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Exciplex systems for Vapor/Liquid Visualization of Fuel Sprays

TABLE OF CONTENTS

	<u>page</u>
SUMMARY.....	2
INTRODUCTION.....	3
EXCIPLEX PHOTOPHYSICS AND SEARCH STRATEGIES.....	5
EXPERIMENTAL APPARATUS AND PROCEDURES.....	10
RESULTS AND DISCUSSION.....	12
AREAS OF FUTURE WORK.....	19
REFERENCES.....	20
APPENDIX (SPECTRA).....	22
PUBLICATIONS.....	23
PERSONNEL ASSOCIATED WITH GRANT.....	24
INTERACTIONS (COUPLING).....	25

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SUMMARY

Under grant 83-0307, sponsored by the Air Force Office of Scientific Research, the University of Texas at Dallas has conducted research on potential new organic exciplex systems for use in fluorescent visualization of the vapor and liquid portions of evaporating fuel sprays. These exciplex systems represent a novel and potentially powerful diagnostic tool for the analysis of the vaporization processes in gas turbine fuel sprays, and as such, possess considerable relevance to Air Force propulsion needs. This final report describes the five best exciplex systems developed to date, the methods used to screen nearly one hundred of potential systems, and the characterization of the naphthalene/tetramethyl-p-phenylene diamine system. This last system has already been used in demonstration experiments to photograph the separate liquid and vapor patterns in an evaporating fuel spray.

INTRODUCTION

Gas turbine and diesel engine combustions are extremely difficult problems, from both a theoretical and experimental standpoint, because both involve chemically reacting, turbulent flows with large mass and temperature gradients. Because the fuel is introduced as a spray, initially the flow is heterogeneous, and the problem is, therefore, even more complex. Literally hundreds of studies, as detailed in recent reviews(1-6), have been made of the behaviour of droplet distributions in these sprays, but there have been very few studies in which both the liquid and vapor distributions have been determined.

The separate measurement of liquid and vapor concentrations by optical techniques, which can be virtually non-intrusive, has been difficult because, for fuel-like molecules, most spectral characteristics are virtually the same in the liquid and vapor phase. Johnston investigated spontaneous Raman scattering but concluded that, in the C-H stretching region near 3000 cm^{-1} , there were insufficient differences between the spectra of the vapor and liquid to allow their separate measurement(7,8). Other optical methods have exploited the index of refraction differences between the liquid droplets and the less dense ambient vapor/air surrounding the droplets; these studies have used direct photography(9,10), laser light scattering(11), or two wavelength laser absorption/scattering(12,13). An alternate strategy, used in this work, is to develop fuel additives which interrogate the spray, and reveal its characteristics in their fluorescence.

In previous work, it has been shown that certain organic exciplex systems, when added to fuel-like liquids and excited with ultraviolet light, result in a blue-green fluorescence from the liquid phase and a purple fluorescence from the vapor phase(14). Thus, these systems possess the unique characteristic that their emissions distinguish the liquid and vapor phases from one another, and hence offer the possibility of seeing the vapor and liquid portions of the evaporating fuel spray separately.

One exciplex system, based on tetramethyl-p-phenylene diamine (M) and naphthalene (N), has already been used to demonstrate the diagnostic potential of the exciplex visualization idea. These molecules were added to hexadecane, and the fuel mixture was sprayed through a simplex nozzle into hot nitrogen. The spray was irradiated with a sheet of laser light (266 nm), and the resulting fluorescence was photographed through filters. Photographs were obtained which showed the liquid portion of the spray without the vapor and vice versa(15,16).

This initial exciplex system is, however, not optimal. The exciplex fluorescence decreases at high temperatures because the exciplex binding energy is not sufficiently high, the emission bands of the monomer M^* and the exciplex E^* are partially overlapped, the vapor phase emission from M^* is subject to quenching by molecular oxygen, and the two exciplex components have significantly different volatilities. Under Air Force sponsorship, grant 83-0307, the University of Texas at Dallas has examined many potential organic exciplex systems in a search for better diagnostic additives. Five systems were found to be promising, and their spectra are included in this report.

The next section summarizes the relevant exciplex photophysics as well as the basic screening criteria and methods. Subsequent to that, the experimental apparatus and techniques are described. The results of the studies are then presented and are discussed in light of the criteria for useful diagnostic systems. Suggestions for future work are outlined and, finally, selected spectra obtained during this investigation are attached as an appendix.

EXCIPIEX PHOTOPHYSICS AND SEARCH STRATEGIES

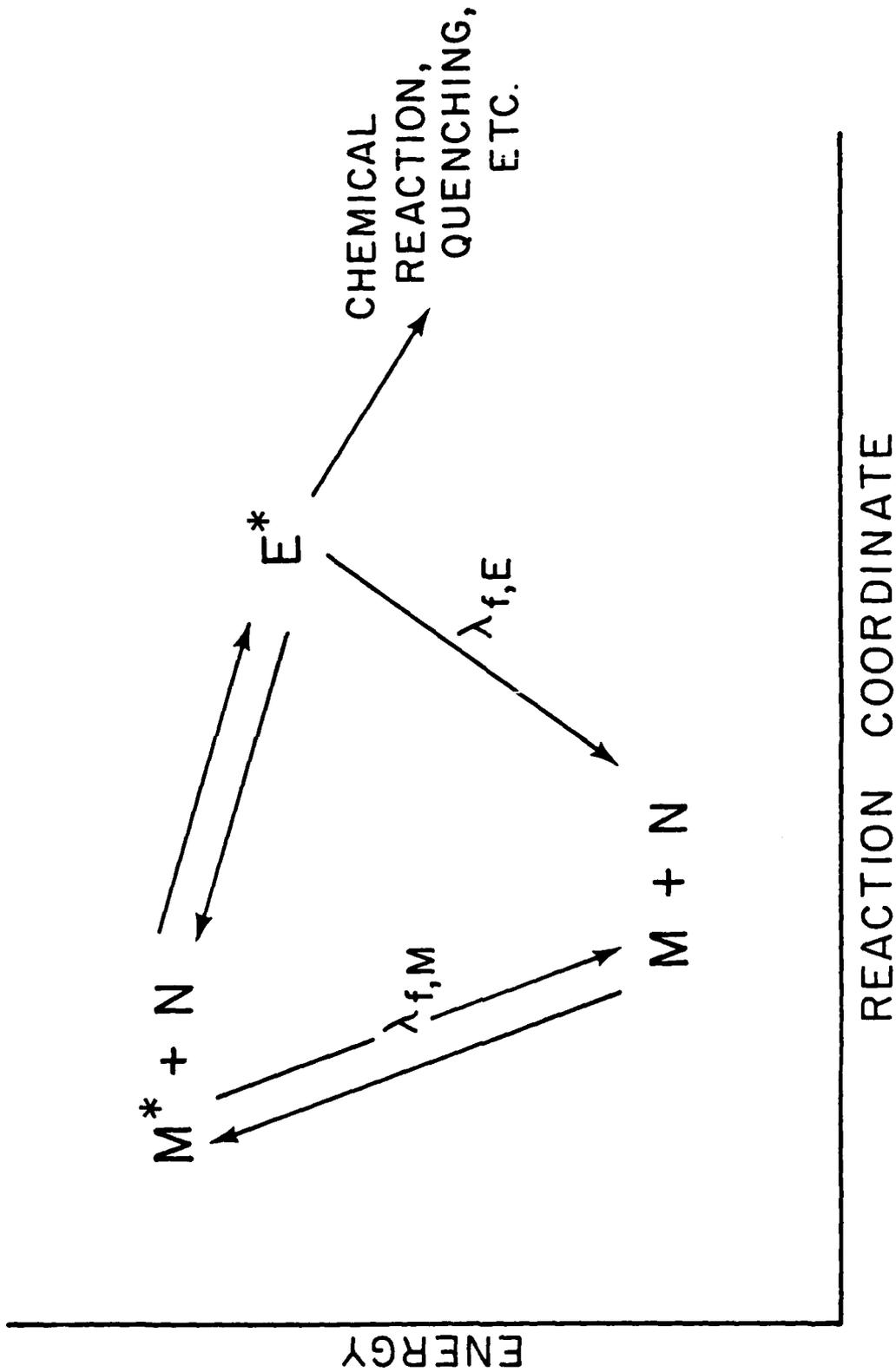
An exciplex (excited state complex) is formed when an excited state molecule reacts with itself or another molecule to form a complex, which is bound only in the excited state. The binding of the exciplex may be quite significant, up to 100 kJ/mole, i.e., 30% of a normal chemical single bond. The ground state is, however, repulsive and the two reactant molecules have no special binding once the excited state has decayed. There is a rich area of organic photochemistry associated with exciplexes as reaction intermediates; however, for the purpose of developing fuel spray diagnostics, we are concerned only with those exciplexes which emit strong fluorescence(17,18).

In Fig. 1, the relevant photophysics for such an exciplex visualization system is shown. A fluorescent organic molecule, M, can absorb light to form the excited species M^* , which may then fluoresce and return to the ground state or may react with another ground state molecule N to form the exciplex E^* . The exciplex is formed in a reversible chemical equilibrium with M^* and may either dissociate back to M^* and N, fluoresce, or undergo further chemical reaction. Only the first two paths are of interest here since fast chemical reaction will disqualify an exciplex system as a diagnostic for fuel sprays.

Two concepts are important in understanding how such a fluorescent exciplex system can be used to distinguish the vapor and liquid portions of an evaporating fuel spray. First, since the exciplex E^* is bound with respect to separated M^* and N, and ground state M and N have virtually no interaction, the exciplex fluorescence is necessarily at lower energy than that of M^* ; indeed this spectral shift of the fluorescence is approximately equal to the binding energy of the exciplex and may be as much as 10000 cm^{-1} . Second, the concentration of N may be adjusted so that in the liquid phase the $M^* + N = E^*$ equilibrium lies far toward the right, i.e., the ratio of the population of E^* to that of M^* is roughly 100. In the vapor phase, the densities are much less and the solvent stabilization of the relatively polar exciplex is much less, hence, the equilibrium lies far toward the left, i.e., the ratio of the M^* population to that of E^* becomes roughly 100(19). In this situation, E^* emission, at its distinct position in the spectrum, is only seen if liquid is present; M^* emission, at its separate spectral position, is only seen if vapor is present. This idealized situation is rarely achieved in full, but nonetheless, a system based on tetramethyl-p-phenylene diamine (M) and naphthalene (N) has been used to photograph the liquid and vapor portions of a hollow cone fuel spray(15,16).

The exciplex systems offer several advantages over the conventional systems based on the analysis of droplets and subsequent calculation of vapor concentrations. The vapor is measured directly, and, since fluorescence is inherently linear in the density of fluorescers, the detected fluorescent intensity should be directly proportional to the mass concentration of the liquid or vapor portion of the spray, as appropriate. The exciplex systems are well adapted to use in modern laser visualization techniques since a slice of the fuel spray may be irradiated with a sheet of laser light, and the resulting fluorescence may be imaged onto an array

FIGURE 1



detector. The fluorescent lifetimes of the emitting species are typically less than 100 nanoseconds(20), and hence independent measurements on a fuel spray can be made at rates greater than one megahertz -- limited not by the photophysics of the detection system but rather by the available repetition rates of laser excitation sources and the capability of high speed cameras and/or digital imaging systems.

The exciplex systems are, however, not without their drawbacks. The equilibrium between M^* and E^* is temperature dependent, and systems must be developed for which the binding of E^* relative to M^* and N is sufficiently strong that the exciplex emission does not vary strongly with temperature during the evaporation of the fuel spray. Excited organic molecules such as M^* are very sensitive to quenching by molecular oxygen, and current measurements indicate that any M^* will be quenched by oxygen on every gas kinetic collision. If this occurs, then the vapor intensity measurements for a fuel spray evaporating in air will be confounded with the penetration of air into the spray, and the results will not be readily interpretable as vapor concentrations. Finally, it should be noted that the additives M and N are not the fuel itself, and hence the emissions from M^* and E^* serve as markers for the fuel vapor and liquid fractions, respectively, but are not the major fuel component themselves. It will be necessary to establish that these emissions are indeed good linear markers in order to interpret the intensity measurements quantitatively.

The initially successful exciplex system was compounded with naphthalene (N) and tetramethyl-p-phenylene diamine (M) with the balance being hexadecane. In light of the promise shown by the demonstration experiments performed with this system and in light of the concerns outlined in the previous paragraph, a search was undertaken to find alternate exciplex systems which would relieve some of the potential drawbacks. In particular it was desired to create systems which would satisfy the following criteria:

i) There should be a large spectral shift between the M^* and E^* emissions so that the spectral overlap of these features would be minimized. It should be remembered that the absorption and emission bands of organic molecules are inherently broad and may easily be $5-7,000\text{ cm}^{-1}$ wide, so large spectral shifts are required if the emissions of M^* and E^* are to be separated.

ii) The exciplex E^* should be strongly bound with respect to the separated M^* and N molecules. If the binding is too weak, then the exciplex equilibrium will shift toward the separated reactants as the temperature is raised. The result is that the fraction of the emission resulting from E^* drops and that resulting from M^* rises. One would then infer that less liquid and more vapor was present. Ideally, the binding energy should be sufficiently high that E^* remains the dominant emitting species from the liquid up to temperatures at which the fuel evaporates, i.e., its boiling point at ambient pressure.

iii) The quenching of the vapor phase fluorescence of M^* by molecular oxygen should be minimized. All present experimental measurements of the fluorescence quenching of organic molecules indicate that molecular nitrogen and aliphatic hydrocarbons are virtually inert(21,22) and that

molecular oxygen is indiscriminately efficient(23,24). Thus, rather than searching for candidates for M^* which might have lower probabilities of quenching in a given bimolecular encounter, we have chosen to examine candidates which have short radiative lifetimes since this parameter determines the number of collisions an excited state molecule undergoes at a given pressure.

iv) In order to make the exciplex system a good marker for the vapor and liquid, one must insure that the ratio of marker to fuel remains constant during the evaporation of the spray droplets. If the vapor pressures of the several components are equal, then the marker and fuel species will rigorously coevaporate. We have chosen to match the boiling points of the three species at atmospheric pressure as closely as possible in order to minimize potential differential evaporation. Recent work by Wang et al supports this matching of boiling points as an effective criterion for coevaporation(25).

v) The exciplex components should be commercially available if possible. Ideally these investigations will result in exciplex systems which will be used by a wide variety of non-chemists and, were specialty syntheses required, the use of the diagnostic systems would be retarded.

Although each proposed exciplex system must be tested individually to determine its suitability, individual systems can be screened for the constraints i) and ii) fairly easily. Rehm and Weller have developed a series of correlations which enable one to calculate the energy at which the maximum of the exciplex fluorescence occurs and the binding energy of the exciplex, if one knows the singlet excitation energy of M^* (available from absorption or emission spectra) and the oxidation/reduction potentials of the donor/acceptor components of the complex as measured in acetonitrile (19). These parameters are available in tabulations, and thus a wide variety of potential exciplex systems can be rapidly screened.

$$h\nu_c^{\max} = [E(D/D^+) - E(A^-/A)] - 0.15\text{eV}$$

$$\Delta H = \Delta E_{O,O} - [E(D/D^+) - E(A^-/A)] - .13\text{eV}$$

where ΔH is the binding energy of the exciplex, $\Delta E_{O,O}$ is the singlet excitation energy, and $E(A^-/A)$ and $E(D/D^+)$ are the oxidation/reduction potentials. The equilibrium constant for exciplex formation is given by

$$K = \frac{[E^*]}{[M^*][N]} = \exp [-(\Delta H - T\Delta S)/RT]$$

where ΔS is found to be approximately -85 J/K-mole over a wide range of exciplexes(20). Consequently, use of the fluorescence spectra compiled by Berlman(26), tables of oxidation and reduction potentials(19,27) and tables of boiling points(28) allows one to assess the probable usefulness of a wide variety of systems prior to testing.

The relative fluorescence yields of the exciplex and the monomer are given by

$$\frac{\phi_e}{\phi_m} = \frac{K_{fe} [E^*]}{K_{fm} [M^*]} = \frac{K_{fe}}{K_{fm}} K [N]$$

The radiative rate constant K_{fe} for exciplexes is typically in the range of 10^6 - 10^7 sec^{-1} (20) and K_{fm} can be obtained from Berlman's compilation.

Using the techniques outlined here we have examined nearly one hundred potential exciplex systems, of which 31 yield fluorescence (a property which is not determined by the correlations given above and which must be separately tested). These systems were then tested against the criteria given above and fluorescence spectra as a function of temperature were measured. Of the 31 potential systems, five showed strong exciplex fluorescence which diminished by less than a factor of two as the temperature was raised from 23 C to 250 C. These systems are presented in detail in the results section.

EXPERIMENTAL APPARATUS AND PROCEDURES

The main body of experimental work in this project was the measurement of fluorescence spectra for test mixtures. The spectra were run on one of three devices: a) a Farrand Mark I spectrofluorimeter, which has a continuously tunable excitation source; b) a specially assembled fluorimeter consisting of a XeCl excimer laser (308 nm), high temperature fluorescence cell, monochromator, phototube, and associated electronics; or c) a specially assembled fluorimeter consisting of a Nd:YAG laser set to produce the fourth harmonic at 266 nm, high temperature-high pressure fluorescence cell, spectrometer, phototube, and boxcar integrator. The Mark I fluorimeter was useful for survey scans, particularly at room temperature, but because of its relatively cramped sample compartment and relatively low excitation intensity, it was rarely used for high temperature measurements. The two specially assembled fluorimeters operated with conventional right angle and front face fluorescence geometries and are described briefly in the following paragraphs.

The excimer laser excited fluorimeter was used at UT-Dallas. The excimer laser source (Lumonics 861S) can produce 80 mJ/pulse at 10-20 hertz, although the typical excitation energies used were only 1-5 mJ/pulse. The beam is focussed onto a high temperature fluorescence cell in such a fashion that, when the 10 x 20 mm quartz cuvet is oriented with the 10 mm wide surfaces perpendicular to the laser beam, the beam does not hit the side walls of the cuvet. If the beam is allowed to fall on these surfaces, unacceptable amounts of scattered light result.

The 10 x 20 mm cuvet is held in an aluminum support so that the assembly can be raised to bring the liquid in front of the laser beam or lowered so that the vapor is in front of the laser beam. The cell holder assembly will also pivot so that the vapor spectra, in which spurious emission from liquid on the walls is a problem, can be taken in a conventional right angle fluorescence geometry and liquid spectra, which must be taken off the front surface since the solutions are optically thick, can be taken with the cell aligned at approximately 45 degrees to the incident laser beam. The cuvet holder assembly can also be translated perpendicular to the laser beam so that the irradiated spot in the front surface experiments will lie on the optical axis of the monochromator. The temperature in an experiment is monitored with an iron-constantan thermocouple inserted in the aluminum cuvet holder approximately 1 mm behind the cuvet. The entire cell assembly is suspended in an insulated box, with quartz entrance and exit windows, and is heated by air which has passed through an electric oven. In some cases, where reaction with or fluorescence quenching by oxygen is thought to be a problem, the air flow is replaced by nitrogen.

In a typical preparation, a few milliliters of solution are mixed in the cell, with the solvent and solids being weighed on an analytical balance and the minor liquid additives being added with a calibrated syringe. In all cases, the solution is purged with nitrogen for at least ten minutes to remove dissolved oxygen and is then stoppered with a teflon plug. This procedure is probably adequate during the heatup phase of an experiment since the increasing vapor pressure inside the cuvet acts to drive air out; however, during the cooldown phase, the pressure in the cuvet becomes subatmospheric and air is drawn into the cuvet. The result is that most

test solutions, which are initially colorless, end up with a color anywhere from amber to deep brown. The thermal oxidation chemistry described here is a minor interference in taking the spectra of these solutions, but would have no effect on the use of the solutions in fuel spray diagnostics since it is orders of magnitude slower than the 50-100 millisecond lifetimes of droplets in typical fuel sprays.

The fluorescence from the cell was focussed through a quartz lens onto the entrance slit of a quarter-meter monochromator (Jarell-Ash) equipped with an RCA 1P28 phototube. The output was taken to an electrometer and thence to a strip chart or X-Y recorder.

In the measurements on the 2.5% naphthalene/1.0% tetramethyl-p-phenylene diamine exciplex system, (performed at United Technologies Research Center with James F. Verdick), the fourth harmonic of a Nd:YAG laser at 266 nm was used to excite fluorescence. This fluorescence was then focussed through a quartz lens into a Spex 1702 monochromator equipped with an EMI 9829QA phototube, and the signal was taken to a PAR 162/164 boxcar, which could be operated in the scanning mode for lifetime measurements or with a fixed delay for spectral measurements. Spectra were taken at temperatures well above the boiling points of the individual components. The cuvet was placed inside a pressure cell and pressurized to 100 psig with nitrogen. The cell had a 7.5 cm diameter by 20 cm high cylindrical cavity and had four quartz windows located at its midsection. The cuvet was placed in an electrically heated 5 cm diameter brass cylinder, which was insulated from the pressure cell with zirconia felt. Since the cuvet was not strong enough to stand a pressure differential of 100 psi, it could not be sealed; instead, a 50 cm piece of thin wall one-eighth inch diameter stainless steel tubing was wound in a conical spiral and fitted into the teflon stopper in the top of the cuvet. This tubing allowed the pressure inside and outside of the cuvet to equalize and at the same time served as a reflux condenser to prevent the solution from getting out of the cuvet and onto the pressure cell windows.

The spectra were digitized and replotted in a standard format by computer. These normalized spectra are collected in the Appendix.

In the exciplex systems described in the later sections, the following commercially available chemicals were used (abbreviation is given in parentheses): 1) Aldrich; 1-methoxynaphthalene (1-MeON) (98+%), 1-methylnaphthalene (1-MeN) (97%), N,N,N',N'-tetramethyl-p-phenylene diamine (TMPD) (98%, sublimed before use), 1-cyanonaphthalene (1-CNN) (tech., sublimed before use), naphthalene (N) (99+%), fumaronitrile (FN) (98+%), trihexyl amine (THA) (98%), 1,2,4-Trimethylbenzene (124TMB) (99+%), hexadecane (C) (99%); 2) Pfaltz and Bauer; heptyl butyrate (purity not stated), N,N-dibutyl aniline (DBA) (purity not stated). Except as noted, the chemicals were used without further purification.

RESULTS AND DISCUSSION

The results presented here fall into two broad categories: 1) the search for new exciplex systems which would not have the limitations of the naphthalene/TMPD system; and 2) the attempts to thoroughly characterize the naphthalene/TMPD system.

A. New Exciplex Systems

As mentioned previously, through use of the correlations developed by Rehm and Weller, and tables of oxidation-reduction potentials, boiling points, fluorescence spectra and emission properties, one can choose potential exciplex systems which will have approximately the right spectral separation of monomer and exciplex emissions and approximately the right binding energy. Each system must be individually tested however to determine whether it emits strongly and whether that emission persists at high temperatures. Nearly one hundred potential exciplex systems were tested for emission at room temperature; thirty-one systems yielded emitting exciplexes, and five of those systems have exciplex emission at 250°C which is no less than a factor of two weaker than their room temperature emissions. These five best systems are summarized in Table I and are discussed individually below.

1) Most Promising Exciplex Systems

Table I summarizes the characteristics of the five most promising exciplex systems found in the search. The spectra for these systems are collected in the Appendix, and each system is discussed briefly below. In each case, the designations M and N are used to indicate whether the molecule is the primary vapor phase emitter and exciplex former (M) or the ground state reactant (N).

a) 15% Naphthalene(N)/0.5% Tetramethyl-p-phenylene diamine (M) (Spectra A1-6, 19-21)

This system, which has already been used in demonstration experiments, forms a strongly emitting exciplex, whose maximum fluorescence falls near 516 nm at room temperature. The major vapor phase emitter, TMPD, has a short radiative lifetime (4.3 nsec), and hence is only modestly sensitive to quenching by molecular oxygen (fluorescence reduced by roughly a factor of six in air at atmospheric pressure). The main drawback of this system is that naphthalene boils at 218°C and TMPD boils at 260°C, hence, the components may differentially distill out of an evaporating droplet, and thus distort the measurements. In addition, the small spectral separation and small binding energy means that the system is only useful up to about 250°C.

TABLE 1

a) Properties of Monomers

MOLECULE	T_{HP} ($^{\circ}C$)	ΔE_{OO} (eV)	$\lambda_{f,max}$ (nm)	τ_f (nsec)	$I_f(\text{nitrogen})/I_f(\text{air})^a$
TMPD	260	3.40	390	4.3	6
Naphthalene	218	3.97	330	96	112
1-Methylnaphthalene	240	3.82	340	67	79
1-Methoxynaphthalene	265	3.74	348	unknown	unknown
1-Cyanonaphthalene	299	3.67	350	15	18
Trihexylamine	263	3.56	275	2.4	4
Dibutylaniline	274	3.76 ^b	352 ^b	2.78 ^b	4 ^b

TABLE I (cont'd)

b) Properties of Exciplexes

EXCIPIEX	ΔH_{calc} (eV)	λ_f , max (nm) (calc)	λ_f , max (nm) (obs)	$I_f(250^\circ\text{C})/I_f(23^\circ\text{C})$	Intensity (N/TMPD=strong)
N/TMPD	0.74	521	516	0.56	Strong
1-MeN/TMPD	0.87	506	510	0.57	Medium
1-MeON/TMPD	0.72 ^c	516 ^c	518	0.82	Strong
1-CNN/DBA	0.94	492	478	0.68	Strong
1-CNN/THA	0.41 ^d	416 ^d	512	0.58	Medium

Spectral and lifetime data from Berlman (26) unless noted; Oxidation/Reduction potentials from Weinberg (27) except as noted.

a Calculated assuming quenching of fluorescence upon every gas kinetic collision with O_2 at 25°C , 0.2 atm pressure.

b Values for Dimethyl aniline

c $E(A^+/A) = 2.65$ eV (29)

d Potentials for tripropyl amine were used.

b) 10% 1-Methylnaphthalene(N)/1% TMPD(M) (Spectra A4-9,22-24)

This system, in which 1-Methylnaphthalene is used to raise the boiling point of the N component (BP=240°C), produces a slightly weaker exciplex fluorescence, but otherwise is very similar to the naphthalene/TMPD system.

c) 10% 1-Methoxynaphthalene(N)/1.5% TMPD(M) (Spectra A4-6,10-12,25-27)

This system, which is nearly coevaporative, displays strong fluorescence and the best thermal stability of any of the exciplex systems tested. In all other respects, it is also very similar to the naphthalene/TMPD system.

d) 0.4% 1-Cyanonaphthalene (M,N)/10% N,N-Dibutylaniline (M,N) (Spectra A13-18,28-30)

In this system, both monomers emit at approximately 350 nm, and hence the vapor phase emission cannot be unambiguously assigned to either species. The spectral separation and thermal stability are typical of the other systems. A closer match of the boiling points could easily be made by substituting appropriate alkyl groups on the aniline.

e) 10% Trihexylamine(N)/1% 1-Cyanonaphthalene (M) (Spectra A13-15,31-33, no spectra were obtained for THA since it does not absorb at 308 nm)

This system possesses excellent separation between the monomer and exciplex fluorescence maxima, has medium strength exciplex fluorescence and has typical thermal stability. It is, however, more sensitive to oxygen quenching than the TMPD systems. As with the previous system, a vapor phase exciplex emission appears and will complicate the use of this system for diagnostic work. This is the only system for which the calculated fluorescence maximum differs significantly from the observed maximum; it is likely that Rehm and Weller's correlations apply only to aromatic systems and not to the aliphatic amines.

Optimal concentrations have not been determined for systems b), c), and e); it is therefore possible that they can still be improved modestly.

In summary, we now have a set of potential exciplex diagnostic systems, each of which has strong and weak points. It is likely that, rather than having one outstanding and universal system, it will be necessary to match the exciplex system characteristics to the demands of a particular problem.

2. Interfering Photochemistry: Examples of Two Promising Systems Which Failed

a) 1,2,4-Trimethylbenzene (M)/Fumaronitrile(N)

On the basis of calculations based on tabulated parameters and the Rehm and Weller correlations, this system was thought to be an excellent candidate for a visualization system. It was estimated to have a large spectral separation, and hence a large binding energy, as well as being a relatively low-boiling (175°C), nearly coevaporative system. The system does show a large spectral separation: the 124 TMB fluorescence peaks at 290 nm and the

exciplex emission peaks at 520 nm. The fumaronitrile itself is not fluorescent, and hence there is no fluorescence interference from that source in the monomer fluorescence region. The fumaronitrile is not very soluble in nonpolar solvents such as hexadecane, and hence a mixed solvent such as hexadecane/heptyl butyrate is used to dissolve the fumaronitrile. This more polar solvent stabilizes the relatively polar exciplex and results in an additional red-shift of the exciplex fluorescence by 10-20 nm. However, as the temperature is raised, both the monomer and exciplex fluorescence decrease rapidly, and above 125°C there is virtually no emission from either species. The electronically-excited alkyl benzenes undergo a thermally-activated internal rearrangement to form a variety of Dewar benzene-like molecules(30), and hence at higher temperatures the monomer excited state disappears before it can fluoresce or react to form an exciplex. The alkyl benzene rearrangement is a unimolecular reaction, and hence, its rate cannot be manipulated by changing the concentration of species in the solution. The system had to be abandoned as a candidate for a vapor/liquid visualization diagnostic.

b) Cyanonaphthalene/TMPD

This potential exciplex system also looks very good on the basis of the Rehm and Weller correlations. It should show a spectral shift of some 180 nm between the maxima of the monomer and therefore, it should be possible to develop mixtures for which the $M^* + N = E^*$ equilibrium would be dominated by E^* even for temperatures as high as the boiling points (265°C) of this nearly coevaporative system. However, when the components are mixed at room temperature, the solution immediately turns yellow: the selection of a highly effective electron donor and a highly effective electron acceptor, chosen in order to develop a system with large binding energy and spectral separation, resulted in the formation of a ground state charge transfer complex which has its own absorption (and possibly fluorescence), and hence this system was not investigated further.

B. Characterization of the Naphthalene/TMPD Exciplex System

This exciplex system was used in the initial demonstration of the exciplex vapor/liquid visualization technique, and with different concentrations, in the demonstration that the exciplex techniques can, even at this stage of development, be used to photograph a two-dimensional slice of an evaporating fuel spray. In order to develop a standard for the characterization of new systems, and in order to understand the underlying photo-physics of these demonstration experiments, a closer study of the naphthalene/TMPD system was made.

Using 266 nm excitation, vapor spectra (A42-45) were taken at temperatures up to 225°C and liquid spectra (A34-41) were taken at temperatures up to 350°C. The key element to be noted in these spectra is that the spectral shapes of the vapor and liquid spectra change as a function of temperature; as a result, broad band filters should not be used to separate the vapor and liquid emissions since the intensity measured will represent a confounding of the density of fluorescers with the changing spectral shape.

The vapor spectra change shape as the temperature rises, primarily because they are a sum of naphthalene and TMPD emissions. Naphthalene (BP 218°C) is more volatile than TMPD (BP 265°C) and its spectrum dominates the low temperature spectrum; TMPD is the stronger emitter and as the temperature rises so that more TMPD is evaporated, its emission eventually dominates the high temperature emission. In addition, however, the first excited singlet state of TMPD lies below that of naphthalene and hence there is efficient energy transfer from excited naphthalene to TMPD; as the vapor density rises, these energy transfer processes result in the eventual disappearance of naphthalene vapor fluorescence in favor of TMPD fluorescence.

It should also be noted that, in earlier work, the vapor emission was shown to have a long tail in the visible and this was suggested to be vapor phase exciplex emission(14). These spectra do not confirm that observation; it was likely due to liquid phase emission. This latter result is the more desirable, for it means that the spectral overlap between the vapor and liquid emission spectra for the naphthalene/TMPD system is significantly less than it was thought to be.

In the liquid phase spectrum the changes are more complicated. The solutions with 2.5% naphthalene, 1.0% TMPD (w/w) show low temperature phenomena not seen in earlier measurements on solutions with 10% and 15% naphthalene concentrations(14). At low temperatures there is a broad band peaking at about 500 nm due to the exciplex, which is strongly favored thermodynamically at these temperatures. However, there are also significant minor emissions at 340 nm and 380 nm from excited naphthalene and TMPD; these emissions occur because the solvent, at these low temperatures, is too viscous for the excited species to diffuse to a reaction partner during its fluorescence lifetime(31). Thus the kinetics of exciplex formation, as well as the thermodynamics become important. As the temperature rises, the viscosity of the hexadecane drops and these monomer emissions become less important relative to the exciplex emission. In addition, as the temperature rises, the exciplex emission itself shifts toward higher energies. This effect, which is not fully understood, has been observed in other exciplex systems(32). Finally, the $M^* + N = E^*$ equilibrium is temperature dependent, and so as the temperature rises, the fraction of the excited state population in the exciplex decreases and the ratio of exciplex emission to TMPD emission decreases. It is this shift in the exciplex equilibrium which fundamentally determines the upper temperature limit for a particular exciplex system. For this system, the highest useful temperature is approximately 250°C.

The naphthalene/TMPD solutions in these experiments were taken to temperatures as high as 400°C, and when returned to room temperature showed only barely detectable discoloration. Hence, the thermal stability of the solutions, in the absence of molecular oxygen, should not be a problem.

In addition to these spectra, the fluorescence lifetime of the naphthalene/TMPD exciplex at room temperature for a 2.5% naphthalene, 1.0% TMPD (w/w) solution in hexadecane was determined to be 51 ± 5 nanoseconds. This value is in the middle of the range of typical exciplex lifetimes, and is consistent with the estimates made in earlier papers.

These results obtained with the naphthalene/TMPD system have implications for the evaluation of other exciplex systems. The following conclusions can be drawn:

1) Reliable high temperature spectra can probably be obtained if molecular oxygen is excluded from the system. Temperature and irradiation with ultraviolet light by themselves do not cause serious degradation of the system.

2) Quantitative work with exciplex systems will probably require that they be compounded so that only one of the monomers is fluorescent. In this manner, one can assure that the vapor phase emission is proportional to the monomer concentration. At present, visualization of the liquid phase is restricted to temperatures at which the exciplex emission dominates that of the monomer; extension to higher temperatures will probably require extensive deconvolution.

3) It is not necessary to compound the exciplex systems so that the monomer emission is completely suppressed at lower temperatures. The kinetic effects shown in the lower temperature 2.5% naphthalene/1.0% TMPD spectra did not interfere significantly with the demonstration fuel spray visualization photographs taken earlier.

AREAS OF FUTURE WORK

The work described in this report was originally part of a three year proposed program for the design and development of fluorescent sensors for fuel sprays. The characterization and testing of new exciplex systems will continue under a subcontract to the University of Texas at Dallas from United Technologies Research Center(USA prime contract DAAG29-84-C-0010). Included also in this subcontract is research on ways to use similar fluorescent systems to determine other fuel spray properties such as droplet temperatures, absolute oxygen concentrations, and fuel/oxygen equivalence ratios.

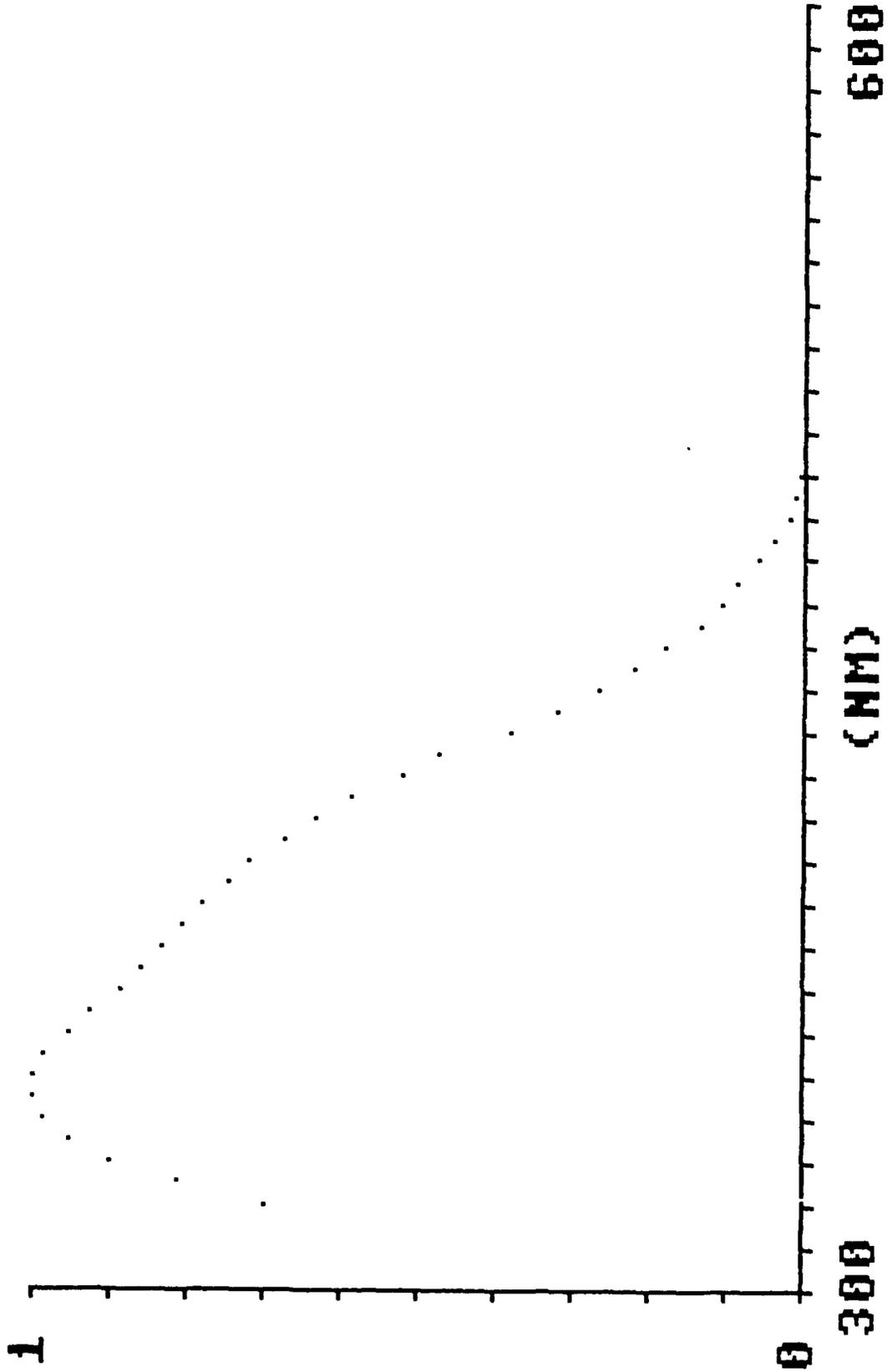
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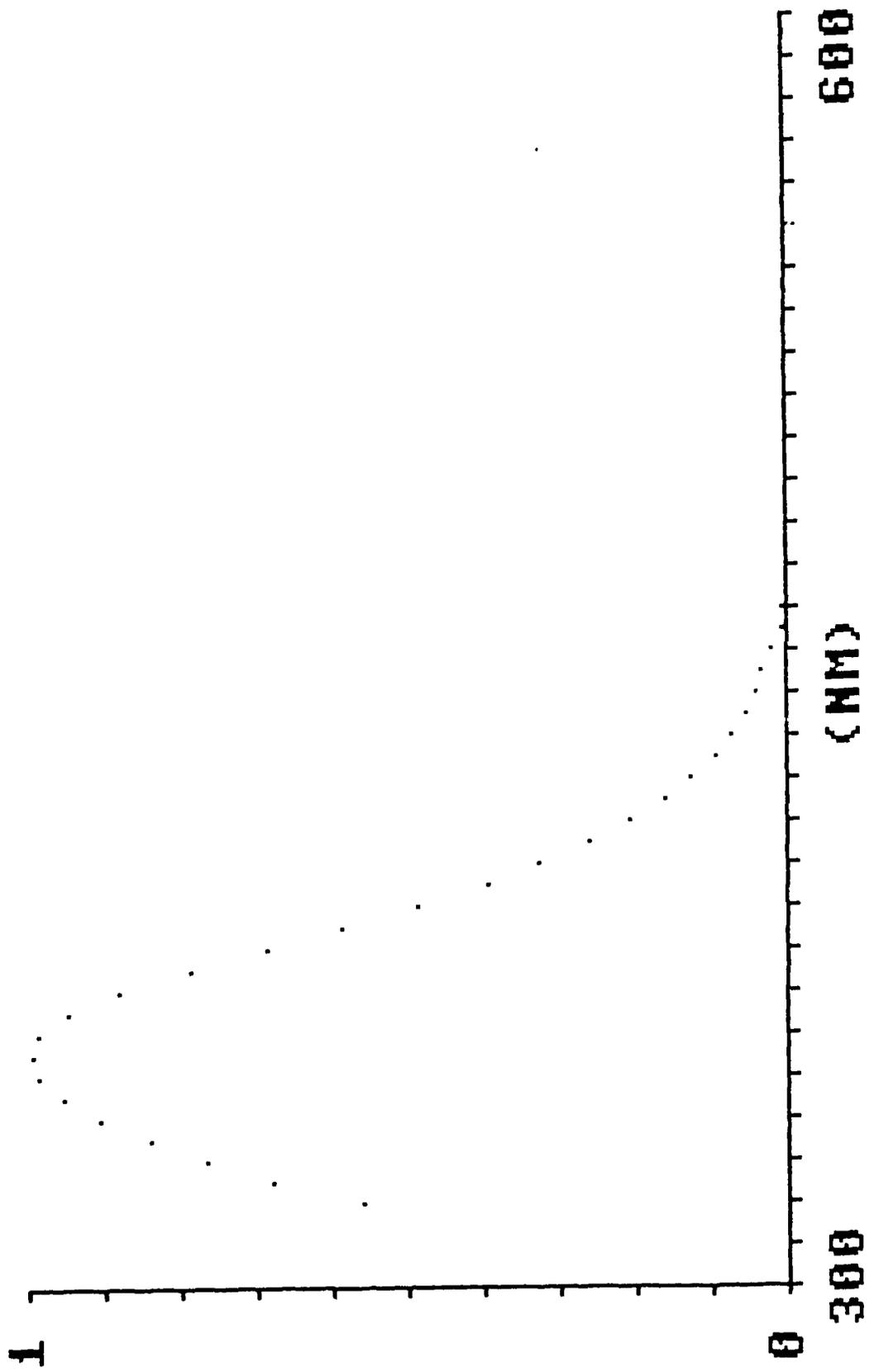
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32. R. A. Caldwell, private communication.

APPENDIX
Fluorescence Spectra

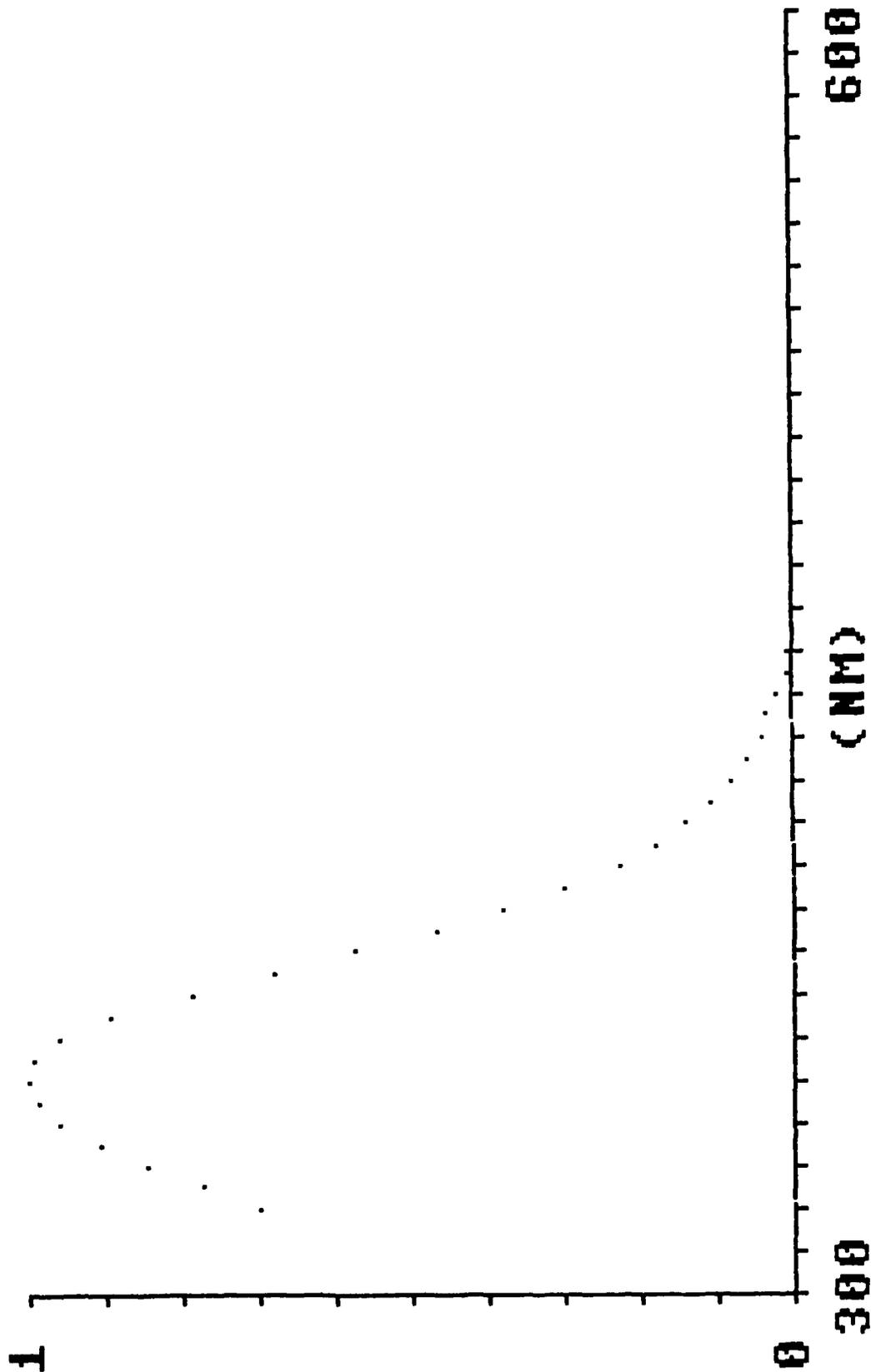
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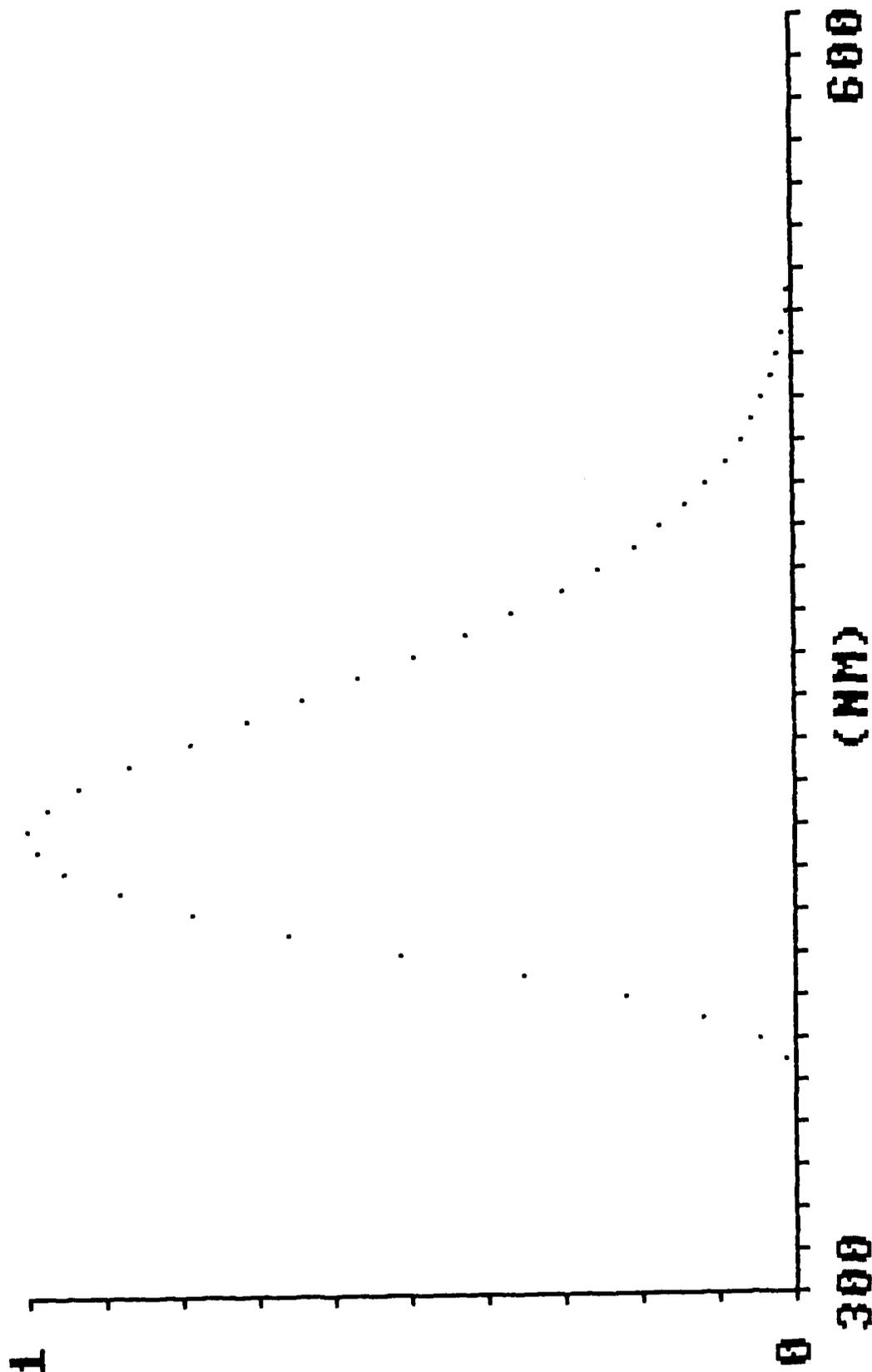
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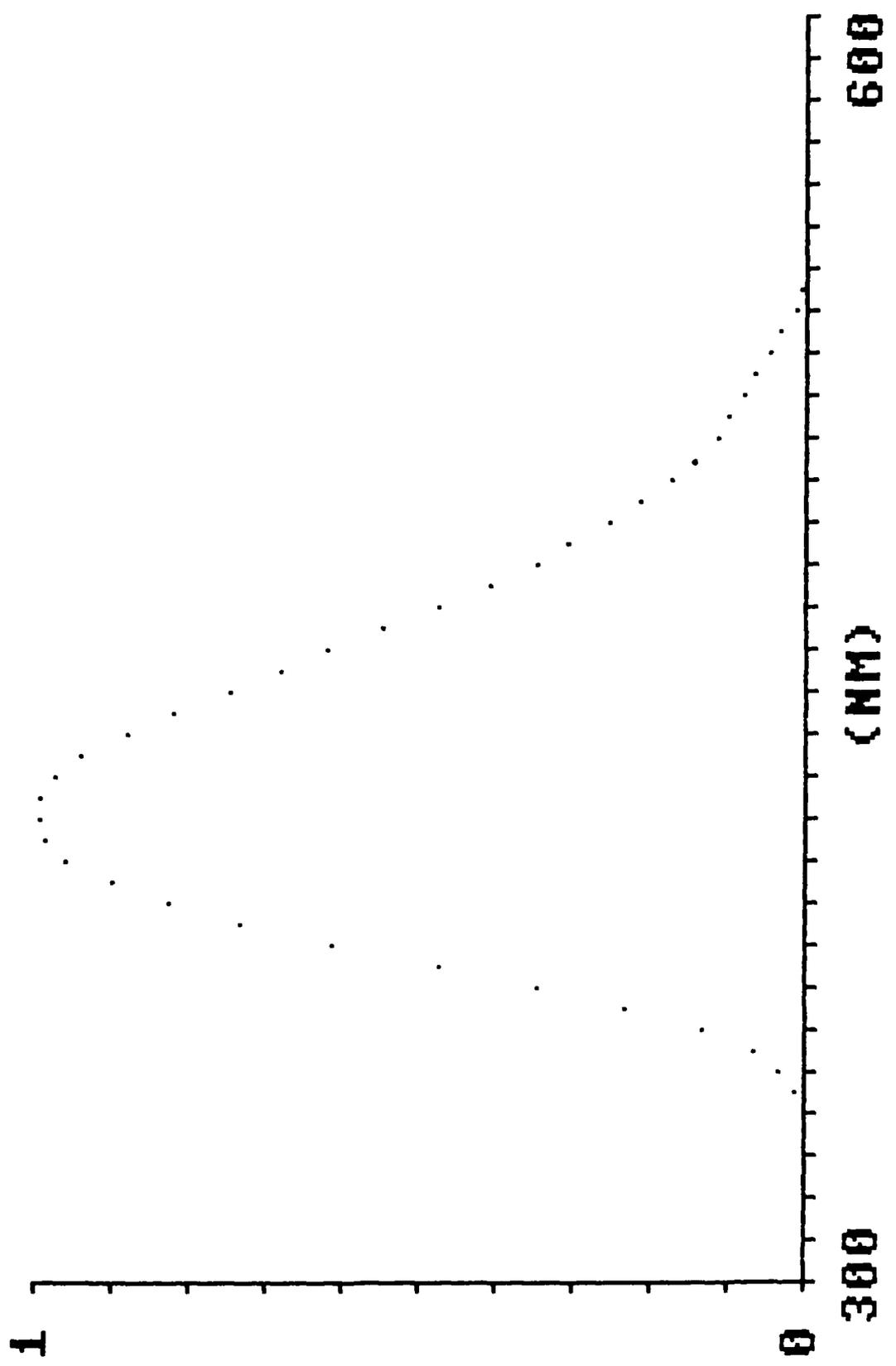
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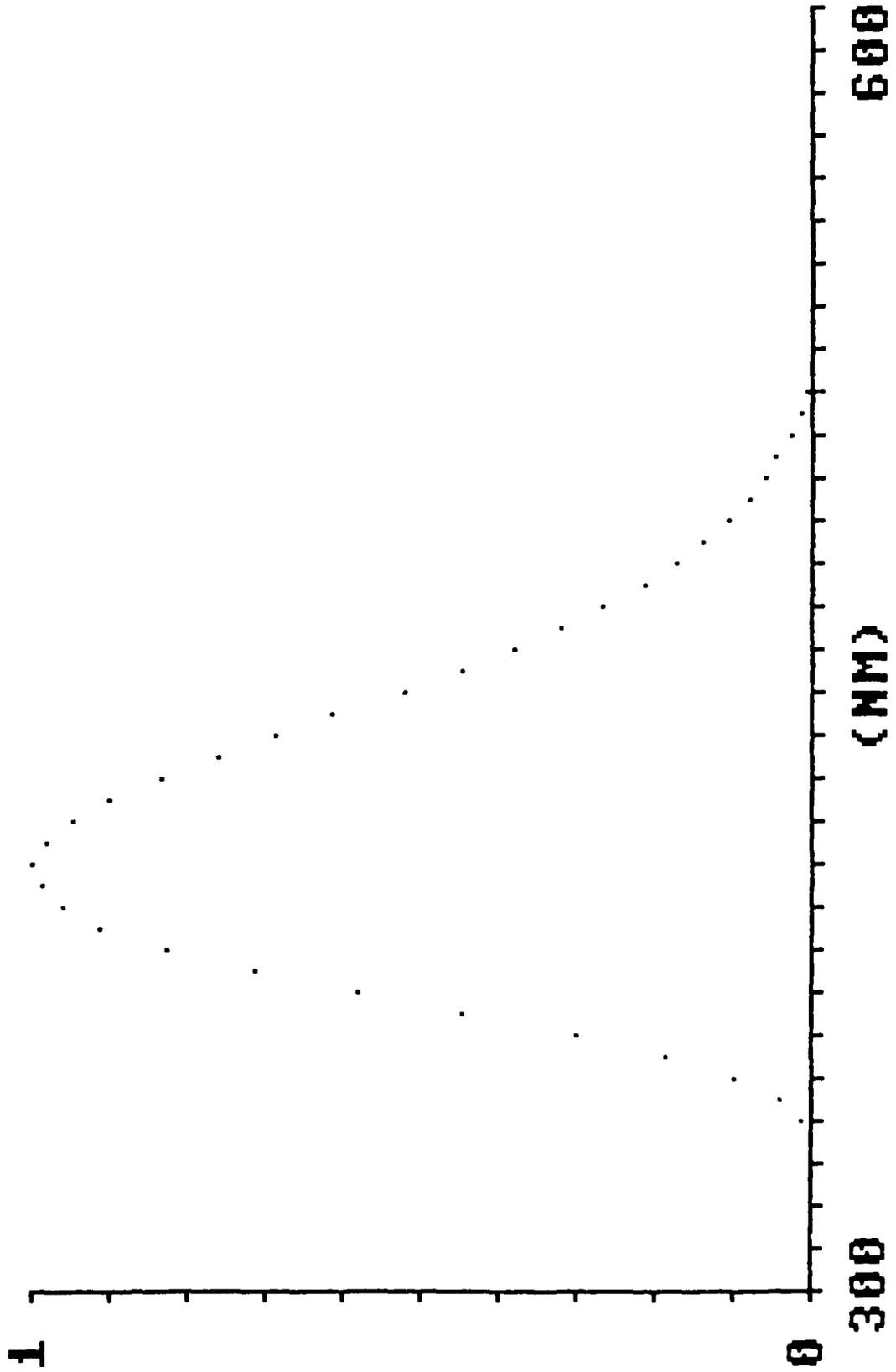
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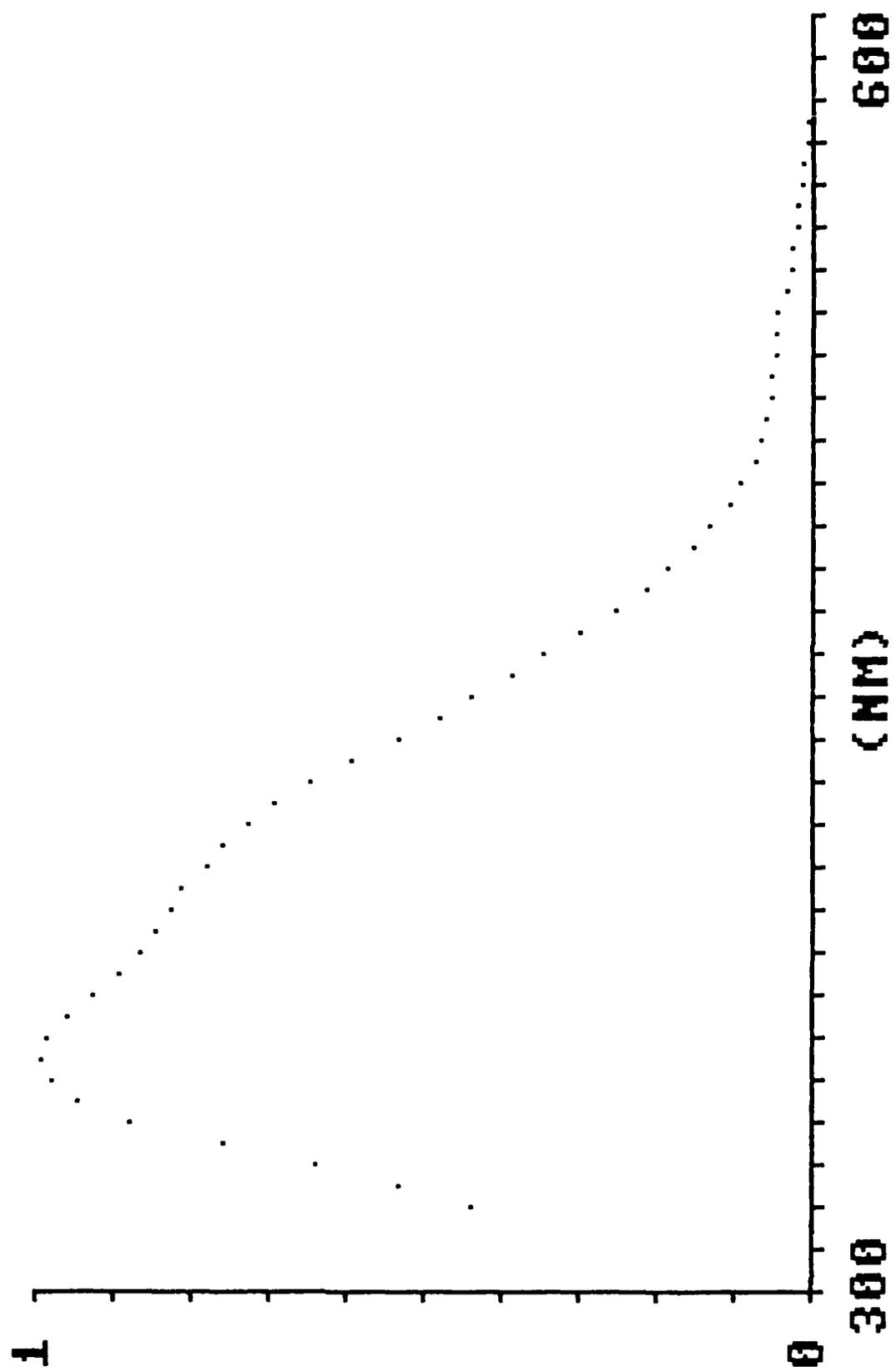
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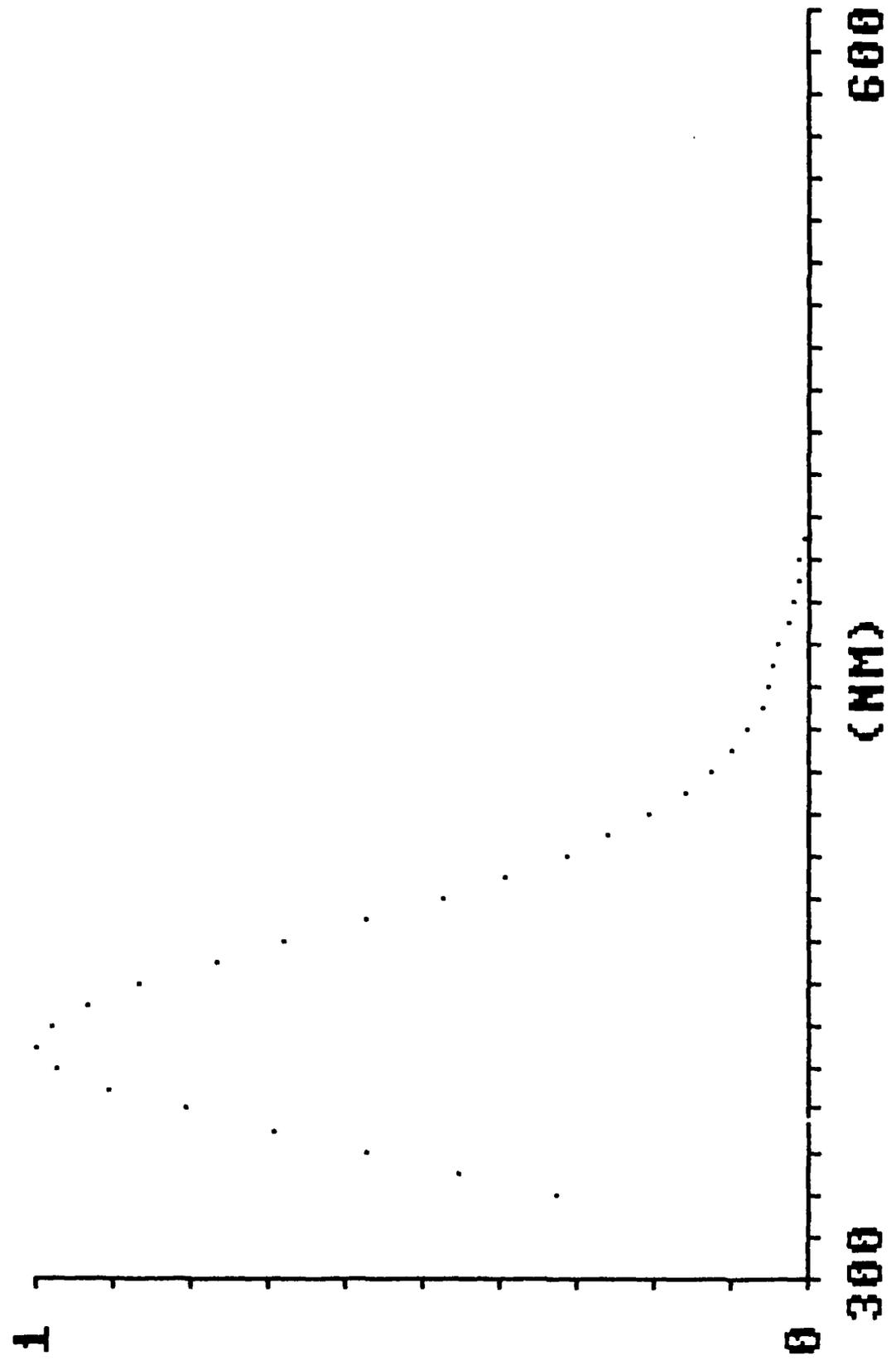
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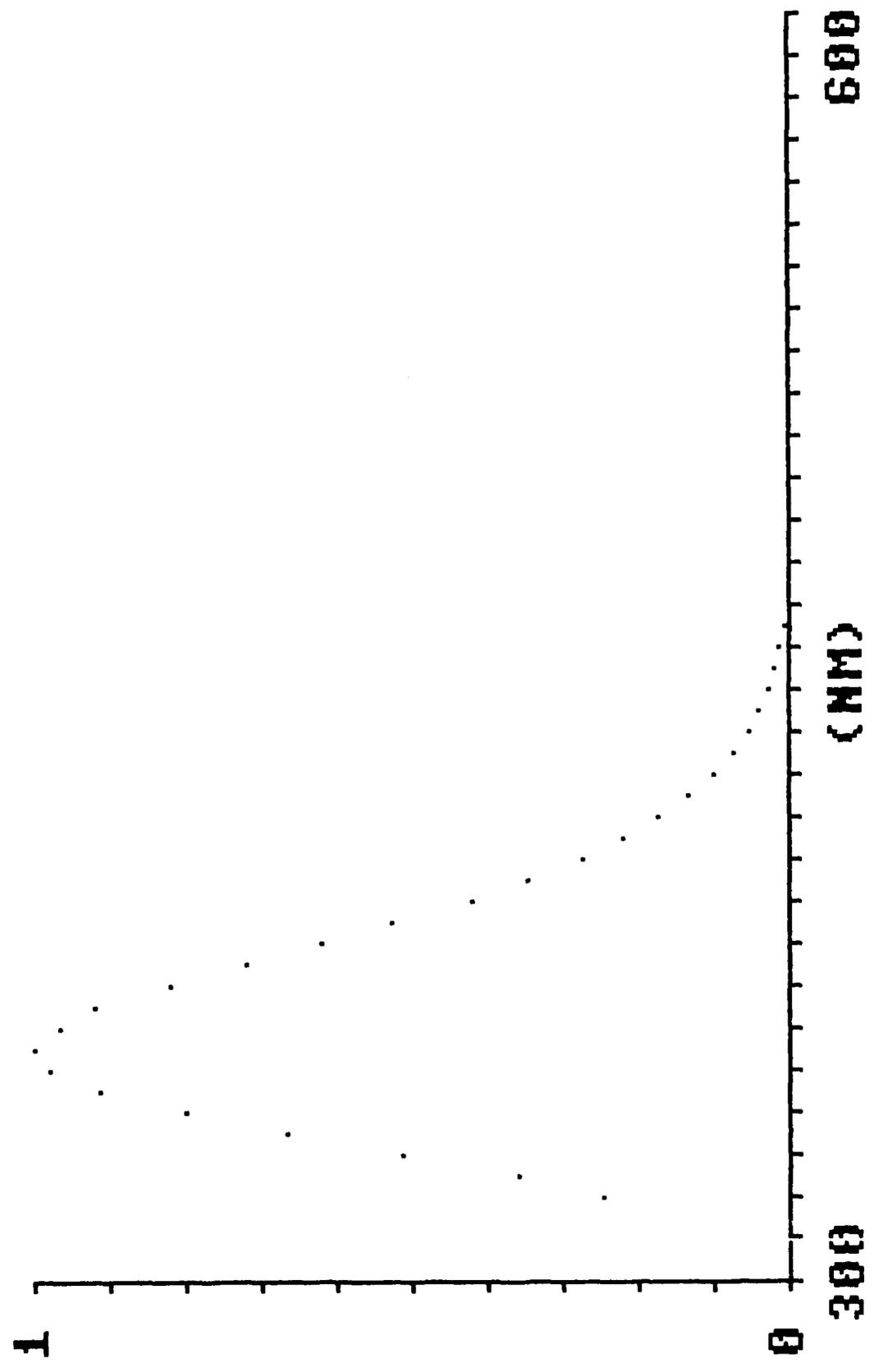
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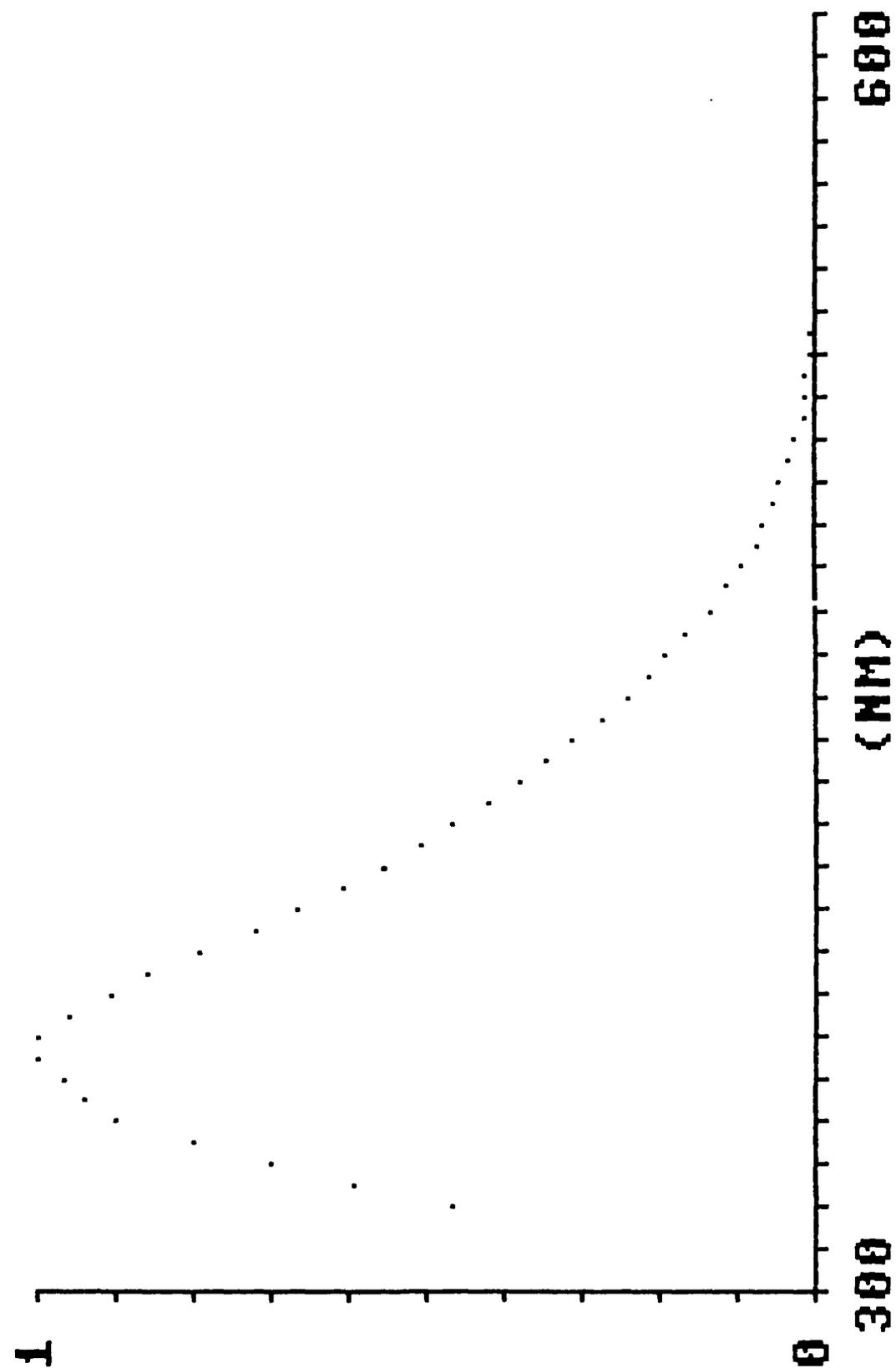
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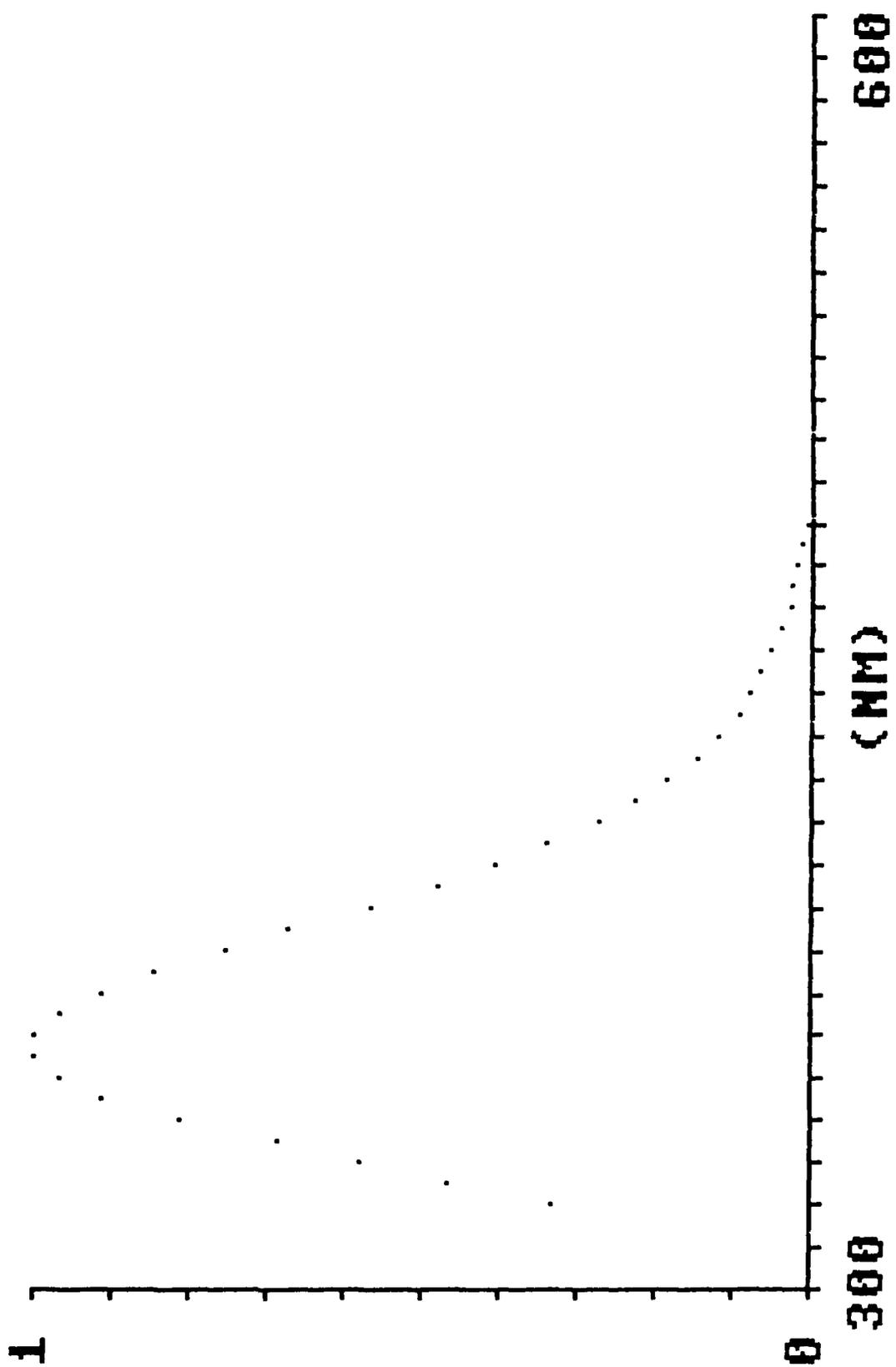
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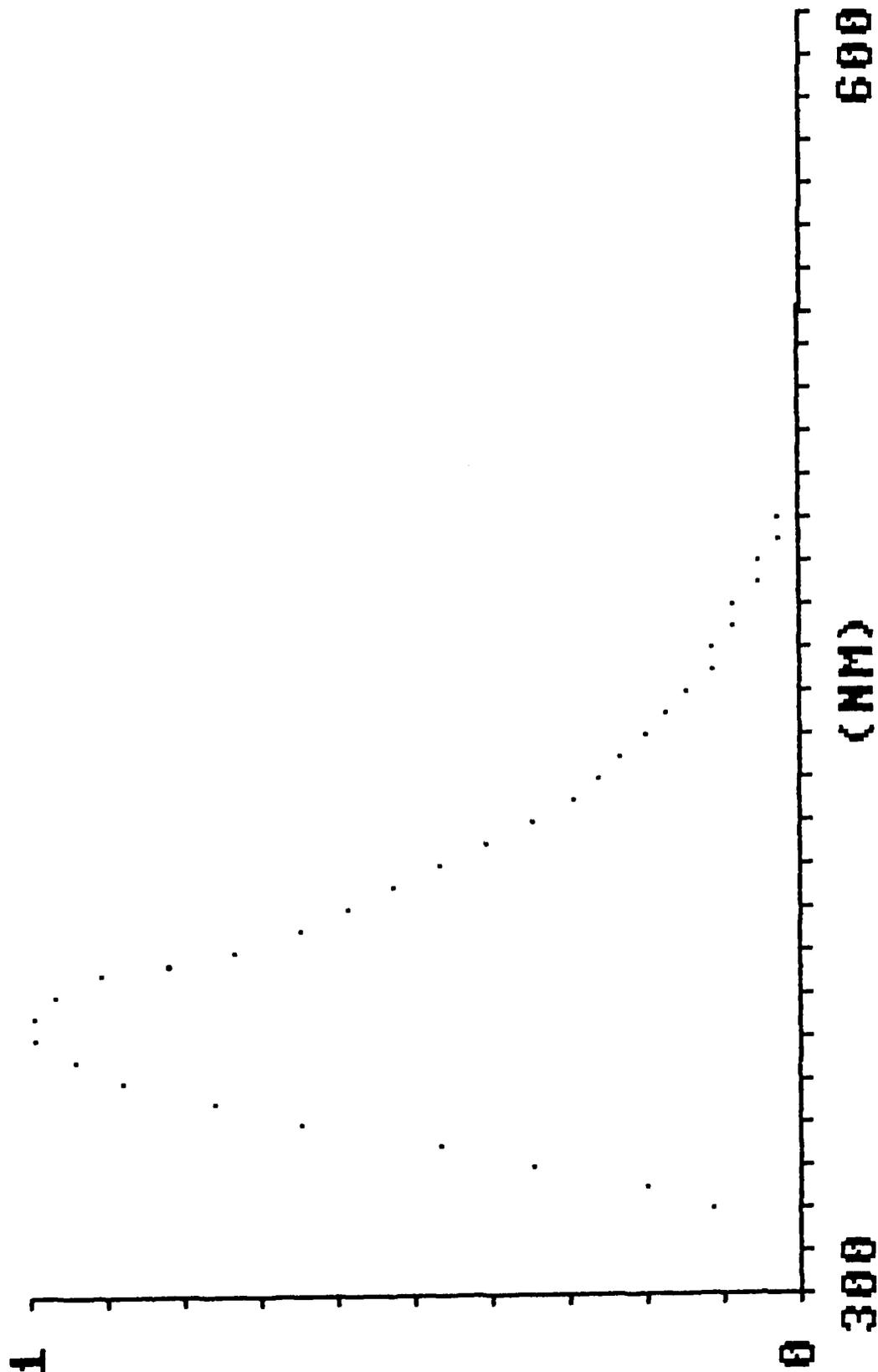
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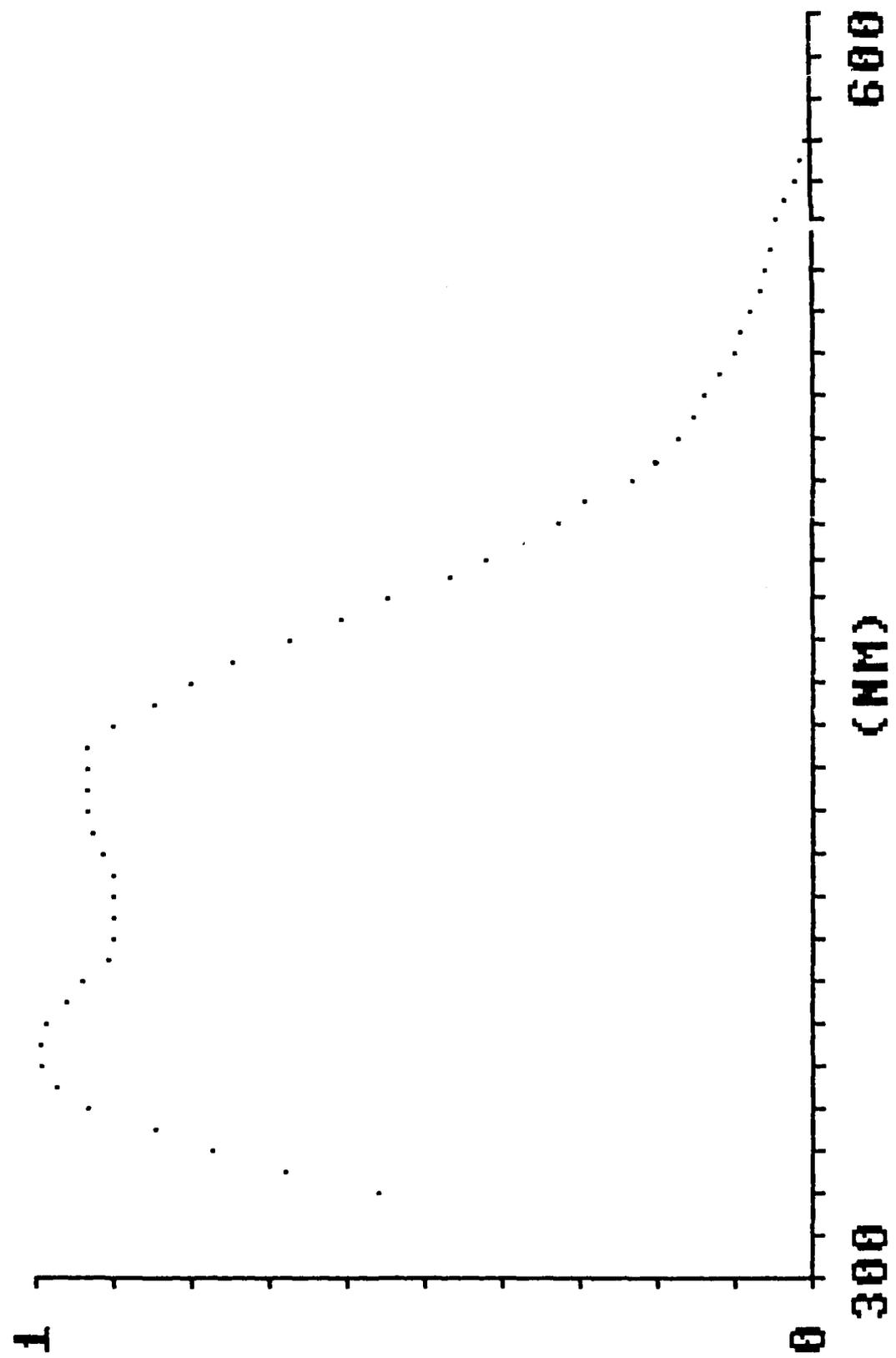
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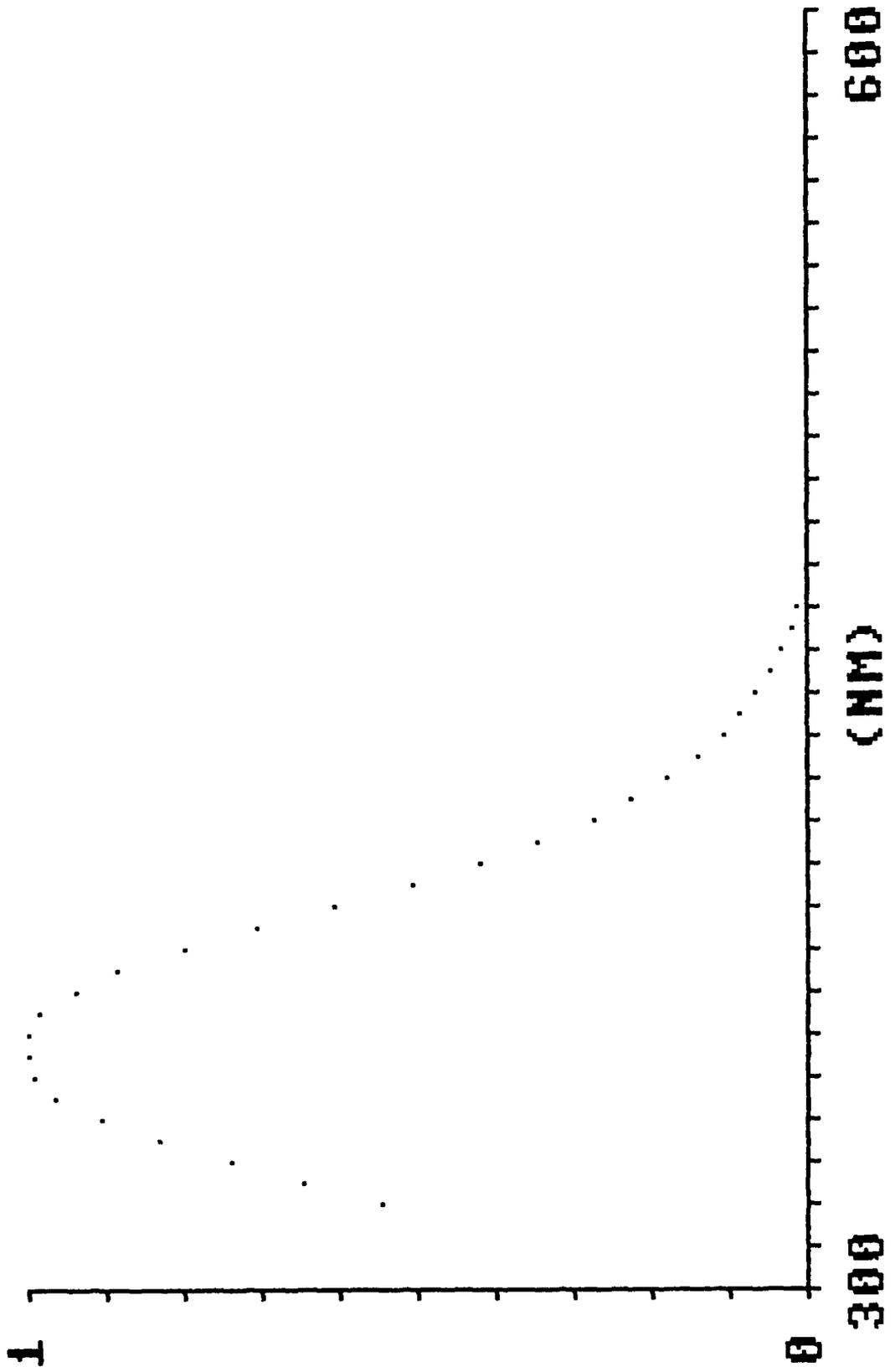
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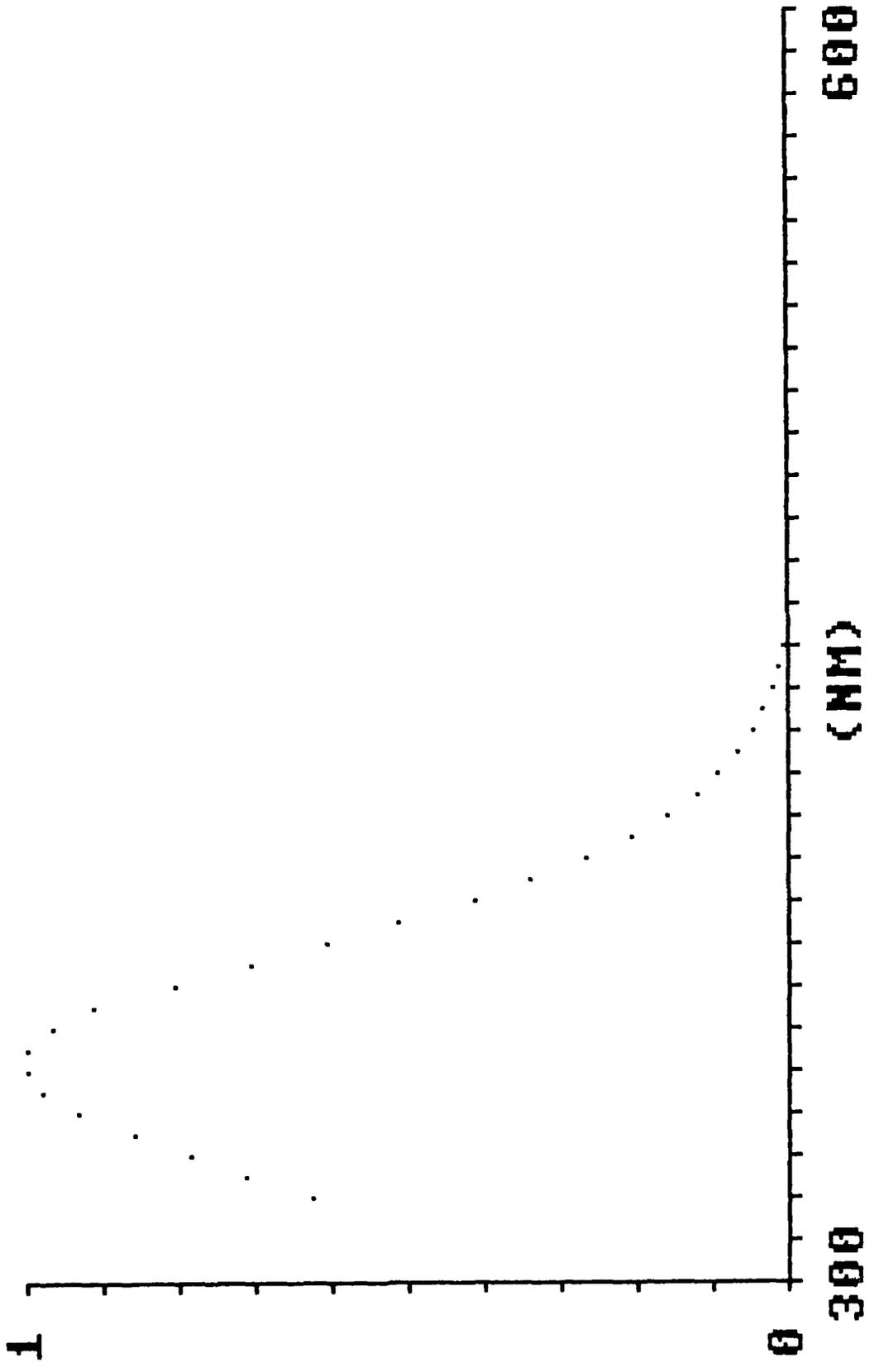
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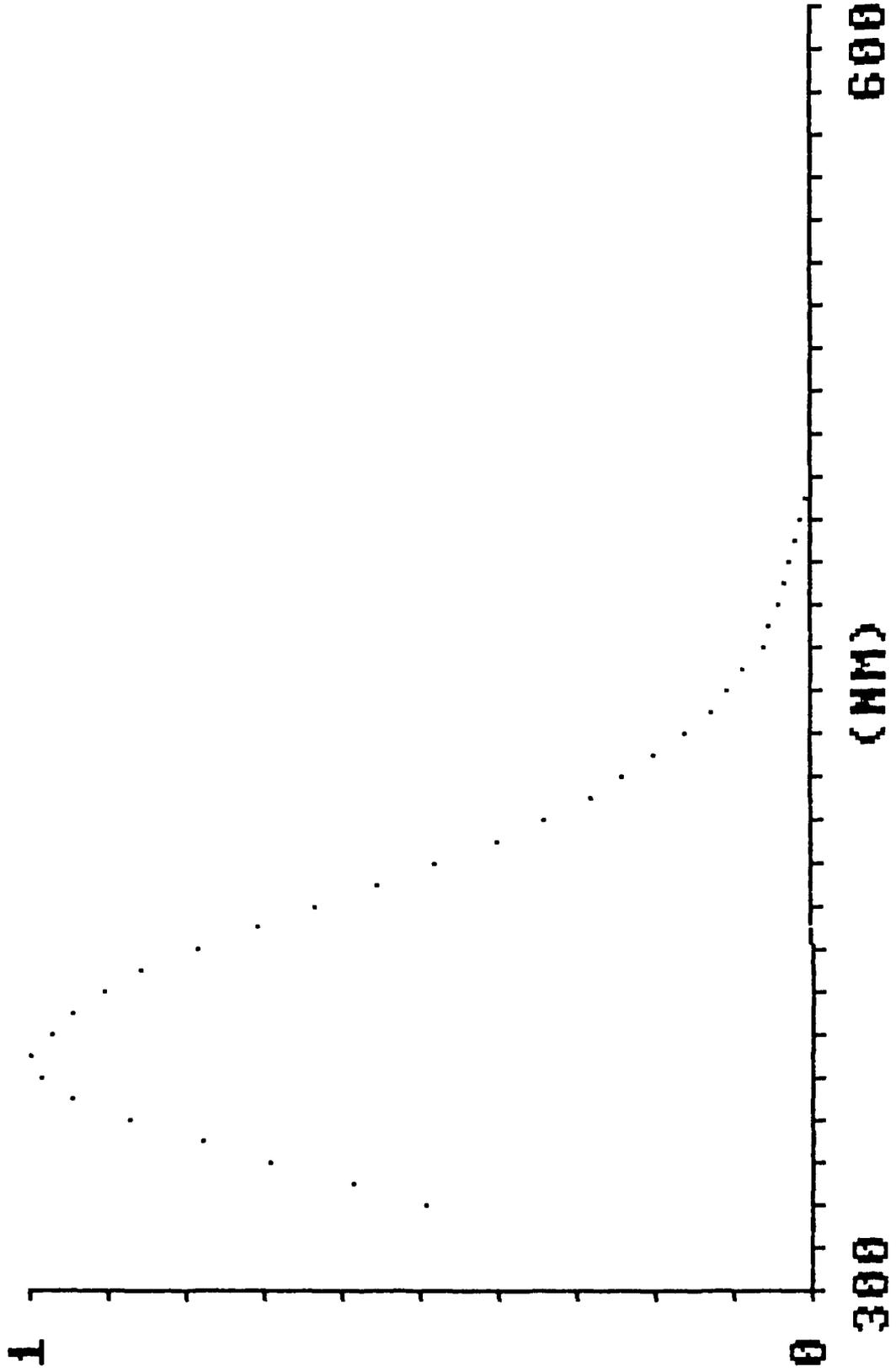
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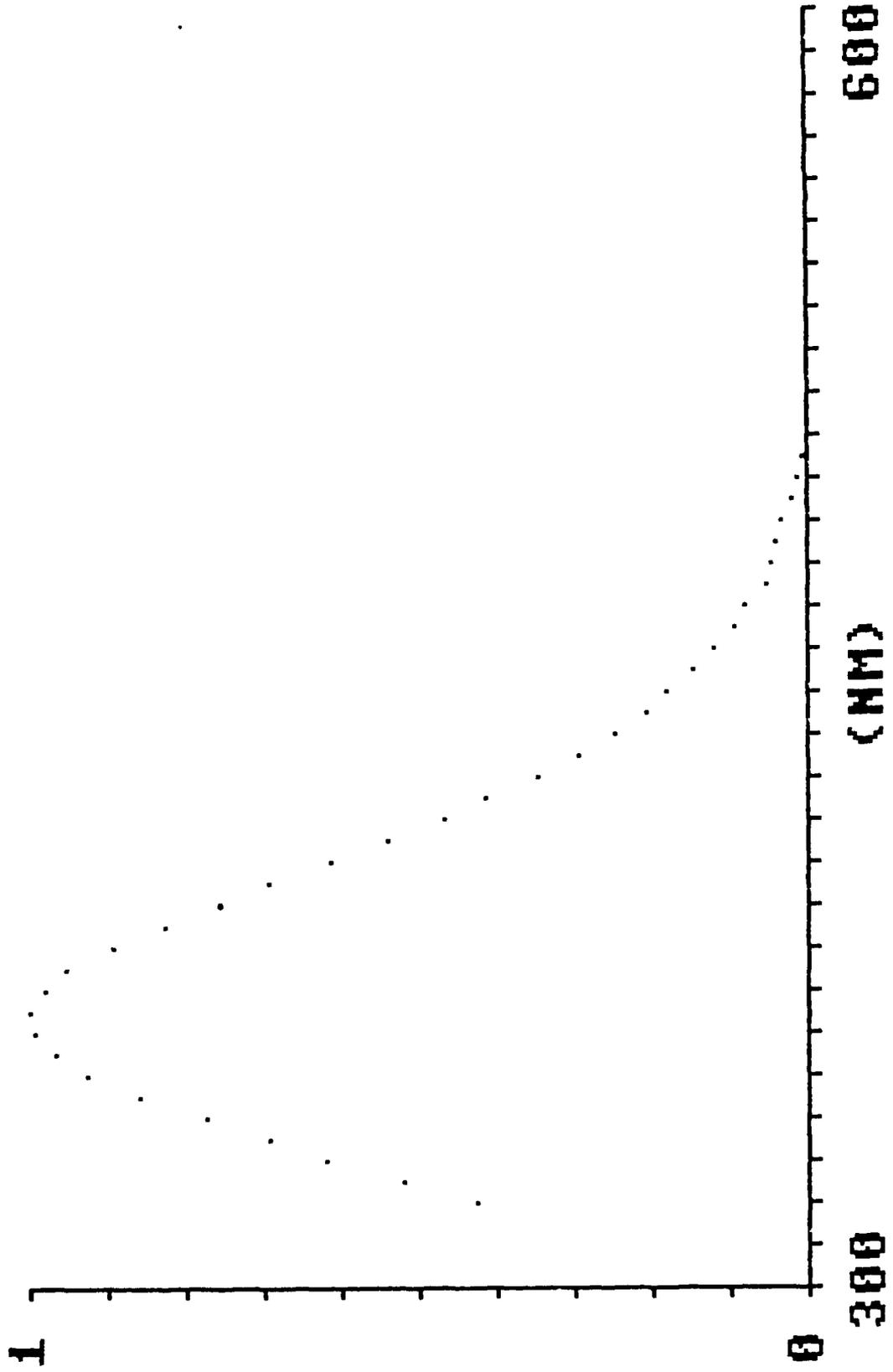
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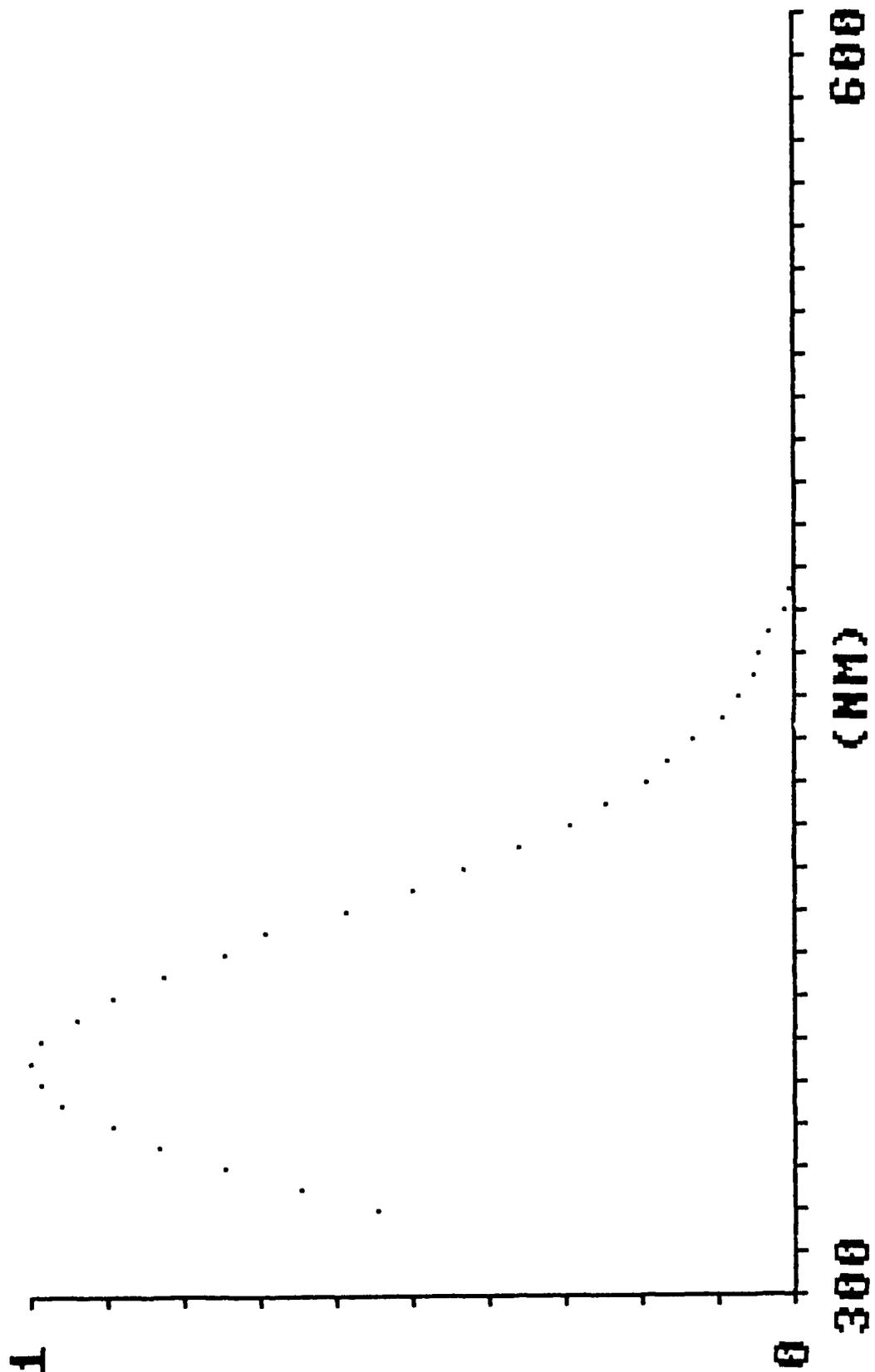
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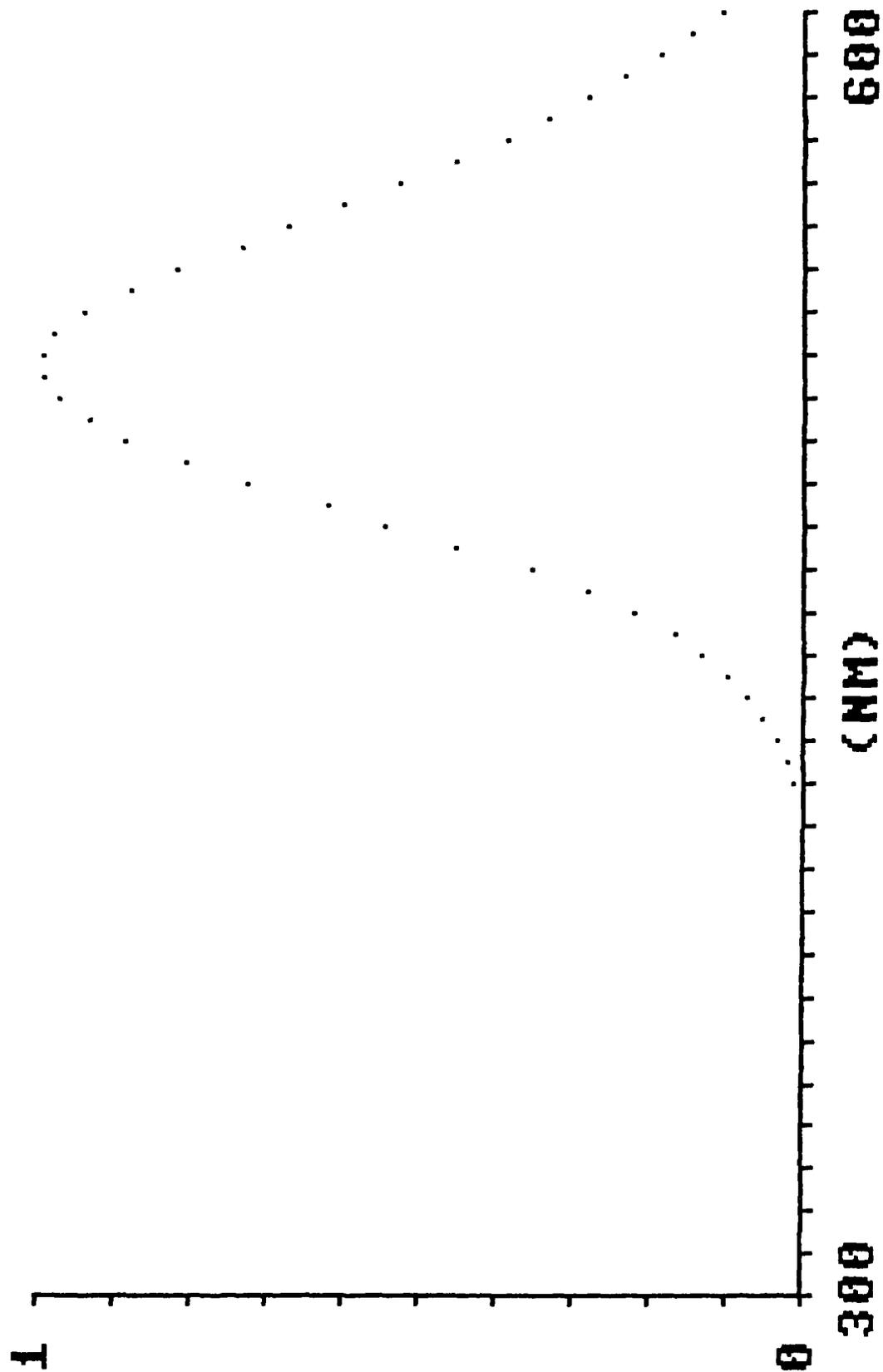
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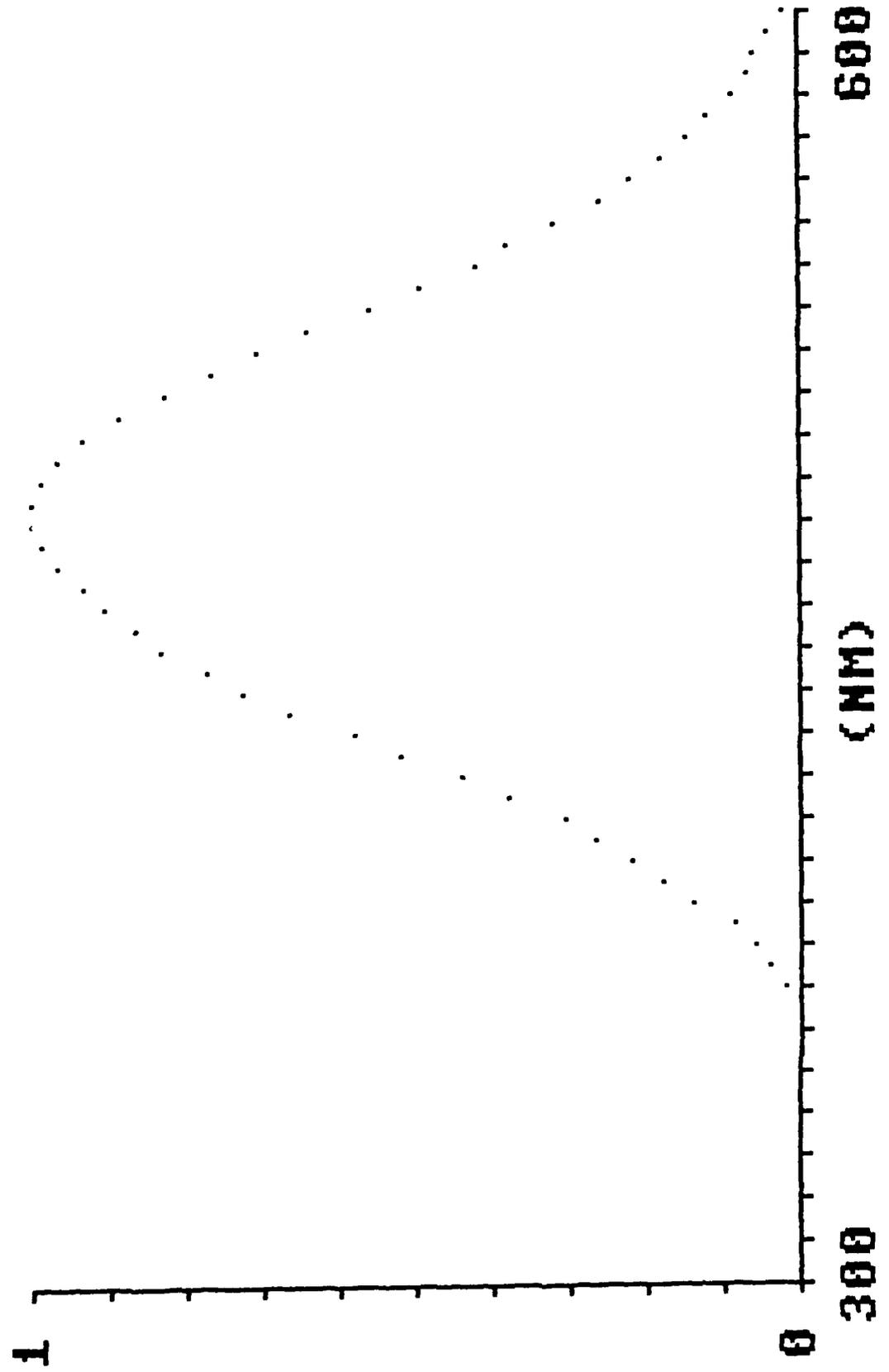
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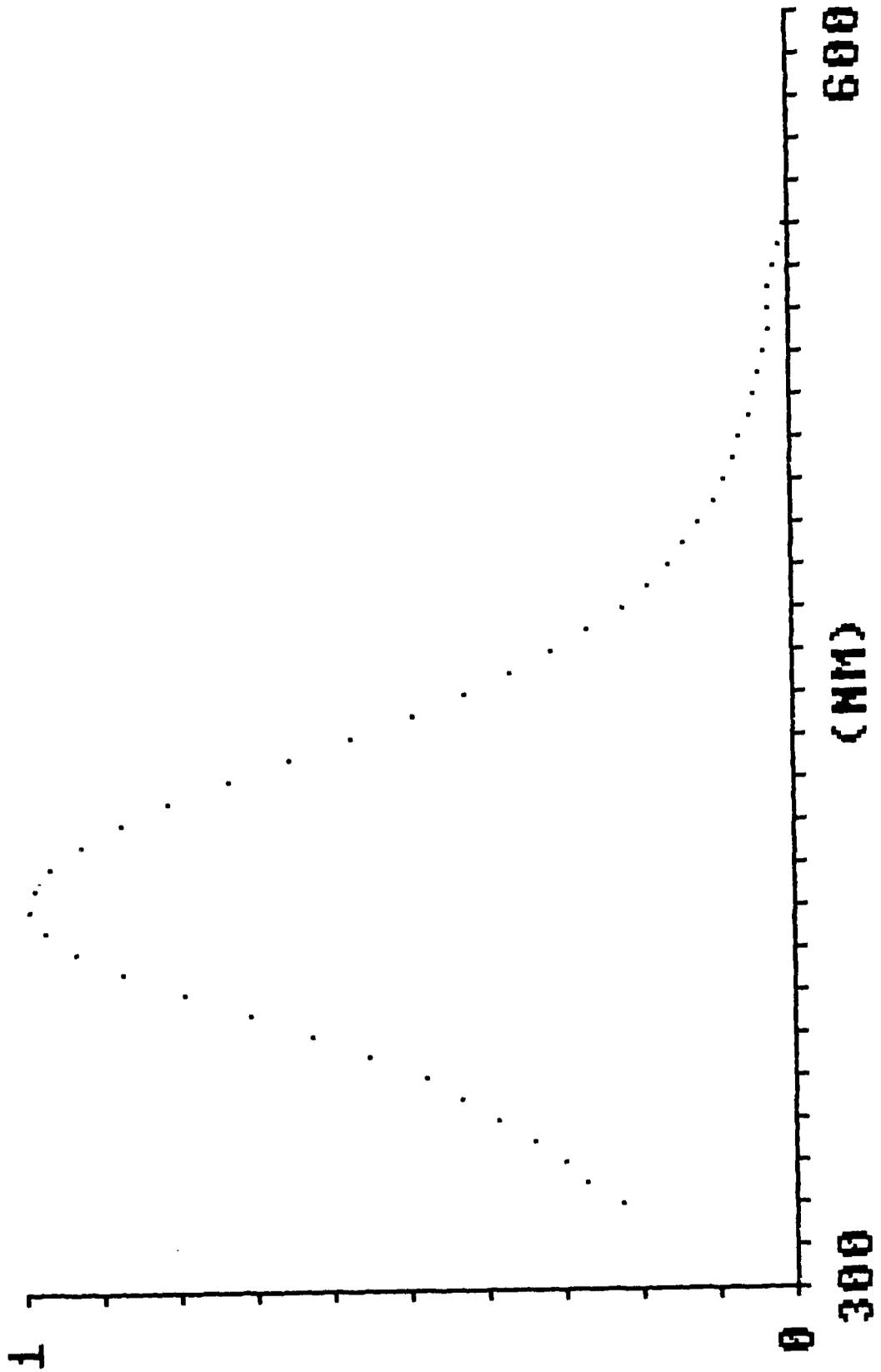
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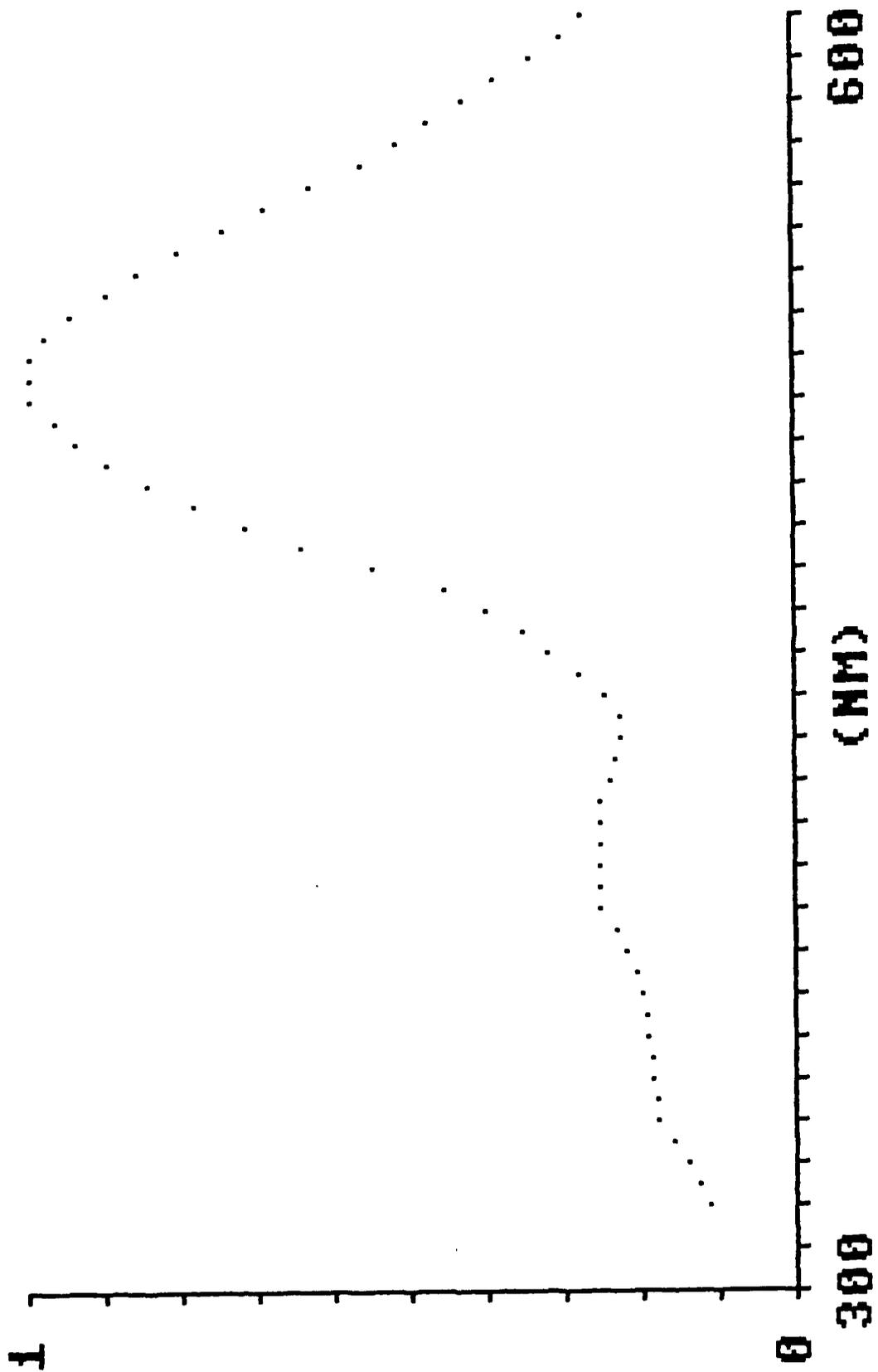
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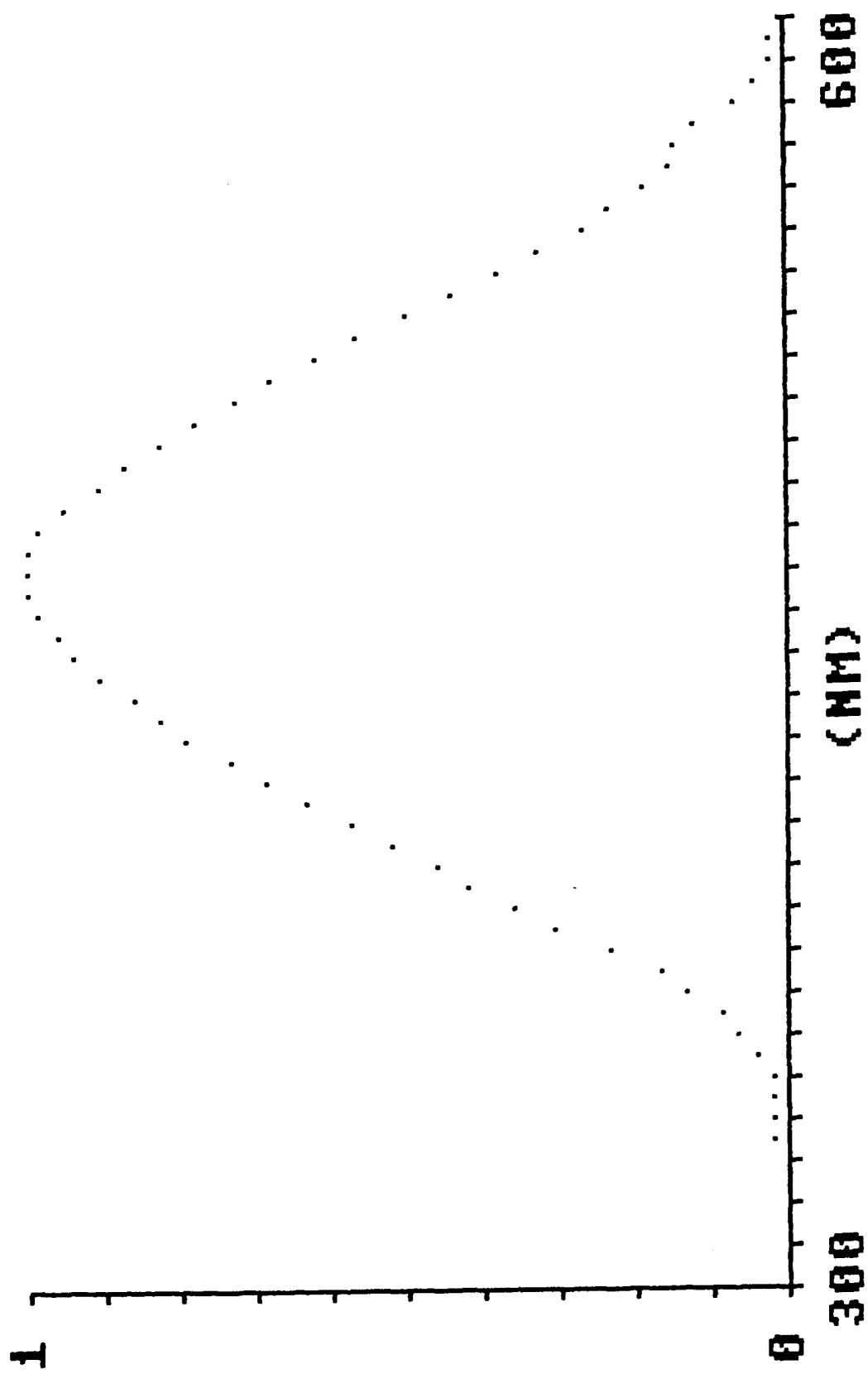
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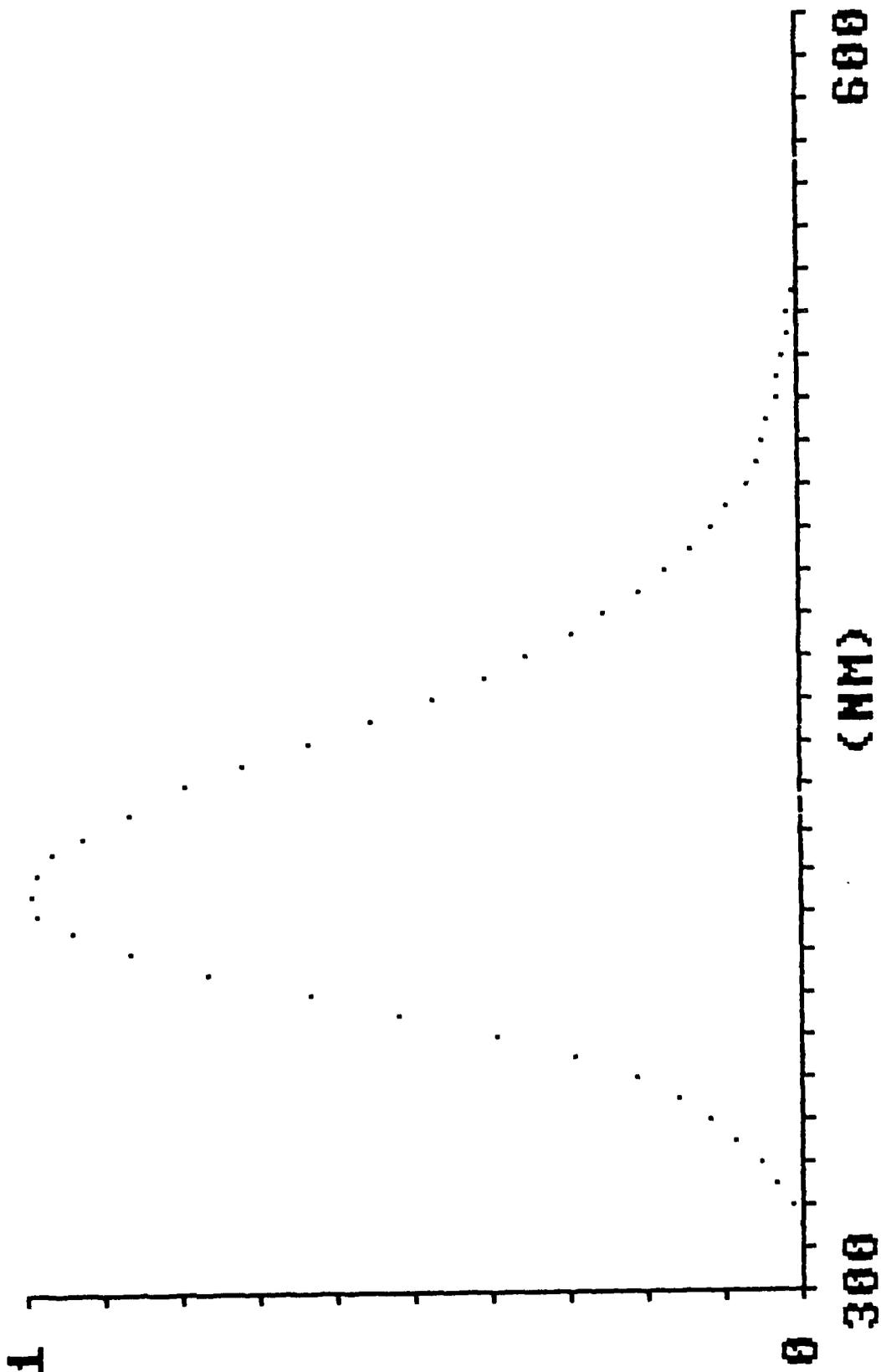
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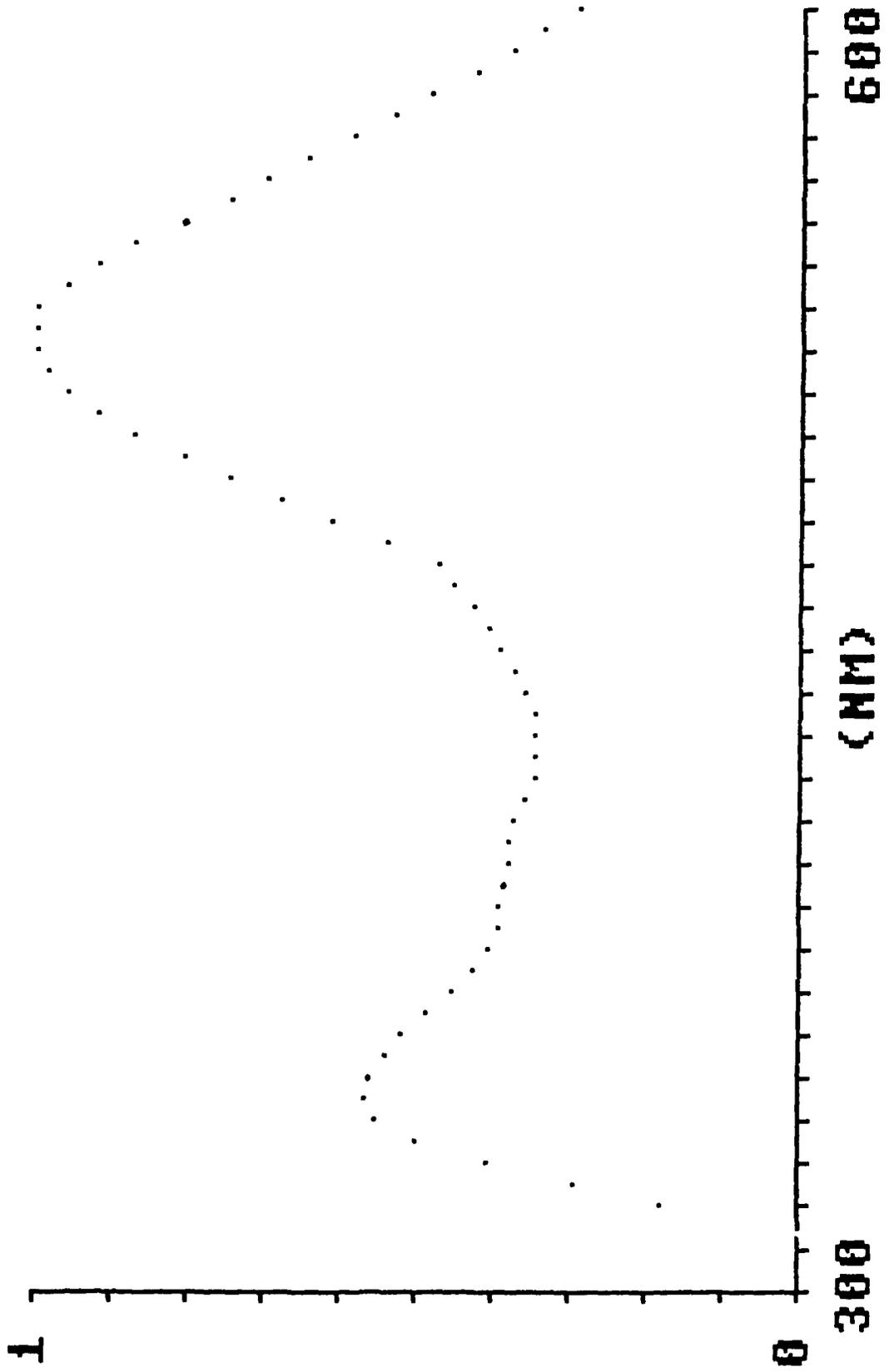
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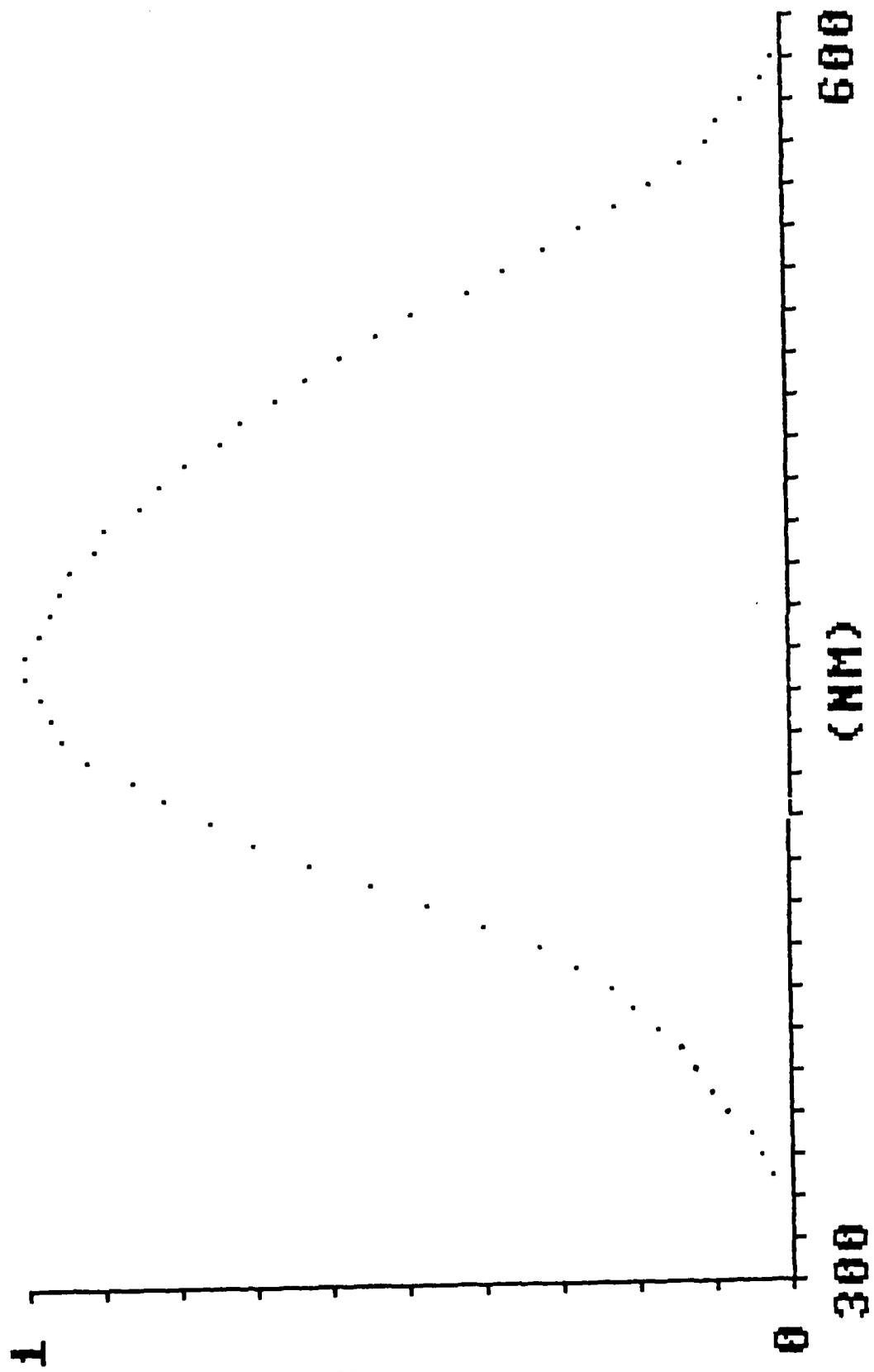
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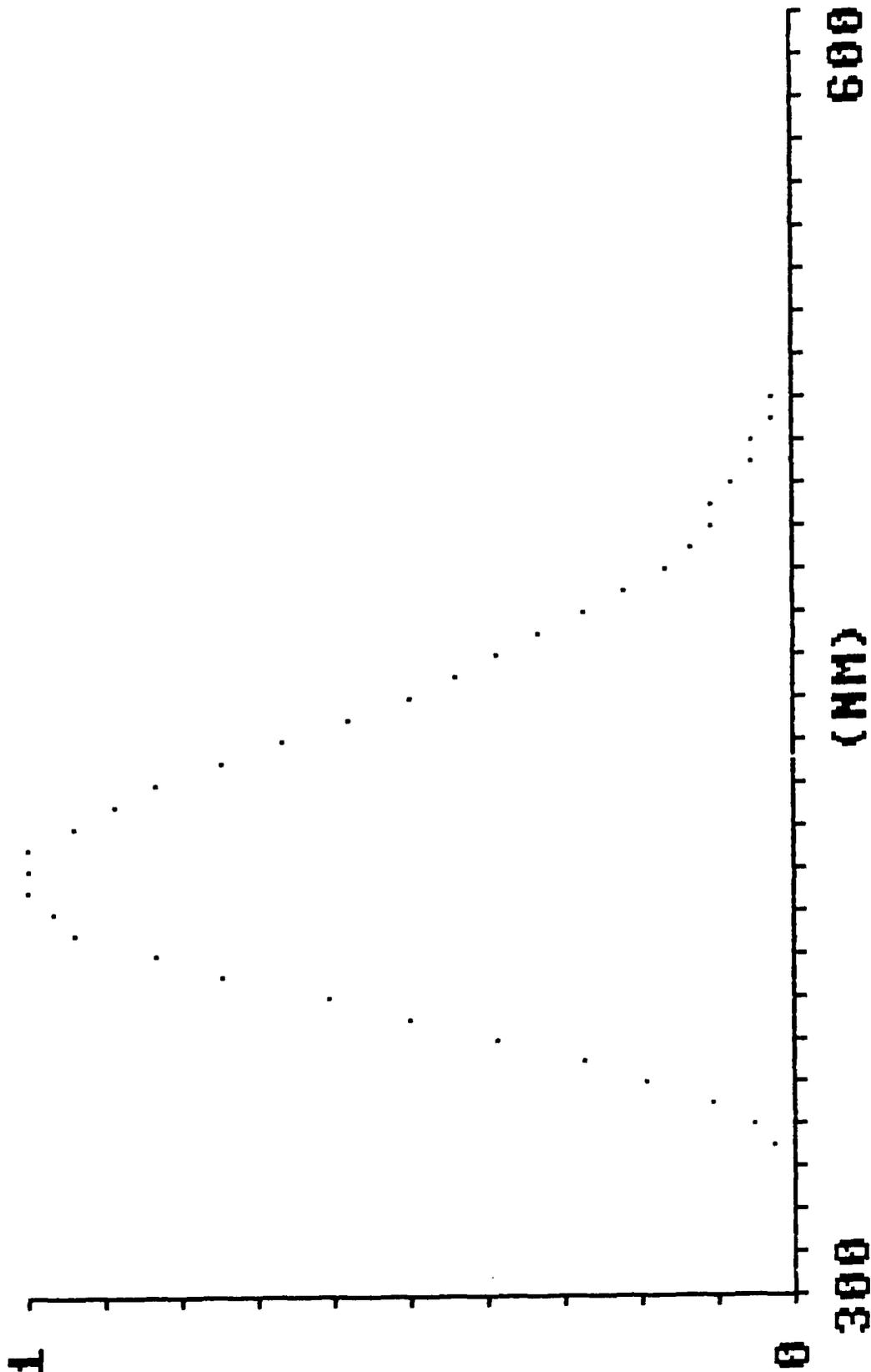
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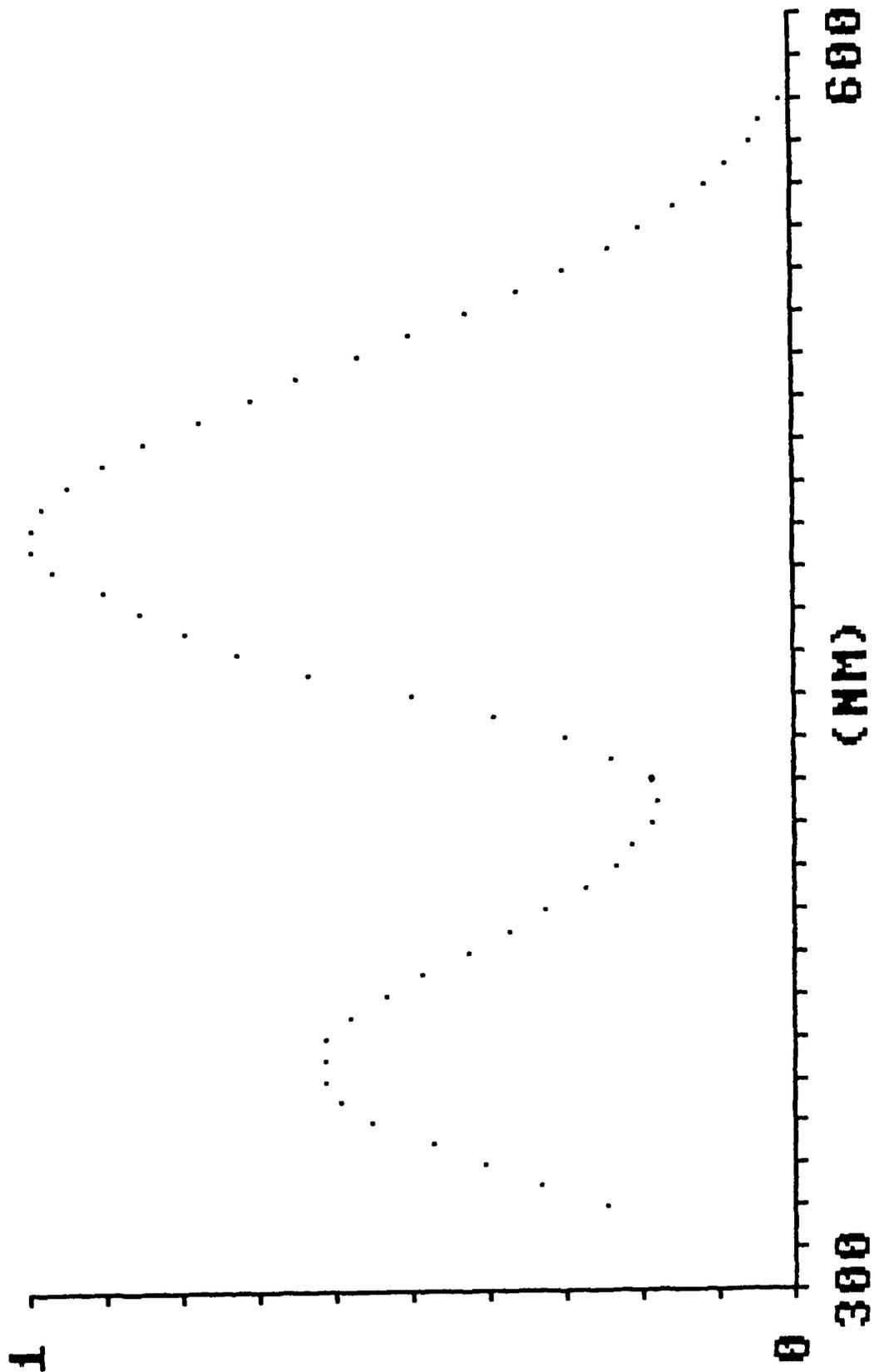
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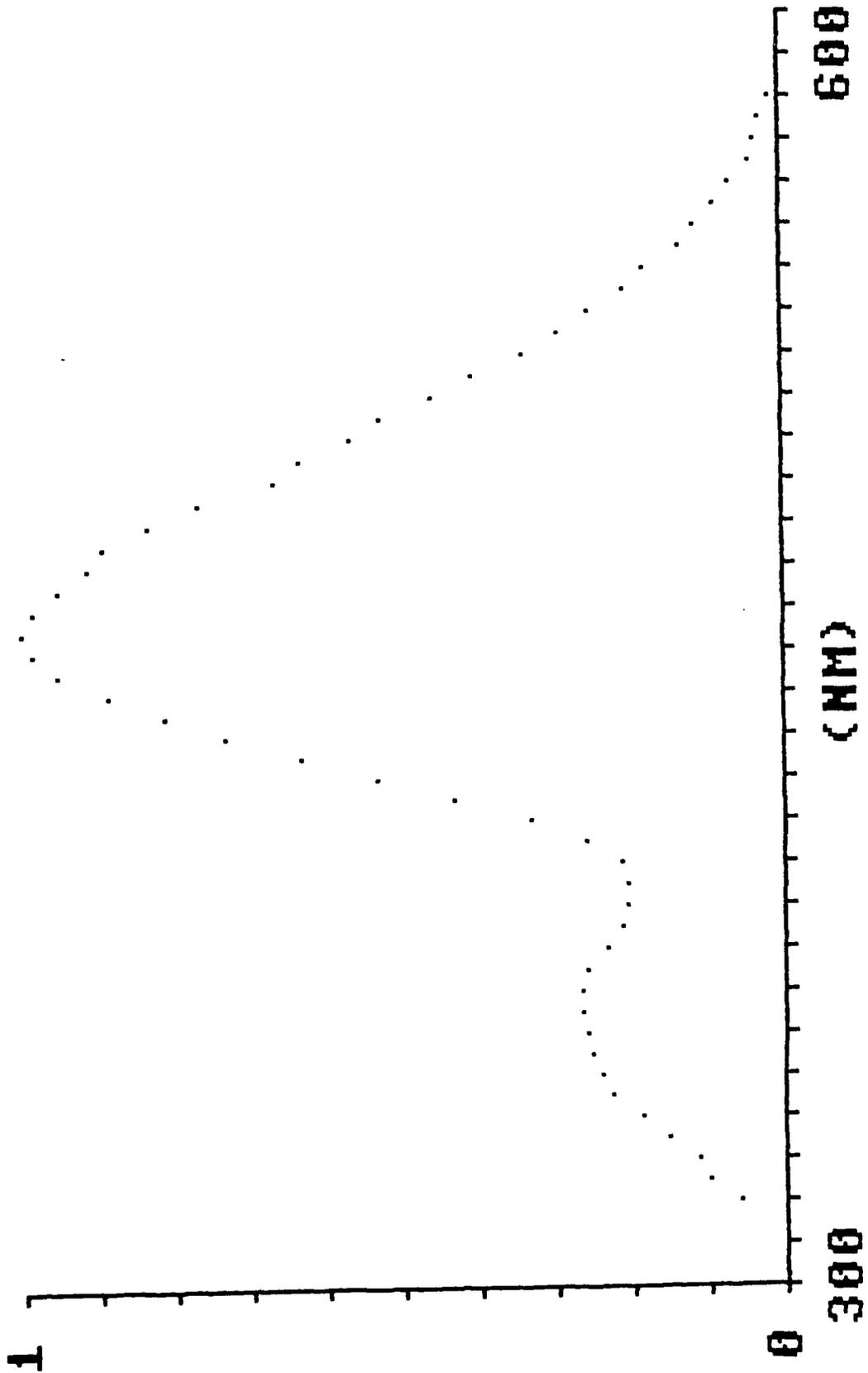
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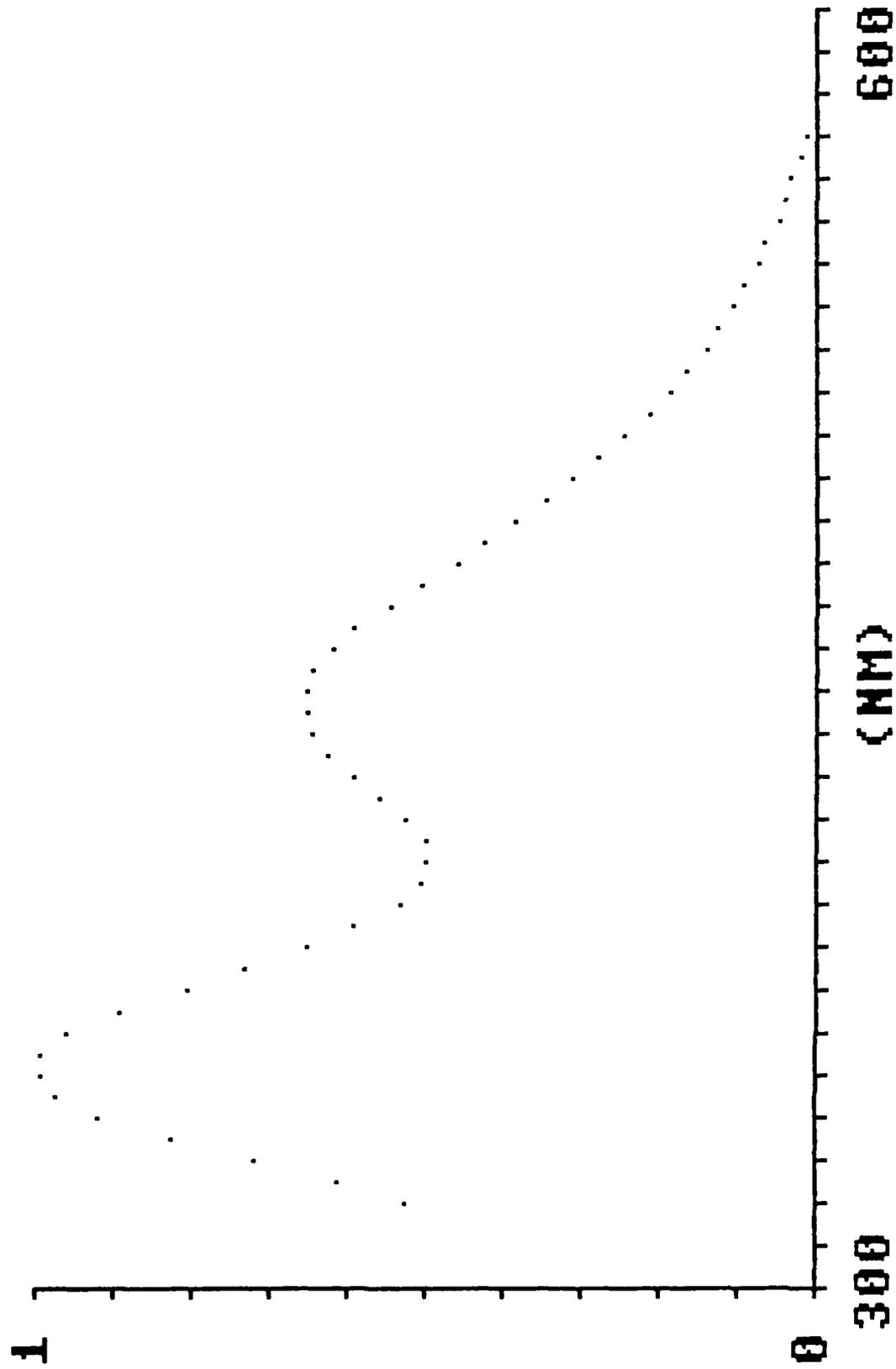
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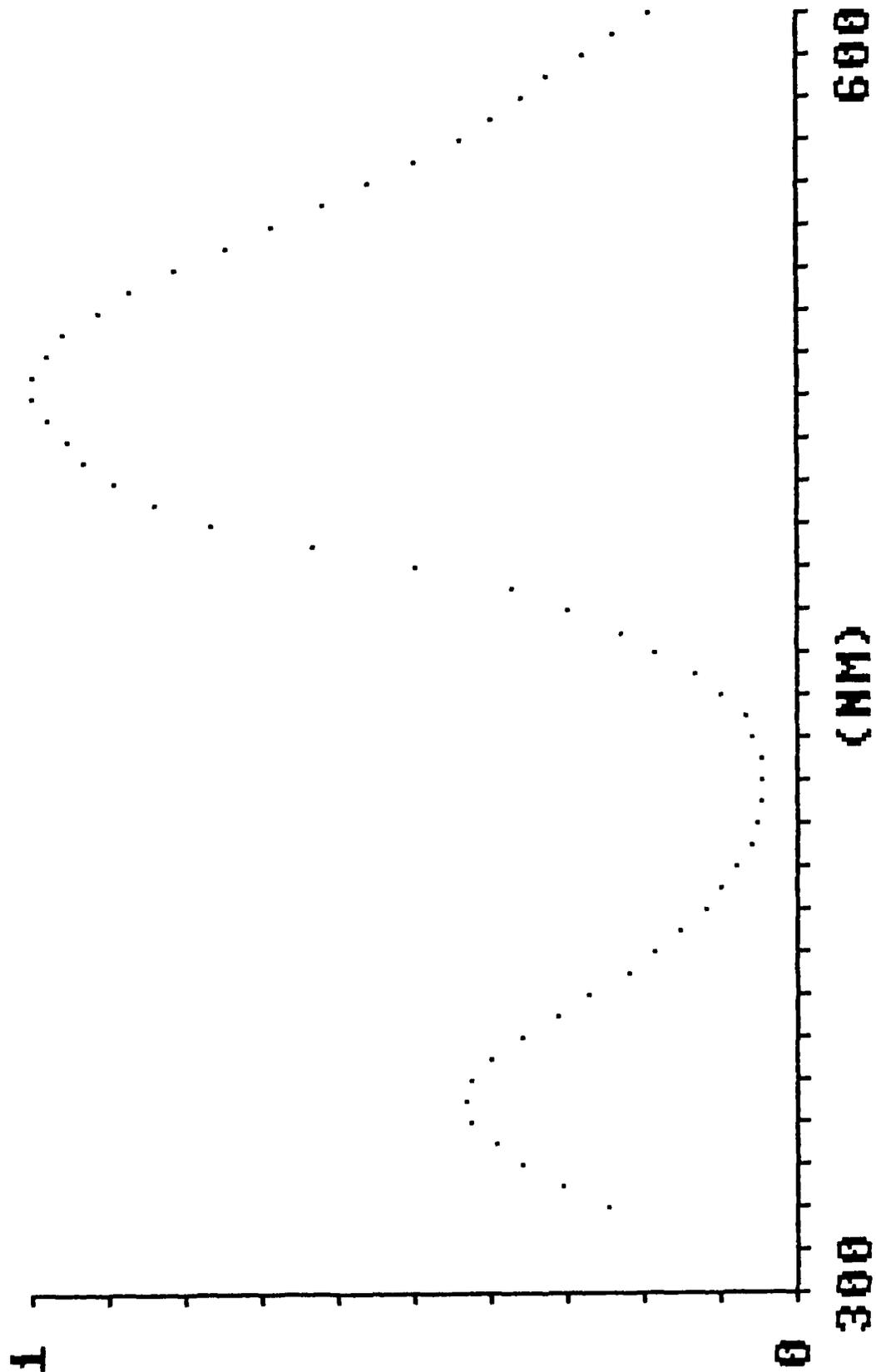
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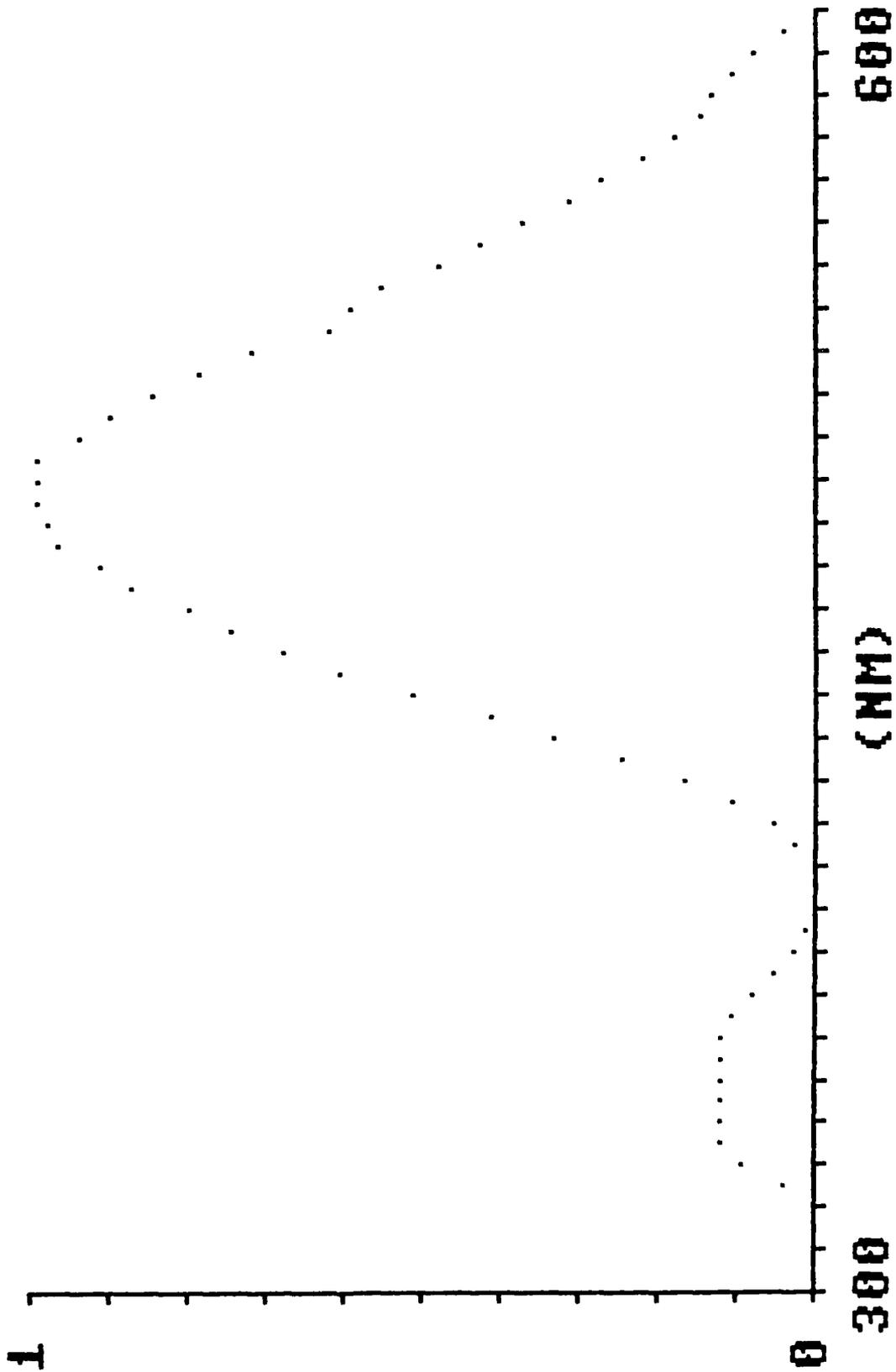
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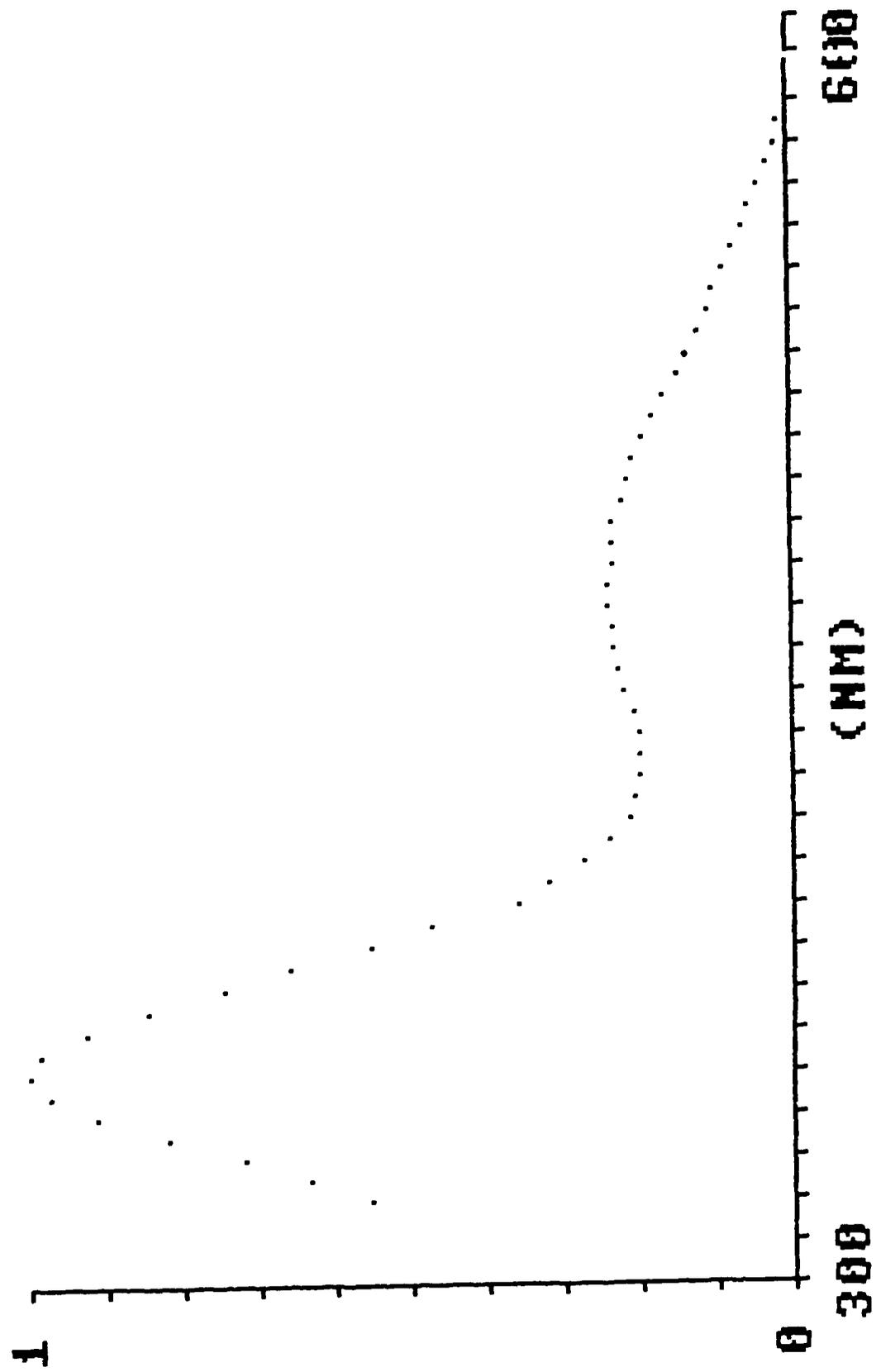
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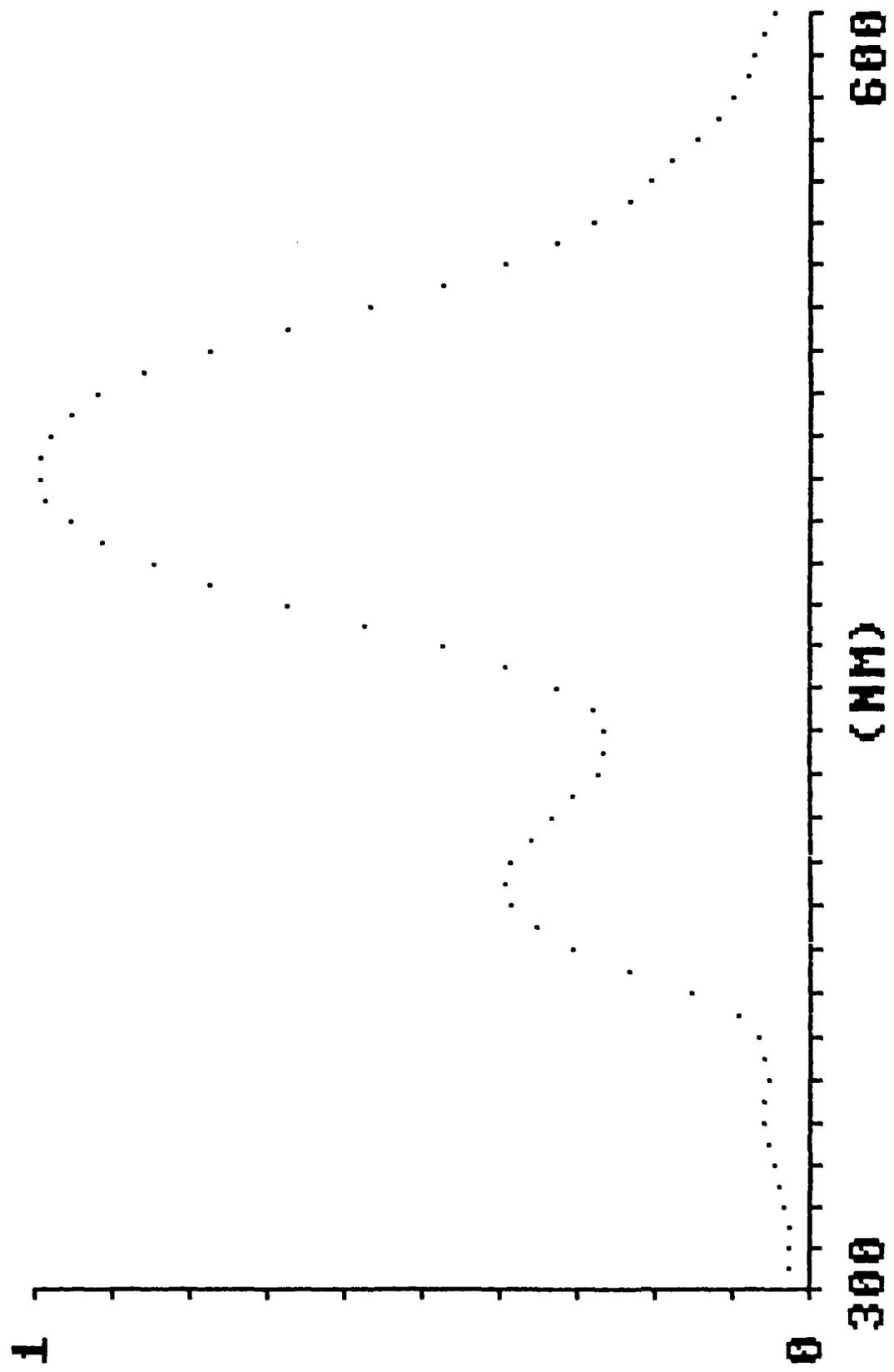
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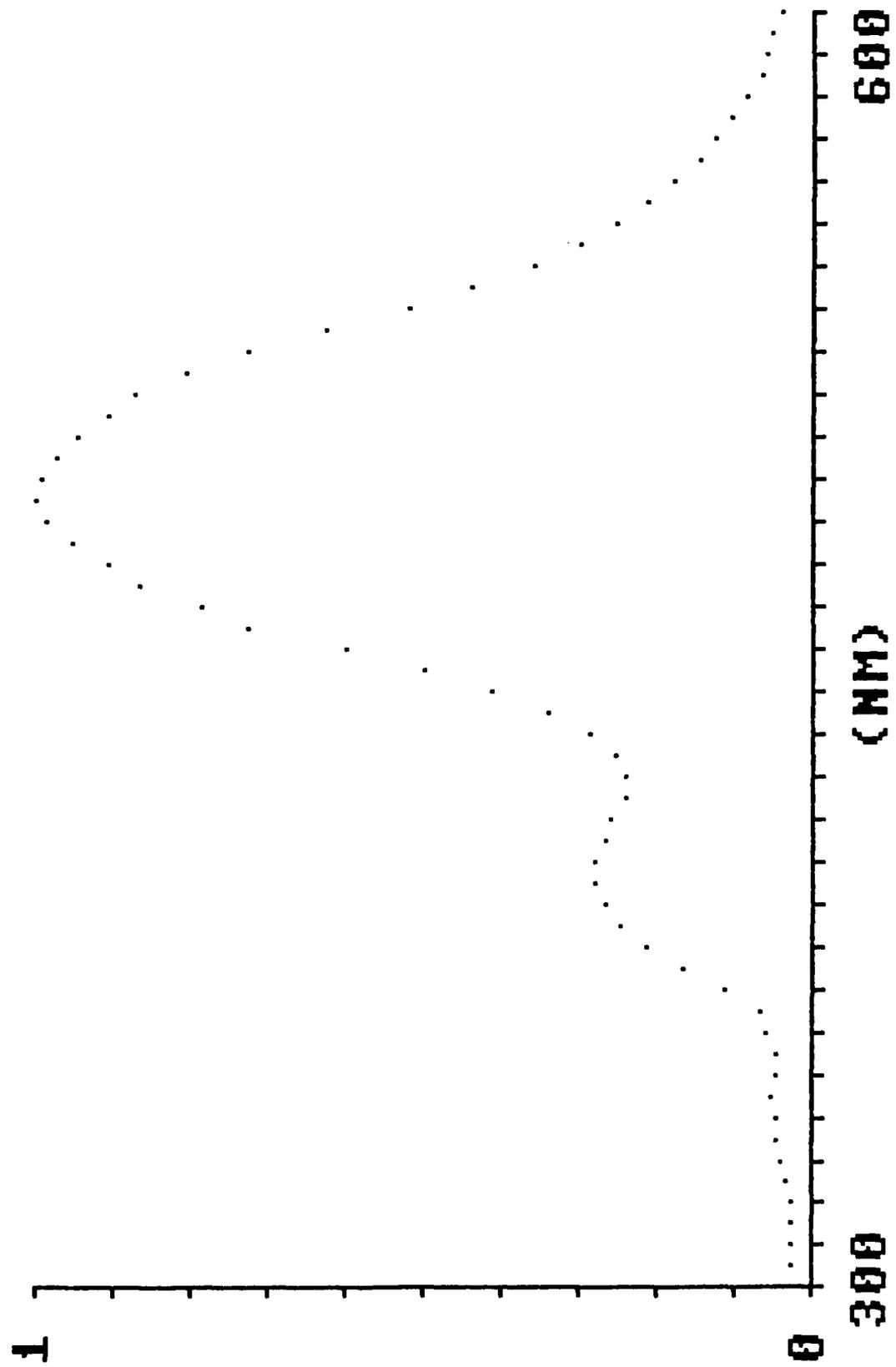
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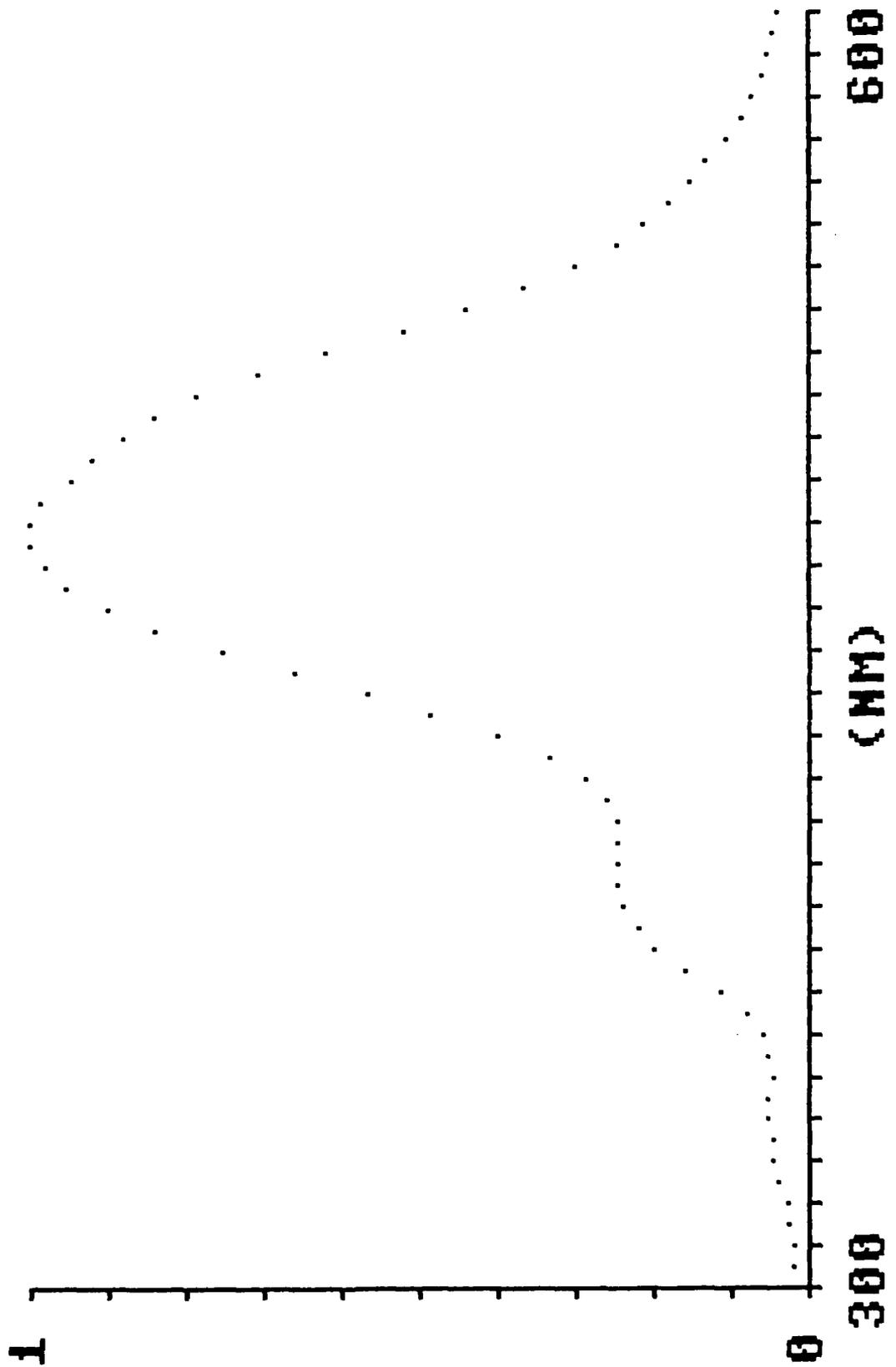
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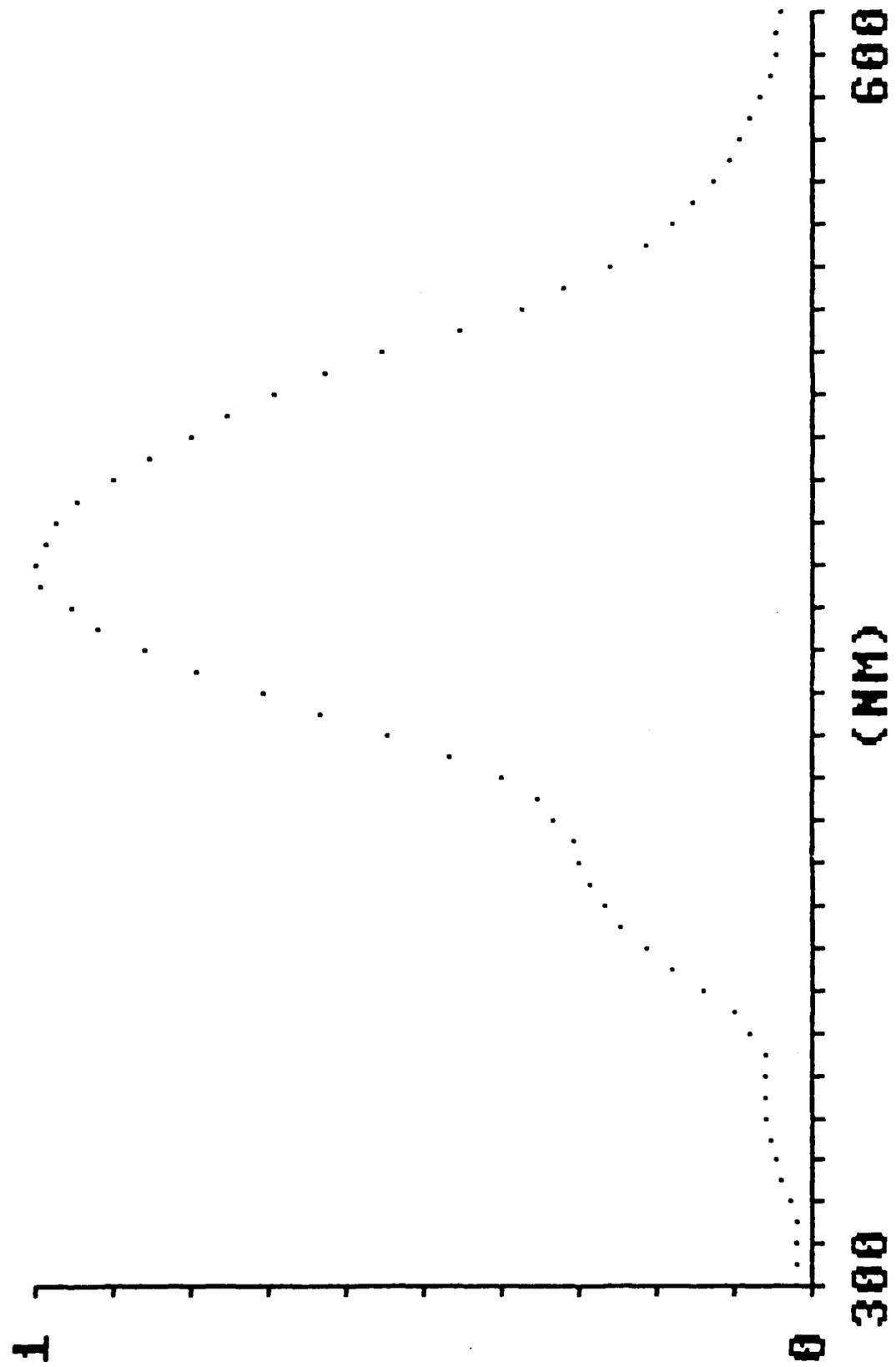
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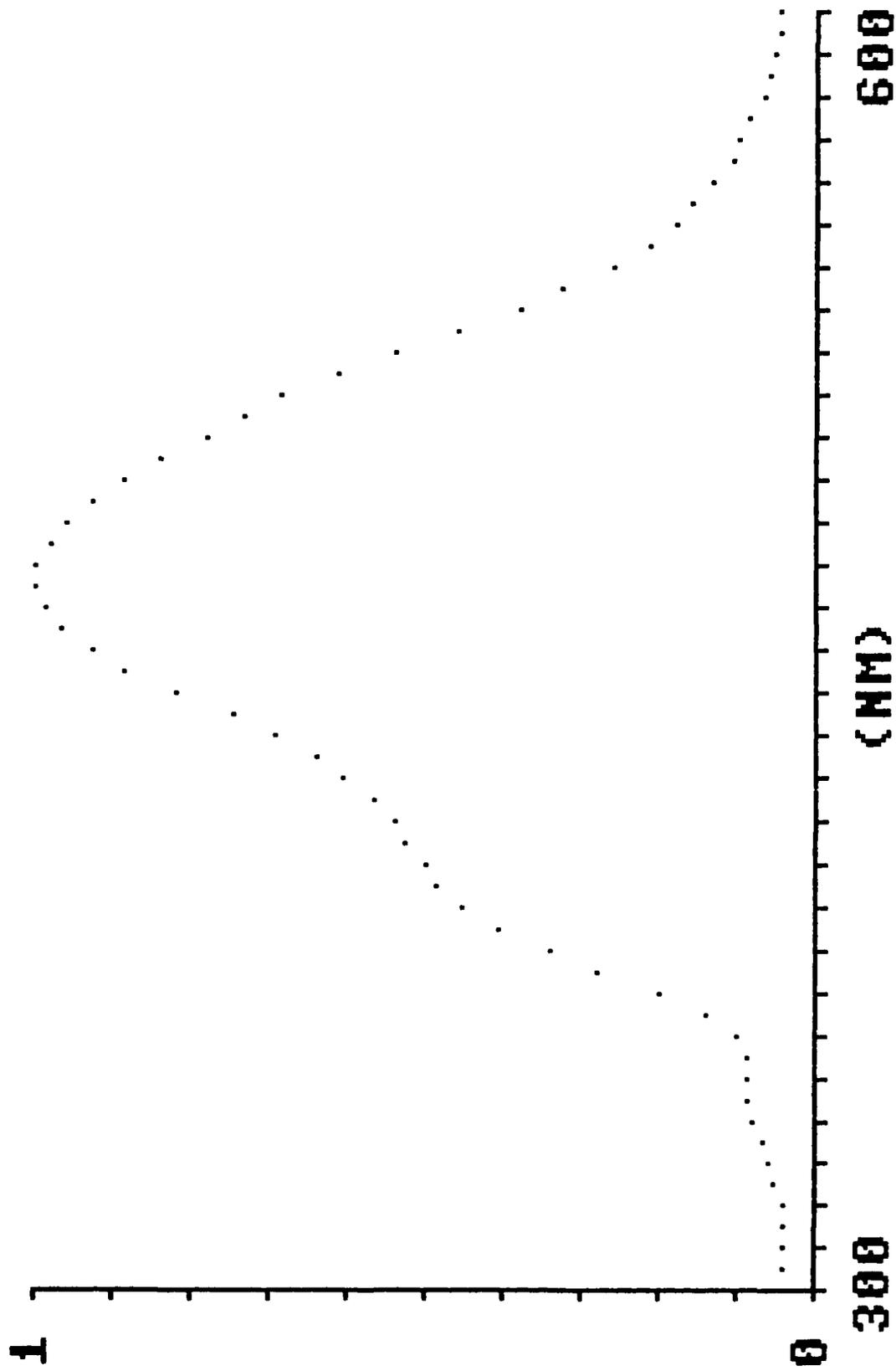
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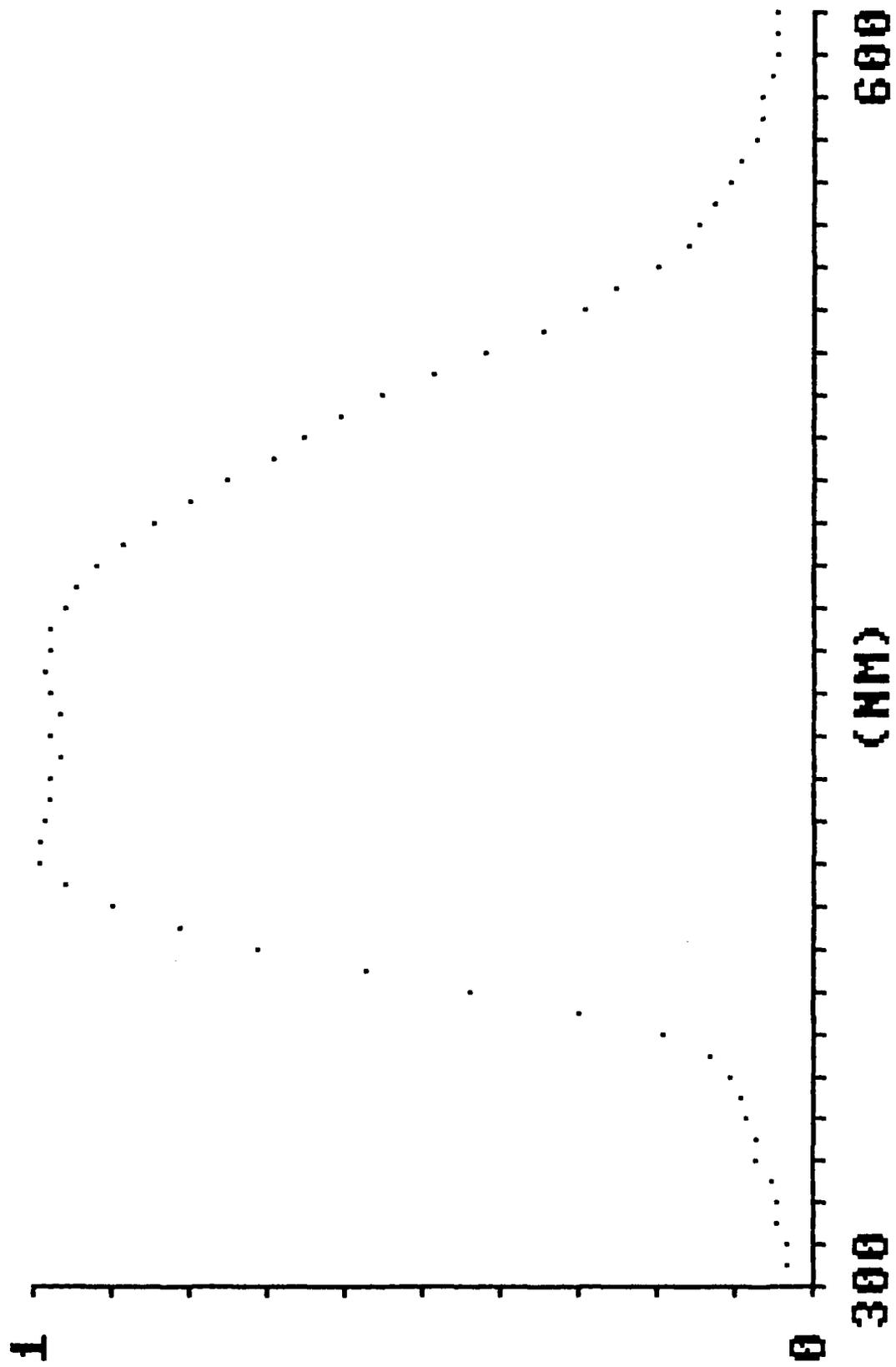
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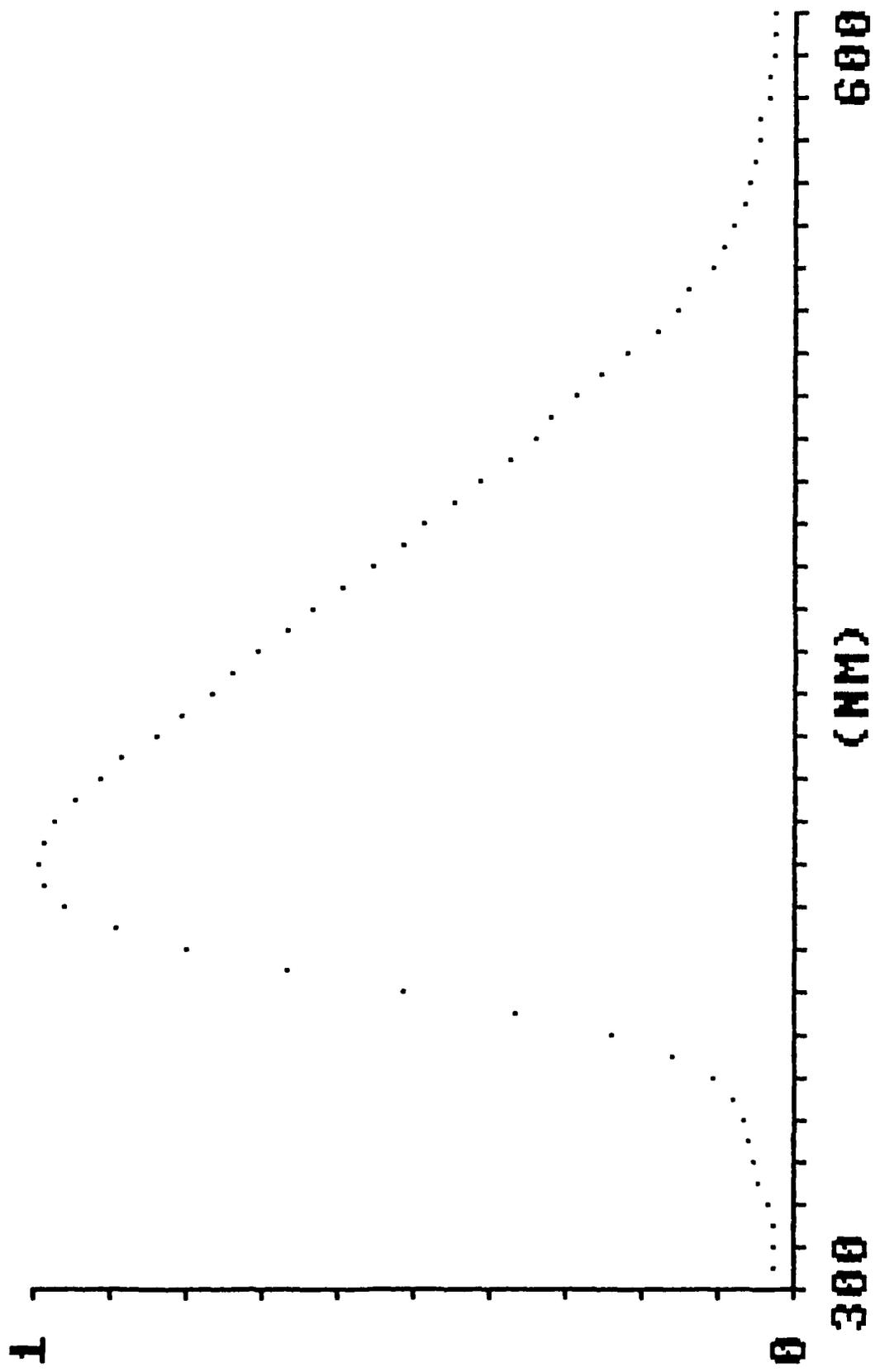
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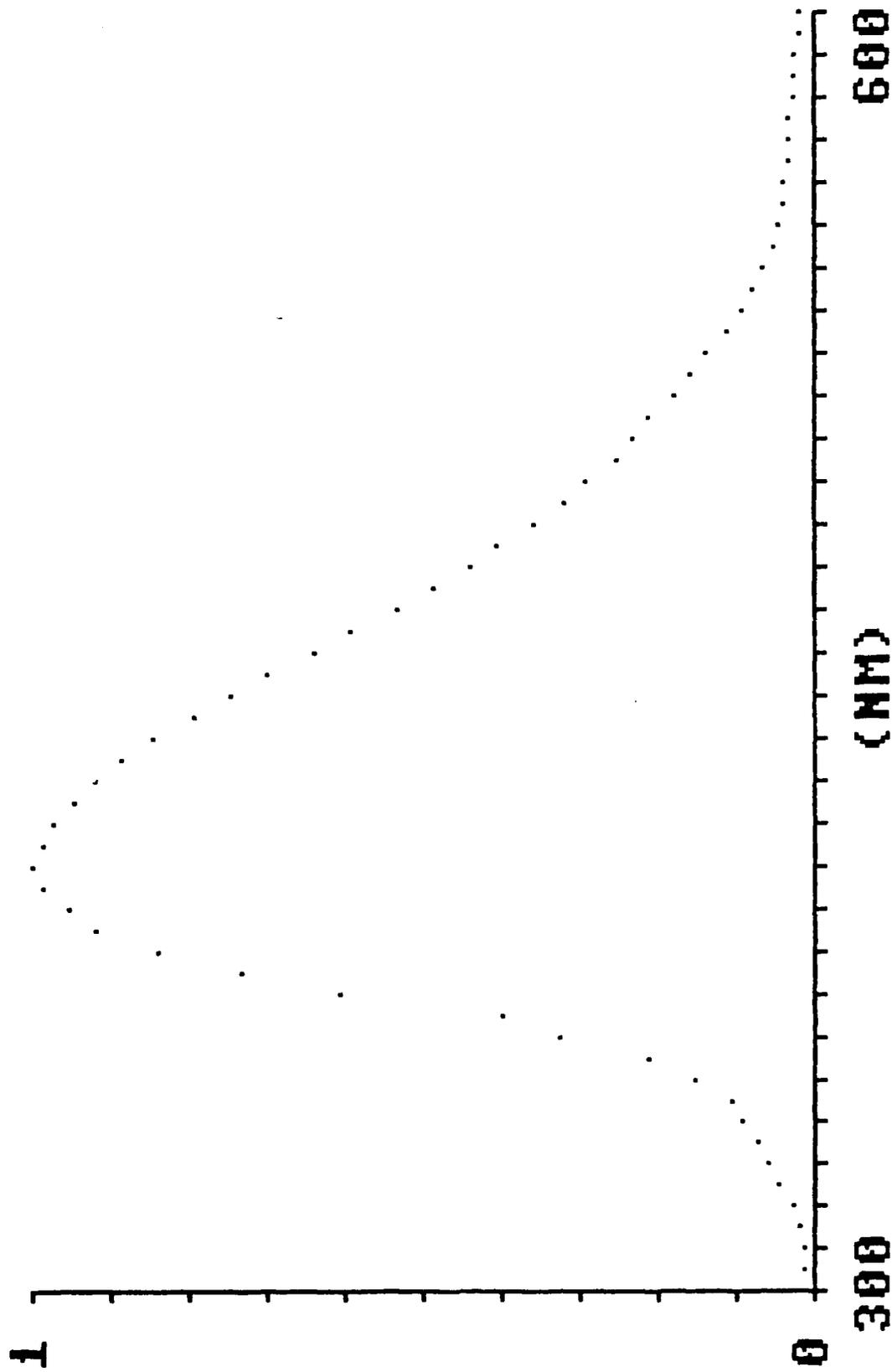
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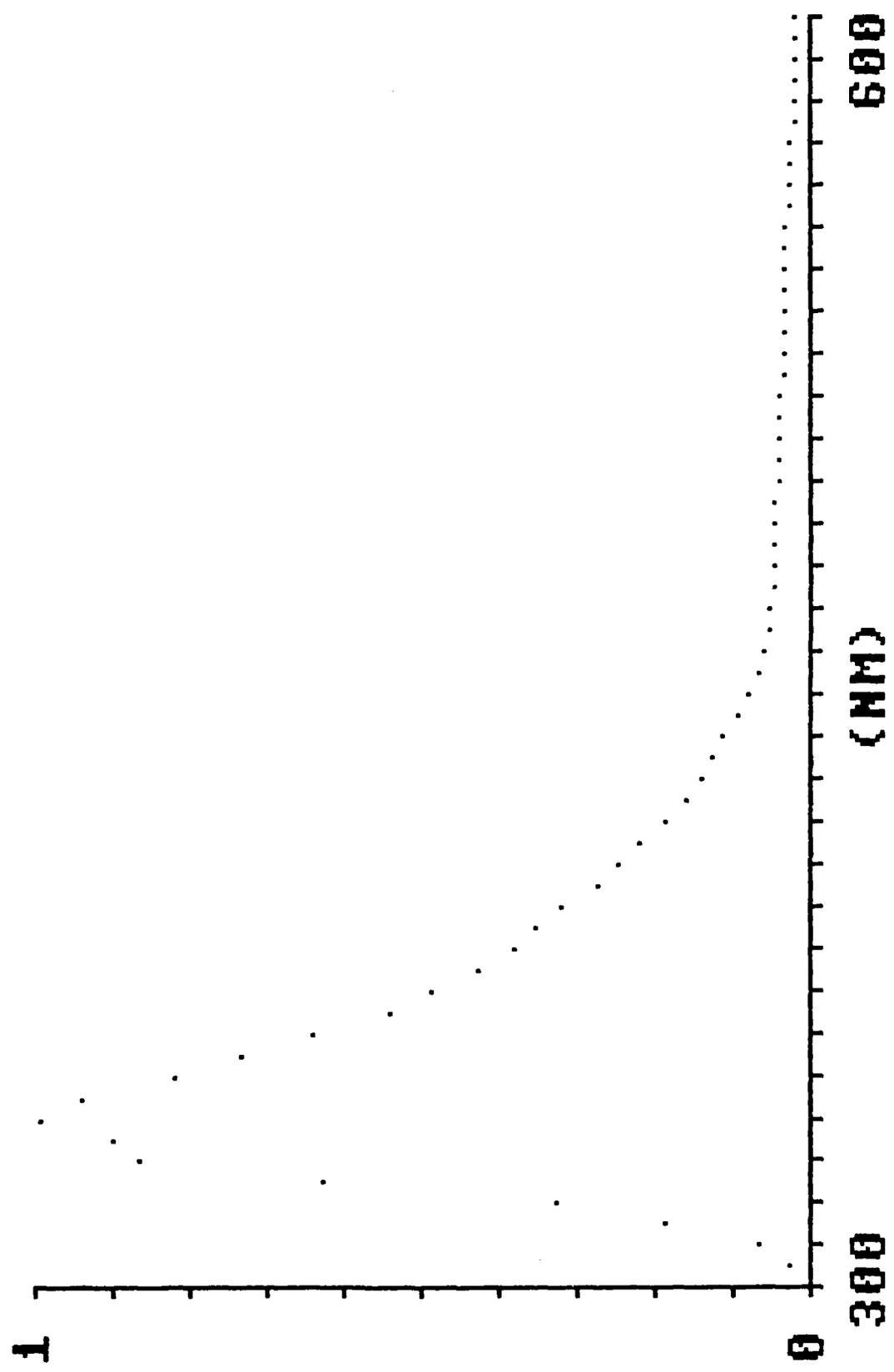
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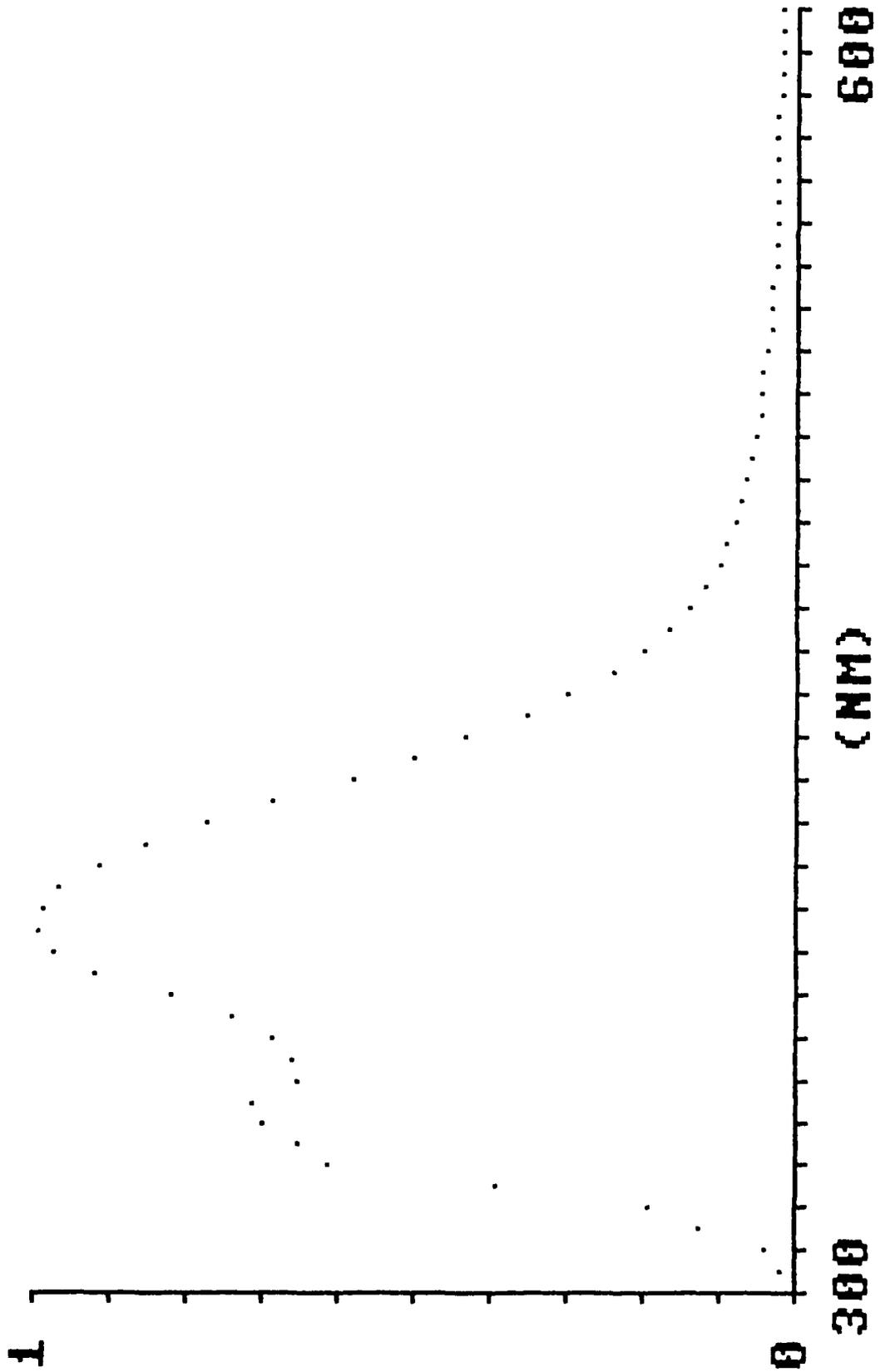
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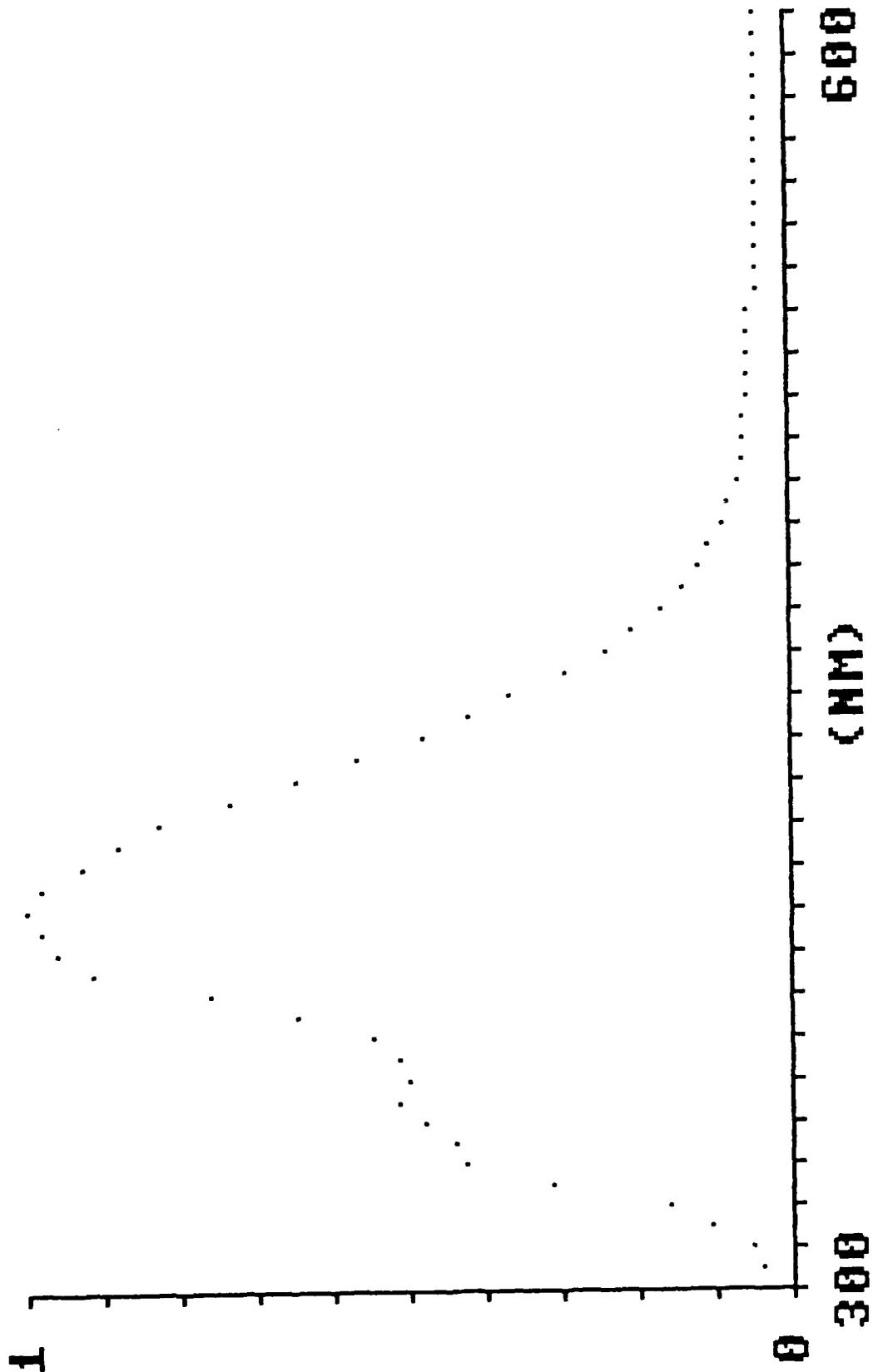
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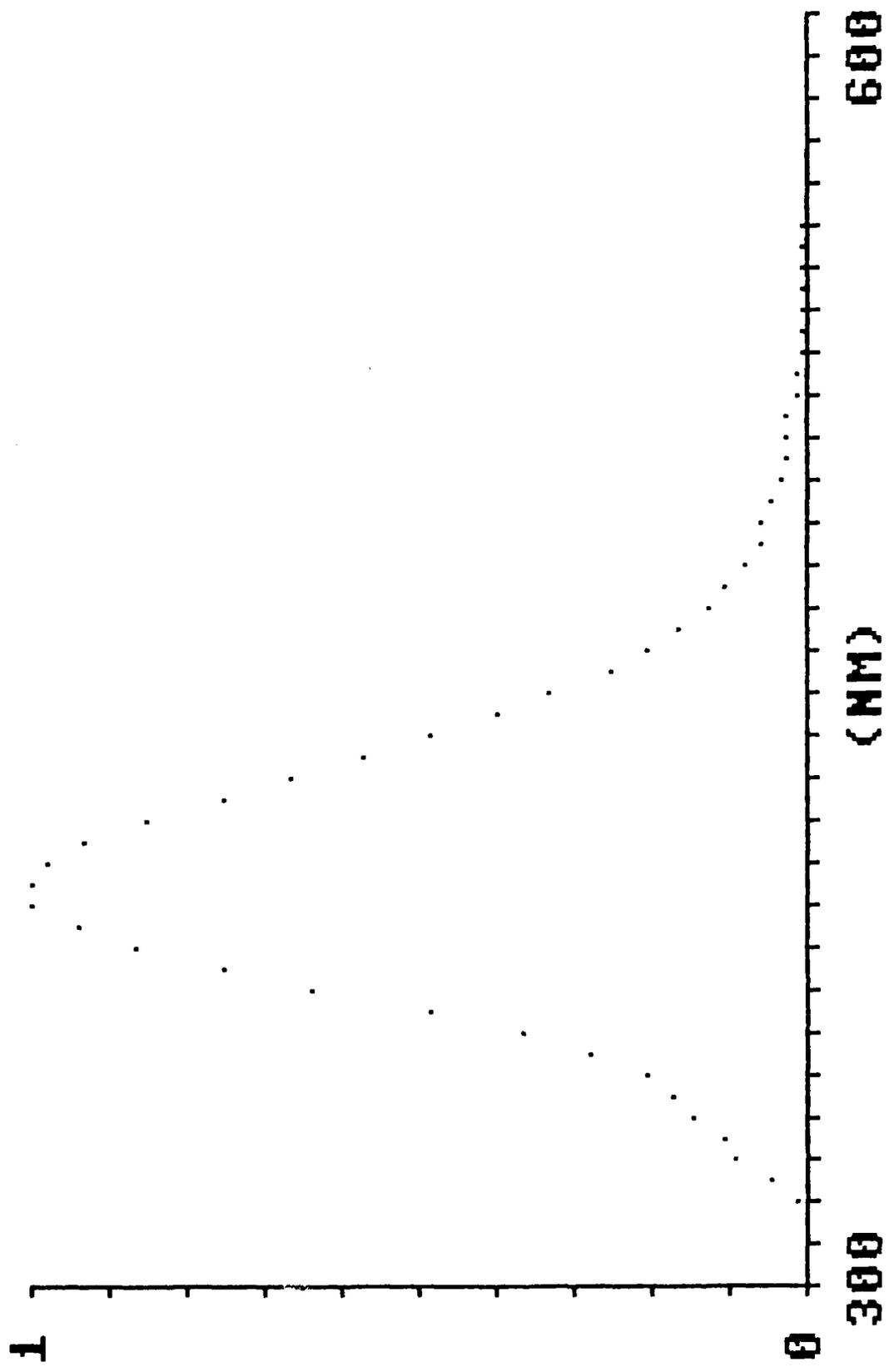
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2.5N/1TMPD/C VAPOR T=200C



2.5N/1TMPD/C VAPOR T=225C



PUBLICATIONS

1. L. A. Melton and J. F. Verdick, "Vapor/Liquid Visualization for Fuel Sprays", *Combustion Sci. and Tech.*, (1984), to be published.
2. L. A. Melton and J. F. Verdick, "Vapor/Liquid Visualization in Fuel Sprays", in *Proceedings, Twentieth International Symposium on Combustion* (The Combustion Institute, Pittsburgh, 1985), to be published.
3. A. M. Murray and L. A. Melton, "New Exciplex systems for Vapor/Liquid Visualization", *Appl. Opt.*, (1985) in preparation.
4. L. A. Melton, J. F. Verdick, and A. M. Murray, "Characterization of Naphthalene/TMPD Exciplex Systems Used in Vapor/Liquid Visualization", *Appl. Opt.*, (1985) in preparation.

PERSONNEL ASSOCIATED WITH GRANT

1. L. A. Melton, principal investigator
2. A. M. Murray, Ph.D, University of Arizona, postdoctoral research associate

INTERACTIONS (COUPLING)

1. L. A. Melton and J. F. Verdieck, "Vapor/Liquid /visualization for Fuel Sprays", paper presented at the Fall Meeting of the Eastern Section of the Combustion Institute, Providence, R.I. , Nov. 1983.
2. L. A. Melton and J. F. Verdieck, "Vapor/Liquid Visualization in Fuel Sprays", presentation of paper #2 above at the Twentieth International Symposium on Combustion, Ann Arbor, Michigan, August 1984.
3. L. A. Melton, seminars on vapor/ liquid visualization at the following institutions:
 - a) Department of Mechanical Engineering, Carnegie-Mellon University, Nov. 1983.
 - b) Combustion Research Facility, Sandia National Laboratory, May 1984.
 - c) Department of Mechanical Engineering, Stanford University, May 1984.
 - d) Molecular Physics Group, SRI International, Menlo Park, CA, May 1984.
 - e) Department of Mechanical Engineering, University of California-Berkeley, May 1984.
 - f) Department of Chemical Engineering, Yale University, July 1984.
4. L. A. Melton spent July 5-August 10, 1984, working with J. F. Verdieck in the Chemical Physics Group (Alan Eckbreth, manager).

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