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TITLE PRODUCTION OF GALLIUM ATOMS BY EXCIMER LASER PHOTOLYSIS OF TRIMETHYL GALLIUM

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PRODUCTION OF GALLIUM ATOMS BY EXCIMER LASER PHOTOLYSIS
OF TRIMETHYL GALLIUM

by

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ABSTRACT

The gas phase kinetics of group III elements such as gallium are important in possible chemically driven energy transfer lasers and in chemical vapor deposition processes in the electronics industry. Excimer laser photodissociation of volatile gallium compounds via multiple photon process provides, in principle, a convenient room temperature source of gallium atoms for study using laser photolysis-laser induced fluorescence techniques. In this paper, we report preliminary results of the multiple photon dissociation of trimethyl gallium at 193 nm. Prompt emission from a number of excited gallium states (5^2S , 4^2D , 6^2S , 6^2P^0 , 5^2D , and 4^4P) has been observed. The time histories of the ground state ($4^1P^0_{1/2}$) and the metastable ($4^2P^0_{3/2}$) have been measured using laser induced fluorescence. The resulting time profiles are complicated even in the absence of a reactant gas by the apparent production of ground state gallium at relatively long times (~ 10 ns) after the excimer laser

pulse. Possible mechanisms for this (i.e., radical reactions to produce gallium, energy transfer cascading from high lying metastable states, ionic processes, etc.) are being investigated. These results indicate that the photodissociation of trimethyl gallium at 193 nm is complex. Photolysis studies at other wavelengths and with other precursors are in progress to find a cleaner source of gas phase atomic gallium for kinetic studies.

INTRODUCTION

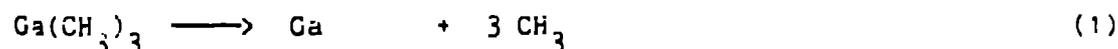
The overall objective of this research is to study the reaction and energy transfer kinetics of gas phase atomic gallium. Data on these processes are necessary to assess a potential chemical laser system based on chemical reaction followed by energy transfer to gallium atoms or which can lase on the $5^2S-4^2P_{3/2}^0$ transition at 417.2 nm. The group III elements, which include gallium, indium, and thallium, are particularly interesting as possible energy transfer laser candidates. Since the lowest $2P^0$ state is split into two spin-orbit components, the ground state ($2P_{1/2}^0$) and the metastable ($2P_{3/2}^0$) state, three level laser schemes are possible with lasing to the higher energy $2P_{3/2}^0$ state. For gallium, these states are 826 cm^{-1} apart.⁸ This is a large enough energy spacing so that there is little thermal population in the metastable state, making it an attractive lower level for a laser. The relatively small energy spacing, however, means that metastable gallium can probably be relaxed fairly efficiently via electronic to vibrational energy transfer by collisions with polyatomic gases. If so, this again would make this an attractive lower level for a laser by minimizing problems with bottlenecking, a buildup of population in the lower laser level.

The reaction and energy transfer kinetics of gas phase gallium atoms and gas phase red cells containing gallium may also play an important role in the deposition of gallium in chemical vapor deposition production of GaAs semiconductor devices. The preparation of a variety of group III-IV compound semiconductors by chemical vapor deposition of organometallic compounds has been demonstrated.² In particular, high purity GaAs has been prepared by such techniques using trimethyl gallium.³ Deposition of gallium metal on quanta substrates has been demonstrated by photolysis of trimethyl gallium at 257 nm using a cw frequency doubled argon ion laser.⁴ Ultraviolet laser photolysis of other organometallics has also been demonstrated as a means of producing a number of different metal films with submicrometer dimensions.⁵⁻⁷ Because metallic gallium has very little vapor pressure except at extremely high temperatures, studies of atomic gas phase gallium generally involve dissociation of some fairly volatile gallium compound, such as trimethyl gallium or the gallium trihalides. Trimethyl gallium has considerable vapor pressure at room temperature and thus, is in principle, a particularly good source of gallium for kinetic studies. This is the compound generally used in the electronics industry for gallium deposition. The ultraviolet spectrum of trimethyl gallium has been measured⁸ and the compound absorbs strongly at 193 nm, the wavelength of an ArF excimer laser. Thus, photolysis of trimethyl gallium would appear to be a particularly good way to produce gallium for study by the laser photolysis-LIF technique.

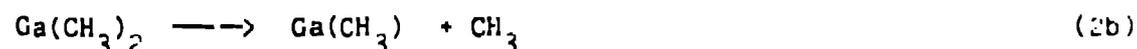
Although laser photolysis of a few organometallic compounds and their corresponding metal halides have been studied in some detail, relatively little has been done with the photochemistry of gallium containing compounds. Lasing

has been demonstrated in atomic gallium following photolysis of gallium triiodide vapor.⁹⁻¹¹ As discussed above, ultraviolet laser photolysis of trimethyl gallium has been used to deposit gallium metals onto surfaces for potential applications in the electronics industry. Recent experiments have detected atomic gallium by multiple photon ionization following photodissociation of trimethyl gallium using a visible laser tuned to atomic gallium resonances.¹²⁻¹³

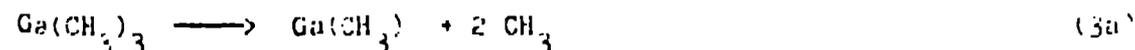
In the ultraviolet, where the absorption spectrum indicates a broad continuum, dissociation to produce gallium atoms occurs presumably either through direct dissociation of trimethyl gallium following absorption of one or more photons, such as



or through a sequential dissociation process, such as:



or



The mean gallium-carbon bond energies in trimethyl gallium have been measured,¹⁴⁻¹⁵ with a recommended value of 57.5 kcal mole.¹⁶ From a pyrolysis study of trimethyl gallium, Jacko and Price¹⁷ have suggested the following:



Based on these thermodynamic measurements, photodissociation of trimethyl gallium at 193 nm to produce gallium atoms must occur via at least a two photon process. The electronic spectra of the monomethyl gallium and dimethyl gallium radicals are unknown, and the excited electronic states are presumably dissociative. With the data available, it is not possible to rule out any of the multiple photon dissociation processes outlined in Sequences 1-3. At high laser fluences, other photofragments may also be produced via higher order processes.

In this paper, we present preliminary results on the production of atomic gallium in both the ground ($^2P_{1/2}^o$) state and in excited electronic states by photodissociation of trimethyl gallium at 193 nm. The implications of these results on the use of this source for gas phase energy transfer and reaction kinetic studies will be discussed.

EXPERIMENTAL

This basic approach in these experiments is to prepare gas phase atomic gallium essentially instantaneously by excimer laser photolysis of some suitable volatile precursor, such as trimethyl gallium or gallium trichloride. The atomic gallium is then detected by laser induced fluorescence in which a laser

is tuned to the resonant wavelength of an atomic transition and then fluorescence from the resulting excited gallium atom is detected. By scanning the time delay between the photolysis laser and the probe laser, the lifetime of the gallium state is measured.

The optical arrangement of the experiment is shown in Figure 1. The photolysis laser is a Lambda Physik EMG-102 rare gas halide excimer laser operating on ArF at 193 nm with unstable resonator optics. Ground state atomic gallium ($^2P_{1/2}^0$) is probed by laser induced fluorescence (LIF) by exciting the $^2S-^2P_{1/2}^0$ transition at 403.3 nm and monitoring the fluorescence from the $^2S-^2P_{3/2}^0$ transition at 417.2 nm. The population of the gallium metastable $^2P_{3/2}^0$ state is monitored similarly by exciting at 417.2 nm and monitoring the 403.3 nm fluorescence. The probe laser wavelengths are generated using a Quanta Ray Nd:YAG pumped dye laser with suitable nonlinear mixing crystals. The 403.3 nm light is obtained by pumping the dye DCM with the doubled output of the Nd:YAG laser and then mixing the dye laser output with the 1.06 μm output of the Nd:YAG laser. The 417.2 nm light is generated by pumping Stilbene 420 dye with the third harmonic of the Nd:YAG laser. The time histories of the $\text{Ga}(^2P_{1/2}^0)$ and $\text{Ga}(^2P_{3/2}^0)$ states are measured by scanning the time delay between the photolysis laser and the probe laser while monitoring the fluorescence. The lasers are aligned collinearly through the flow cell using suitable Suprasil 2 lenses and a dichroic mirror. For studies of the effect of emission intensity with laser fluence, a fraction of the excimer laser beam is sampled using a quartz flat and the laser energy measured using a Laser Precision Model RJ-7200 energy meter interfaced to the computer. The laser energy could be systematically varied by attenuation using quartz flats.

The fluorescence is imaged through a 0.25 m monochromator equipped with variable slits or through a dielectric filter onto the element of an RCA 31034 photomultiplier tube. The photomultiplier signal is amplified and sent to either a Tektronix R7912 transient digitizer or to PAR Model 162 boxcar signal averager. The processed signal is then recorded on a Nova 3 computer and transferred to a larger computer for analysis. For studies of gallium states produced electronically excited in the multiple photon dissociation, the signals are processed using the transient digitizer to measure their lifetimes. The transient digitizer is also used for fluence studies in which the integrated intensity from a given electronic state is measured as a function of the fluence (energy/cm²) of the photolysis laser. The boxcar averager is used in the LIF experiments of the ground state (²P_{1/2}^o) and metastable (²P_{3/2}^o) gallium time profiles by integrating the LIF signal as the time delay between the photolysis laser (which produces the gallium atoms) and the probe laser is scanned.

A schematic of the vacuum system is shown in Figure 2. Gases are slowly flowed (~0.1 slm) to avoid a buildup of photolysis products. The flows of a precursor mixture and buffer gas are measured and controlled using Tylan mass flow controllers. Argon is generally used as a buffer gas to minimize diffusion effects and to translationally equilibrate the photofragments. The precursor, trimethyl gallium, is generally flowed from a 1% mixture in argon. Flows are chosen so that the viewing region will be completely swept out between laser shots. Pressures are measured with a MKS capacitance manometer. The windows where the laser beams enter and exit are purged using a buffer gas to minimize window deterioration by buildup of gallium on the windows from the photolysis. Typical conditions for these experiments are approximately 20 torr

of argon and 1 mtorr of trimethyl gallium. Under these conditions, the concentrations of trimethyl gallium and the resulting gallium atoms are low to minimize complications due to radical-radical processes or product buildup and to minimize problems with radiation trapping of the fluorescence. .

The trimethyl gallium is electronic grade (99.9995%) purity and was obtained commercially. One percent precursor mixtures of trimethyl gallium with argon are prepared in an all welded Teflon-lined stainless steel cylinder to avoid decomposition or exchange problems. The argon used is research grade (99.999%).

RESULTS

Initial experiments monitored the production of $Ga(2S)$ produced directly in the photolysis of trimethyl gallium at 193 nm. Emission at 403.3 and 417.2 nm from the $5^2S-4^2P_{1/2}^0$ and $5^2S-4^2P_{3/2}^0$ transitions, respectively, was observed. The signal strength of this emission as a function of excimer laser fluence is shown in Figure 3. An analysis of this data indicates an apparent second order dependence of the signal on laser energy, indicating at least a two photon process for the production of $Ga(5^2S)$.

Laser induced fluorescence experiments to detect ground state $Ga(4^2P_{1/2}^0)$ and measure its lifetime were then begun. The temporal behavior of the ground state gallium for a typical set of conditions is shown in Figure 4, for a mixture of argon and approximately 1 mtorr of trimethyl gallium. The very fast rise from zero corresponds to direct production of ground state gallium in the photolysis of trimethyl gallium and includes contributions from excited states that rapidly radiate down to the ground state. A slower rise, is noted in the signal followed by a much slower decay, presumably from diffusion and perhaps

reaction with the precursor. Initially, the slow rise in the signal was thought to arise from electronic relaxation by collisions with argon of the metastable $^2P_{3/2}^0$ state produced in the photolysis. The lifetime of the $^2P_{3/2}^0$ state under the same conditions was then measured using LIF. The result is shown in Figure 5. The slow decay of the metastable state does not correlate with the slow rise in the ground state population indicating that the ground state rise is not due to simple collisional quenching of the $P_{3/2}^0$ state process but that other more complicated processes are involved. Perhaps other metastable states are involved in the energy transfer to the ground state.

To investigate this further, an emission spectrum was taken of the excited photofragments produced in the dissociation. Numerous lines were observed as shown in Figure 6. Assignments of the spectrum reveal that the bands near 314 nm, 390 nm, and 430 nm arise from emission from electronically excited CH radical produced in the photodissociation, corresponding to the C-X, B-X, and A-X transitions, respectively.¹⁸ The remaining lines can be assigned to emission from electronically excited gallium atoms produced in the photodissociation. The energy level diagram for atomic gallium is shown in Figure 7. The states from which emission has been observed are labeled and the transitions observed in this experiment are shown. It is interesting to note that not only are dipole allowed transitions observed but also the spin forbidden transition from the 4^4P state. Preliminary studies of the dependence of the excited state populations on photolysis laser fluence indicate that the prompt emission arises from a process requiring 2-3 photons with the higher gallium energy levels having higher dependence on laser fluence. Experiments are in progress to quantify these results.

The temporal behavior of each of the excited gallium electronic states can be characterized by two components. A fast component corresponding to the initial production of the excited state by the multiple photon dissociation of trimethyl gallium. This component has a lifetime characteristic of the excited state. For the dipole allowed transitions, these lifetimes are approximately the radiative lifetimes which are short, 6-200 ns,¹⁹ for the dipole allowed transitions and quenching is not important under these conditions. For the ⁴P state, which is coupled to the ground state via a spin-forbidden transition, a somewhat longer lifetime is observed and the effects of electronic quenching by collisions with argon may be significant. The second component of the signals is a much longer slow rise on the order of 10 μ s followed by a much longer decay on the order of 100 μ s. The process that produces excited gallium atoms at long times may well be the same process that gives rise to the complex time behavior of the ground state gallium. Experiments are in progress to check this and to measure the dependence of both the prompt signals and the long-lived component of the emission on trimethyl gallium pressure and photolysis laser fluence.

DISCUSSIONS AND CONCLUSIONS

Emission from a number of electronically excited states of gallium atom (5^2S , 4^2D , 6^2S , 6^2P^o , 5^2D , and 4^4P) has been observed following multiple photon dissociation of trimethyl gallium at 193 nm. The dependence of the signals on laser fluence indicates that these states are being produced by processes involving 2-3 photons. This fluence dependence agrees with the thermodynamic calculations presented earlier but does not clarify which of the three dissociation sequences is occurring. The observed fluence dependence

seems to increase with increasing energy levels of the gallium. Emission from these states is also observed at longer times apparently arising from collisional processes. Possible explanations include cascading from high lying metastable states of gallium produced in the photodissociation, radical reactions with triethyl gallium or other radicals, energy transfer from excited metastable photofragments, and ionic processes since the energy of a 193 nm photon is above the ionization limit of atomic gallium. A significant number of gallium ions may be produced similarly. Since this process used 2-3 photons, an enormous amount of energy is potentially available for excitation of the photofragments.

The time behaviors of the ground state ($^2P_{1/2}^0$) and of the metastable ($^2P_{3/2}^0$) state are complicated. The ground state population shows a risetime that cannot be explained by radiative cascading from the observed electronically excited states initially produced in the photodissociation or from the metastable ($^2P_{3/2}^0$) state, but may be due to cascading from metastable states produced in the photolysis or from processes such as those described above to account for the long-time component of the excited gallium atoms. Further work is in progress to explain this behavior and to correlate it with the time behavior of the excited gallium states.

The observation of electronically excited CH radicals indicates that the photodissociation of trimethyl gallium at 193 nm is a very violent process. The CH emission shows a dependence on photolysis laser fluence similar to that of the excited gallium states. It is not clear if the excited CH arises from a dissociation of trimethyl gallium, monomethyl gallium, dimethyl gallium or methyl radicals. With the energy of 2-3 193 nm photons, an enormous number of dissociative channels are energetically possible. The A $^2\Delta$ state of CH has a

radiative lifetime of 538 ± 5 ns.²⁰ From the observed spectrum, by comparison with the excited gallium atom emission, the production of CH(A) would appear to be significant but not out of the major dissociative channels. Experiments have not yet been done to measure the amount of ground state CH radical produced.

These results indicate that trimethyl gallium photodissociation at 193 nm is complex. Mechanistic considerations suggest that a cleaner source might be achieved by using longer wavelengths or other precursors. Work is in progress to evaluate production of atomic gallium at these longer wavelengths, such as 246 nm, where ionization of the atomic gallium should not be important and to consider other volatile precursors, such as gallium trichloride. Gallium trichloride photochemistry should be simpler since complicated channels such as those possible with CH₃ will not be present. Similarly, any secondary chemical processes should be less important than appears to be the case for trimethyl gallium, since Cl atoms should behave differently from methyl radicals. The temporal behavior of the gallium atoms produced by photolysis of trimethyl gallium at 248 nm is quite different than that at 193 nm. This may be an encouraging result for future kinetics studies.

ACKNOWLEDGMENTS

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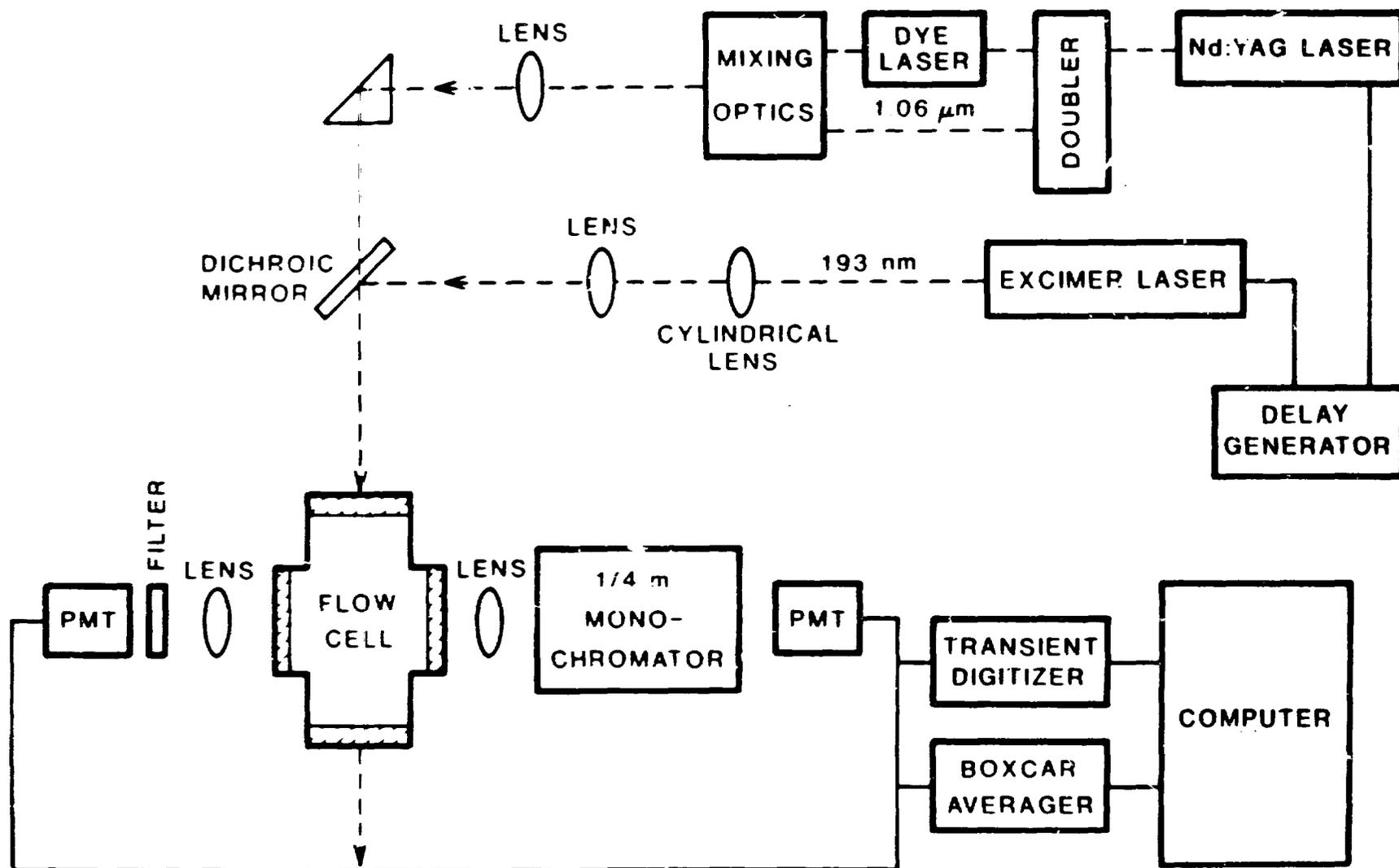
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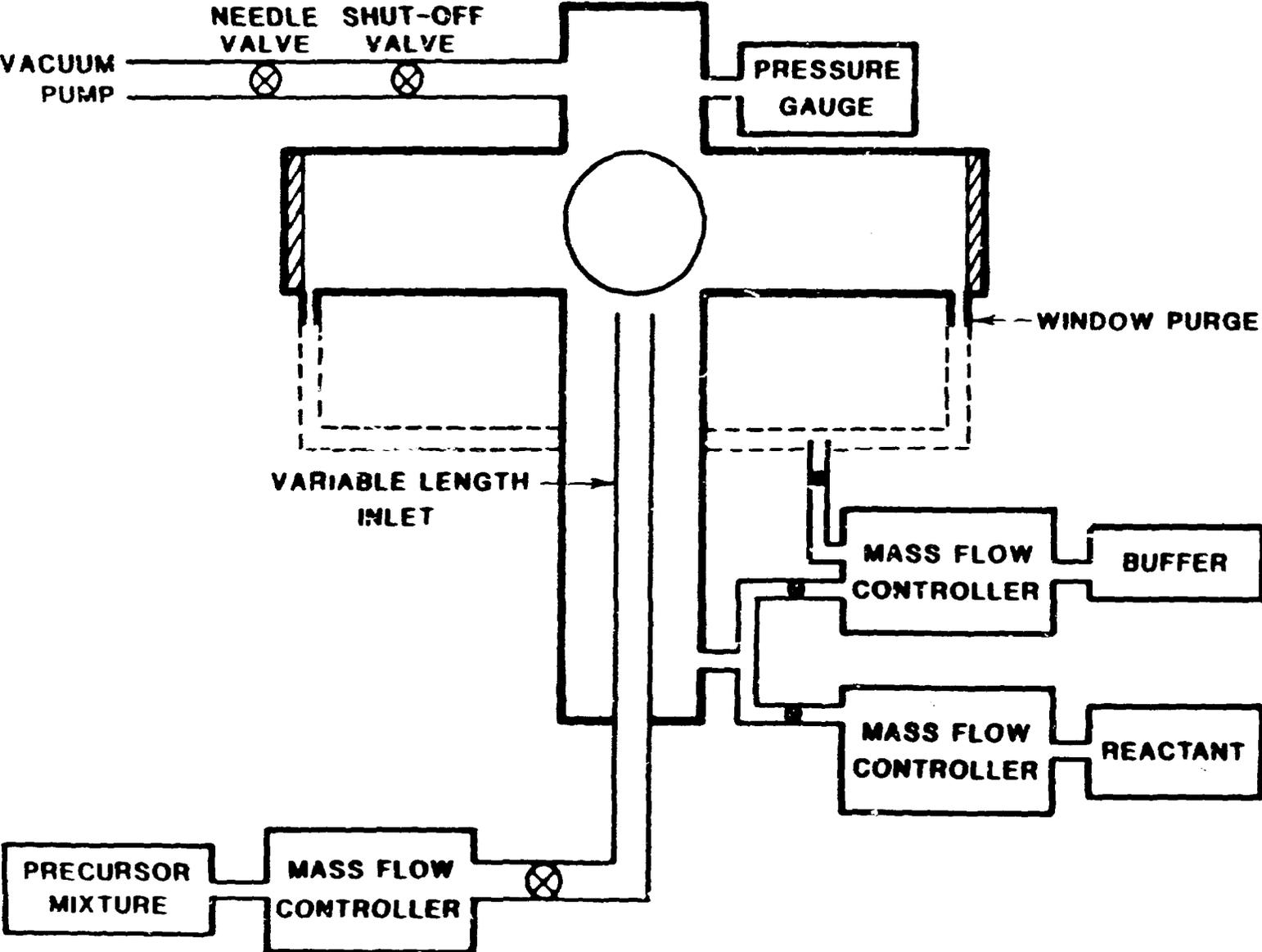
FIGURE CAPTIONS

- Fig. 1. Optical schematic for kinetic experiments using the laser photolysis LIF probe technique.
- Fig. 2. Schematic of the flow system and gas handling system.
- Fig. 3. Dependence of the Ga(5^2S) emission on 193 nm laser fluence in trimethyl gallium photolysis.
- Fig. 4. Time behavior of the ground state gallium ($4^2P_{1/2}^0$) density following 193 nm photolysis of trimethyl gallium. The sharp rise corresponds to the excimer laser firing.
- Fig. 5. Time behavior of the metastable gallium ($4^2P_{3/2}^0$) density following 193 nm photolysis of trimethyl gallium. The sharp rise corresponds to the firing of the excimer laser.
- Fig. 6. Prompt emission spectrum resulting from 193 nm photolysis of trimethyl gallium. The transitions from electronically excited gallium atoms and CH radicals are identified.
- Fig. 7. Energy level diagram for atomic gallium showing the observed transitions.

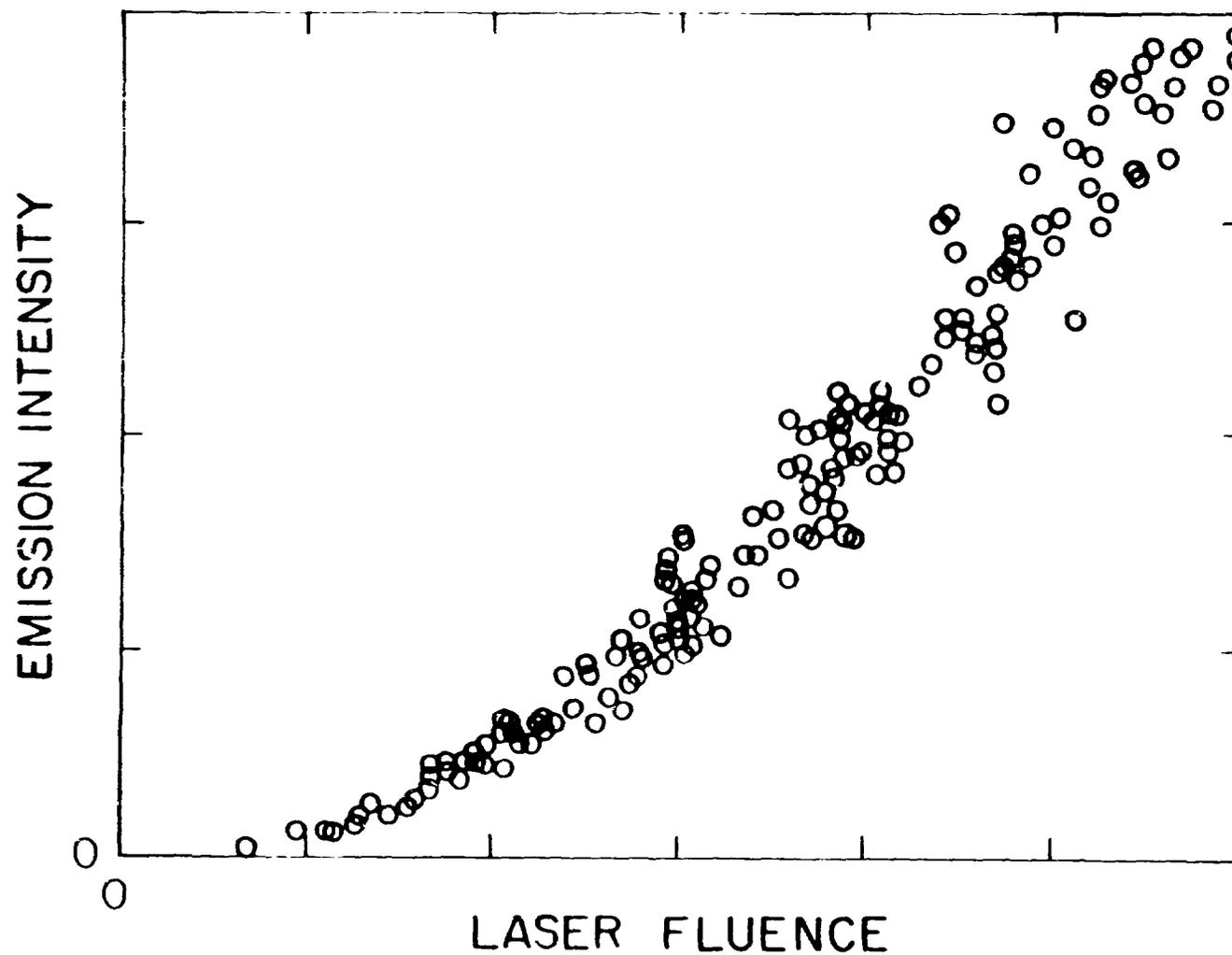
OPTICAL SCHEMATIC FOR KINETICS EXPERIMENTS USING THE LASER PHOTOLYSIS/LIF PROBE TECHNIQUE



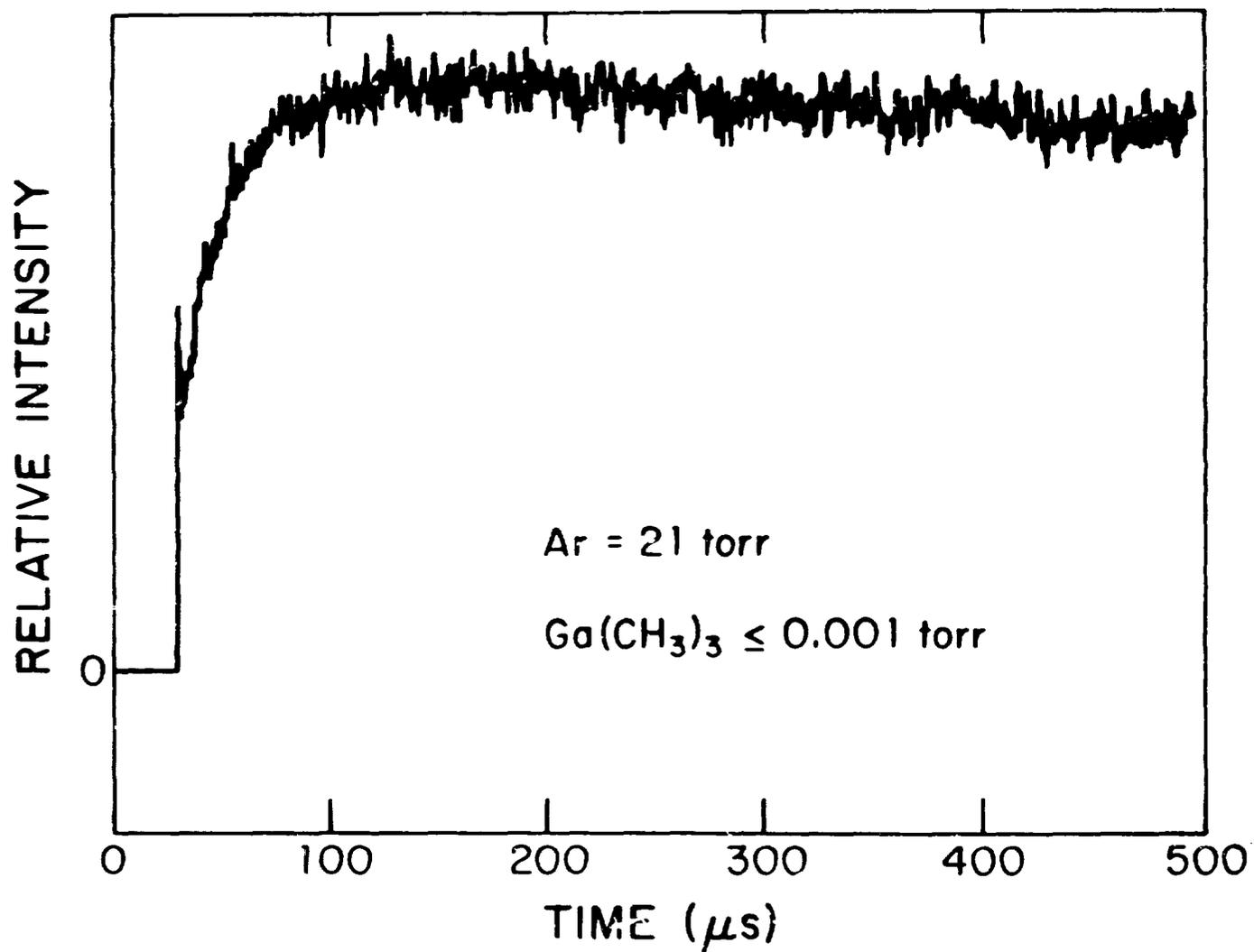
FLOW SYSTEM SCHEMATIC



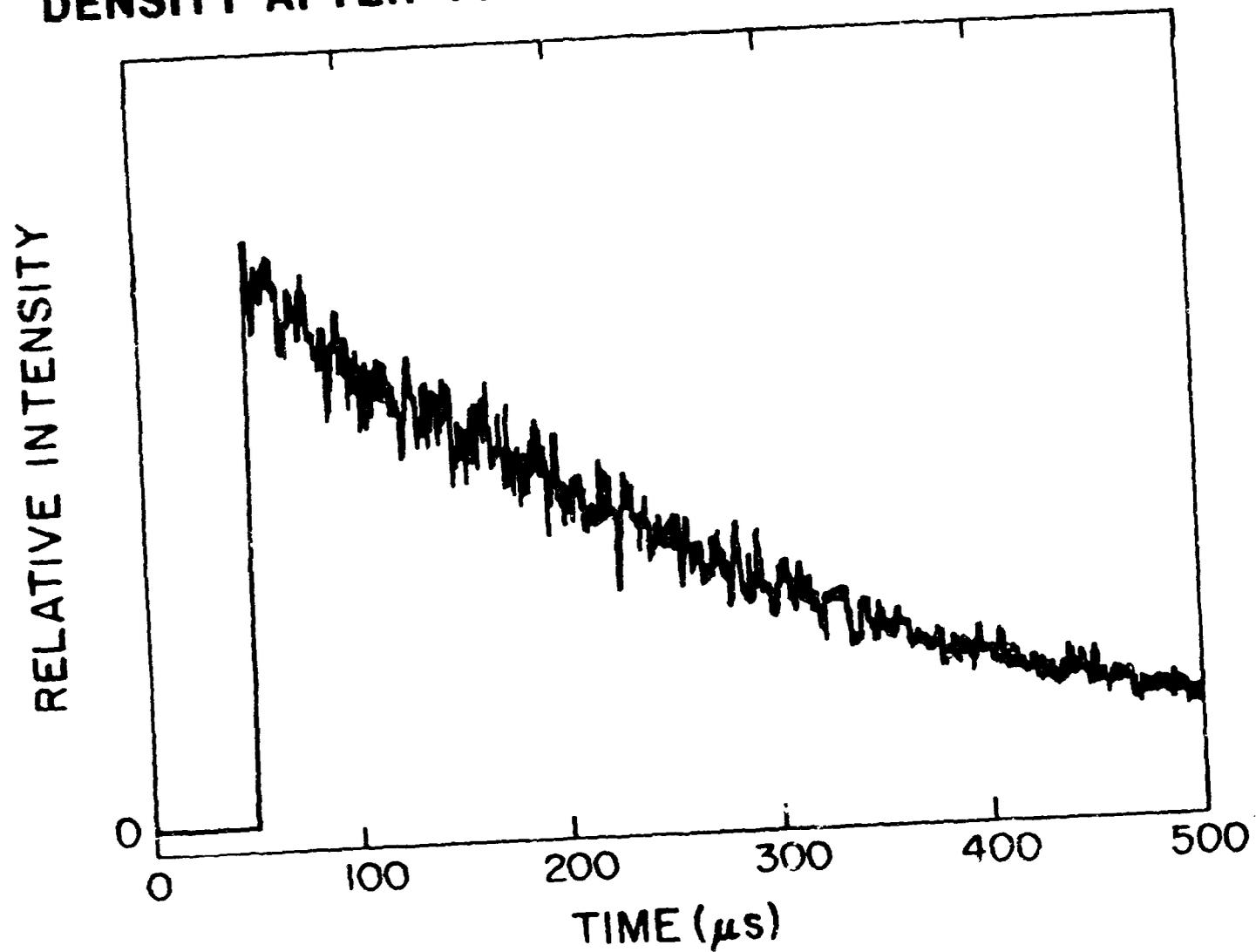
DEPENDENCE OF $G_{\alpha}(5^2S)$ EMISSION ON 193nm LASER FLUENCE IN $Ga(CH_3)_3$ PHOTOLYSIS



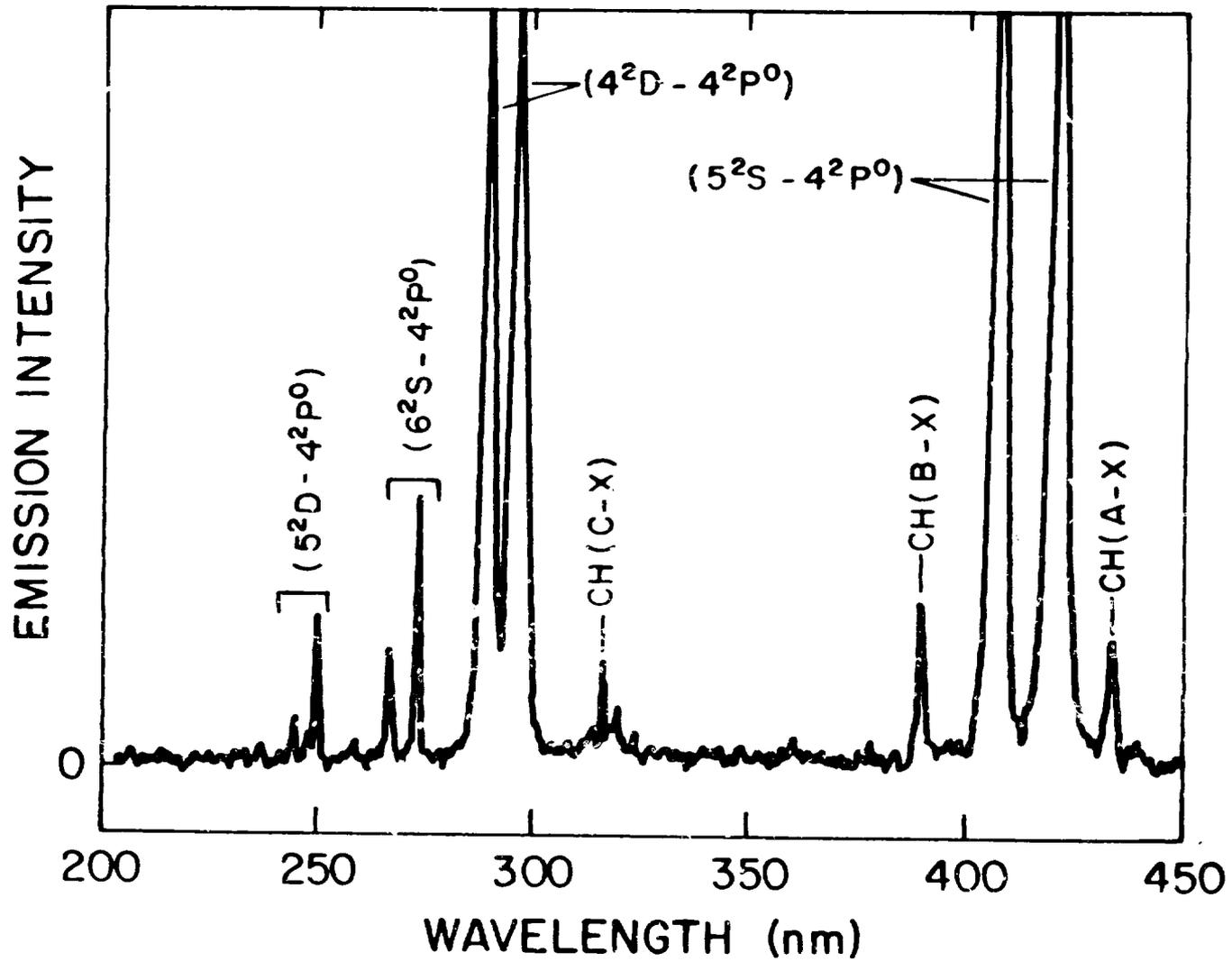
TIME BEHAVIOR OF GROUND STATE GALLIUM ($4^2P_{1/2}$)
DENSITY AFTER 193 nm PHOTOLYSIS OF $\text{Ga}(\text{CH}_3)_3$



TIME BEHAVIOR OF METASTABLE GALLIUM ($4^2P_{3/2}$)
DENSITY AFTER 193 nm PHOTOLYSIS OF $\text{Ga}(\text{CH}_3)_3$



**EMISSION SPECTRUM RESULTING
FROM 193 nm PHOTOLYSIS OF Ga(CH₃)₃**



GALLIUM ENERGY LEVELS

