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ELECTRONIC STRUCTURE OF CYANINE DYES

by

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ABSTRACT

The absorption of a set of four symmetrical cyanine dyes was investigated at ordinary and liquid air temperatures. The results are presented in tabular form and graphically with optical density plotted vs. wavelength. All bands show better definition and are narrower at liquid air. A plot of n (number of double bonds in the conjugated chain) vs. λ is given for all the peaks at room and liquid air temperatures. The graphs are mostly linear in rough agreement with the predicted theoretical expectation. The main absorption peak shifts toward longer λ as n increases and the total width of absorption increases also. The small peaks at short λ , which appear practically for all the dyes, are sharper and more intense for n = 1 and 3 than for n = o and 2. The room temperature results are, in order of increasing λ , 4254 A, 5638 A, 6558 A, 7595 A. with an average error of $\pm$ 10 A. The theoretical values as given by Pitzer are 4530, 5530, 6530, 7530 A which are not in good agreement for the lower wavelengths.

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INTRODUCTION

This is an experimental study of the optical absorption of a set of conjugated organic compounds known as cyanine dyes. Much work has been done already on cyanine dyes by Brooker and by others at room temperature. The maximum absorption in the visible, its intensity, its dependence upon chain length, and other aspects were investigated experimentally and many attempts were made toward their interpretation.

One of the theoretical models, the free electron model (1), assumes the electrons that are in π orbitals, π e's, are "free" like valence electrons in metals. Another, "the particle in a box"(2), assumes the electrons to move within a box provided by the molecule, in a periodic potential arising from the ion cores. There are still other models like the LCAO (3) and the valence bond (4) which give more detail and more satisfactory results, but are more complicated. None, however, of the various models is capable of a complete description of all the observed facts, and where one model fails another may succeed.

At the beginning, we expected to extend the range of our study down to the UV, and to investigate the absorption of thin crystals of the different dyes. This in addition to a review of the absorption of the same dyes in solution. All of these were to be done both at room temperature and at liquid air temperature, on a spectrograph of high resolution, large Hilger. However, some difficulties stood in the way of making thin crystals and necessitated the elimination of the UV region completely. The apparent unstability of most of the compounds was the main source of difficulty. So we confined our efforts to a study of solutions in the visible region only, at both room and liquid air temperatures.

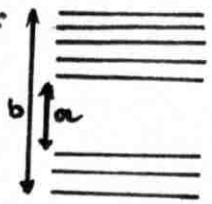
THEORETICAL CONSIDERATIONS

Spectroscopy is, in a sense, the study of the energetic make-up of systems (atoms, molecules, or ions) in any phase. A spectrum refers to an orderly sequence of things or their totality; e.g., frequency spectrum of an oscillator, energy, wavelength, etc., spectrum of an atom, eigenvalue spectrum of an operator, etc. A spectrum could be discontinuous where two consecutive items differ by a discrete amount, continuous where the number of items is infinite or the difference between two consecutive items is vanishingly small, or quasi-continuous where the items are discrete but are too close to be resolved under certain conditions of temperature, pressure or phase.

The energy spectrum of a system can be obtained by two ways: by exciting the system to a high energy state and observing the energies it emits as it reverts to the ground state, or by noting the energies it absorbs from a continuous spectrum. The first is an emission, the second is an absorption spectrum. In principle, any system possesses both spectra, but, sometimes, the emission cannot be obtained experimentally, because the system under study breaks up under excitation. This necessitates the use of absorption for its study, which limits the amount of information to few energy states above the ground state. Thus we get a simpler spectrum at the expense of information.

A molecule composed of a number of atoms has a complicated spectrum compared to that of an atom. The total energy of a molecule includes the binding energy of the electrons, the vibrational energy of the atoms, and the rotational energy of the whole molecule and the radicals therein. Although in the condensed phases the rotational activity is hampered, yet the spectrum is still complex, because the number of vibrational energy states

depends upon the number of modes of vibration which is 3N-6 for a molecule of N atoms. So the electronic energy levels are more like energy bands with the vibrational energy levels superimposed upon them. As a result the system, in any energy level, can possess a number of energies corresponding to the possible vibrational states associated with that level. Changes in energy due to transition from one level to another (absorption, say) spread over a certain range (b-a) which produces a spectral band consisting of many lines instead of one. The band as such is discontinuous, but there are many factors which make it look continuous. The molecule in a solution is interacting (electrically, mainly) with other molecules of solute and solvent and this introduces broadening of the energy levels. If the excitation energy is of the order of the dissociation (5) energy, continuous absorption takes place and the bands broaden and tail off toward shorter wavelengths.



molecular energy levels

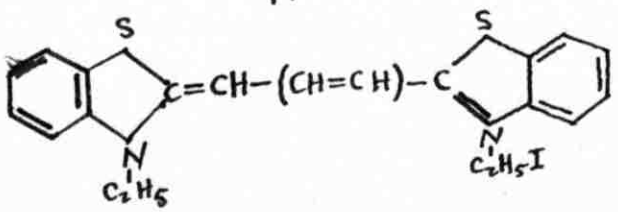
Consider a number (n_o) of identical particles in a certain state of aggregation and a certain energy state e_o. If we shine polychromatic continuous radiant energy on the system, n_i particles absorb energy e_i and rise to the i-th state. So we can say that the transition probability (P_t) to the i-th state or probability (P_a) of absorption of energy e_i is proportional to n_i/n_o. The total energy absorbed $E_i = n_i e_i$ is a function of both n_i and e_i. If the incident energy of the i-th type is E_{oi}, the transmitted energy $E_t = E_{oi} - E_i$ decreases as E_i increases indicating an increase in absorption and hence an increase in absorbing particles. So we can relate P_a to $E_{oi}/(E_{oi} - E_i) = E_{oi}/E_t$ which says that as E_t decreases there is probably more molecules absorbing, which is reasonable. If $\log E_{oi}/E_t = A$, the probability consideration still holds. $A = \log E_{oi}/E_t$ is a function of n_i and e_i.

But A/n_i depends only on e_i and type of absorber. If we take n_i as the number of particles per unit area, A/n_i reminds us of Bouguers law which says $A/cl = a$ (absorptivity), where C = concentration in moles per litre, l = length of light path in the solution in cm. Therefore $A/n_i = a/N_o$ where N_o is Avogadro's. Thus, with this argument we could relate the transition probability to the absorbtivity, which can be shown to be true by a more rigorous argument (6). For continuous absorption P_t is shown to be related to $\int a\, d\nu$, where ν is the frequency.

Cyanine dyes are groups of colored organic compounds used for sensitization of silver halide photographic emulsions. Since these dyes are colored, their absorption is in the visible region. One can visually tell the range of absorption because it is complementary to the color of the dye. Very roughly the connected colors in the diagram are complementary.

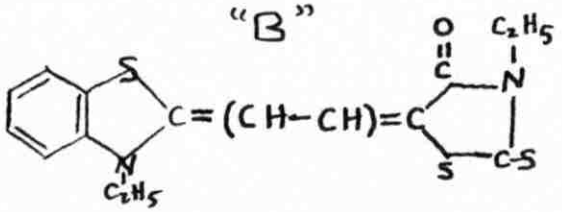
Every set of dyes is characterized by a general structure with fixed terminal groups, and with the length of the connecting chain differing in different members of the set. The following are general structural formulas for the two sets, of four dyes each, we are studying here.

"A"



Brooker, JACS, 62, 1119.

"B"



Brooker, JACS, 73, 5347.

The double bonds in the connecting chain are conjugated (they alternate) and they are the color producing elements (chromophores) in these dyes. If we assume that every double bond contributes 2 electrons moving freely in a box determined by the length of the conjugated chain, we get a fairly

good account for the observed absorption of some dyes (A) and hence their colors (7). For the dyes (B), a better fit with experiment was obtained if the electrons were assumed to move in a periodic potential provided by the carbon atoms in the conjugated chain (2). However no satisfactory account of the intensity was given by either model.

EXPERIMENTAL METHODS

Few but excellent pieces of equipment are available for the study. There is a large Hilger spectrograph with interchangeable quartz and flint optics offering an over all range of 12000 - 2000 A. A Baird Associate recording densitometer (automatic), with an optical density range of 0 - 2, is used for the study of the photographic plates. Ilford R.40 pan plates were used in the region 6500 - 3500 A, and Kodak IR - ER plates in the region 8000 - 6500 A.

The absorption of the various dyes in solution was studied. The solvent (EA) used was a mixture of 95% ethyl alcohol and ethyl ether in the ratio 2/5. Quartz cells 1 x 1 x 4 cm^3 were used to expose the solutions. Five cm cells were used when higher concentrations were desired for the detection of weak absorptions.

Because of the low solubility of the compounds, the solutions could not be prepared quantitatively. That required the use of either small masses of solute with a small practical volume (5-10 ml) of solvent, or large volumes of solvent with bigger masses. The latter requirement is not practical, because the solutions were short-lived and they had to be renewed every run. The former needed a micro-balance, reading 0.01 mg or less, which was lacking. Under these circumstances, we had to use saturated solutions, old enough (5 to 30 minutes in EA) to show sufficient absorption. It was noticed that the long-chained compounds were more soluble than the short-chained ones.

UNSTABILITY OF THE COMPOUNDS - Most of the dyes were unstable; their solutions changed color on exposure to radiant energy. Even visible radiation affected some of them, and the unstability increased with chain length. In fact, the n = o compound (yellow) is stable under irradiation

or heating up to the melting point - I mean no apparent change of color occured. All the others changed color to a greater or less degree before melting. On exposure to ordinary light, the longest chained one changed color in a day, while the next longest in few days.

This unstability was a stumbling block in the way of any study of these dyes in the UV or in thin crystals. The solutions changed color rapidly under UV irradiation, which definitely indicated a change in the character of the solute. Either it decomposed or was oxidized or both. Since all conjugated systems are known to be chemically active, one can give a high probability for oxidation without eliminating the possibility of dissociation. At room temperature and under visible irradiation the discoloration takes a day or more, so for exposures of 10 minutes or less under similar conditions, one may neglect the effect of oxidation. And assuming a dissociation energy of about 3 ev (4000 A), this effect is negligible with a visible source like tungsten which has a weak emission around 4000 A. For very active compounds, however, it is preferable to use evacuated cells. This reduces oxidation but does not stop decomposition initiated by UV photons. The n = 3 compound in solution in evacuated cells, was exposed to UV irradiation from a hydrogen lamp (Beckman), and in about 10 minutes changed from blue to colorless. This same solution left in ordinary light for few days, changed color from blue to green to yellow. The direct change in color in the absence of oxygen may be caused by dissociation, but the gradual change from one color to another is most probably due to a gradual change in the character of the compound as incurred by saturation of π e's thru oxidation.

THIN CRYSTALS - Three different methods were tried for the preparation of thin crystals. Two of which required the application of heat up to

the melting point, which the n ≈ o compound only could stand. In one method, the compound is put in a test tube which is heated in an oven up to sublimation and thin crystalline films are collected on a filter paper put on the top of the test tube under a crucible lid (8). This needed few mgms for every trial, which we could not afford because of our small sample. The second method required the heating of a sample between two glass or quartz plates up to melting. The n ≈ o dye could stand this but, anyway, it did not form uniform films. The third method required the deposition of the compound from solution, by vaporizing the solvent. This saves much material and does not need heat, but it did not yield uniform crystals. Type of solvent, concentration of solution, and rate of deposition affect the crystal produced.

Those were some of the technical difficulties which we met, and our success in dealing with some of them decided the orientation of our work.

LOW TEMPERATURES - Low temperature studies provide access to finer structural details which are obscured by thermal interference at room temperature. Part of our study was carried out around 80° K (liquid air temperature). The work in this region is more taxing and rather tedious. It requires more care, vigilance, and refinement than at room temperature. A plate requires from 2 to 4 hours. So blunders are costly and unjustified.

SOLVENTS - Since any solvent at such a low temperature is a solid, one has to choose the proper solvent or mixture of solvents which will yield a transparent glass and still possess sufficient dissolving power. Furthermore, it should not contract much on cooling and produce a deep miniscus. Mixture solvents are usually used rather than pure solvents, because they meet the above requirements, especially transparency, better.

We could prepare two suitable mixture solvents from the pure solvents available to us. One consisted of two hydrocarbons, methylcyclohexane (6 parts) and iso-octane (1 part). The proportions could be raised to 10/1, but could not be lowered much below 6 because that affected the stability and transparency of the glass. The dissolving capacity of this solvent was low. The other solvent and the one which we used much possessed higher dissolving capacity and cost much less. It consisted of ethyl ether (5 parts) and 95% ethyl alcohol (2 parts). This mixture (EA) is used much in the visible region but with an extra part of isopentane, then it is known as EPA. Unfortunately we could not get isopentane. This ingredient, perhaps, improves the stability and/or the transparency at lower temperatures.

The constituents of EA are both polar, which accounts for its high dissolving power, especially for polar solutes. But it has a disadvantage over the other mixture solvent in that it introduces perturbing fields which broaden the vibrational levels and obscure the vibrational structure in the absorption bands. So, solvents of low dielectric constant (1st mixture) are recommended when a study of vibrational structure is desired.

Solutions should be well degassed before cooling. Air is less soluble at low temperatures and so it forms bubbles which reduce the transparency. So special glass-stoppered vacuum tight cells were used. The cell was connected to a vacuum pump and degassed for 3-5 minutes, then closed and removed. A liquid air trap was used to stop any vapors from reaching the pump. With stable solutes which can stand moderate heating, degassing is easily achieved by warming the filled cell for few minutes before closing it.

After degassing, the cell is half dipped into liquid air and left for about ten minutes before exposure. It can be dipped all into liquid

air, and this certainly speeds up the cooling, but that introduces many complications. The air bubbles and the variable impurity content of liquid air interfere with reproducibility. Furthermore, the selective absorption of the liquid oxygen may overlap the sample's absorption; it has three strong bands at 4770, 5770, and 6300 A. The general absorption and scattering due to impurities and bubbles decrease the intensity much, and hence necessitates the use of longer exposures which are already twice their value at room temperature. An air blast should be kept blowing on the windows of the dewar flask to prevent fogging which cut down transmission almost to zero.

There are really many factors involved that render reproducibility difficult. Evacuation of cell, its position in dewar which is not fixed, impurities sticking to the cell walls and inner windows from the liquid air, fog on the inner and outer windows, variation of source voltage, and others count among the difficulties. Notice that all of these troubles can be reduced; they are only difficult to deal with.

The cells had narrow and tall necks (3-4 cm), and filling and emptying were nasty. This, in turn, made their cleaning with detergent, which required many rinses, lengthy, tedious, and hazardous. So we used syringes with needles which were a bit shorter than the neck - we could not find longer ones - and that almost solved the problem of filling which became quicker and less messy. But emptying was done by shaking off the the cell which was not safe and lengthy. Longer needles were needed.

Wave Length Calibration - There was no direct way of reading off the wavelength of a line or band on the photographic plate. One could print on every plate a mm scale only. We calibrated this scale in Angstroms for a wavelength drum setting of 80-32. This calibrated the range 6500 - 3200, determined by the sensitivity of the R.40 plate, to within $\pm$ 1.5 A on

the average. The error could be reduced to less than 1 A. But the drum setting was variable, and the relative position of the spectrum and the scale was reproducible to within $\pm$ .5 mm which amounts to about 20 A around 6500 A and to 8 A around 4000 A. The scale setting, however, is quite reproducible relative to the spectrum. But there is a possible shift of the total spectrum-plus-scale due to racking of the plate to get more than one exposure on it. And the direction of shift depends on whether one racks up or down. For very accurate work, the latter defect is corrected by use of the Hartmann slits. However, for one using the same range all the time, this calibration is good. But for one using different ranges or needing more accuracy, this is neither convenient nor dependable.

The other method used is independent of the scale. A rich line spectrum printed next to every absorption spectrum serves as a reference for identification of the absorption peaks. One is no more bound by any setting of the wavelength drum.

The iron spectrum was chosen as a reference because it is rich in wavelengths with few gaps all over the visible region (8000 - 4000) A. It is even richer between 5000 A and 2300 A. We identified over 300 Fe lines in the range 6500 - 4000 A, and over 50 Ne lines between 5850 A and 9000 A. Identification done with the help of iron spectrum was done by interpolation to within a fraction of an Angstrom, while with Neon, due to the fewer Ne lines, a Hartmann dispersion equation was used (9), with an accuracy of 0-1 A. But the error due to the width of the absorption peaks was much more than that, about ten times and sometimes more.

The arc used was after the recommendation of Pfund (10), only thicker electrodes were used sometimes.

The Fe and Ne spectra were densitometrized with such speeds of carriage and chart as would render every 2.1 mm on the plate into one inch.

From a density chart of the absorption, the peak position was determined in mm relative to a spectral line in the comparison spectrum. The chart was divided in half inches. Fractions thereof were measured by a ruler reading 0.5 mm. Then the wavelength corresponding to this distance was found from the Fe or Ne spectrum chart. The error inherent in the measurement was about 0.2 X dispersion in A/mm. One could halve the 0.2 by doubling the chart speed, but since other errors (peak width) were still few times bigger (2 or more), not much would be gained.

Calibration of Emulsion (11) - Among the things which one is usually interested in, is the intensity of absorption or the integraded intensity which is proportional to the transition probability. What one gets in practice is the density on the photographic plate. This depends upon the radiant intensity and the exposure time. A relation between density and intensity can be obtained by plotting D vs log t with I_o constant in $E = I_o t$, where E is sort of effective intensity and it is called the exposure. The density difference $D_1 - D_2$ is changed by the graph to log $\frac{E_1}{E_2} = A$ which is the absorbance of the solution where E_1 belongs to solvent and E_2 to solution. If the concentration of the solution is known, A gives "a" the absorptivity (see theory p. 3), and a d which is proportional to the transition probability, is the area under the absorption peak after transforming the plot from D to A to "a".

As I mentioned above, the concentrations of our solutions were unknown and so we could not get the absolute integrated intensity.

It is worth mentioning that we tried a long sector for calibration, but we found on theoretical grounds that it gave D vs log $(E_1/E_2 + 1)$ instead of log E_1/E_2 which we were interested in.

RESULTS

The results of the study are grouped in a table on (p. 18). It contains the absorption maxima of each dye (set A) both at room and at liquid air temperatures. The width of each absorption band was found by doubling the half width of the band measured from the center of the height to the sharper edge of the band which is usually to the longer wave length side. The height of the band is given in optical density units. The error in λ is determined wholly by the estimation of the position of the absorption peak. For broad bands the uncertainty in the estimation went as high as 1 mm, and it did not drop below 0.2 mm for other bands. This uncertainty multiplied by inverse dispersion (A/mm) gives the error in Angstroms shown in the table. In addition to that, a plot of density (D) versus wavelength is given for each dye at both room and liquid air temperatures. In two cases I had to impose a plot of the second weaker absorption which did not show well in the exposure for the strong peak. A higher exposure time was required to give the weak absorption, then the optical density around the strong peak went above 2 which is the maximum reading limit for the densitometer. This was due to the non-uniformity of the source emission. There is a graph of n which appears in the structural formula for the dyes A (p. 4), vs λ max at both room and liquid air temperatures.

DISCUSSION

Our aim was to get an accurate and detailed picture of the electronic make-up of conjugated systems, the set of dyes under study being one of them. Our claim to accuracy and detail is based on the fact that the spectrograph used (large Hilger) is superior in resolution and dispersion to any spectrophotometer, the instrument which is usually used for such study. The use of low temperatures can provide more detailed information about band structure,

hence energy levels not possible at room temperatures.

If we look at the graphs of the four dyes, we notice that all of them display a smooth rise on the long wave length side, and a slower uneven fall on the short wave length side; they all have shoulders on this side, which make one suspect the presence of a peak or peaks. There is sort of a limit on the lower energy absorbed (p. 4), and a limit on the high energy, both determined by selection rules, but the upper limit is less rigid due to the presence of more excited levels.

Now if we compare the band widths (b w in table) for the same dye at both temperatures, we notice that all bands are narrower at low temperatures, and a second peak, weak and at shorter λ , is resolved and it is quite sharp and intense for the odd n's (1 and 3), while for n = o and 2 it is much less intense and quite flat relative to the main peak. If we assume that an excited state is less densely populated at lower temperatures (Boltzman distribution), i.e. most of the systems are in the lower states, the transitions to the first excited state are more restricted because they are starting up from few vibrational states, while at room temperatures they originate from more vibrational states. This accounts for the narrowing and the splitting of the bands.

But the sharper and more intense peaks for the dyes with odd n both at room and liquid air temperature is not clear.

From the plots of n vs λ we see that the absorption maximum increases linearly from 1 to 3 with n or chain length or number of mobile electrons. This conforms with theory which gives the energy proportional to the chain length (6, 7). The graphs are similar at both temperatures. But at low temperatures the position of λ max shifts a little to the red while another λ appears at lower wavelengths. The apparent shift to the red could be due

to a better definition of the absorption peak at lower temperature and to the increase in the refractive index of the solid solution (12).

Platt (7) and Pitzer (6) give theoretical formulae for the calculation of the energy based on the free electron model. Pitzer's gives a better fit.

$$\lambda = 500(N-3.06)\ A$$

where N = 6, 8, 10, 12, and λ = 4530, 5530, 6530, 7530 A, with a constant difference of 1000 A. The high wavelengths fit the experimental results better than the lower ones, and the difference is also about 1000 A except for the lower two (1384 A). However, as I said before, no theoretical model can account for all the observed facts; they give mostly a partial account.

Our values compare well with the experimental results of Brooker which are: 4230, 5575, 6500, 7580 A.

The second peak which is resolved at low temperature - it appears as a shoulder at room temperature - and on the short wavelength side of the main absorption peak is not accounted for by the said model. It is most probably due to a change in vibrational energy accompanying the main electronic transition and equal to the energy separation of this small peak from the main one. In fact the difference which is about 1100cm^{-1} (0.8 ev), is of the order of magnitude of a vibrational separation. Also, the shoulder that flanks the main peak (and lies between the two peaks) corresponds to a vibrational transition of energy less than 1100 Am^{-1}.

ACKNOWLEDGEMENTS

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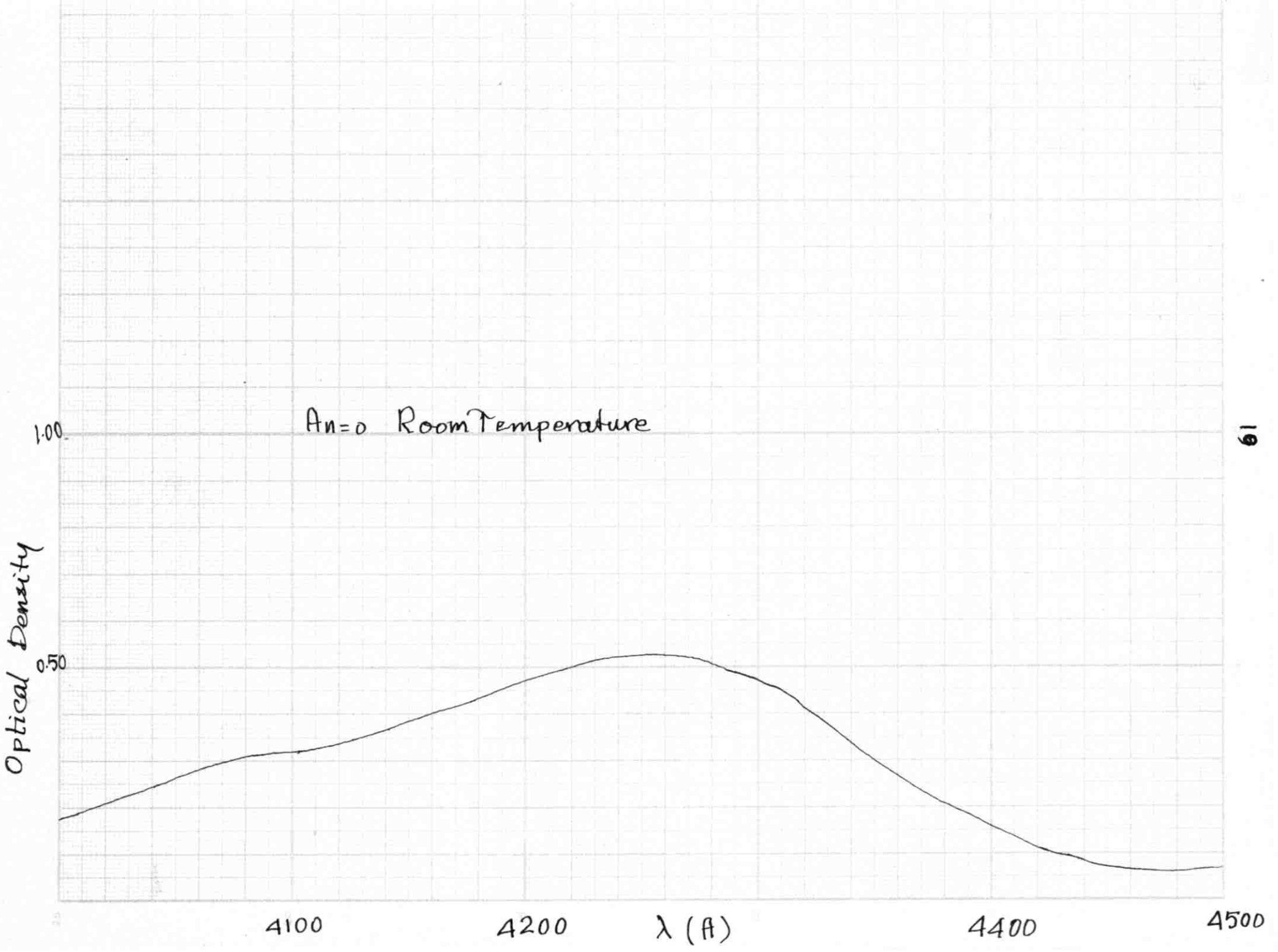
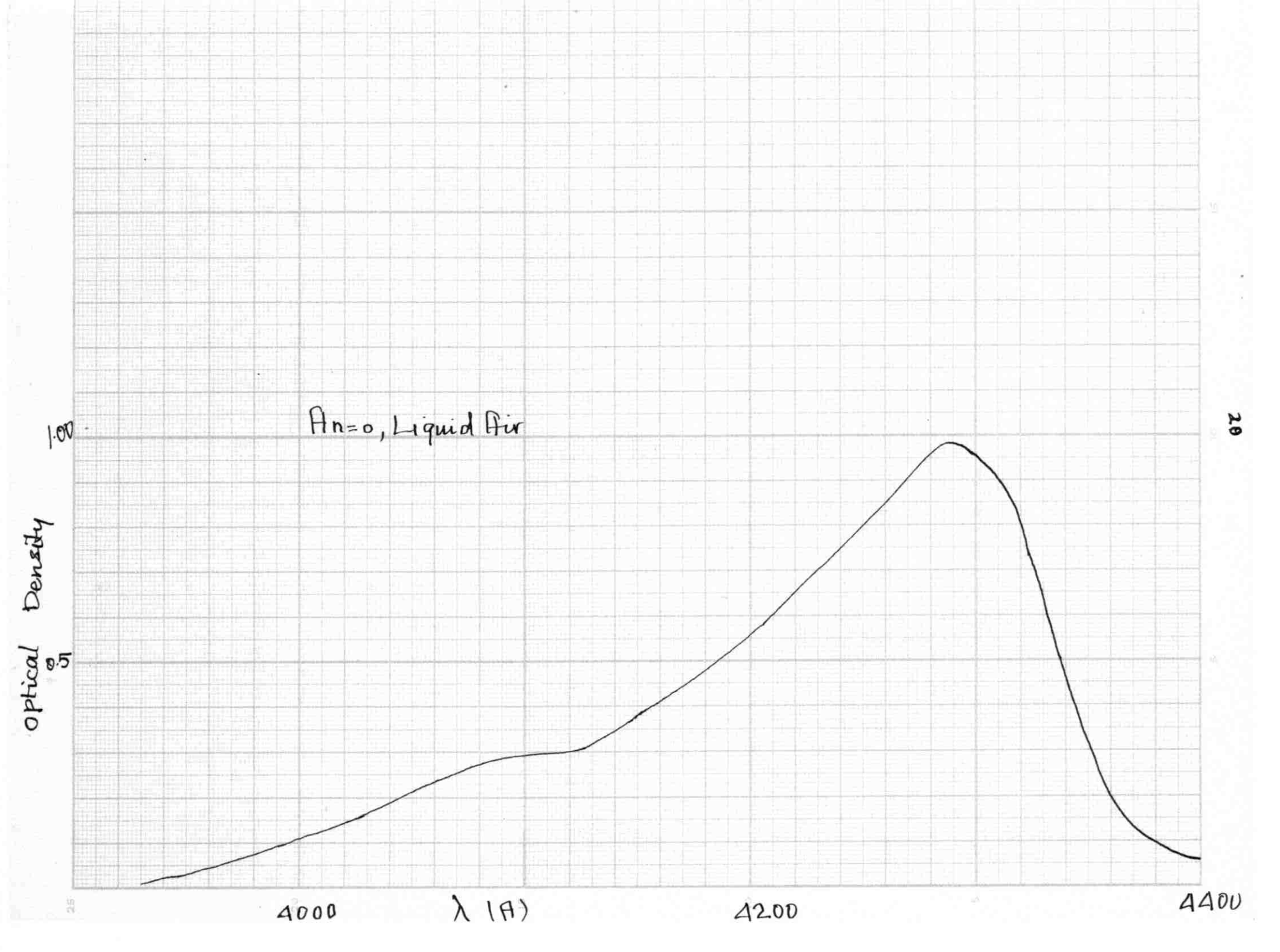
TABLE OF RESULTS

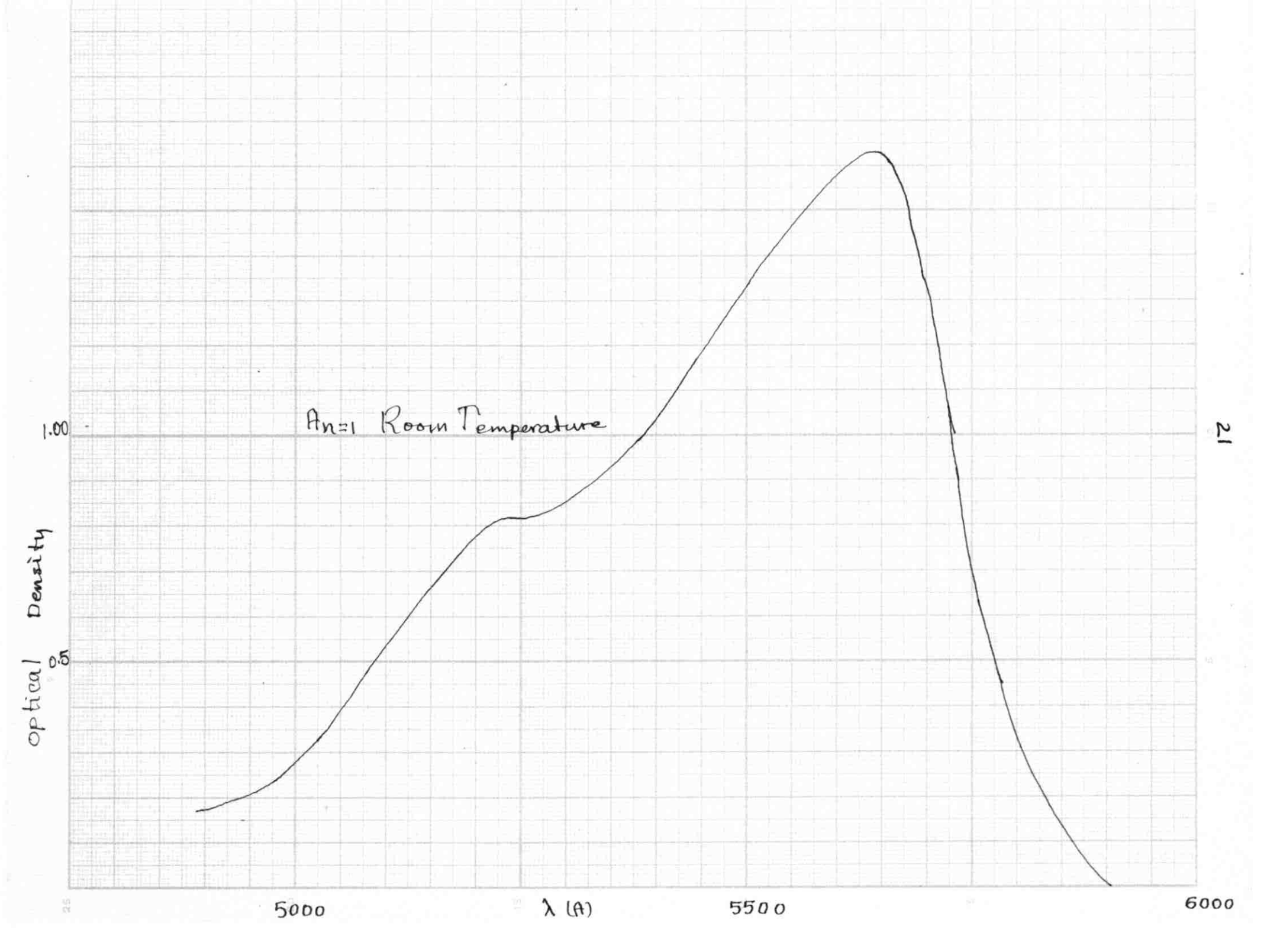
Dyes "A"

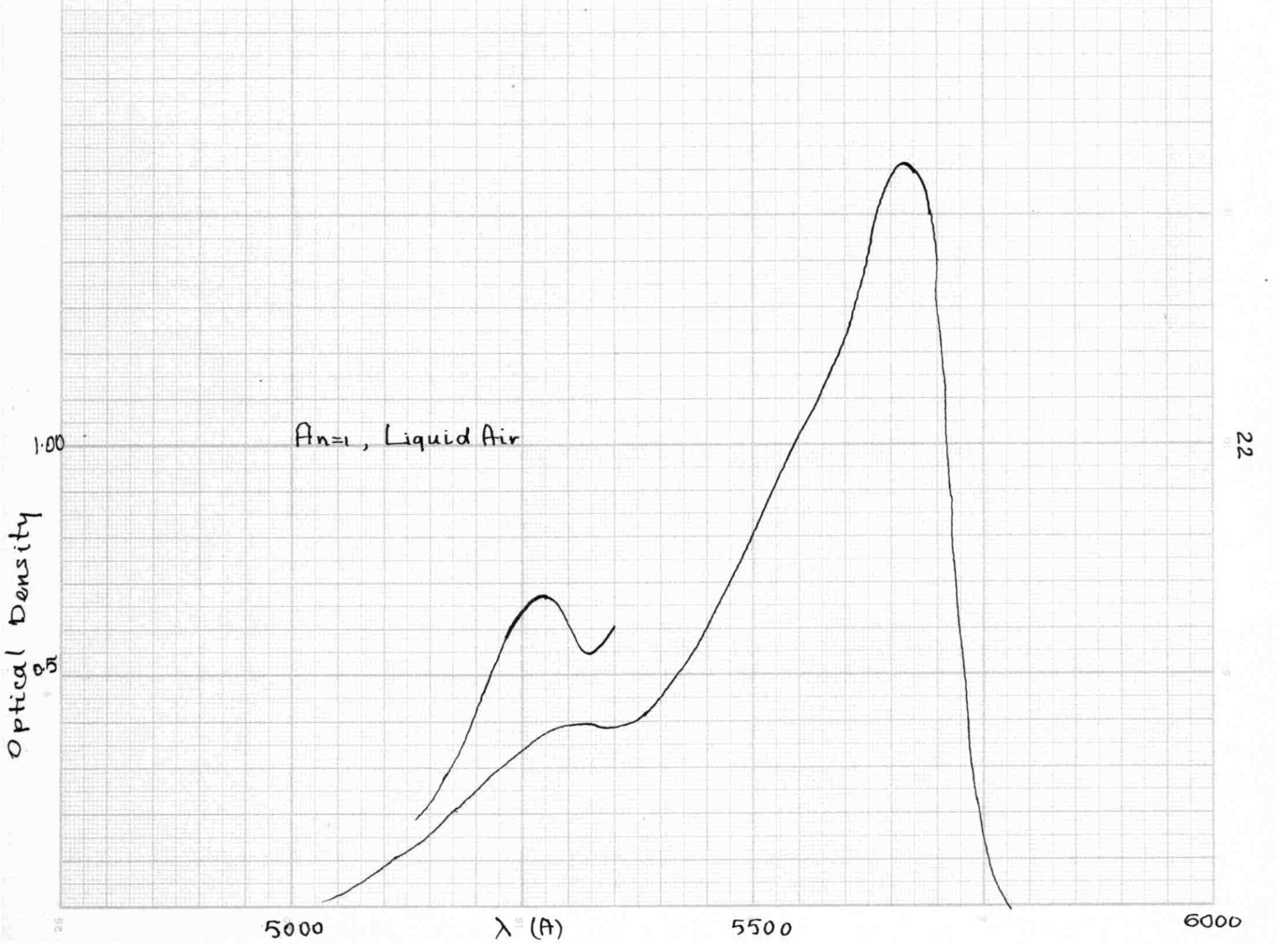
Dye	Room Temperature				Liquid Air Temperature							
	λ A	ν Cm^{-1}	b w Cm^{-1}	h D	λ_1 A	ν_1 Cm^{-1}	b w Cm^{-1}	h D	λ_2 A	ν_2 Cm^{-1}	b w Cm^{-1}	h D
$A_n = 3$	7595 ± 5	13170 ± 10	920	0.80	7719 ± 5	12980 ± 9	600	1.25	7083 ± 6	14130 ± 12	800	.98
$A_n = 2$	6558 ± 10	15250 ± 25	860	0.43	6671 ± 4	14990 ± 8	280	0.84	6150 ± 8	16260 ± 20	840	.19
$A_n = 1$	5638 ± 5	17730 ± 15	580	1.62	5660 ± 3	17670 ± 10	320	1.61	5269 ± 6	18980 ± 20	920	.67
$A_n = 0$	4254 ± 15	23510 ± 20	960	0.52	4288 ± 8	23320 ± 15	520	.95	4100	-	-	-

λ is the wavelength at maximum absorption, ν the corresponding frequency, bw is the band width, h is the height of the absorption at λ in optical density units.

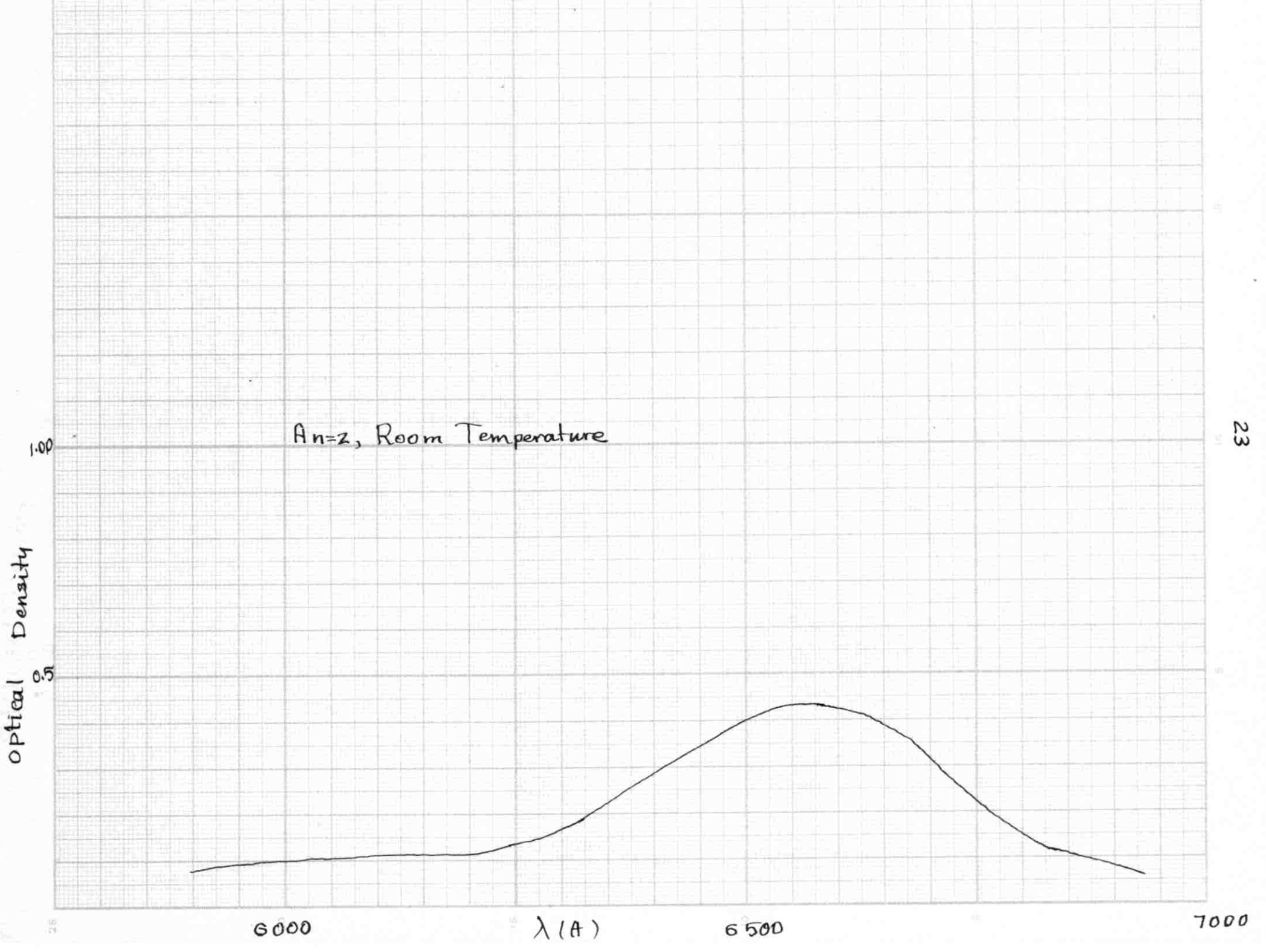

An=0 Room Temperature
1.00
0.50
Optical Density
4100
4200
λ (A)
4400
4500

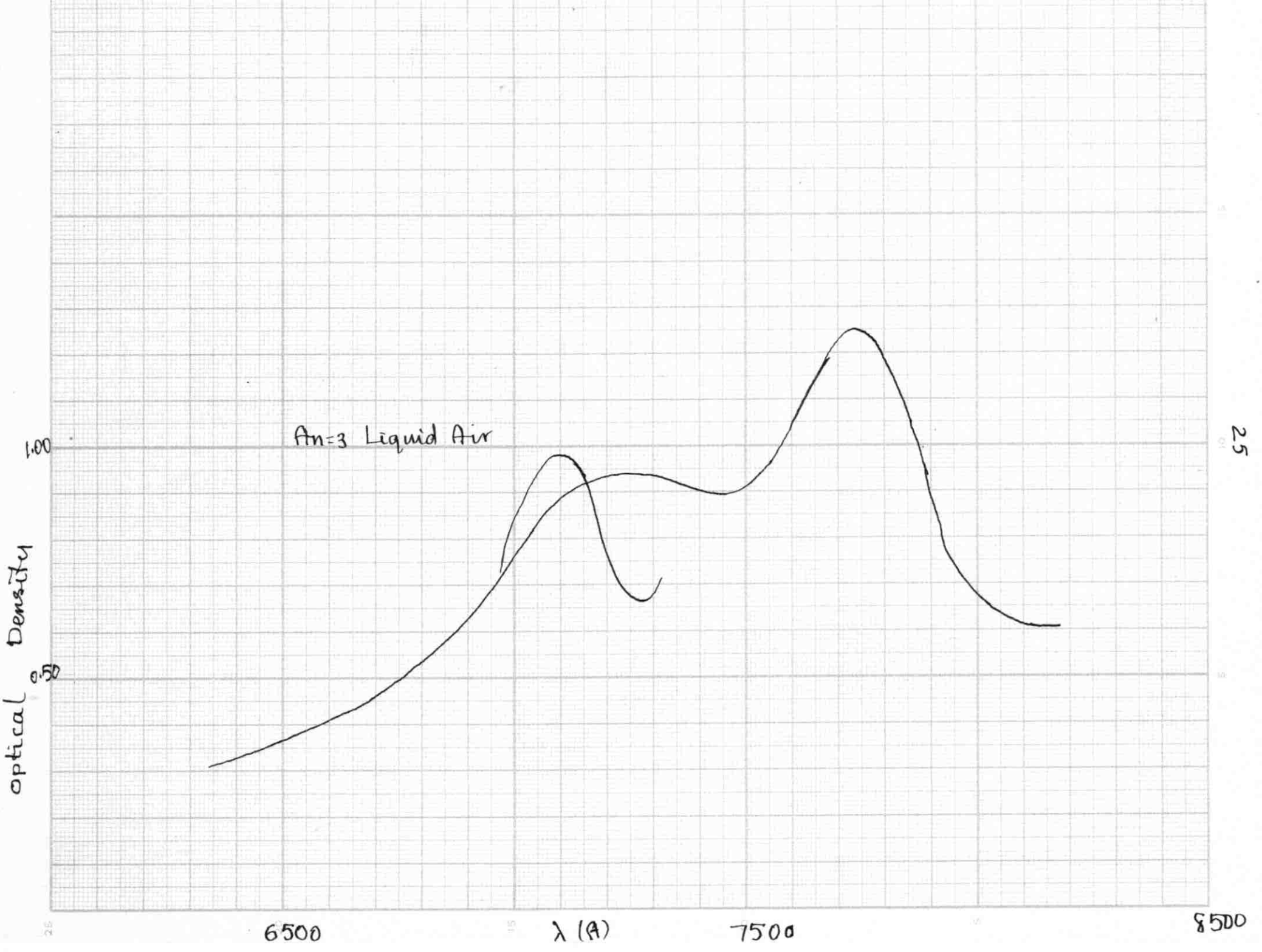

Δn=0, Liquid Air
1.00
.5
optical Density
4000
λ (Å)
4200
4400
29

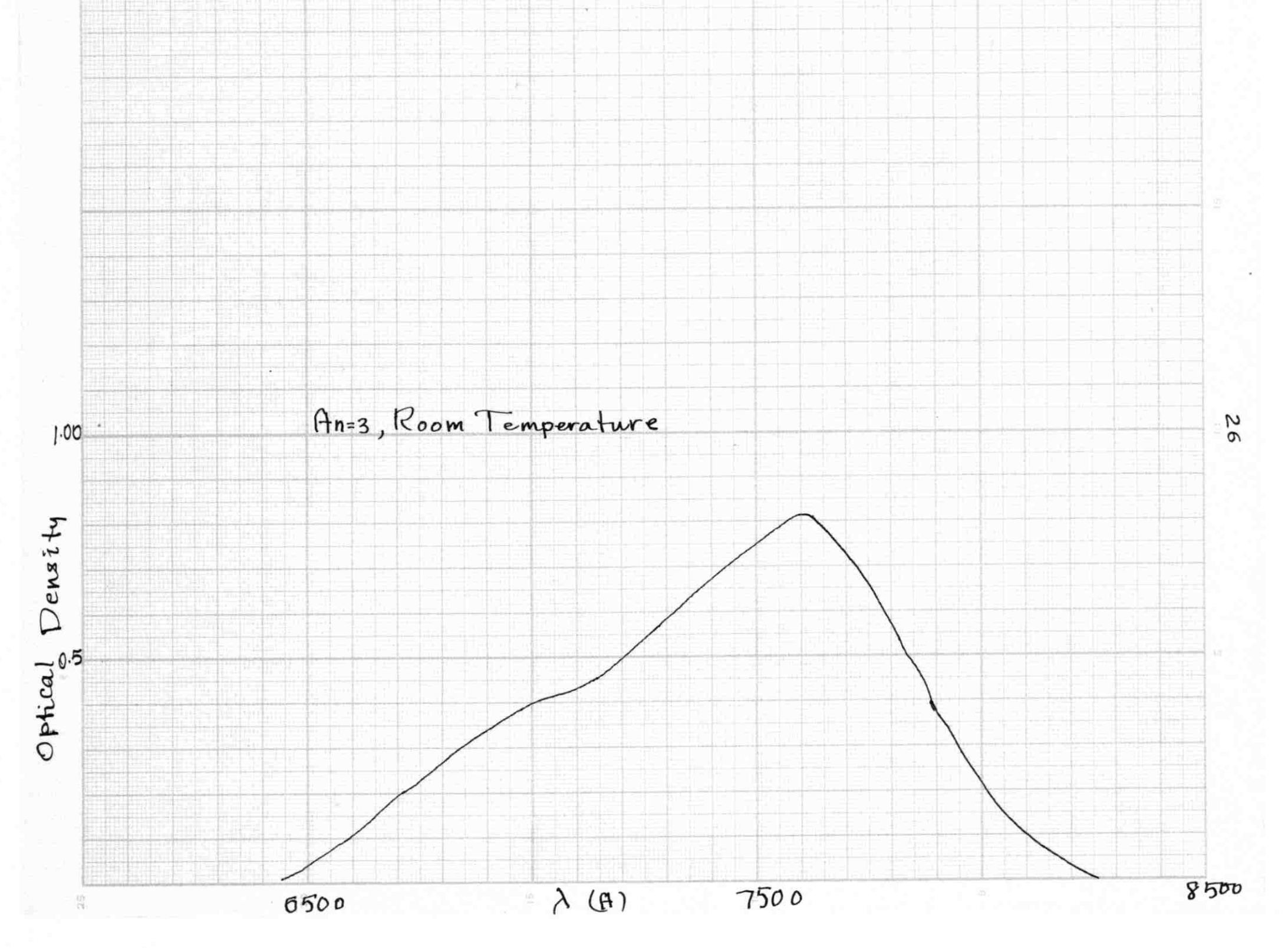

An=1 Room Temperature
1.00
0.5
optical Density
5000
λ (A)
5500
6000


An=1, Liquid Air
1.00
0.5
Optical Density
5000
λ (A)
5500
6000
22

An=2, Room Temperature




An=3 Liquid Air
1.00
0.50
optical Density
6500
λ (A)
7500
8500
25


An=3, Room Temperature
1.00
0.5
Optical Density
6500
λ (Å)
7500
8500
26

400
500
600
λ (mμ)
700
800
0
1
2
3
n us λ
LA λ2
RT
LA λ1