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TITLE: *LASER INDUCED RECOVERY OF DEUTERIUM OR TRITIUM FROM WATER*

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AUTHOR(S): *REED J. JENSEN AND JOHN L. LYMAN*

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PAPER

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NAME OF AUTHOR Reed J. Jensen and John L. Lyman, Los Alamos Scientific Laboratory, California, Los Alamos, New Mexico, USA, 87544

SESSION NUMBER III

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A laser method for recovery of deuterium or tritium from water is proposed. The two-step photolysis method utilizes a known coincidence of the $P_1(8)$ line of the DF laser with HDO and D_2O absorption lines coupled with a water filtered xenon flash lamp to selectively photolyze HDO and D_2O in the presence of H_2O. CO is to be added to the photolysis mixture to remove the O atom from the OH photolysis product. The isotopic material is to be collected as D_2. The reaction kinetics for this experiment has been modeled with a computer calculation based on rate processes. The dependence of isotopic selectivity on various vibrational energy transfer processes is discussed.

Introduction

The need for tritium removal from water for fission reactor waste management and the need for deuterium production for fusion reactor feed has stimulated us to develop a method for hydrogen isotope separation from water. Deuterium fuel requirements for fusion reactors operating on the D-T fuel cycle are approximately 0.1 g/MWd. Hence, a 1000 MW reactor, 40% efficient, will burn 250 g D_2 per day. Thus, 1000 such reactors will require 91,000 kg of D_2 per year.

Because of the above requirements, it is necessary to perform the extraction from water or an industrial feedstock compound with a flow of 1.6 thousand metric tons per day, or greater. As can be seen from the above consideration, an inexpensive selective method for deuterium recovery from water could result in a substantial savings.

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The ultraviolet room temperature absorption spectrum of water is discussed in Ref. 6. The onset of absorption at 186 nm (53,760 cm^{-1} or 6.66 eV) is well above the 5.113 eV or 41,250 cm^{-1} dissociation energy of water into H + OH fragments, (Ref. 7) and absorption in this region is known to produce the dissociation fragments (Ref. 8) with a quantum yield near unity (Ref. 9).

We believe that a very selective, energy conservative, two-photon dissociative process can be devised by coupling this ultraviolet absorption process with a preliminary selective vibrational excitation. The absorption spectrum of the vibrationally excited water molecules should be similar in form to a spectrum shown in Ref. 6, but shifted to longer wavelengths by an amount that is at least as great as the vibrational excitation.

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The present price of D_2O is about ¢/gm. The cost of the laser-induced pro- ess may be estimated as follows: each ole of HOH bonds broken requires 6.4 x 10^5 J which must be supplied by the laser. If the lasers are 1% efficient in converting electrical energy to photon energy, then 6.4 x 10^7 J or 18 kwh of electrical energy would be required at a cost of 27¢. The resulting energy cost of D_2O would then be 1.3 ¢/gm.

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Figure 1 shows the infrared spectrum of water (Ref. 10) from 1 to 15 μm. Fundamental vibrational frequencies for the various isotopic species are listed in Table 1 (see Ref. 11). Notice that the HOT and HOD frequencies of the ν_1 mode are well separated from each other and especially from the H_2O frequency. It should be an easy matter to excite HOT and HOD from contaminated or pure water vapor while leaving the HOH in the ground state. It should also be possible to selectively excite H_2O^{18} in the presence of H_2O^{16} if appropriate lasers can be found.

Absorption coefficients have been measured for H_2O, HDO, and D_2O vapor with individual HF and DF laser transitions. The absorption coefficient, α, is defined by

$$I/I_o = e^{-\alpha\rho\ell}$$

where I and I_o are the transmitted and incident laser energy, ℓ is the path length in meters and ρ is the water vapor density in mol/m^3. The results are summarized in Table 2. Note that D_2O can be preferentially excited by several DF laser transitions, and that HDO can be preferentially excited by several HF laser transitions. Laser intensities used in these measurements were in the range of 5 to 100 kW/cm^2.

The very high oscillator strength and anharmonicity of water give rise to strong overtone absorptions at 1.2 and 1.35 μm, shown in Fig. 1, and 0.8227, and 0.7957, and 0.6994 μm discussed in Ref. 12. The very strong overtone at 1.35 μm is especially interesting because of its near coincidence with a number of good lasers, such as the tunable lithium niobate optical parametric oscillator and the iodine laser. The iodine laser can also be tuned somewhat with a magnetic field to bring it into precise coincidence with absorption lines.

Exciting the water overtone will permit the use of a longer wavelength uv source. The advantages of longer wavelength are that uv sources are more readily available, absorption by atmospheric O_2 is decreased, and absorption by unexcited water is further reduced.

Photolysis produces OH and H enriched in D or T. In order to recover the enriched hydrogen it must be in a form that is easily separable from water, and it cannot undergo isotopic exchange reactions. Any species that
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The OH radicals can be c
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Al alternative recovery
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Apparatus

A 150 cm path length cell
designed to obtain the uv abs
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The OH radicals can be converted to H atoms by reaction with CO. The H atoms can then be scavenged by ethylene. After radiolysis, the reaction mixture is recompressed, and the purified water will condense leaving the CO and ethylene gases ready for another scavenger cycle. It should be emphasized that the amount of scavenger gas needed for an operation is extremely small and that its periodic distillation should be sufficient to remove the attached isotopically enriched ethane from the material. The final chemical form of the enriched hydrogen will be as ethane or one of its derivatives.

An alternative recovery scheme would be to react the OH with CO and then simply allow the hydrogen atoms to recombine to molecular hydrogen which is easily recoverable from water.

Apparatus

A 150 cm path length cell has been designed to obtain the uv absorption spectrum of vibrationally excited D_2O by a double resonance method. The light from a uv flash lamp is passed through the cell to a monochromator. At some time during the 10 μs flash the D_2O vapor is irradiated with a DF laser pulse. The DF laser pulse is short (120 ns) compared to the uv flash and the laser intensity is sufficient to excite about 10% of the D_2O molecules to the ν_1 or ν_3 vibrational level. The absorption of the uv radiation by the vibrationally excited D_2O will cause a decrease in the intensity of the transmitted uv flash. The time response of the uv absorption will also give a better understanding of the vibrational energy transfer processes that occur in water vapor.

The same apparatus will also be used to collect deuterium enriched hydrogen from partially deuterated water by this two-photon photolysis technique. Basic kinetics data on the scavenging process should be obtainable from this same apparatus.

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[illegible] mixture of H_2O, HDO, and D_2O vapor and CO diluent will be irradiated simultaneously with a uv flash lamp and a DF laser. The DF laser pulse will be absorbed by D_2O and to a lesser extent by HDO. A water optical filter will be used to transmit only the uv radiation with wavelengths longer than 186 nm. Thus, only vibrationally excited water molecules will be photolyzed. The hydrogen produced will be analyzed for isotopic enrichment by mass spectrometric methods.

Computer Modeling

A computer code has been written to model the reaction kinetics of these experiments. The code will be used to guide the experimental program and to interpret the data obtained. Many of the rate coefficients for reactions occurring in these experiments have been measured. Reasonable estimates have been made where measured rate coefficients are unavailable. A sample of 1 torr (0.053 mol/m^3), of D_2O irradiated simultaneously with a 100 mJ/cm^2 DF laser pulse (110 ns-pulse idth) and a 1 W/cm^2, 5 μs uv flash at 90 nm gives a transmitted uv signal as hown in Fig. 2. The incident flash is he dotted line. Conditions for a econd computation were 1 torr (0.053 ol/m^3) of water with an isotope ratio f D/H = 1 irradiated with a 100 mJ/cm^2, 00 ns DF laser pulse with a 1 kW 5 μs, 90 nm uv flash. The water was diluted ith 10 torr (0.53 mol/m^3) of CO. The oncentrations of the vibrationally excited water species are plotted in Fig. 3. he isotope ratio of the resulting hydrogen was D/H =, 8.4 and the D yield was .3 x 10^{-6} mol/m^3/pulse. For the same onditions with ten times the water vapor 0.53 mol/m^3) the isotope ratio was D/H = .7 and a D yield of 9.8 x 10^{-6} mol/m^3.

Higher yields of enriched hydrogen ill require further laser development in oth the near infrared and ultraviolet pectral regions. The requirements of ood selectivity and high concentration f the vibrationally excited species can est be met with a high power tunable ear infrared laser.

The candidates being considered for his laser are first, the lithium niobate ptical parametric oscillator (OPO) pumped with frequency doubled iodine Nd:YAG laser radiation. Second, the iodine laser tuned with a magnetic fi the $LiNbO_3$ OPO is tunable over the sp tral range from 0.5 to 4 microns with ergies on the order of a few millijou in 60 to 80 ns (Refs. 13, 14, 15). T iodine photodissociation laser may be tuned over a limited range by applyin uniform magnetic field.

An iodine laser is currently bei constructed to be tuned by one of the bove methods.

Tunable uv lasers between 185 an nm may be achieved by doubling a tuna dye laser; however, the shortest wave achieved by this method to date is 2 (Ref. 16). Another promising method frequency upconversion of a tunable laser by two-photon pumping of a nona lowed atomic metal vapor transition. Bloom et al. (Ref. 17) have demonstra that several CO_2 laser lines could be converted to the 350 nm region by two photon pumping of a nonallowed sodium transition. It has been proposed (Re 18) that this method could be used to tune over the spectral region from 4 138 nm. This latter method seems mos promising and will be pursued.

In addition to the laser develo described above, some chemical proces development will be required to perf the method of extracting the deuteri rich photolysis products. The entyl and CO scavengers will have to be fra tionated periodically to remove CO_2 deuterated ethylene. If the method extended to O^{18} recovery the CO_2 rem would be rich in O^{18}.

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In addition to the laser developments described above, some chemical process development will be required to perfect the method of extracting the deuterium-rich photolysis products. The ethylene and CO scavengers will have to be fractionated periodically to remove CO_2 and deuterated ethylene. If the method were extended to O^{18} recovery the CO_2 removed would be rich in O^{18}.

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Table 1

Fundamental Frequencies of Isotopic Water Molecules

Molecule		Frequencies (cm^{-1})	
	ν_3	ν_1	ν_2
H_2O	3935.59	3825.32	1653.91
HDO	3883.8	2820.3	1449.4
D_2O	2883.79	2758.06	1210.25
DTO	2830.7	2357.1	1117.9
T_2O	2436.12	2296.63	1017.89
HTO	3882.6	2365.0	1374.6

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Table 1

amental Frequencies of Isotopic Water Molecules

		Frequencies (cm^{-1})	
ecule	ν_3	ν_1	ν_2
$_2$O	3935.59	3825.32	1653.91
DO	3883.8	2820.3	1449.4
$_2$O	2883.79	2758.06	1210.25
TO	2830.7	2357.1	1117.9
$_2$O	2436.12	2296.63	1017.89
TO	3882.6	2365.0	1374.6

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Table 2

Absorption Coefficients for Absorption of HF and DF Laser Radiation

Laser Transition	α (m^2/mol)		
	H_2O	HDO[a]	D_2O
HF $P_1(4)$	< 0.05	0.453 ± 0.047	--
(5)	0.240 ± 0.071	< 0.05	--
(6)	0.116 ± 0.77	< 0.05	--
(7)	< 0.05	< 0.05	--
(8)	< 0.05	0.100 ± 0.047	--
$P_2(3)$	< 0.05	< 0.05	--
(4)	< 0.05	< 0.05	--
(5)	< 0.05	< 0.05	--
(6)	0.095 ± 0.060	< 0.05	--
(7)	< 0.05	< 0.05	--
(8)	0.079 ± 0.062	< 0.05	--
$P_3(3)$	--	< 0.05	--
(4)	--	0.048 ± 0.056	--
(5)	--	< 0.05	--
(6)	--	< 0.05	--
(7)	--	< 0.05	--
DF $P_1(5)$	--	0.221 ± 0.206	--
(6)	--	0.114 ± 0.049	< 0.19
(7)	--	< 0.09	--
(8)	--	1.08 ± 0.32	4.81 ± 0.06
(9)	--	0.633 ± 0.187	2.47 ± 0.17
(11)	--	0.088 ± 0.079	--
$P_2(4)$	--	0.752 ± 0.131	--
(5)	--	0.268 ± 0.075	0.311 ± 0.13

(6)	0.116 ± 0.77	< 0.05	--
(7)	< 0.05	< 0.05	--
(8)	< 0.05	0.100 ± 0.047	--
P_2(3)	< 0.05	< 0.05	--
(4)	< 0.05	< 0.05	--
(5)	< 0.05	< 0.05	--
(6)	0.095 ± 0.060	< 0.05	--
(7)	< 0.05	< 0.05	--
(8)	0.079 ± 0.062	< 0.05	--
P_3(3)	--	< 0.05	--
(4)	--	0.048 ± 0.056	--
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(6)	--	< 0.05	--
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(7)	--	< 0.09	--
(8)	--	1.08 ± 0.32	4.81 ± 0.06
(9)	--	0.633 ± 0.187	2.47 ± 0.17
(11)	--	0.088 ± 0.079	--
P_2(4)	--	0.752 ± 0.131	--
(5)	--	0.268 ± 0.075	0.311 ± 0.13
(6)	--	0.086 ± 0.024	0.369 ± 0.05
(8)	--	< 0.05	

[a] These are the actual absorption coefficients measured for a 1:1 mixture of H_2O and D_2O and the contributions from H_2O and D_2O have not been subtracted.

2

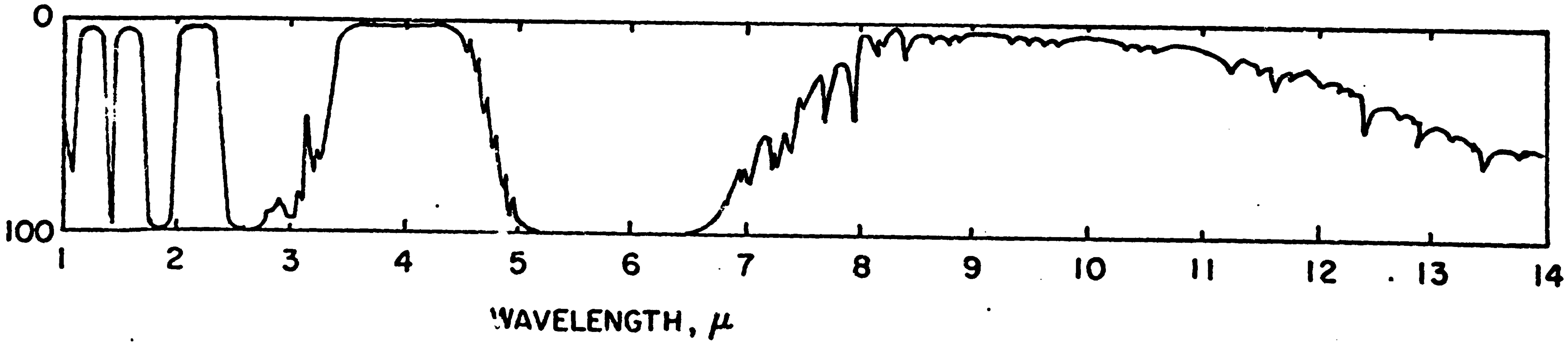

Fig. 1. Infrared absorption spectrum of water

From: W. Wolfe, "Handbook of Military Infrared Spectroscopy" p.228 Office of Navel Research, Department of the Navy, Washington D.C.

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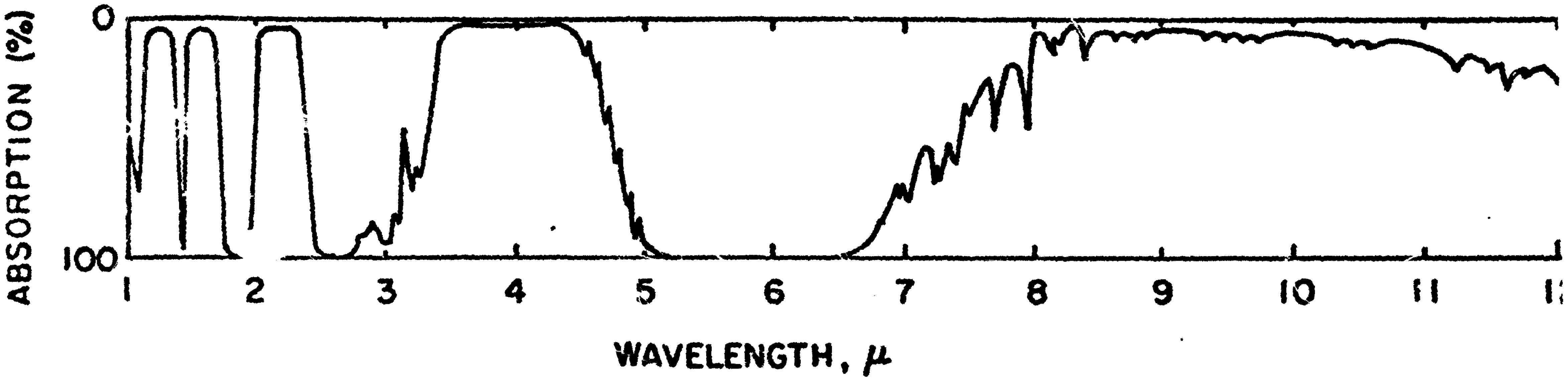

Fig. I. Infrared absorption spectrum of water
From: W. Wolfe, "Handbook of Military Infrared Spactroscopy" p.228 Office of Novel Research, Department of the Navy, Washington D.C.

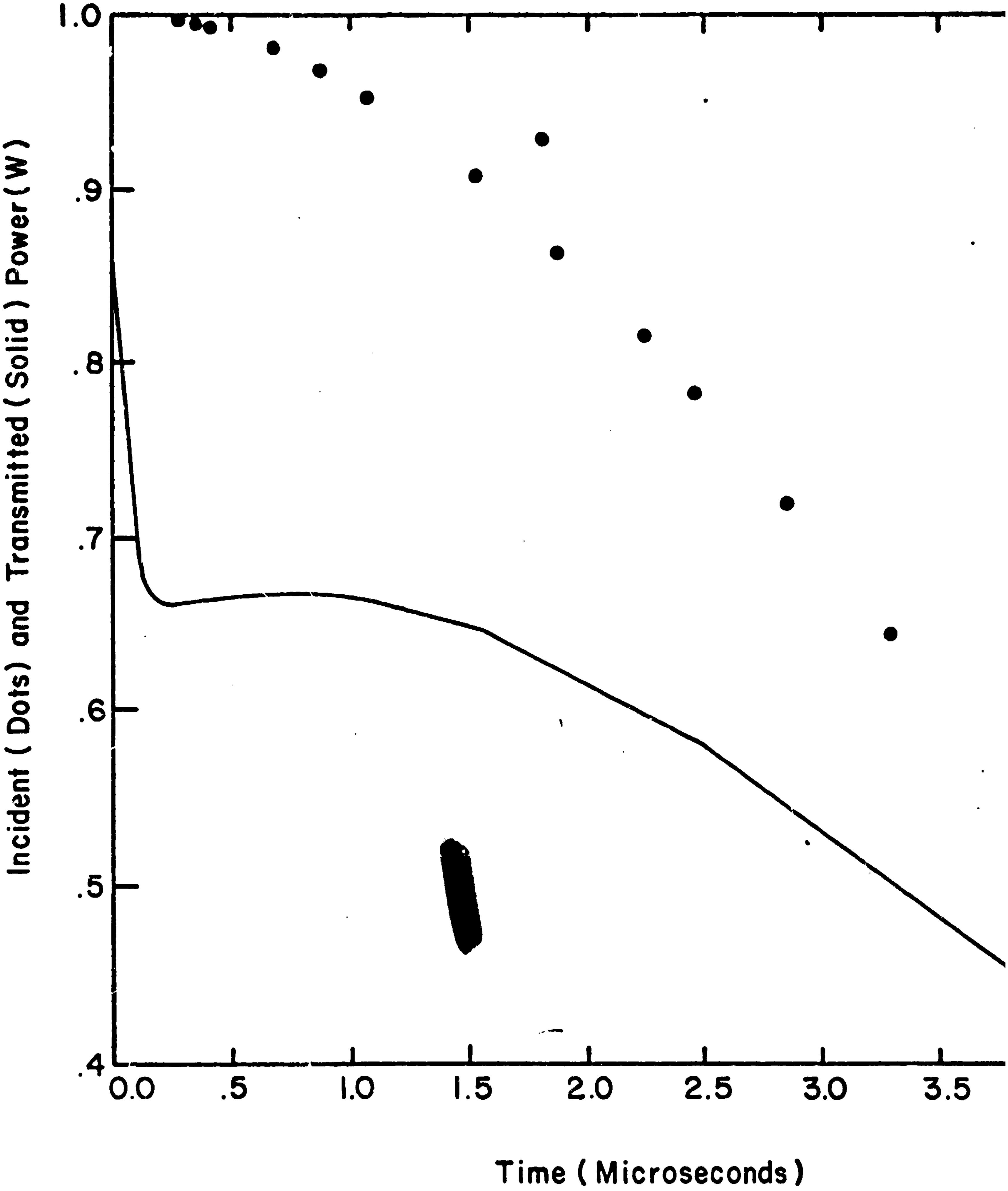

Fig. 2. uv transmission for 10 torr of $H_2O + D_2O$ in 160 c

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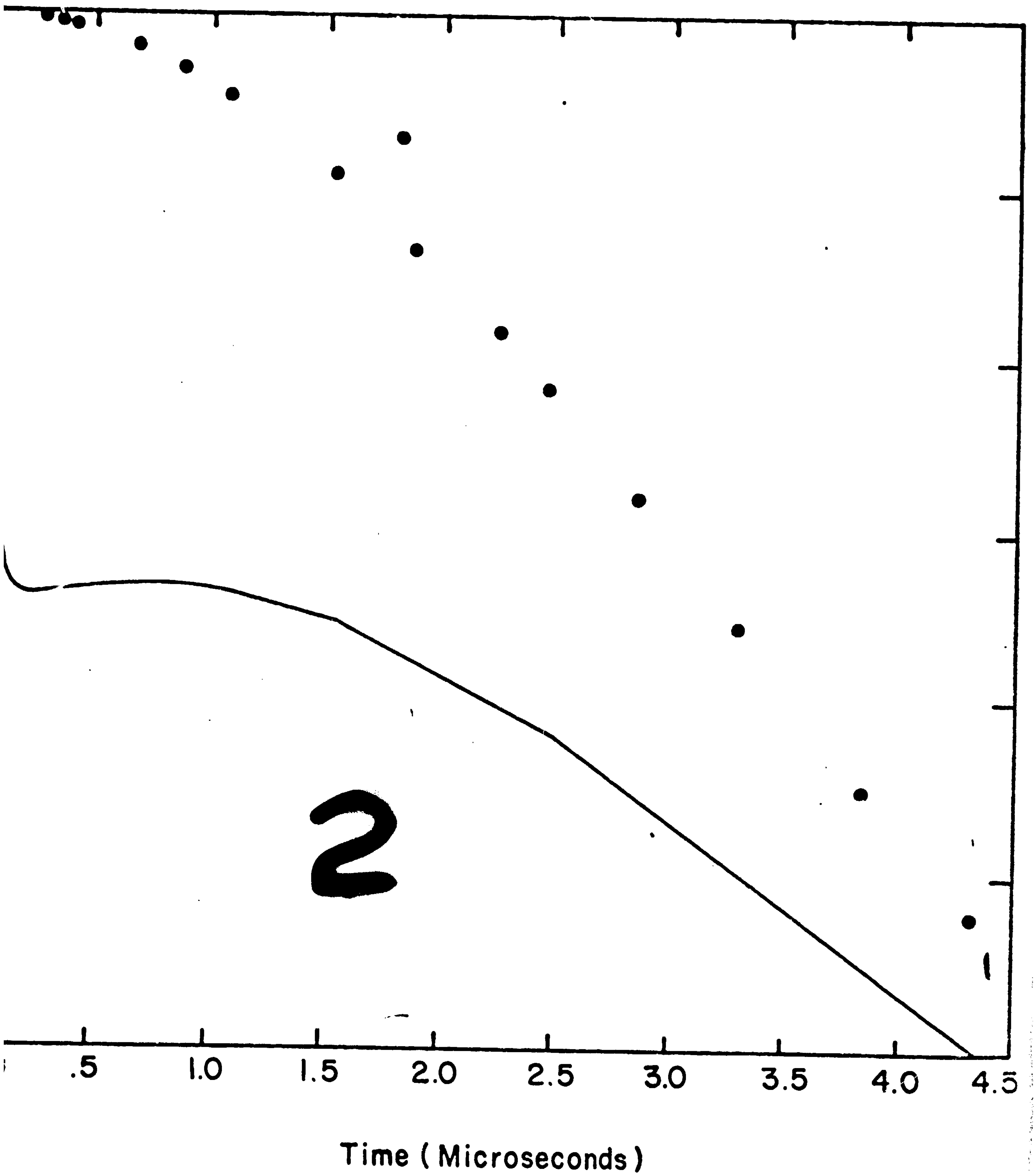

ig. 2. uv transmission for 10 torr of $H_2O + D_2O$ in 160 cm cell.

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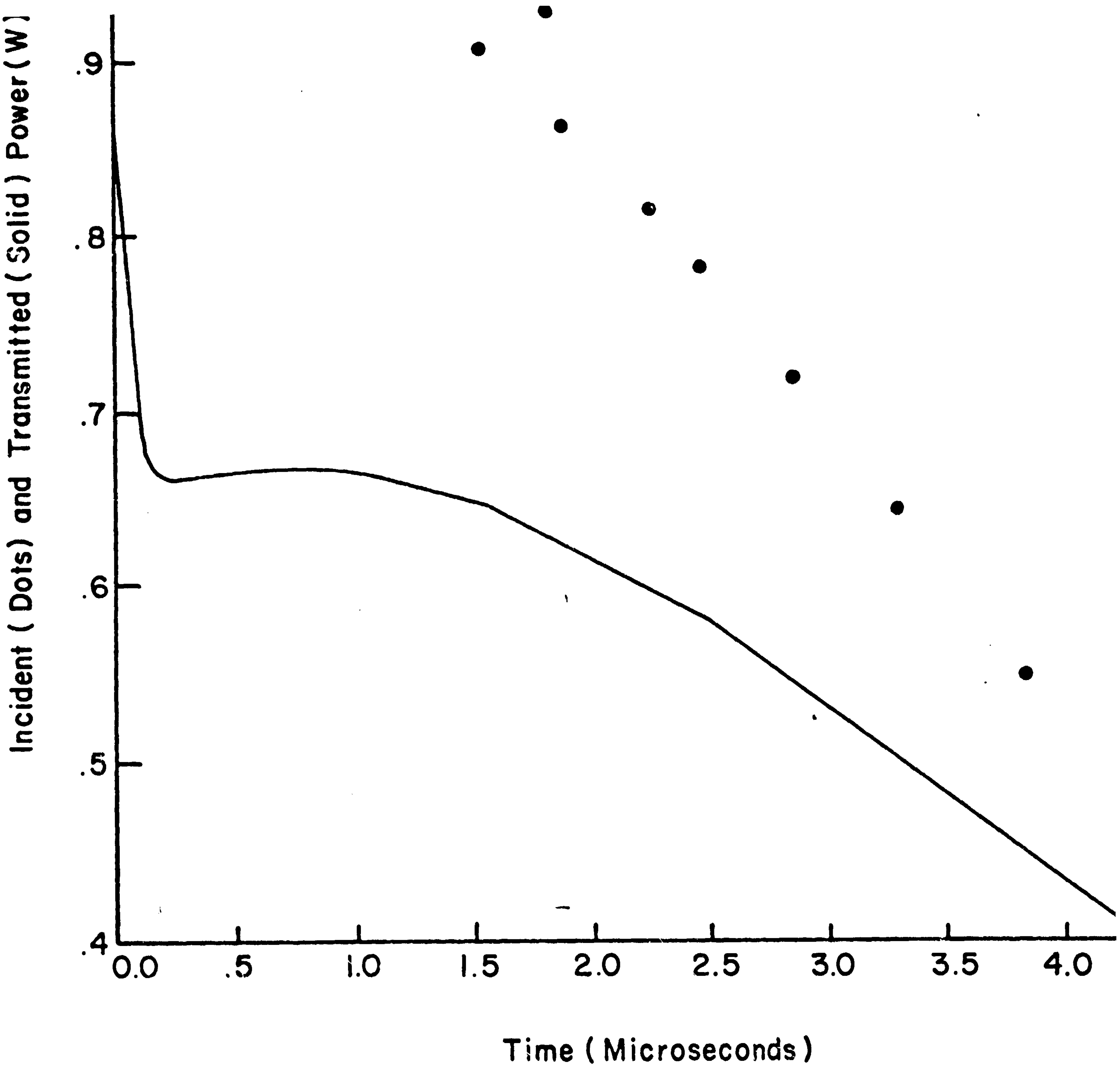

Fig. 2. uv transmission for 10 torr of $H_2O + D_2O$ in 160 cm cell.

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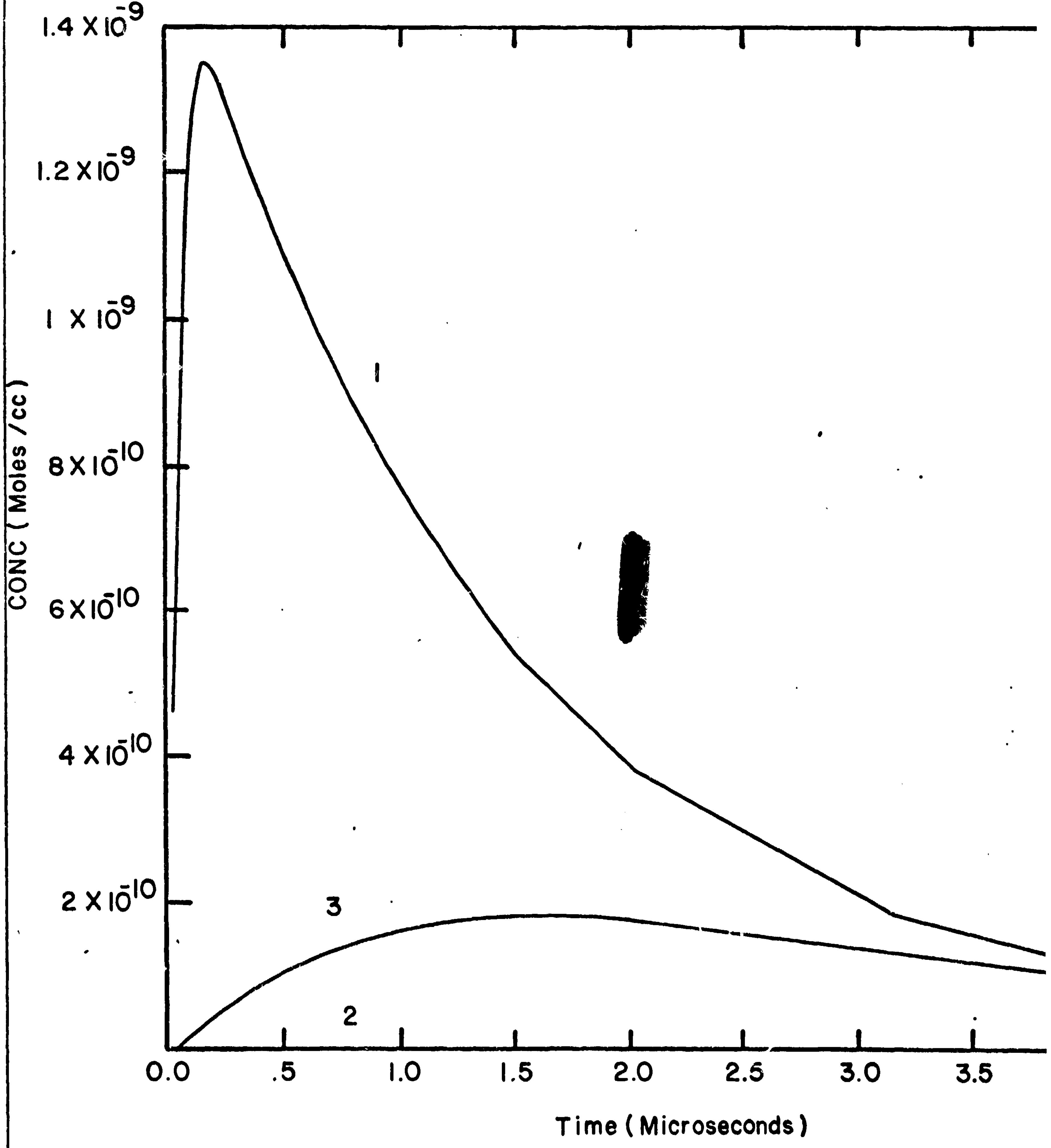
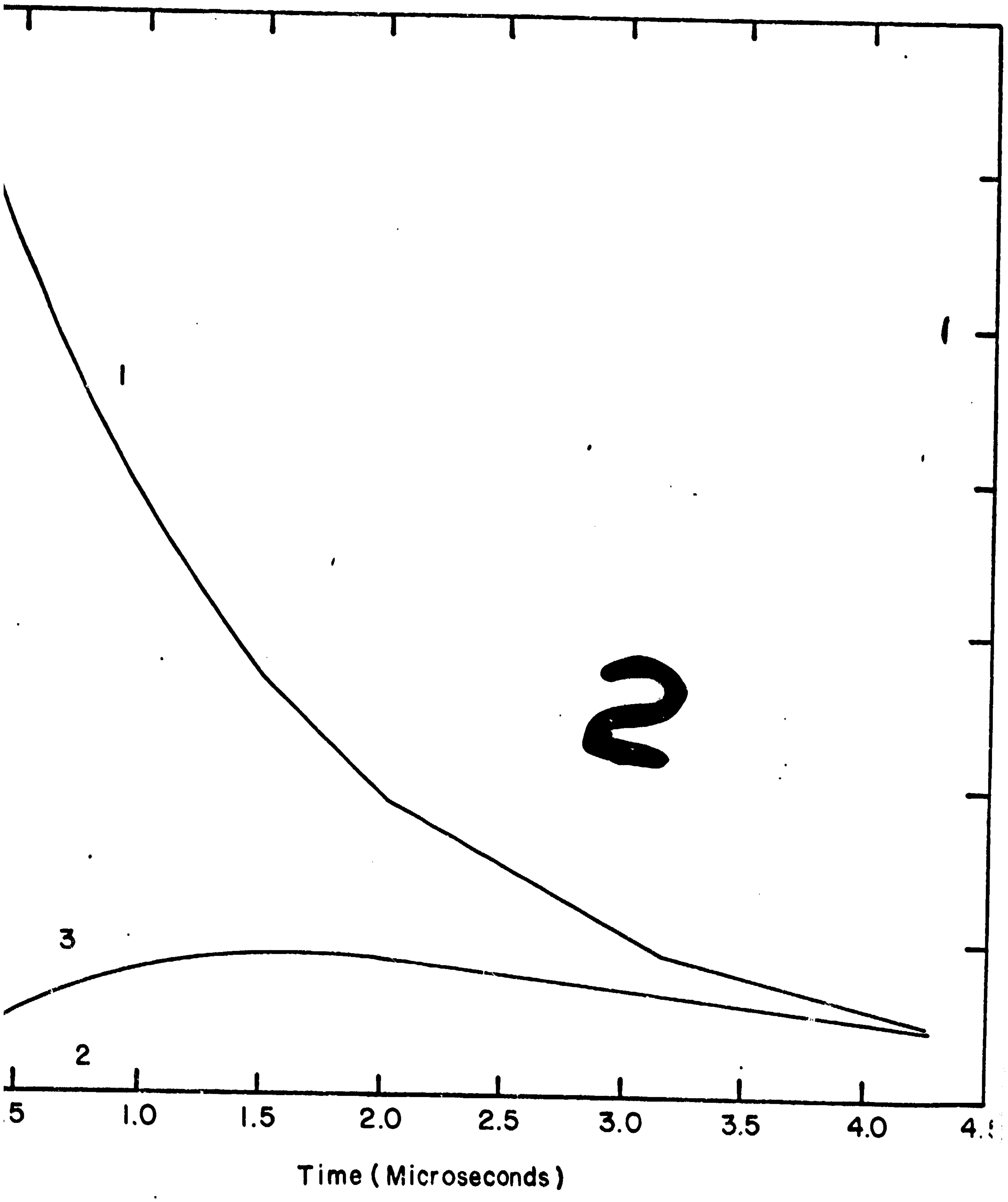


Fig. 3. I concentration of excited D_2O, 1; H_2O, 2; and HDO, 3



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