955 2885	1455 1380	
Propane	−185	2955 2880	1455 1375	
n−Butane	−130	2945 2865	1455 1375	
n−Hexane	25	2910 2855	1450 1370	
n−Heptane	25	2920 2860	1450 1370	720
n−Decane	25	2920 2850	1460 1380	725

TABLE 2

INTENSITIES OF BANDS IN LIQUID HYDROCARBONS

Compound	Bands Involving CH Stretch		Bands Involving CH_2 and CH_3 Deformations	
	$S_{CH} = \int k(\nu)d\nu$ cm^{-1}	S_{CH}/M_{CH} $cm^{-1}/(mole/liter)$	$S_\delta = \int k(\nu)d\nu$ cm^{-1}	S_δ/M_c $cm^{-1}/(mole/liter)$
Methane	4.4	0.040	5.7	0.207
Ethane	12.2	0.107	2.2	0.058
Propane	9.1	0.086	2.8	0.070
n-Butane	11.2	0.108	2.6	0.063
n-Hexane	13.2	0.123	4.1	0.089
n-Heptane	12.3	0.112	2.7	0.057
n-Decane	12.0	0.106	3.1	0.060

mean[a] = 0.107 ± 0.007   mean[a] = 0.066 ± 0.009

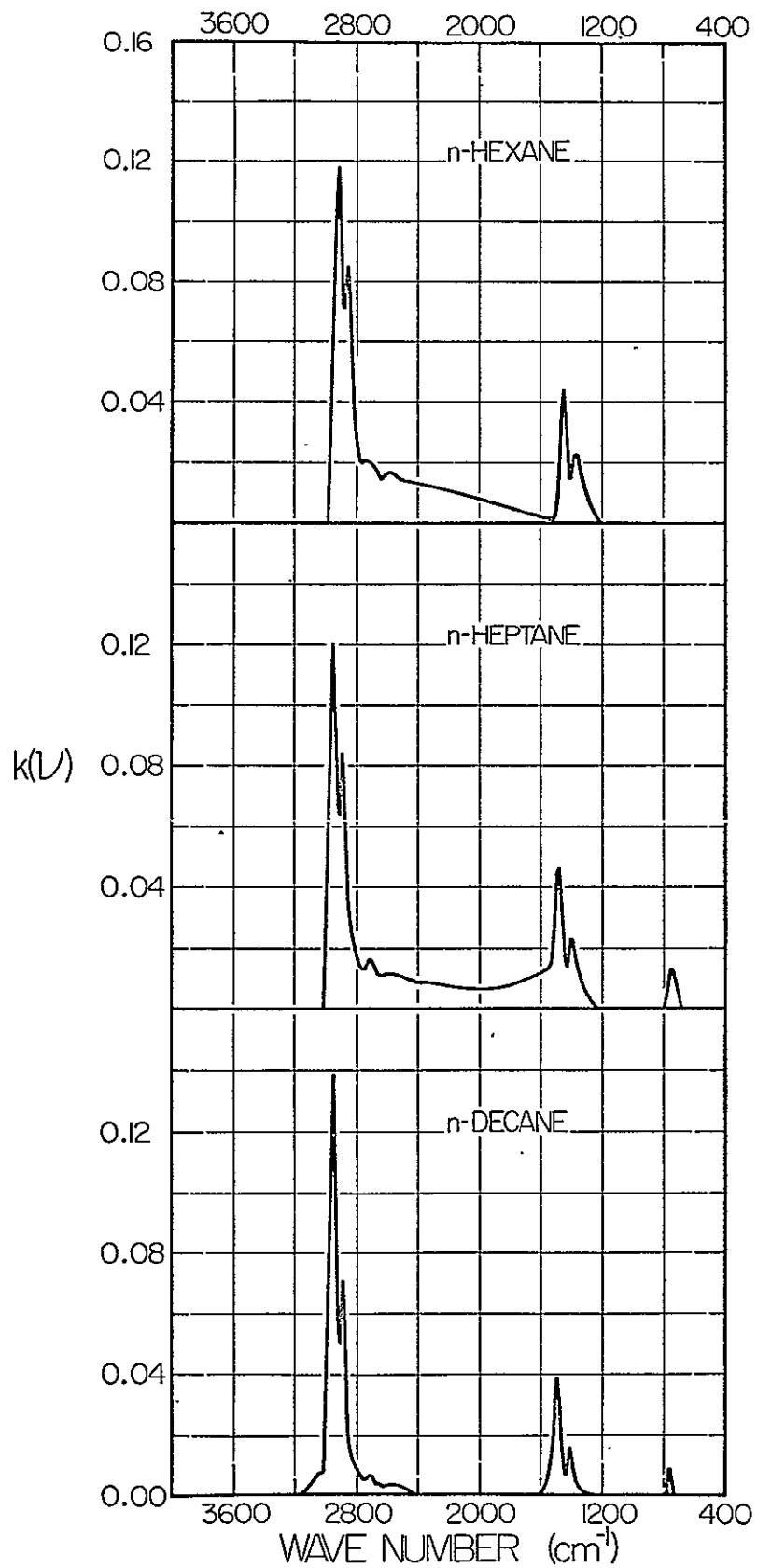a) Excluding methane.
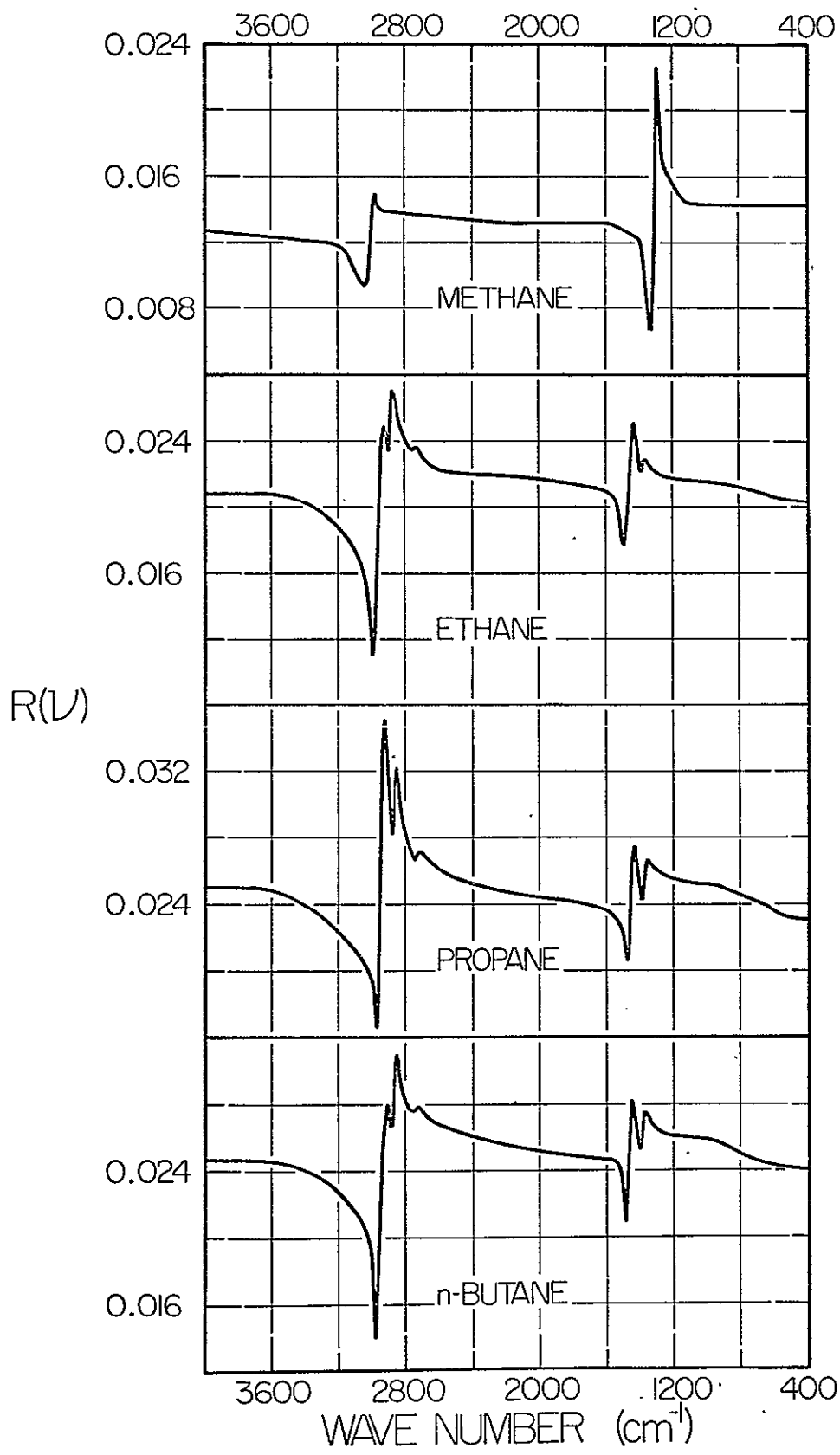
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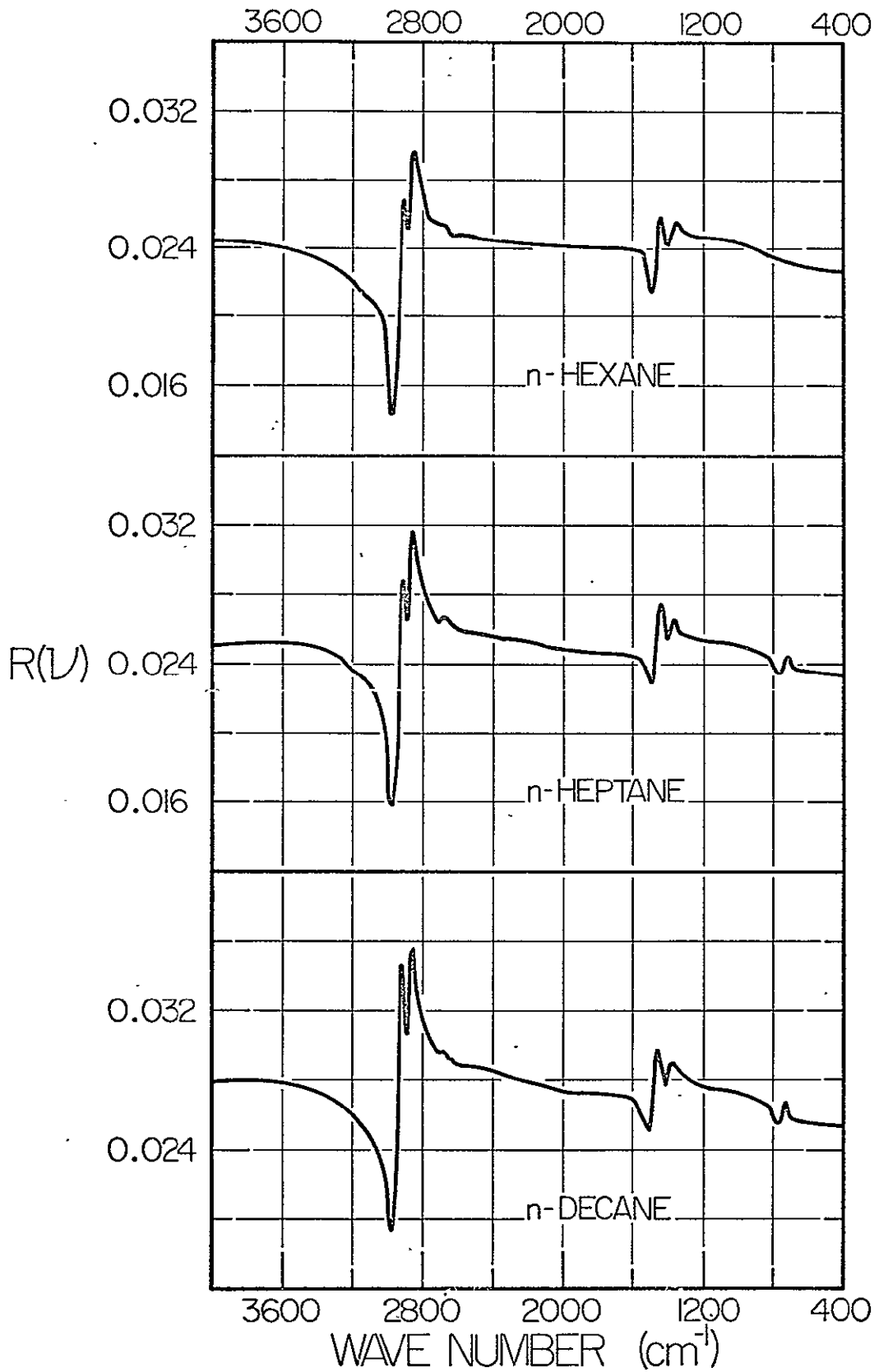
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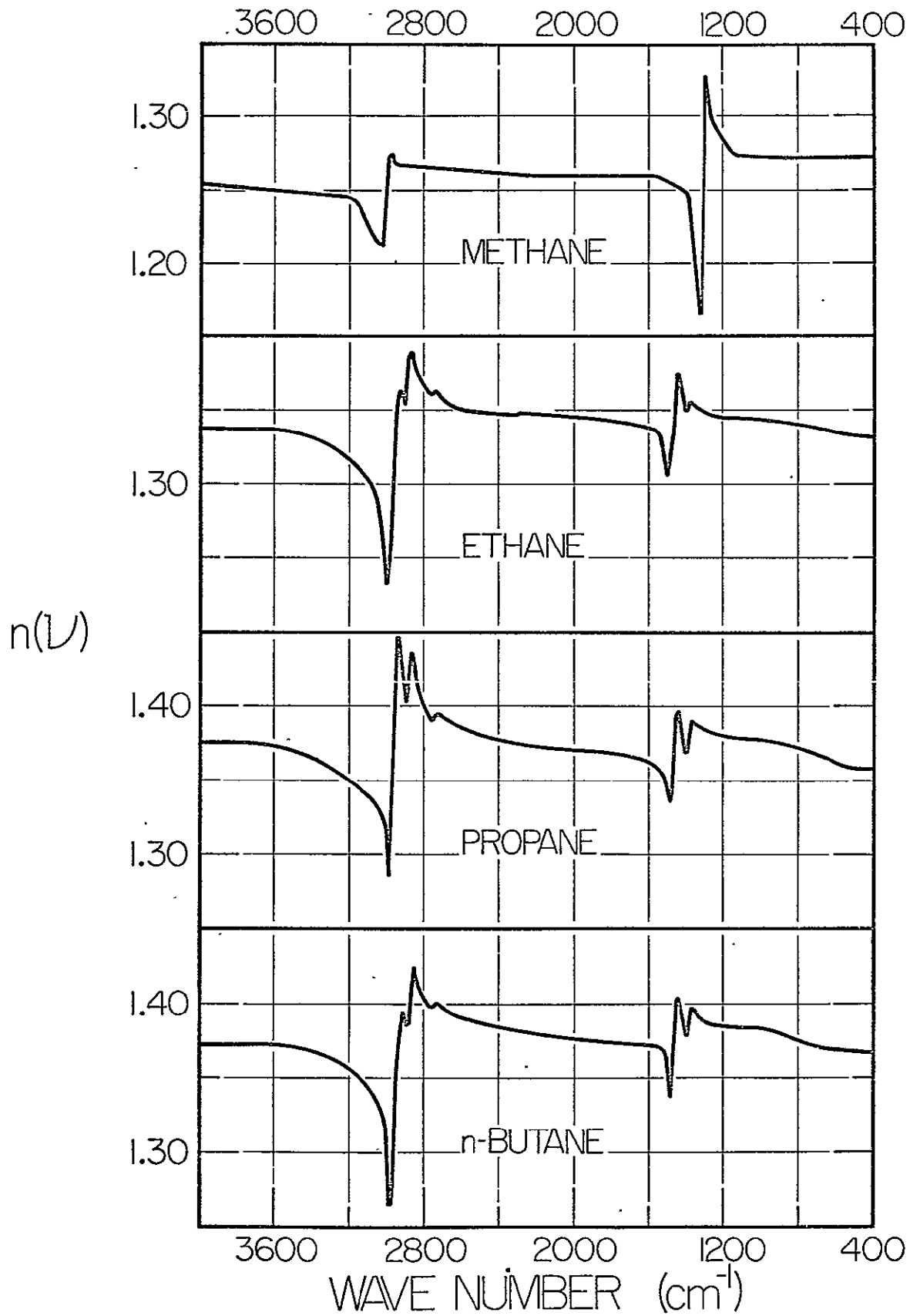
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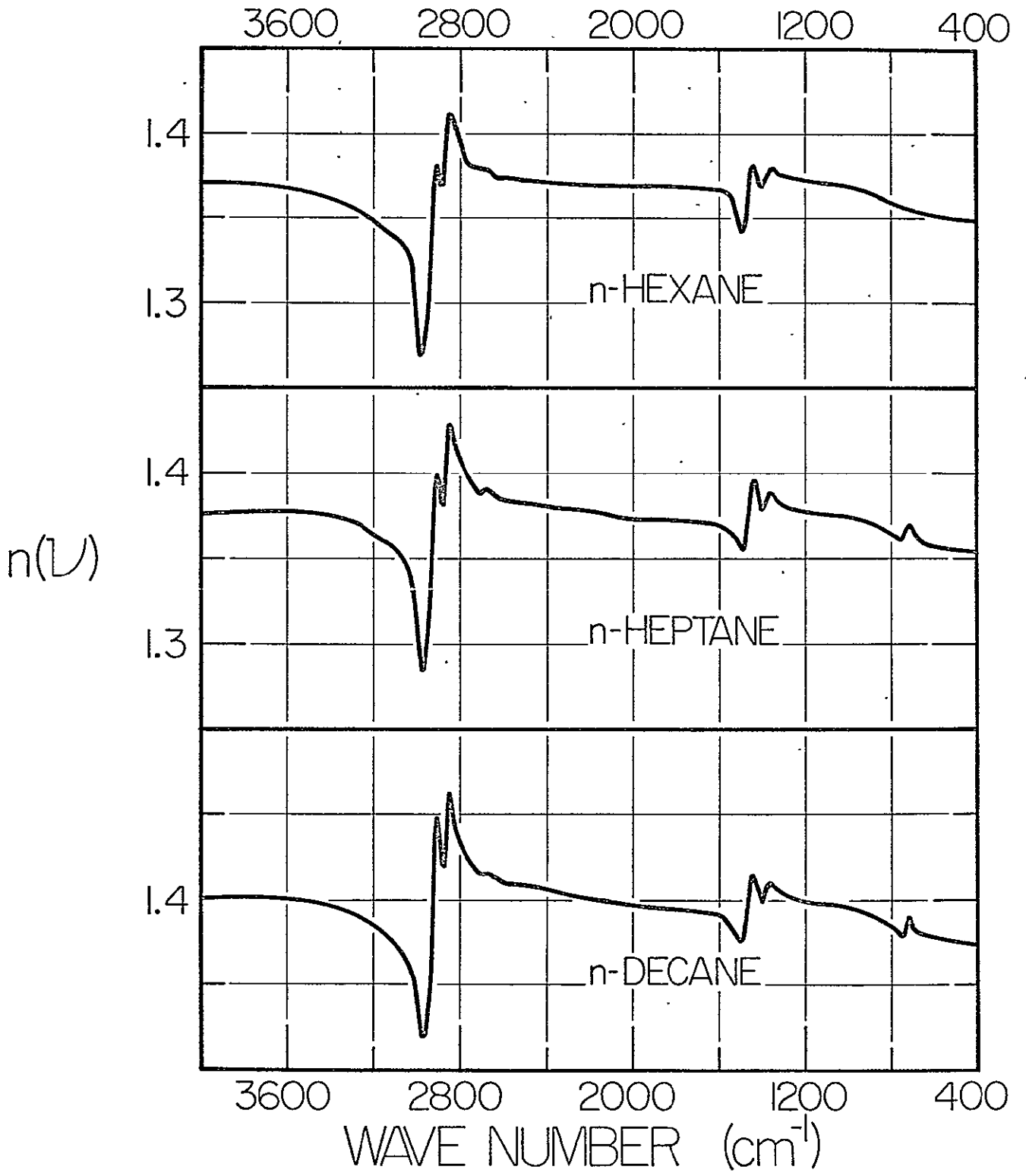
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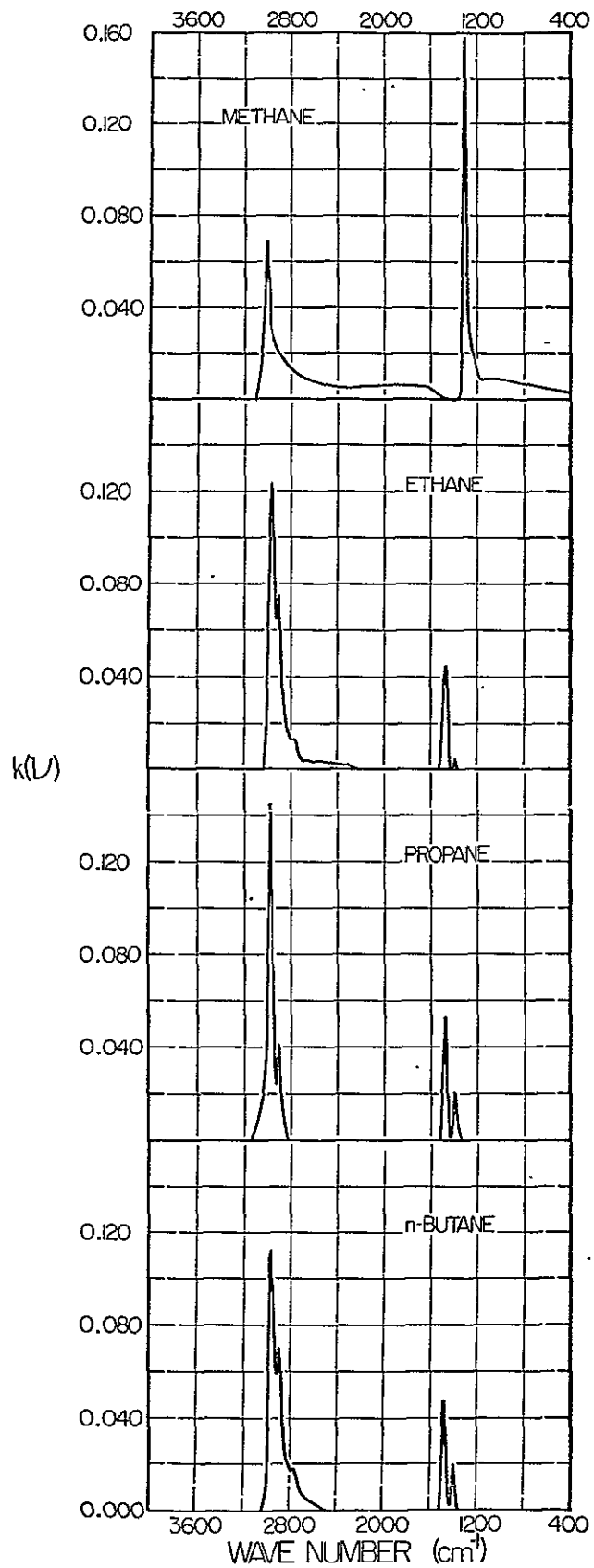
Fig. 5.

Fig. 6

INFRARED BAND INTENSITIES IN AMMONIUM HYDROXIDE AND AMMONIUM SALTS*

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ABSTRACT

We have applied Kramers-Kronig analysis to reflection spectra to determine the optical constants of ammonium hydroxide and of aqueous solutions of ammonium chloride and bromide. From considerations of the absorption indices $k(\nu)$ we conclude that ammonium hydroxide consists of a solution of NH_3 in water, in which NH_3 molecules are hydrogen-bonded to neighboring water molecules. The spectrum of ammonium hydroxide differs from the spectra of ammonium salts, in which bands characteristic of NH_4^+ ions are prominent. The existence of ammonium hydroxide as an aerosol in planetary atmospheres is briefly discussed.

1

In view of the discovery of small amounts of water vapor in the atmosphere of Jupiter and the presence of large amounts of ammonia in the Jovian atmosphere, it has been suggested that ammonium hydroxide may also be present in the Jovian atmosphere. Although previous attempts[1] to observe infrared absorption by gaseous ammonium hydroxide in the laboratory have been unsuccessful, it seemed desirable to make further studies of ammonium hydroxide solutions and to compare their infrared spectra with the spectra of solutions of ammonium salts.

In the present study we have used the methods of reflection spectroscopy[2] to obtain characteristic band intensities in the spectra of ammonium hydroxide and of ammonium halides in aqueous solution. The experimental work has involved a careful measurement of the spectral reflectance $R(\nu)$ at near-normal incidence as a function of wave number ν in the spectral range 6800 cm^{-1} to 350 cm^{-1}. On the basis of the measured values of $R(\nu)$, we have employed Kramers-Kronig phase-shift analysis to determine the real $n(\nu)$ and imaginary $k(\nu)$ parts of the complex index of refraction $\hat{N}(\nu) = n(\nu) + ik(\nu)$ for the solutions. In the present work we have been chiefly interested in the absorption index $k(\nu)$ and have used the phase-difference techniques described earlier[3] to obtain differences between $k(\nu)_{sol}$ for the solutions and $k(\nu)_{w}$ for water at 27°C. The use of the phase-difference technique enables us to determine more precise values for the difference $k(\nu)_{sol} - k(\nu)_{w}$ than for the absolute values of either $k(\nu)_{sol}$ or $k(\nu)_{w}$. We have found[4] that in certain cases the difference $k(\nu)_{sol} - k(\nu)_{w}$ is directly proportional

to the molar concentration of the solute.

The infrared reflectance spectrum $R(\nu)$-vs-ν of a 4.3M solution of ammonium bromide is shown in Fig. 1 for the range 5200 to 400 cm^{-1}. Except for slight frequency shifts, the major dispersion features in the 3600–3200 cm^{-1}, the 1700–1600 cm^{-1}, and the 800–400 cm^{-1} regions are similar to the corresponding major features in the reflectance spectrum of water. Superposed on these major features are smaller features in the 3200–2800 cm^{-1} region and the 1600–1400 cm^{-1} regions that are characteristic of the NH_4^+ ion. Other ammonium bromide and chloride solutions have reflection spectra that are in general similar to the spectrum shown in Fig. 1.

Our work on several ammonium chloride solutions is summarized in Fig. 2, which shows a plot of a quantity $[k(\nu)_{sol} - ak(\nu)_w]/M$ as a function of wave number. The term $k(\nu)_{sol}$ is the absorption index for a solution of molar concentration M; $k(\nu)_w$ is the absorption index for pure water and a is the ratio of the molar concentration of H_2O in the solution to the molar concentration of H_2O in pure water. The plot thus gives an account of the influence of the solute on the water bands and of the additional bands due to the solute itself. The large positive peak near 3500 cm^{-1} represents a shift of the ν_1 and ν_3 bands of water to higher frequency. The large negative excursion near 800 cm^{-1} followed by the rise near 500 cm^{-1} is a result of the shift of the librational band ν_L of water to lower frequency. Shifts of this kind have been observed in our earlier studies of alkali halide solutions.[5] The other absorption peaks can be attributed to absorption by the NH_4^+ ion.

The band with three apparent peaks in the 3000 cm^{-1} region represents the overlapping ν_1 and ν_3 fundamentals of the NH_4^+ ion.[6] The small peak at 1600 cm^{-1} can be attributed to the weak ν_2 fundamental of NH_4^+ but may also

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involve a slight shift in the ν_2 fundamental of water in this region. The sharp absorption band near 1500 cm^{-1} corresponds to the ν_4 fundamental of the NH$_4^+$ ion.

Our results for ammonium bromide solutions are given in the corresponding plot in Fig. 3. Although the influence of the solute on the water bands is different from the influence noted for the ammonium chloride solutions, the observed band shifts are to be expected on the basis of our earlier studies of other chlorides and bromides[5]. We note that there are characteristic NH$_4^+$ bands in Fig. 3 that can be attributed to the known absorption bands of the ion. These bands appear in the same spectral regions as those in Fig. 2 and have comparable intensities.

In our studies of ammonium hydroxide solutions we employed exhaust pumps to remove ammonia gas from the light path in the region above the free surface of the solutions. Because ammonia is continuously evolved from the solution surface we were careful to use freshly prepared samples for only brief periods during reflectance measurements in order to minimize effects due to changes in measured concentration.

In Fig. 4 we show the observed reflection spectrum of a 5.4M ammonium hydroxide solution. The major features in the spectrum are remarkably similar to those of water. There are, however, changes in the shapes of the dispersion feature between 3600 and 3200 cm^{-1} and in the vicinity of 1700-1600 cm^{-1}. A small additional dispersion feature appears in the 1200-1100 cm^{-1}. There are no apparent effects due to absorption of gaseous ammonia in the radiation path.

Our work on ammonium hydroxide is summarized in Fig. 5, which shows plots of $k(\nu)_{sol} - ak(\nu)_w$ for several different concentrations. Three characteristic absorption bands with intensities proportional to concentration can

be noted: (1) a broad band in the 3500-2700 cm^{-1} region, (2) a band with two branches in the 1800-1500 cm^{-1} region, and (3) a sharp band near 1100 cm^{-1}. These ammonium-hydroxide bands differ in frequency and contours from the NH_4^+ bands observed for the ammonium halide solutions. The most obvious differences between the ammonium-hydroxide spectrum and the spectrum of the ammonium-halide solutions are the presence of the sharp peak at 1100 cm^{-1} in ammonium hydroxide and its absence in the ammonium-halide solution and the absence from the hydroxide spectrum of the characteristic strong NH_4^+ band at 1450 cm^{-1}. In connection with Fig. 5 we note that the absorption maxima at frequencies below 1000 cm^{-1} may be due to shifts in the librational band of water but may be spurious; the intensity of these apparent absorption bands is not proportional to the concentration of the solutions as are the intensities of the characteristic bands.

Because the characteristic NH_4^+ bands are not present in the ammonium hydroxide spectrum we conclude that the concentration of the NH_4^+ ion in ammonium hydroxide is negligibly small. Consideration of the characteristic absorption bands of ammonium hydroxide indicates that these bands form a pattern that is similar to the pattern of the bands in gaseous[7], liquid[8], and solid ammonia[9]. In the upper part of Fig. 6 we give a schematic comparison of the spectrum of ammonia in its various phases with the observed ammonium hydroxide spectrum; we have attempted in the figure to maintain the measured band intensities $S = \int k(\nu)d\nu$ and to degrade the observed spectrum of the gas to the low resolution used in obtaining the absorption spectrum of the condensed phases.

When NH_3 gas condenses, hydrogen bonds are formed between NH_3 molecules. Hydrogen bonding decreases the frequencies of the ν_1 and ν_3 bands involving the valence vibrations of the NH units and increases the frequency of ν_2 bands that involve molecular bending vibrations in which the motion of hydrogen

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atoms is involved. This is also the case when water vapor condenses; the valence vibrations ν_1 and ν_3 decrease in frequency while the bending frequency ν_2 increases; the hydrogen bonds between water molecules are stronger than the hydrogen bonds between ammonia molecules. The observed spectrum of ammonium hydroxide can be interpreted in terms of NH_3 molecules that are hydrogen-bonded to surrounding water molecules. Because the hydrogen bonds between NH_3 molecules and H_2O molecules are stronger than hydrogen bonds between NH_3 molecules, the shifts of the frequencies of NH_3 in aqueous solution are greater than of ammonia in condensed phases.

In the lower part of Fig. 6 we list the bands due to the NH_4^+ ions. The frequencies and the intensities of these bands are markedly different from the bands attributed to NH_3 hydrogen-bonded to water molecules. This is especially evident in the case of the ν_2 and ν_4 bands.

We have summarized our results on the intensities of the NH_3 and NH_4^+ bands in Table I, in which we list the values of the quantity $\int \{[k(\nu)_{sol} - ak(\nu)_w]/M\} d\nu$ in $cm^{-1}/(Mole/liter)$ for each band. It is to be noted that the characteristic NH_3 bands in the ammonium hydroxide solutions differ from the bands in the ammonium salts in characteristic intensity as well as in frequency. Unless otherwise noted in the table, the band intensities are subject to an uncertainty of approximately ± 15 percent of the values listed.

Our study indicates that ammonium hydroxide consists of a solution of NH_3 gas in water without spectroscopically appreciable numbers of NH_4^+ ions; this conclusion is in agreement with much chemical evidence. If ammonium hydroxide exists as an aerosol in the atmospheres of the outer planets, its optical constants are nearly the same as those of water except for concentration dependent differences near $3000\ cm^{-1}$, $1600\ cm^{-1}$, and $1100\ cm^{-1}$. We have obtained no evidence to indicate that NH_4OH exists as a chemically bonded molecule; there is no reason to expect its presence as a gas in planetary atmospheres

FOOTNOTES AND·REFERENCES

* Supported in part by grants from the National Aeronautics and Space Administration and the Office of Naval Research.

† Now at Lockheed Space and Missiles Co., Huntsville, Alabama.

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TABLE I. Characteristic Band Intensities[a]

	ν_1, ν_3	ν_4	ν_2
NH_3 Bands in Ammonium Hydroxide	2.34	0.24 ± 0.06	0.28

	ν_1, ν_3	ν_2	ν_4
NH_4^+ Bands in:			
NH_4Cl	2.81	0.19 ± 0.07	1.77
NH_4Br	2.78	0.31 ± 0.07	1.95
$(NH_4)_2SO_4$	$-^b$	$-^b$	1.96

[a]The intensities are given by $\int \{[k(\nu)_{sol} - k(\nu)_w]/M\}d\nu$ and are stated in $cm^{-1}/(Mole/liter)$.

[b]Shifts in nearby water bands prevent accurate intensity measurement of these bands.

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LEGENDS FOR FIGURES

Fig. 1   The near-normal spectral reflectance $R(\nu)$ of a 4.3M solution
         of ammonium bromide in the infrared.

Fig. 2   Molar absorption index of ammonium chloride as a solute.

Fig. 3   Molar absorption index of ammonium bromide as a solute.

Fig. 4   The near-normal spectral reflectance $R(\nu)$ of a 5.4M solution of
         ammonium hydroxide.

Fig. 5   The absorption indices for ammonium hydroxide solutions for
         various concentrations: 1.35M, 2.70M, 4.05M, and 5.40M.

Fig. 6   The upper part of the figure compares the characteristic bands
         of ammonium hydroxide with the bands of gaseous, liquid, and
         solid NH_3. The lower part of the figure gives the bands char-
         acteristic of the NH_4^+ ion in solutions and in a crystal. The
         spectrum shown for the crystal NH_4Cl is taken from E. L. Wagner
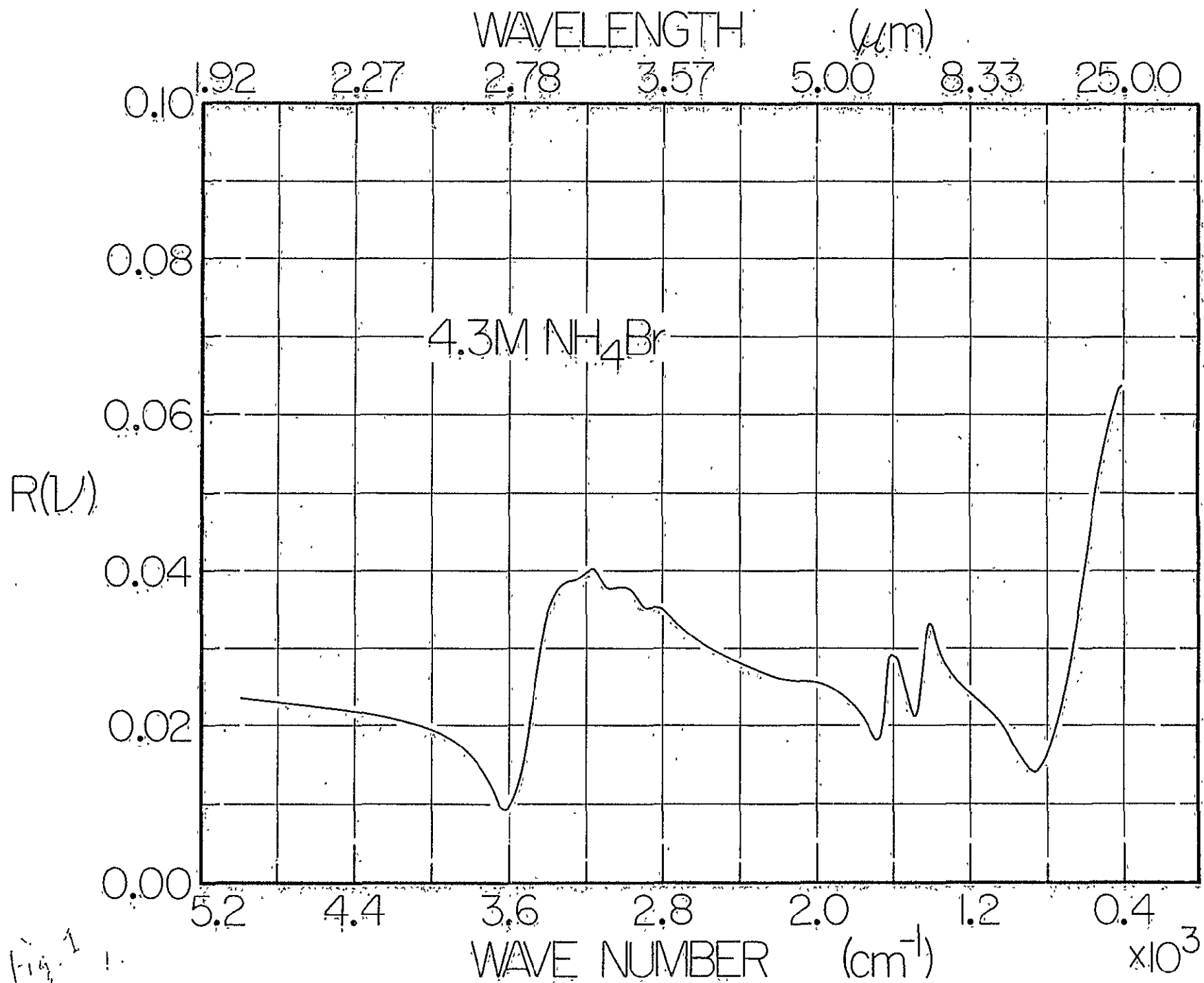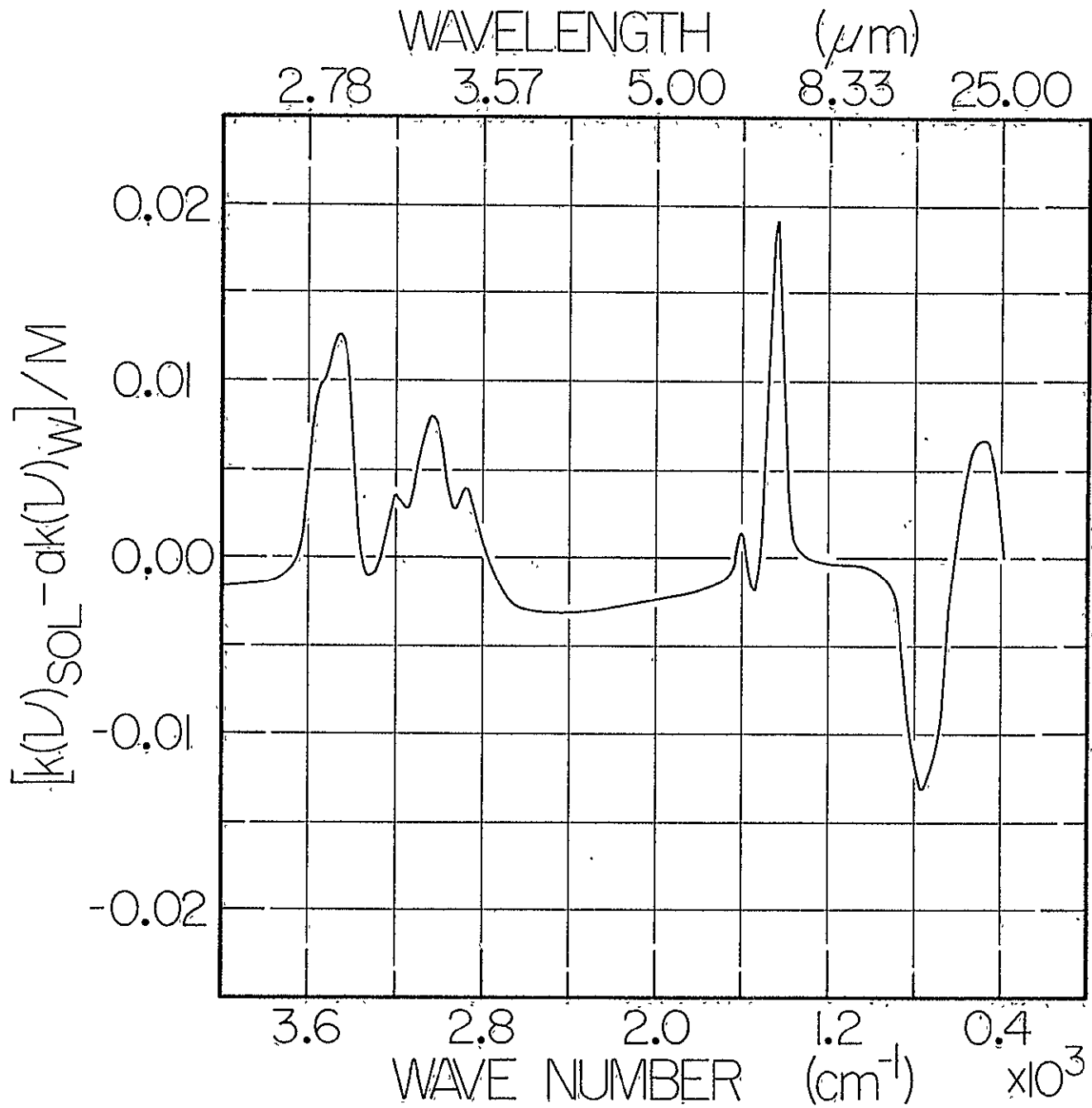   and D. F. Hornig, J. Chem. Phys. 18, 296-304 (1950).
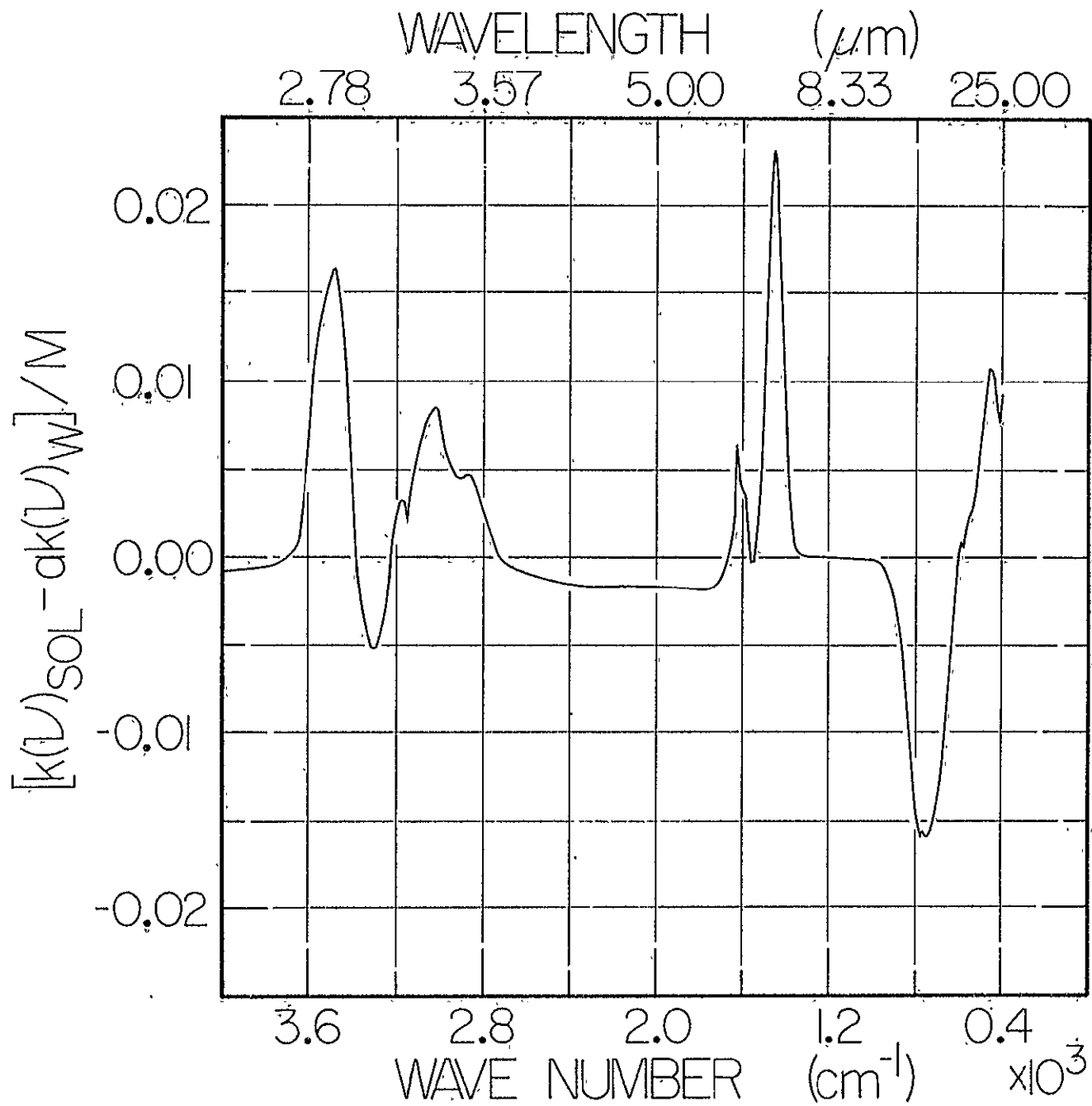
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WAVELENGTH (μm)

4.3M NH$_4$Br

R(ν)

WAVE NUMBER (cm^{-1})

Fig. 1

Fig 2

Fig. 3

Fig 4

Fig 5

Fig. 6