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ABSTRACT

The sodium-ammonia solution system permits investigation of an array of compositions spanning the transition from non-metallic to metallic bonding. Reflection spectra in the range 1 - 20 μ were measured for solutions of mole ratio 5.5 to 168 NH_3 per Na. The dilute solutions show peaks characteristic of the vibrations of ammonia and a strong peak near 1.5 μ which is assigned to the solvated Na_2 species. Concentrated solutions show high reflectivity over broad wavelength ranges. The results for nearly saturated solutions are fitted reasonably by the free electron model, but in the range of mole ratio 10-15 a complex array of energy absorption processes of finite frequencies are required to fit the spectra.

Introduction

While the nature of the transition from ionic to covalent bonding is now well understood, much less is known concerning the transition from metallic bonding to either sort of non-metallic bonding. There are not too many series of compounds or solution systems where the non-metallic to metallic transition can be observed, but several are now known. Solutions of metals in liquid ammonia constitute one of the most familiar and convenient systems for such a study. In this paper we report reflection spectra for sodium solutions in liquid ammonia at concentrations spanning the transition from metal to non-metal, and discuss these and other data with respect to the nature of the electronic binding. Solutions of sodium metal in liquid ammonia offer a continuously variable composition from the very dilute to the saturated state above the critical temperature -41°C. Phase separation occurs below this temperature. The conductance measurements of Kraus[1] demonstrate very well

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(1) C. A. Kraus, J. Am. Chem. Soc., 43, 749 (1921) and C. A. Kraus and W. W. Lucassee, J. Am. Chem. Soc., 43, 2529 (1921); 44, 1941 (1922).

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that these solutions range in their properties from those of a rather strong electrolyte (very dilute solutions) to those of a liquid metal (concentrated solutions).

Experimental Method and Procedure

Transmission measurements have been performed on the very dilute solutions of sodium in ammonia. However, the infrared extinction coefficients of these solutions are so large that transmission spectroscopy becomes totally impracticable at concentrations above about 0.1 molar. Thus, in order to study these solutions over a wide range of concentrations it was necessary to employ a reflection technique, the light reflected from a suitable optical surface being analyzed spectroscopically. These measurements are related to the energy absorption processes by a somewhat less direct path, but they provide the only means of investigation in the case of a highly absorbing material.

Reflection might be measured from either the interface between ammonia gas and the top surface of a solution or the interface between a suitable optical window of transparent material and a solution. The former of these involves the problem of light absorption by the ammonia vapor as well as the problem of surface disturbances such as bubbling. The latter involves the complications that very few materials are both transparent in the desired spectral region and insoluble in ammonia and, further, that many of the usable materials are susceptible to thermal shock breakage when being cooled to a low temperature. Both methods were tried, but the solution-window interface proved to be the more satisfactory optical surface for study.

Apparatus. - The reflection cell is illustrated in figure 1 and the optical arrangement used with the cell is illustrated in figure 2. The spectrophotometer used in this research was a Perkin-Elmer 12c equipped with an amplifier of laboratory design. Lithium fluoride, sodium chloride, and potassium bromide prisms were used with this instrument.

The cell is constructed from two glass tubes. At its top the inner tube is connected to the vacuum system through a spherical joint; at its bottom this tube is bent outward and sealed through the second glass tube and is ground flat so that a window can be sealed tightly and held by a steel template and clamp. The outer tube is sealed at its top in a ring-seal around the inner tube, while at its base it is closed to a hemispherical end. The inner tube serves as the solution cavity while the outer tube serves as a cooling jacket. Coolant enters this jacket through a glass tube in back of the window area so that the window is kept as cold as possible. The outer vessel shown in figure 1 maintains a protective vacuum around the cell and contains the necessary windows, etc.

In the optical arrangement, light from a glowbar source was focused by an extra set of standard Perkin-Elmer source optics at the interface between the window and the solution with an angle of incidence of approximately forty degrees. The reflected light entered the spectrometer through the usual optical system on the Perkin-Elmer instrument.

Acetone was the cooling fluid used in these experiments. The acetone was pumped from a cold reservoir through the cell by a centrifugal pump. The reservoir was cooled by a copper coil through which acetone in thermal contact with a dry ice bath was pumped. A knife blade heater was also inserted in the reservoir which was regulated to + or -0.5°C. This system was capable of maintaining a constant temperature of -40°C. for over twenty hours.

The windows which were used with this reflection cell were quartz, lithium fluoride, barium fluoride, and polyethylene supported by cesium iodide. The first three, at least, are fairly common infrared materials, of limited transparency. However, no common window material was available for use in contact with liquid ammonia for the spectral region beyond twelve microns. For this region a special window was prepared by sealing a thin polyethylene sheet to a cesium iodide window. Since this seal must endure through a rather large temperature drop, it could not be rigid. Consequently, Kel-F grease was used, and the sheet of plastic was rolled onto the window until most of the grease was squeezed out. This seal held under vacuum and did not crack as the temperature was reduced.

Experimental Procedure. - The sdutions of sodium in liquid ammonia were prepared in an atmosphere of ammonia gas at -40°C. The ammonia was first dried by distillation into a bulb containing waste sodium at a temperature of -70°C. A small amount of hydrogen was pumped off. The dry ammonia was distilled into the cold reflection cell by allowing this bulb to warm gradually to room temperature. Sodium pellets were added to the ammonia in

the reflection cell through a glass addition tube sealed into the vacuum system just above the top plate of the outer vessel. The pellets were stored in vacuo in side arms of this addition tube so that when the tube was rotated these arms could be tilted downwards toward the cell, allowing the desired number of pellets to pass into the ammonia.

Sodium pellets were prepared by cutting a solid block of sodium into many small cubes, rejecting those cubes which had been at or near the surface of the original block; this operation, and all subsequent handling of the sodium, was performed under thiophene free benzene. The cubes were weighed individually under benzene and were placed in the arms of the addition tube in known order. Once the tube was connected to the system, the benzene was distilled away and the reflection apparatus was evacuated overnight. Since the initial volume of ammonia in the cell could be read from calibration marks and since the total weight of sodium in the solution could be derived from the number of pellets and their weights, the concentration of a given solution was known. This concentration was recorded as dilution V, the number of liters of ammonia per gram atom of sodium, but it is also indicated in terms of the mole ratio. The error should not exceed 5%.

Analysis of Results

Theory of Reflection Spectra.[2] - A wave equation for light in

(2) J. R. Partington, An Advanced Treatise on Physical Chemistry, Vol. IV, Physico-Chemical Optics, Longmans, Green and Company, 1953.

a transparent and isotropic medium of dielectric constant D can be derived readily from Maxwell's equations. In this relation, it is found that the transverse solution wave travels through the medium with a velocity equal to c (the velocity of light in vacuo) divided by $\sqrt{D\mu}$ where μ is the magnetic permeability and is usually unity. Since it is this ratio of the velocities which defines the refractive index of the material, we see that the optical constants may be related to the electrical constants in this way. The refractive index, n, of this simple material is equal to the square root of D.

If the material absorbs light but is still isotropic, the dielectric constant is a complex number given by $D' = D - \frac{4\pi\sigma}{\omega}i$. Hence, the refractive index of the absorbing medium is also a complex number, $(n - ik)^2 = D'$. Here, n is the real refractive index while k is the absorption coefficient.

Application of the Helmholtz boundary conditions to the incidence of a plane wave of light upon a planar surface of this material gives the following expression for the amplitude reflectivity (normal incidence):

$$r = \frac{n - ik - n_0}{n - ik + n_0} \qquad (1)$$

where n_0 is the refractive index of the material in which the light is incident and the reflectivity gives the ratio of reflected to incident amplitude. The measurable quantity is the luminous reflectivity R which is equal to the value of $|r|^2$.

$$R = \frac{(n - n_0)^2 + k^2}{(n + n_0)^2 + k^2} \qquad (2)$$

Thus the observation of reflection is indirectly related to an observation of absorption; reflection of light must always accompany the absorption process, being especially strong when the absorption is great.

Drude's theory of dispersion, in turn, relates the microscopic absorption processes to the macroscopically observed optical constants. Drude assumed that a dielectric material could be pictured as an array of oscillators bound to equilibrium positions and having frequencies ω_1. The displacement of a given oscillator under the influence of an applied periodic field, such as a light wave, is given by the equation of motion:

$$m(d^2x/dt^2) + m\gamma(dx/dt) + m\omega_0^2 x = - eE \exp(i\omega t) \qquad (3)$$

where m is the oscillator mass, x is the displacement, γ is the damping constant, ω_0 is the frequency of the oscillator, e is the charge and $Ee^{i\omega t}$ represents the electric field of the light wave. Since the displacement is related to the dielectric constant of the material, expressions for the optical constants may be obtained.

$$n^2 - k^2 = 1 + 4\pi \sum_i \frac{(N_i e_i^2/m_i)(\omega_i^2 - \omega^2)}{(\omega_i^2 - \omega^2)^2 + \gamma_i^2\omega^2}$$

and (4)

$$nk = 2\pi \sum_i \frac{(N_i e_i^2/m_i)\gamma_i\omega}{(\omega_i^2 - \omega^2)^2 + \gamma_i^2\omega^2}$$

where N_i is the density of each sort of oscillators.

Drude's formulae may be used even in consideration of the free electrons of metals. Since these electrons are unbound,

according to classical notions, they represent oscillators of zero frequency. The formulae which result from this substitution predict the optical constants with good accuracy.

A variety of absorption processes in the liquid ammonia-sodium system will cause reflection of light. For instance, both bound and free electrons must exist in these solutions. The bound electrons will produce reflection peaks associated with the absorption frequencies, while the free electrons will yield a general reflection in the infrared with varying intensity. The vibrational motions of ammonia molecules will also give some contribution although, because of the larger masses, we expect these to be small in magnitude.

Observed Spectra. - In measuring the reflection spectrum of any material one must observe both the reflected and incident intensities or the spectrum under identical conditions of some reflection standard whose optical constants are known throughout the region of study. In this research liquid mercury was used as a standard reflector for several reasons. It could be placed inside of the cell where its reflection spectrum could be taken under conditions identical to those at which the solutions were studied. Also, liquid mercury obeys the Drude formulae for a metallic reflector so that the solutions were compared directly to a classical metal. No attempt was made in this research to obtain the optical constants of these solutions from the observed spectra. Either one would have to make observations at several different angles of incidence (which is clearly impractical with the reflection cell illustrated) or one would have to apply the

Robinson and Price method[3] of calculating the phase angle as a function of wavelength (which would clearly not be accurate in a case where absorption spreads over a large region of the spectrum). Instead, the reflection was indicated as a percentage ρ obtained by dividing the solution spectra by the corresponding mercury spectra.

(3) T. S. Robinson and W. C. Price, Molecular Spectroscopy, Rept. Conf., Inst. Petroleum London 1954, 211 (Pub. 1955).

Figures 3 and 4 show the spectra taken with the LiF window. The spectra taken with the quartz window contain no additional information.[4] Regions of intense atmospheric absorption are omitted. The spectra taken with BaF_2 and polyethylene-CsI windows contain only relatively narrow regions of good observation between regions of absorption by atmospheric constituents or the window materials. The Kel-F grease which sealed the thin polyethylene to the CsI plate apparently flowed enough to vary in thickness and hence results are unreliable even in regions where it absorbed only moderately. The resulting reflectivities[4] (relative to mercury) in each region of good observation were interpolated to even concentrations and are shown in figure 5. The small peaks near 3μ are omitted in figure 5.

(4) Figures showing all of the spectra are included in the Ph.D. Dissertation of Tad Alan Beckman, University of California, 1960 (Lawrence Radiation Laboratory Report UCRL-9330).

Assignment of Reflection Bands. - Review of the spectra of the dilute solutions indicates that several reflection bands, or maxima, exist; these are to be found at 6200 cm^{-1}, 3370 cm^{-1}, 3190 cm^{-1}, and 1030 to 1050 cm^{-1}. The three low frequency peaks can all be associated with fundamental vibrations of the ammonia molecule. For instance, the 3190 cm^{-1} reflection seems best assigned to the ν_1 vibration of ammonia which is observed by transmission to lie at 3223 cm^{-1} in the crystal.[5] The

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(5) F. P. Reding and D. F. Hornig, J. Chem. Phys., 22, 1926 (1954).

3370 cm^{-1} band can be assigned to ν_3 which absorbs at 3378 cm^{-1} in the crystal. And 1030 to 1050 cm^{-1} is easily assigned to ν_2 which is 1060 cm^{-1} in the crystal. The reflection peak at 6200 cm^{-1} is, however, a property of the sodium-ammonia system as a whole. The concentrated solutions show high reflectivity over wide regions with little or no fine structure.

Discussion

Our interpretation of the spectra will be divided into two parts. In dilute solutions the principal solute species can be inferred by the concentration dependence of various phenomena. Also many other investigations have yielded various types of data for dilute solutions. Our spectra are consistent with this knowledge from other sources. The concentrated solutions and the two phase region offer a more difficult problem and only some preliminary conclusions will be given here. Other experiments will be needed before a very detailed understanding of the concentrated solutions is possible.

In view of the recent and complete reviews by Jolly[6] and

(6) W. L. Jolly, Progress in Inorganic Chemistry, 1, 235-281 (1959).

by Symons[7] an extensive bibliography is unnecessary and only the

(7) M. C. R. Symons, Quart. Revs., 13, 99 (1959).

most pertinent evidence will be cited.

Dilute Solutions. - Most of the properties of dilute alkali metal solutions in ammonia can be attributed to the species in the equilibrium

$$M_2 = 2M^+ + 2e^-_{am} \qquad (5)$$

Here M^+ is just the familiar solvated ion and e^-_{am} is an electron solvated by oriented ammonia molecules with presumably a cavity at the center.[8] The species M_2 was first suggested by Huster.[9]

(8) J. Jortner, J. Chem. Phys., 30, 839 (1959).

(9) E. Huster, Ann. Physik, 33, 477 (1938).

The nature of the species M_2 is not established in detail but it contributes to neither the electrical conductance nor the paramagnetic spin resonance. Presumably the Na^+ ions are solvated by ammonia and two such ions are bound together by two electrons of antiparallel spin. Additional species, such as solvated electron pairs or solvated metal atoms, have been proposed

but the evidence indicates that they are at most minor species in $Na-NH_3$ solutions.

Yost and Russell[10] discuss the evidence for M_2 and Becker,

(10) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry", pp. 144-5, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1946.

Lindquist, and Alder[11] calculate the equilibrium constants for reaction (5) for potassium solutions at 298, 274 and 240°K. The magnetic data[12] show that the equilibrium constant for sodium

(12) C. A. Hutchison and R. C. Pastor, J. Chem. Phys., 21, 1959 (1953).

is indistinguishable from that for potassium at 240°K and that its change with temperature is a little more rapid for sodium than for potassium. Only a short extrapolation is required to 233°K, the temperature of our experiments, where we find $K = 3.5 \times 10^{-8}$ if concentrations are in moles per liter. Even in our most dilute solution, V = 4.14 or 0.24 M, this K predicts only 4% dissociation of Na_2. Consequently, the reflection spectra for relatively dilute solutions in the range 0.24 to 1 M must be dominated by features arising from Na_2 as well as NH_3, of course. At still lower concentration, however, where absorption spectra are measured, the dissociated ions Na^+ and e^-_{am} become major species. Thus the fraction dissociated is roughly 50% at 0.01 M while at 0.001 M it is greater than 95% at the temperature of spectral measurement.

The reflection spectra of the dilute solutions, figure 3, show just one distinct feature attributable to the metal solute--the peak near 1.5μ. While the equilibrium constant for dilute solutions indicates little dissociation of Na_2 in the concentration range of figure 3 (V = 0.67 to V = 4.14), we have little independent evidence concerning the concentration of larger clusters Na_n with $n > 2$. Our spectra show just a gradual increase in intensity as the concentration increases to V = 1.0, but at higher concentration the reflectivity at wavelengths longer than 4μ increases more rapidly than that at the 1.5μ peak. This additional reflectivity at longer wavelength presumably indicates the appearance of some larger clusters. The 1.5μ peak may be assigned to the Na_2 species and calculation indicates λ_a corresponding absorption wavelength of approximately 2μ. The nature of the reflection process is such that the reflection peak is observed at shorter wavelength than the absorption peak.

Unfortunately the concentration range for good reflection measurement does not overlap with that for absorption measurement, hence a direct comparison is impractical. The absorption spectra[13]

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(13) R. C. Douthit and J. L. Dye, J. Am. Chem. Soc., 82, 4472 (1960).

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show a peak in this same region with a maximum at 1.4μ for very low concentration of either Na or K. This band is assigned to e^-_{am}. As the concentration increases above 0.01 M the maximum shifts slowly to longer wavelength (about 1.5μ at 0.05 to 0.1 M) and small differences are noted between sodium and potassium

solutions. This shift is in the direction expected as the amount of Na_2 (or K_2) increases. In the case of both the reflection and absorption spectra the intensity corresponds to that of an allowed transition by most if not all of the solute present. The near equality of frequency for e^-_{am} and for solvated Na_2 may be either accidental or of fundamental significance; we shall hope to learn which in the near future.

Concentrated Solutions. - The fully metallic nature of very concentrated metal-ammonia solutions was recognized in the early work. The equivalent conductance of a saturated solution of sodium is 6 times that of mercury. Presumably the metal ions are solvated as in the species M_2 but now the electrons have metallic orbitals which pervade the entire solution. One of us[14]

(14) K. S. Pitzer, J. Am. Chem. Soc., 80, 5046 (1958).

has pointed out the analogy between the phase separation below -41.6°C in these solutions and the vapor-liquid phase separation in pure sodium. In the solutions the ammonia solvates the solute species but is otherwise a dielectric medium within which a condensation phenomenon can occur. The metallic solutions are those in the liquid-like range, i.e. more concentrated than the critical composition of 4.15 atom % Na.

Exploratory calculations were made of the reflectivity on the free electron model. Equation (4) was used with $\omega_1 = 0$ and N_1 taken from the known concentration. The observed electrical conductance σ yields γ_1 from the relationship

$$\gamma_1 = N_1 e_1^2 / \sigma m_1 \qquad (6)$$

where e_1 and m_1 are the electronic mass and charge respectively. Figure 5 shows as dashed lines the calculated curves for the concentrations V = 0.135 and V = 0.3. In the nearly saturated solution where the mole ratio is 5.5 NH_3 to one Na the calculated reflectivity curve resembles the experimental curve rather closely. The agreement is good except that the drop in ρ in the region 3 to 0.5μ is actually more gradual than that calculated. Doubtless some refinement of the model would remedy this discrepancy. We shall not attempt such modifications at present but rather emphasize the general success of the simple free electron model for the nearly saturated solutions.

At V = 0.3, however, the agreement with the free electron model is much poorer. The difficulty near 1μ remains and in addition the trend with wavelength in the 15-25μ region is wrong. Several more complex models were tested in an effort to fit the observed curve for V = 0.3. The curve shown as a dot-dash line on figure 5 was calculated for a model with three different absorption processes of finite frequency in addition to a small population of free electrons with a damping constant fitted to the electrical conductance. The following parameters were used:

$$N_1 = 4 \times 10^{19},\ \gamma_1 = 1.2 \times 10^{13},\ \omega_1 = 0$$
$$N_2 = 2.5 \times 10^{20},\ \gamma_2 = \omega_2 = 1.5 \times 10^{14}$$
$$N_3 = 5 \times 10^{20},\ \gamma_3 = \omega_3 = 3 \times 10^{14}$$
$$N_4 = 5 \times 10^{20},\ \gamma_4 = \omega_4 = 1 \times 10^{15}$$

The values of γ_i were taken equal to ω_i for each non-zero frequency since relatively broad bands would be expected and there was no justification for independent adjustment of the various γ_i. While the fit of this calculated curve is by no means perfect, it is good enough to confirm this general type of model.

The model for the dot-dash curve may be interpreted as representing a small concentration N_1 of conduction electrons, a rather high concentration N_4 of dimeric, solvated Na_2, and high concentration $N_2 + N_3$ of a distribution of larger clusters Na_n $(n > 2)$ which have primary electronic frequencies distributed over the range indicated by ω_2 and ω_3. Such larger clusters were suggested by Schmidt[15] on the basis of x-ray data.

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(15) P. W. Schmidt, J. Chem. Phys., 27, 23 (1957).

No significance should be attached to the exact values given for N_2, N_3, ω_2, ω_3, etc. This interpretation is plausible on the basis of our knowledge of the more dilute sodium-ammonia solutions and of critical and condensation phenomena in general.

These results indicate that solutions significantly more concentrated than the critical composition, such as $V = 0.3$, do not constitute the sort of simple free-electron metal which is represented by the saturated solution or the pure liquid or solid alkali metal. The clustering of the solute, however, need not be primarily to spherical clusters. It seems likely that much more irregular shapes are involved including threadlike regions sometimes interconnected throughout the solution.

Research is being continued on these systems which will include further experimental measurements as well as discussion of the results in terms of quantum theory of the valence electrons.

Acknowledgments. - We thank Dr. Marvin Ross for certain exploratory calculations and Professor W. L. Jolly for comments and suggestions. This research was carried out under the auspices of the U. S. Atomic Energy Commission.

Captions for Figures

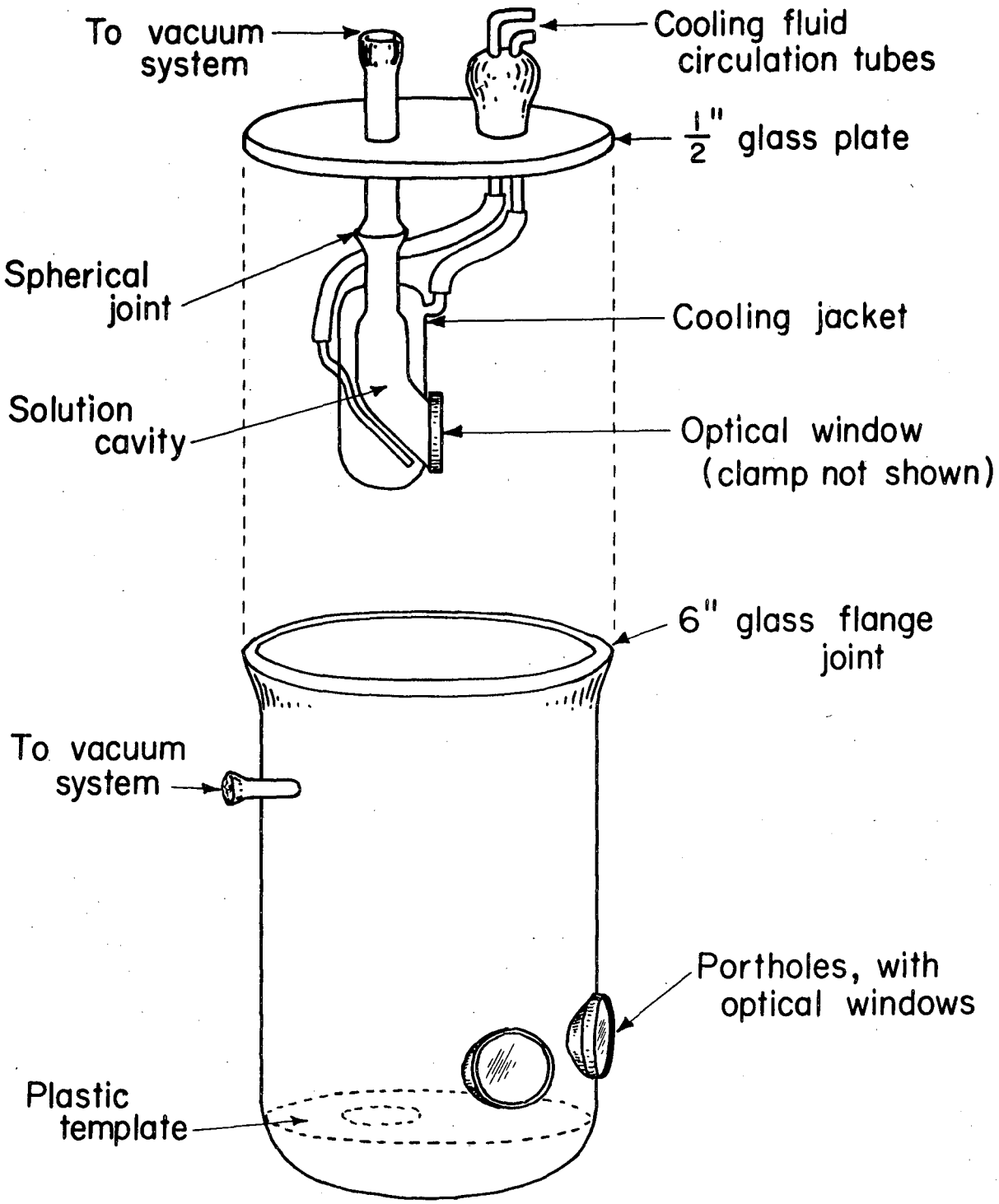
Fig. 1 - Reflection cell.

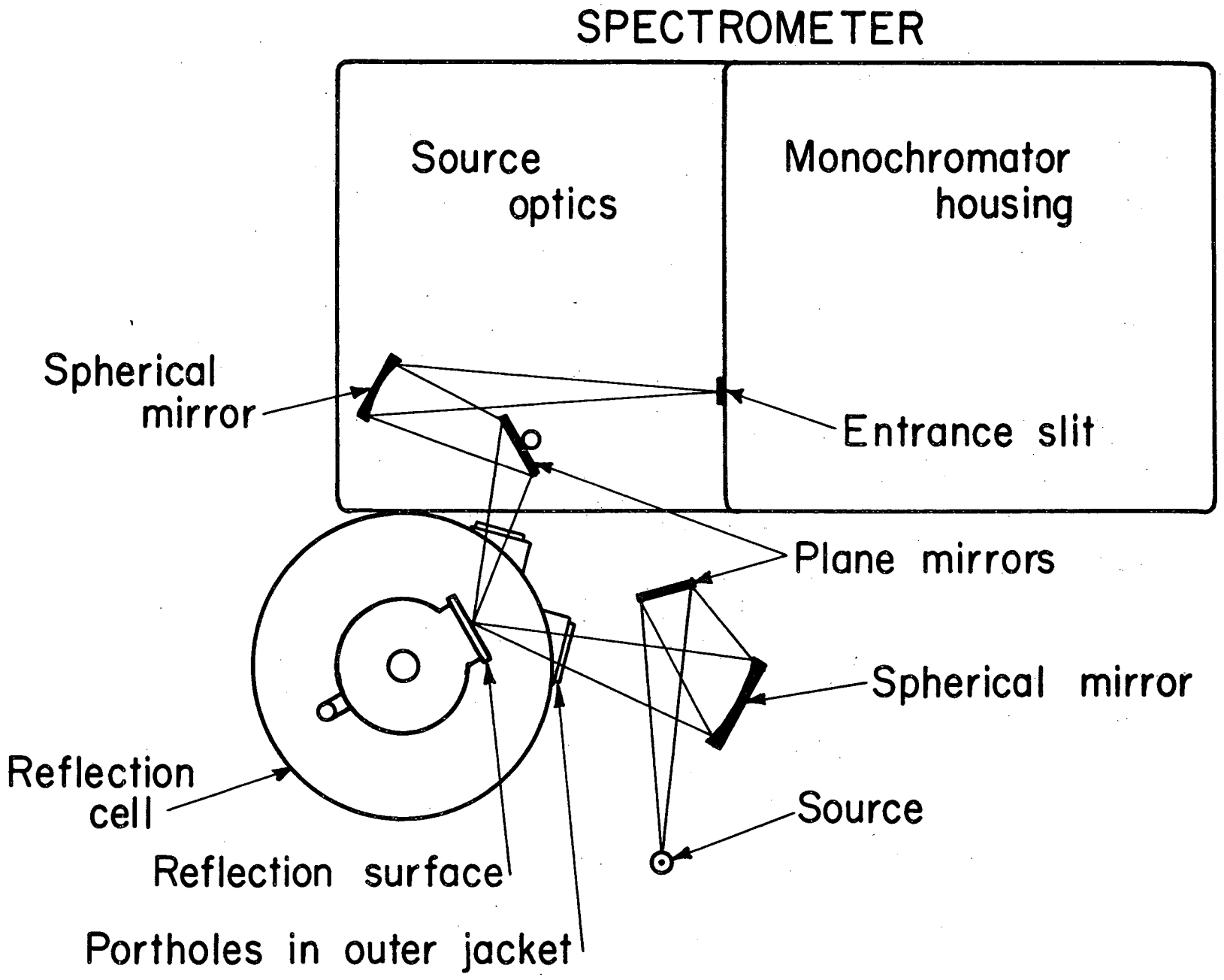
Fig. 2 - Optical arrangement.

Fig. 3 - Reflection spectra for dilute solutions in the LiF region. The concentration is given in liters of NH_3 per mole Na and (mole ratio NH_3 to Na).

Fig. 4 - Reflection spectra of more concentrated solutions. Concentration given as in Fig. 3.

Fig. 5 - Reflectivity (relative to Hg) for Na-NH_3 solutions of the dilution in liters of NH_3 per mole of Na indicated. Dotted curves are calculated for free metallic electrons; the dot-dash curve for $V = 0.30$ is calculated for a more complex model given in the text.


To vacuum system
Cooling fluid circulation tubes
½" glass plate
Spherical joint
Cooling jacket
Solution cavity
Optical window (clamp not shown)
6" glass flange joint
To vacuum system
Portholes, with optical windows
Plastic template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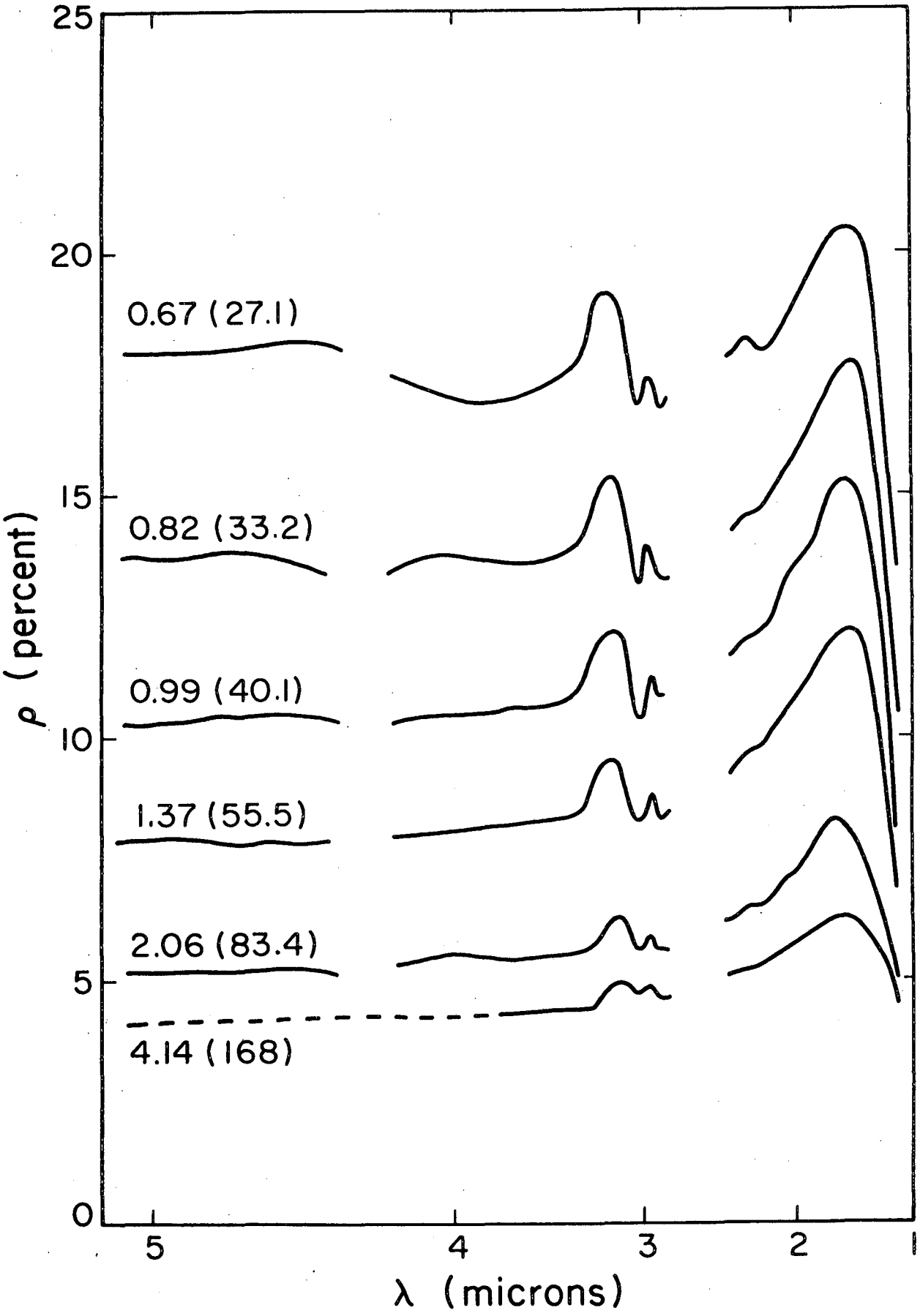
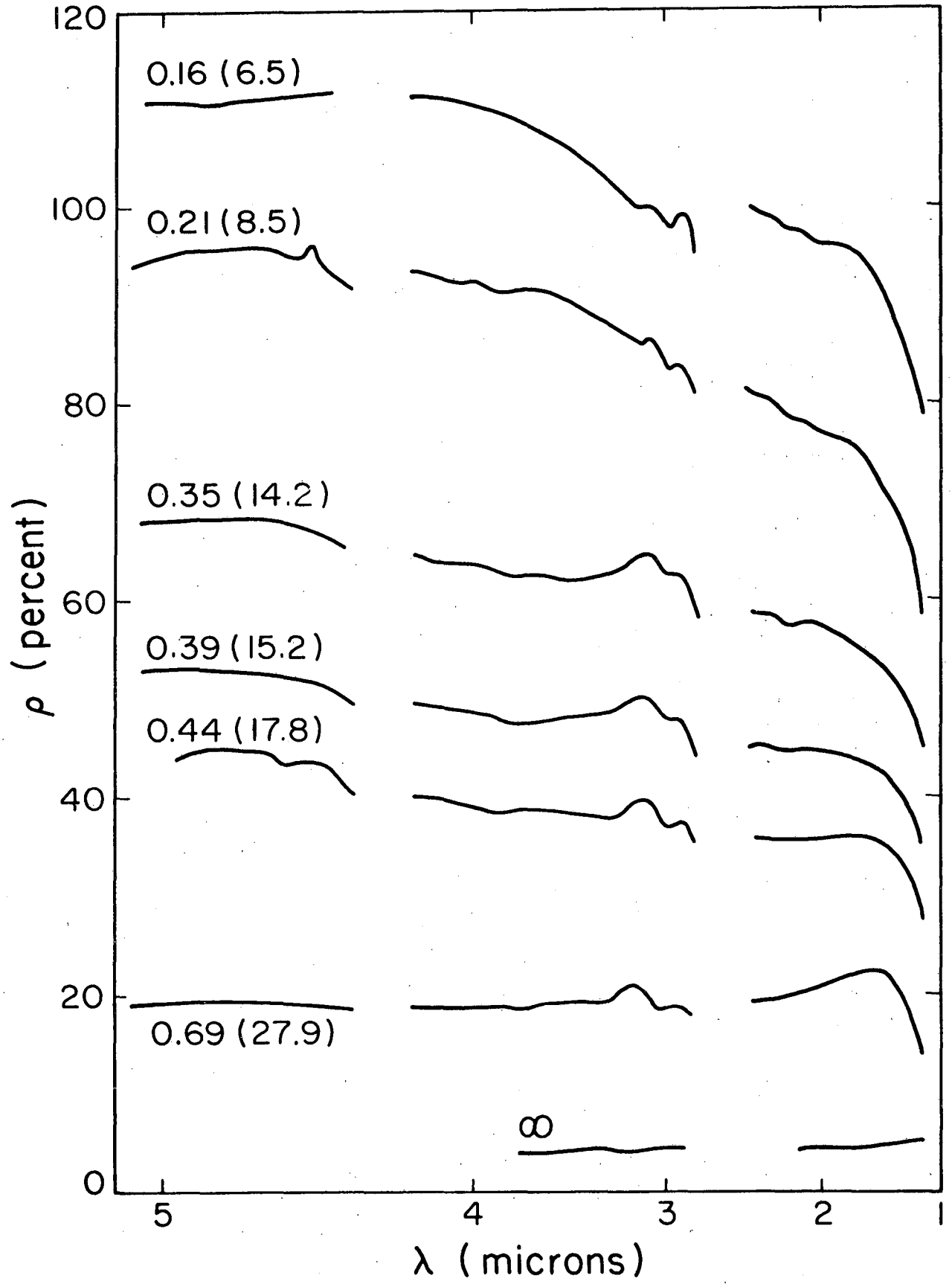
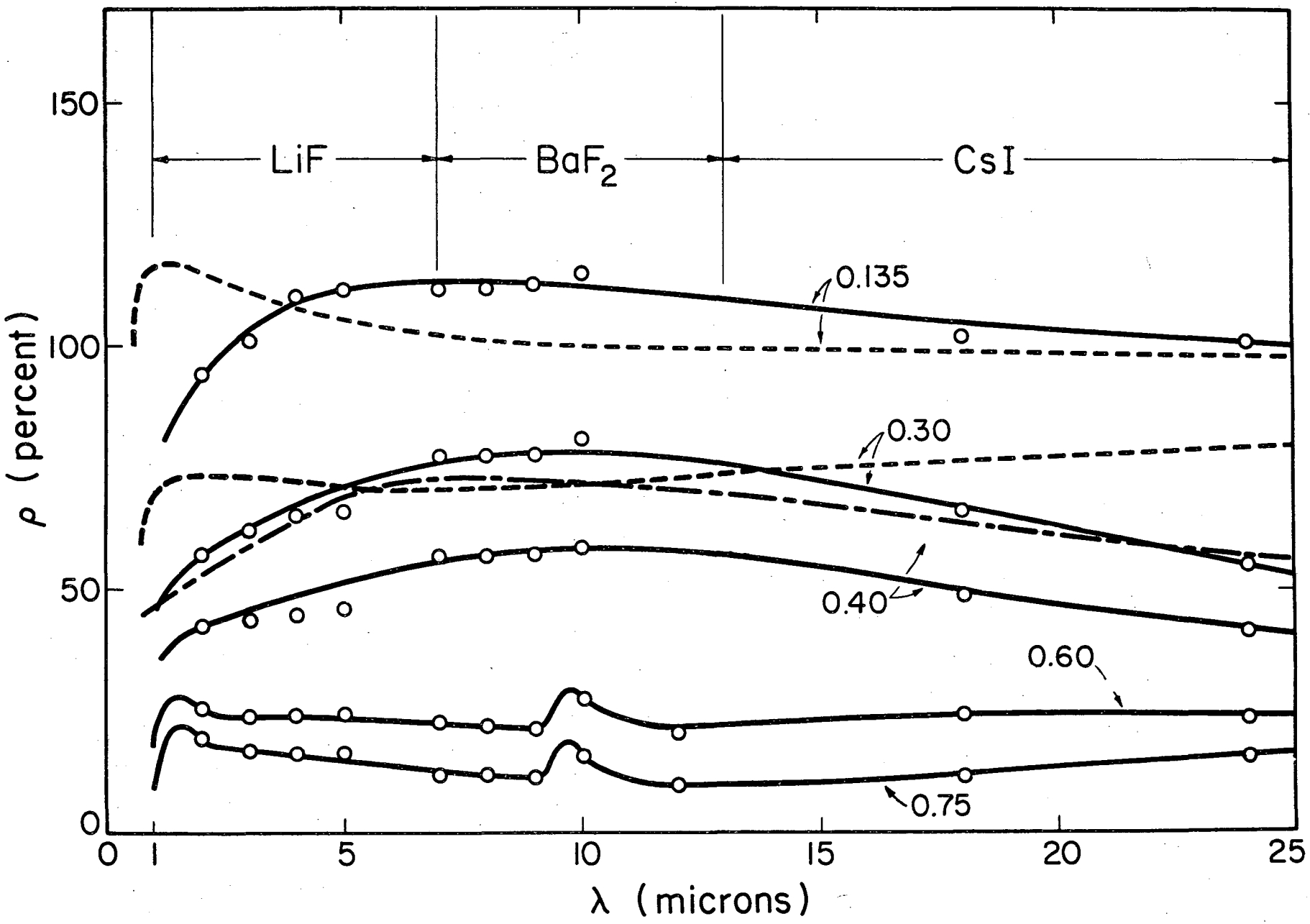
Monochromator housing
Spherical mirror
Entrance slit
Plane mirrors
Spherical mirror
Reflection cell
Source
Reflection surface
Portholes in outer jacket


25
20
15
10
5
0
ρ (percent)
0.67 (27.1)
0.82 (33.2)
0.99 (40.1)
1.37 (55.5)
2.06 (83.4)
4.14 (168)
5
4
3
2
λ (microns)


120
100
80
60
40
20
0
ρ (percent)
0.16 (6.5)
0.21 (8.5)
0.35 (14.2)
0.39 (15.2)
0.44 (17.8)
0.69 (27.9)
∞
5
4
3
2
1
λ (microns)


LiF
BaF2
CsI
0.135
0.30
0.40
0.60
0.75
ρ (percent)
λ (microns)
150
100
50
0
0
1
5
10
15
20
25