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A MEASUREMENT OF VIBRATIONAL EXCITATION IN NO PRODUCED IN THE P--ETC(U)

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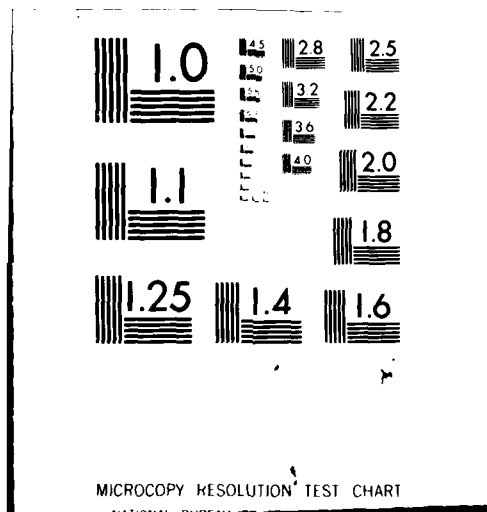
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IN THE PHOTODISSOCIATION OF NOCl AND NOBr at 193 nm

by

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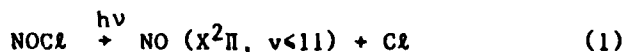
Abstract

Infrared emission has been observed from the vibrational state v_n (n equals 1 to > 16) of the nascent NO ($X^2\Pi$) photofragment produced in the photodissociation of NOCl and NOBr at 193 nm. The photodissociation was observed to be a single photon process. Models and mechanisms of photodissociation are discussed in view of experimental observations.

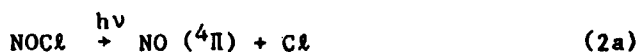
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I. Introduction

The U.V. photochemistry of the nitrosyl halides, especially NOCl, has been of continuing interest since 1930, when Kistiakowsky observed the production of NO in the photodissociation of NOCl at wavelengths from 365 to 635 nm.¹ In 1962 Basco and Norrish observed vibrational excitation up to $v=11$ in NO via absorption measurements during the flash photolysis of NOCl.² They postulated two mechanisms for the dissociation.



or



followed by



Though it was not possible for them to make a definitive choice between either of the mechanisms, they found that the rate of production of vibrationally excited NO was independent of added inert gas or chlorine or NO. This indicated that (1) was the likely mechanism for production of vibrationally hot NO. Busch and Wilson found that a directly dissociative mechanism was responsible for production of NO when NOCl was dissociated by 347 nm radiation.³ NOCl was photodissociated in a molecular beam photofragment spectrometer and the results indicated that the NOCl dissociated in less than 8×10^{-14} seconds from a state of A^- symmetry.

The NO($^4\Pi$) state involved in mechanism 2 was first predicted in 1932 by Mulliken to be a bound state 4.5 eV above the ground state.⁴ Since then, it has been suggested that this state is responsible for predissociation in the $\delta(C^2\Pi-X^2\Pi)$ band which occurs above $v'=1$ ^{5,6} and for the absence of emission from

the higher vibrational levels of the $B^2\Pi$ state, a result of a potential curve crossing of the 4Π and $B^2\Pi$ states.⁷ There have been a number of studies utilizing optical spectroscopy in which observed bands are assigned to transitions involving the 4Π state though spectroscopic assignments are less than definitive.⁸⁻¹¹ However, Frueholz, et. al., have recently observed the transitions $X^2\Pi \ v=0 \rightarrow a^4\Pi \ v'$ ($v'=4-8$) using electron impact spectroscopy.¹² From their data the energy of the $a^4\Pi \ v'=4$ state is 5.22 (± 0.02) eV above the ground states.

A comparison of the amount of vibrational excitation in the NO fragment at the limited number of discrete photolysis wavelengths used previously indicates that as the photolysis wavelength decreases, the percentage of available energy partitioned into vibration increases. At photolysis wavelengths of 480 nm or longer Grimley and Houston saw no initial infrared emission from the NO photofragment when viewing combined emission from the NO $v \rightarrow v-1$ ($v=1,2,3$) transitions during NOCl photodissociation.¹³ At 355 nm they observed that approximately half of the total fluorescence amplitude was immediate (detector response limited) which they assigned to initial vibrational excitation in these levels. The data of Busch and Wilson at 347 nm allowed for the production of NO ($v=1,2,3$). However, their recoil energy distribution was also accurately predicted by an impulsive model in which all of the NO fragments were formed in $v=0$. The results of Basco and Norrish indicated that highly vibrationally excited NO may be produced at shorter wavelengths. A population inversion has been obtained in the photodissociation of NOCl in a number of studies.¹⁴⁻¹⁶ In his work Deutsch observed laser action up to $v=11$ from flash photolyzed NOCl.¹⁶ Welge has photolyzed NOCl in the vacuum ultraviolet and has observed NO($A^2\Sigma^+$) for photolysis wave-

lengths of 160 nm or shorter.¹⁷ These photodissociation studies, although performed at a limited number of discrete wavelengths, indicate that the percentage of available energy partitioned into vibration increases rapidly with increasing photolysis energy with electronically excited NO observed at wavelengths shorter than 160 nm.

II. Experimental

The laser used in these experiments was a Lambda Physik excimer laser operating on an ArF(193 nm) lasing mixture. The repetition rate was varied from 1-10 Hz and the energy of the beam was typically 5-7 mJ/pulse measured by a calibrated thermopile at the photolysis cell front. The energy was contained in a beam which was confined to an approximate 2 cm diameter by an iris immediately in front of the cell. Laser energy varied $\leq 3\%$ during a measurement.

The stainless steel photolysis cell had dimensions of 3.5 cm diameter and 20 cm length. It was equipped with CaF_2 windows in the beam path and NaCl windows at right angles to the beam.

The gases were flowed through the cell from a reservoir held at 1-3 atmospheres pressure. Cell pressure was measured by a capacitance monometer, and flow rates were controlled by two metering valves, one before and one after the cell. The gases were trapped by a series of liquid nitrogen traps before diffusion and rough pumps. In these experiments a sufficient rate of flow was maintained for signal intensity to be independent of flow rate. During a measurement cell pressure varied by less than 3%.

Emission was viewed using a photovoltaic Au:Ge detector with a response time of 1.05 μsec when biased at 5k Ω .¹⁸ The output of the detector was

amplified using an Advanced Kinetics amplifier, digitized by a Biomation 8100 digitizer, and averaged using a Nicolet 1170 averager. Signals were stored and analyzed using a Data General Nova 4 computer.

A circular variable interference filter (CVF) placed between the cell and the detector was used to isolate specific spectral regions of 30 cm^{-1} width (FWHM). (or 50 cm^{-1} , for a 1% cutoff) with a slit width of .040" and a spectral width of 100 cm^{-1} (1% cutoff) with a slit width of .50". The NO anharmonicity constant is approximately 28 cm^{-1} .¹⁹ To determine the degree of vibrational excitation in the NO fragment, the CVF with a slit width of .040" was scanned from an initial spectral region of $5.21\text{--}5.35\text{ }\mu\text{m}$ to a spectral region of $6.85\text{--}7.08\text{ }\mu\text{m}$. In this way the vibrational manifold ($\sim v=1\text{--}18$) of NO was scanned, viewing at most 3 adjacent transitions at a time. It was not possible to isolate single transitions with the CVF.

NOCl was obtained from Matheson with a minimum purity of 97%. NOBr was prepared by mixing equal pressures of NO (Matheson, 99%) and Br_2 (Mallinckrodt, ACS) in a glass bulb. After 12 hours or more any unreacted NO was distilled off at 138°K and the NOBr was then drawn off at 189°K .

III. Results

Figure 1 displays a signal obtained after 1024 laser pulses with 50 millitorr of NOCl in the photolysis cell under flowing conditions. The CVF was used with the .040" slit, isolating a spectral region from 1500 cm^{-1} to 1550 cm^{-1} (1% cutoff). The $v=14\rightarrow 13$ and $v=13\rightarrow 12$ transitions are at approximately 1512 cm^{-1} and 1540 cm^{-1} , respectively.¹⁹ The initial amplitude of the fluorescence is due to NO ($v=13,14$) formed in the primary photolytic step of the photodissociation of NOCl . Similar instantaneous amplitudes were obtained

when scanning the lower NO ($v \leq 12$) transitions resulting from NOCl photodissociation. The higher transitions, $v=15 \rightarrow 17$, were insufficiently strong at this pressure for definite observation of an immediate rise. Initial fast rises were also present in signals obtained with 100 mtorr of NOBr when viewing NO ($v=13,14$) or lower transitions. At pressures of 300 mtorr, the transitions NO $v \rightarrow v-1$ ($v=15 \rightarrow 17$) produced from either NOCl or NOBr were observed to possess initial rises which, as in the above cases, rose with a detection limited rate.

The percentage of molecules dissociated per pulse at energies of 15 mj/pulse or less was found to be $\leq 3\%$ for NOCl and $\leq 1\%$ for NOBr. This was determined by measuring the increase in cell pressure as a function of the number of laser pulses. With 5 torr in a sealed photolysis cell and a laser repetition rate of 2 Hz, the rise in cell pressure was linearly dependent on the number of laser pulses for both NOCl and NOBr. The slope was used to calculate percentage dissociation.

Figure 2 is a plot of the integrated fluorescence intensity from the transition NO $v \rightarrow v-1$ ($v=13 \rightarrow 17$) of NOBr as a function of laser energy. The range of laser energy is that used in the reported measurements. These transitions were isolated using the CVF with a slit width of .50". A similar linear plot was obtained for the integrated fluorescence intensity from NO ($v=13 \rightarrow 17$) for NOCl photodissociation at laser energies up to 17 mj/pulse.

When scanning through the vibrational transitions of the NO photofragment using the CVF, a general trend is noted (Figure 3). For both NOCl and NOBr, the lower transitions ($v=1-4$) exhibit an initial immediate emission intensity of amplitude $> 1/2$ of the maximum. After the initial rise, these signals possess

an additional rise at short time and a fall at longer time. As the CVF is scanned and transitions higher in the vibrational manifold are viewed, the percentage of amplitude attributable to the slow rise diminished, with complete disappearance of the slow rise at approximately NO $v=6,7$. It should also be noted that as the higher transitions are viewed, the observed rate of the fall increases. As stated previously, vibrational excitation was definitively observed up to NO ($v=16$) for both NOCl and NOBr, but the spectral resolution (± 1 transition) did not allow us to determine if the degree of vibrational excitation in the NO fragment produced from NOBr and NOCl was identical.

Discussion

A rapid rise in emission from NO is observed for the $v=1 \rightarrow 13$ states on a μsec timescale at 50μ pressure of NOCl. Thus any process that was collisional that was involved in the production of excited NO would have to possess a cross-section that was $\sim$ twice gas kinetic. Due to insufficient signal to noise ratios, higher states in NO resulting from the photolysis of NOCl and all NO states resulting from the photolysis of NOBr could not be viewed at this pressure. However, NO states resulting from NOBr photolysis could be viewed at pressures as low as $100\mu - 300\mu$ as could NO states above $v=13$ from NOCl. Thus even for these states in these systems a collisional process, if involved, would have to have a cross-section of $1/3$ gas kinetic to gas kinetic.

If the process in equation 2 were involved in the production of vibrationally hot NO following photolysis of NOCl, it is reasonable to expect that process 2 would be applicable for all vibrational states in the photolytically produced NO. Thus by this reasoning, unless process 2b could occur with

greater than gas kinetic cross-section, it is possible to rule out process 2 as being involved in the production of $\text{NO}(^2\Pi)$ hot vibrational states in the photolysis of NOCl . Though for NOBr our actual experimental observations only allow us to rule out processes of type 2b with cross-sections less than gas kinetic, the similarity of the distributions of NO produced from the photolysis of NOCl and NOBr would argue that equation 2 is not important for either NOCl or NOBr .

Similarly, other processes leading to vibrationally hot NO can be ruled out as the source of the initial fast rise that we observe. NO^* can be produced via the reaction

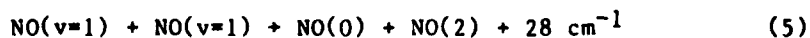


This reaction has been shown to produce NO only in low lying vibrational states ($v=0-3$) and even for these states the measured rate constant of reference 13 of $5.40 \pm .47 \times 10^{-12}$ cc molecule $^{-1}$ sec $^{-1}$ would produce a rise time of >50 μsec under our conditions. In reference 13, a similar rate constant has been measured for the analogous NOBr reaction. A faster rate constant for the reaction



of 3.6×10^{-10} cc molecule $^{-1}$ sec $^{-1}$ has been measured in reference 20. This would give a rise time of ~ 1 μsec under our conditions. However, this would only produce NO in the low lying ($v=0-3$) levels.

Energy transfer processes can be ruled out as the source of the initial excitation in high lying levels. The process



has a rate constant of $1.24 \pm 0.27 \times 10^5$ sec $^{-1}$ torr $^{-1}$.²¹ Virtually any energy transfer process of this type can be ruled out since the total NO concentra-

tion is only at most 3% of the NOCl concentration and the cross-section for the process in equation 5 is significantly (~ 100 times) less than gas kinetic.

Energy transfer from excited chlorine atoms to NO may also be ruled out. The $\text{Cl}(^2\text{P}_{1/2})$ level is at 881 wave numbers and could not be expected to be efficient at populating even $\text{NO}(v=1)$. $\text{Br}(^2\text{P}_{1/2})$ is at 3678 wave numbers. Reference 22 and 23 provide an upper limit for the rate constant for energy transfer from $\text{Br}(^2\text{P}_{1/2})$ to NO which is less than gas kinetic. Even if this process occurred it would only populate $v=1$ or 2. Other plausible energy transfer processes would seem to require multiple collisional events.

From the above evidence it can be concluded that the source of the initial vibrational excitation in NO produced in the photolysis of either NOCl or NOBr is not due to collisional processes. Thus a direct dissociation process of the type illustrated in equation 1 is the source of vibrationally hot NO.

A slower rise following the initial fast rise is observable for the lower levels of the NO vibrational manifold (fig. 3). This is followed by a slow fall. The source of this rise and fall is likely due to energy transfer processes of the type illustrated in equation 5 convoluted with processes that involve NOX as a collision partner. The fact that the slow rise is only observed for the lower states in the NO manifold ($v=1-5$) suggests that it is due to V-V and $V + T/R$ relaxation processes following the formation of NO^* which lead to equilibration or partial equilibration of the NO vibrational manifold. It is only seen in the lower NO states since equilibration of the NO manifold population should cause a build up of population in these states.

The slow fall seen in all the states would then represent the further relaxation of the equilibrated or partially equilibrated vibrational manifold. Depending on the relative magnitude of V-V and $V + T/R$ steps for the various vibrational states, the observed increase in rate of the slow fall as a func-

tion of v could be due to a combination of the following factors:

(1) High lying states in a highly excited system appear to relax at v times the rate of the $v=1$ state if all states are coupled on the timescale of the fall by processes of the type:^{24,25}



(2) Direct $V \rightarrow T/R$ relaxation of $\text{NO } v$ to $\text{NO } v-1$ would be expected to increase as n increases for both NO and NOX as collision partners since the $v \rightarrow v-1$ energy gap decreases as a function of increasing v .

(3) Energy transfer of the type



could increase as v increased due to the increase in dipole moment of NO as a function of v .

Three types of models have been formulated to treat NOCl_2 dissociation. Natanson^{26,27} applied an extension of the method of Rosen²⁸ to predict vibrational excitation in the NO fragment and the lifetime of the excited state NOCl_2 . He studied the probability of transitions from a discrete state of two coupled oscillators to a continuum state as a function of the original energy distribution in the oscillators and magnitude of the oscillator coupling terms. The results indicated that under some circumstances, a high degree of vibrational excitation could be achieved in the NO fragment and that the excited state lifetimes could be less than 10^{-14} second. Natanson assumed his model would apply only to photodissociation at wavelengths of ~ 500 nm or longer. The absorption spectrum of NOCl_2 possesses definite vibrational structure in this region.^{29,30} Busch and Wilson have suggested that this model may also be appropriate for other photolysis wavelengths.³

Basco and Norrish used a purely impulsive linear model to predict NO

vibrational excitation.² In their model, all available energy is initially converted to translational energy of the N and Cl atoms which undergo repulsive interaction. As the nitrogen atom separates from the chlorine atom, subsequent to repulsive interaction, the nitrogen atom interacts with the oxygen atom imparting vibrational energy to the NO diatomic. The maximum percentage of energy channeled into NO vibration would be 38% of available energy. This is at least 2 quanta less than the degree of vibrational excitation experimentally observed by Basco and Norrish. The discrepancy between their model's result and our data is even greater, at least 7 quanta.

Busch and Wilson used a modified impulsive model. The model is modified so that translational energy is also imparted to the oxygen atom during the repulsive interaction of the chlorine and nitrogen atom. With this model at most 34% of the available energy is channeled into vibration, a percentage similar to that of Basco and Norrish. This model fit the data of Busch and Wilson well. Again however, it does not predict the high degree of vibrational excitation observed in this study.

Mitchell and Simons proposed that the vibrational excitation observed by Basco and Norrish was due to a greatly extended NO bond length in the excited state of NOCl.³¹ While the bond length of NO and of the NO group in ground state NOCl are virtually identical (~ 1.14 Å), the predicted NO bond length in the excited state of NOCl is 1.5 Å. Bond length was estimated using bond orders obtained from M. O. calculations on NOF, which was assumed to have electronic states similar to NOCl. Their results predict the high degree of vibrational excitation at the photolysis wavelengths used in the present study as well as the lesser degree of vibrational excitation achieved at longer wavelengths. Of all the proposed models, this model appears to be the most

generally applicable.

Of course it would be quite interesting to investigate the predictions of a number of the elegant recently formulated theories of photodissociation with regard to the degree of vibrational excitation expected in NO following NOCl or NOBr photodissociation at 193 nm and other wavelengths.³²⁻³⁴

V. Conclusion

From this study it is concluded that the photodissociation of NOX is via a direct mechanism such as that shown in equation 1. NO up to $v=16$ and perhaps up to $v=17$ is observed in the photodissociation of both NOCl and NOBr. A number of existing impulsive models for NOX photodissociation seriously underestimate the degree of NO vibrational excitation at 193 nm. The calculations of Mitchell and Simons predict a high degree of vibrational excitation in accord with our results. The model of Mitchell and Simons also predicts the lesser degree of vibrational excitation obtained at longer wavelengths and makes assignments of specific spectroscopic transitions to the various photolysis wavelengths.

The validity of these models can be further investigated through the study of NO vibrational excitation in NOX photodissociation at a greater number of photolysis wavelengths than those used previously. This work is now in progress.

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FIGURE CAPTIONS

Figure 1. Emission from NO observed from 1500 cm^{-1} to 1550 cm^{-1} (1% T cutoff) upon photolysis of NOCl₂ with 193nm radiation. The NO $v=14 \rightarrow 13$ and $v=13 \rightarrow 12$ transitions are in this spectral region. A constant NOCl₂ pressure of 50 millitorr was maintained in a flowing system.

Figure 2. The integrated intensity of NO emission in the 1400 cm^{-1} to 1500 cm^{-1} spectral window plotted in arbitrary intensity units versus laser energy in mj/pulse. The spectral window corresponds to the NO transitions $v \rightarrow v-1$ for $v=13-18$. The parent gas was NOBr at 330 millitorr under flowing conditions.

Figure 3. NO emission from the indicated transitions on photolysis of 300 millitorr of NOCl₂. The transitions were observed through a circular variable filter with a spectral width of 50 cm^{-1} (<1% T cutoff). The prepulse baseline for each signal is shown as a solid line. Traces start immediately after the laser pulse so that the $t=0$ level of the trace is the amplitude subsequent to the fast rise discussed in the text.

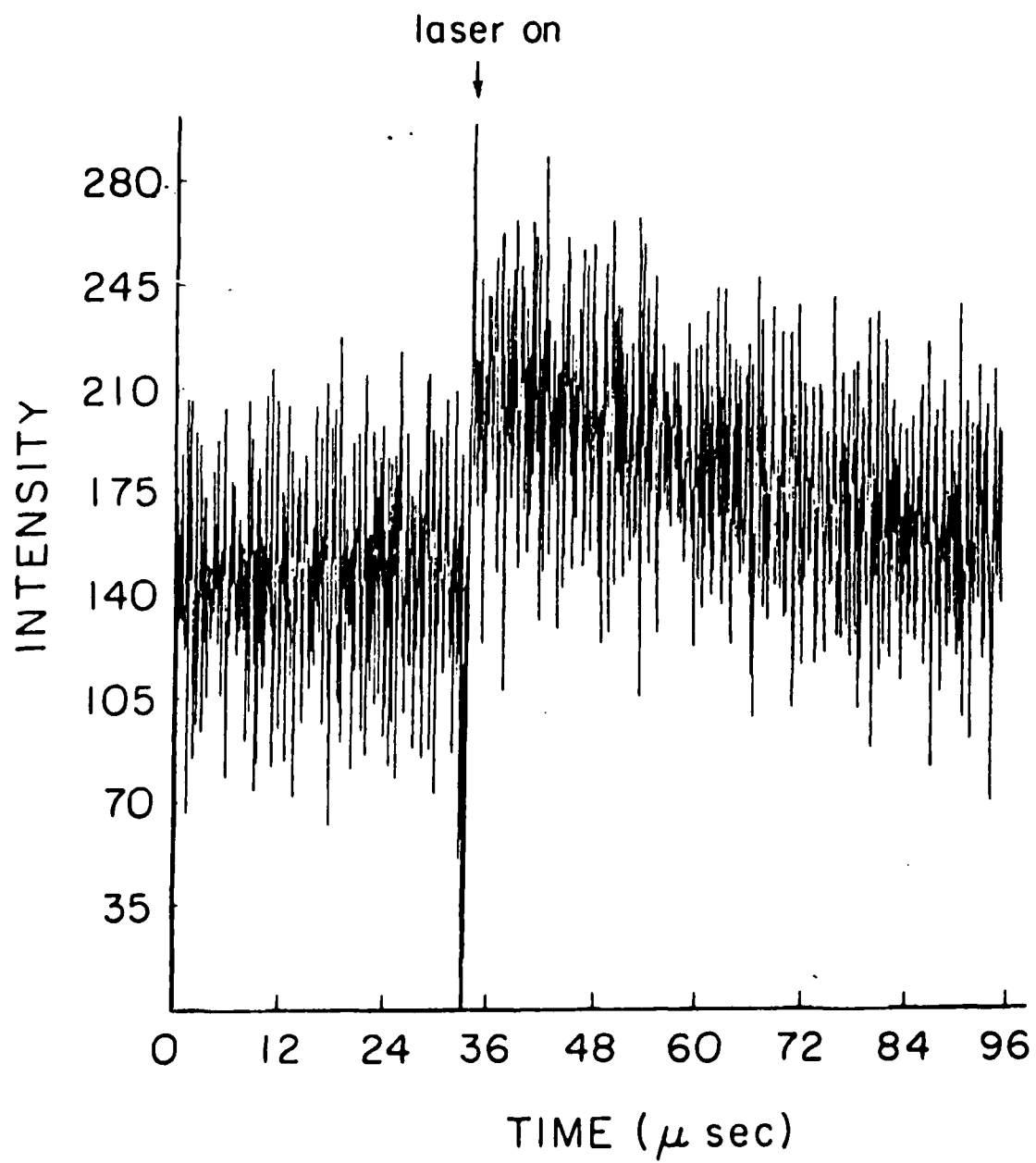


Figure 1

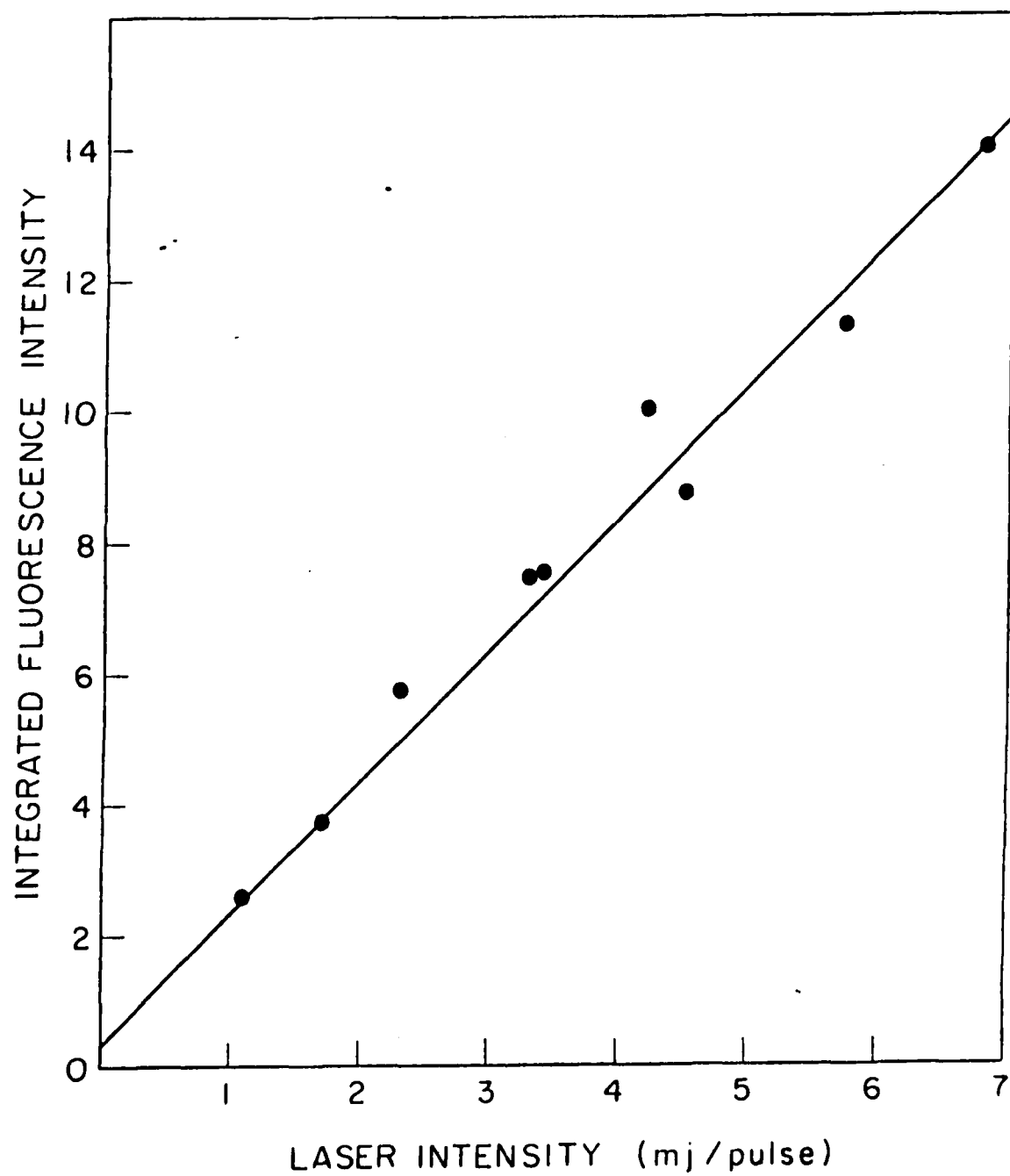


Figure 2

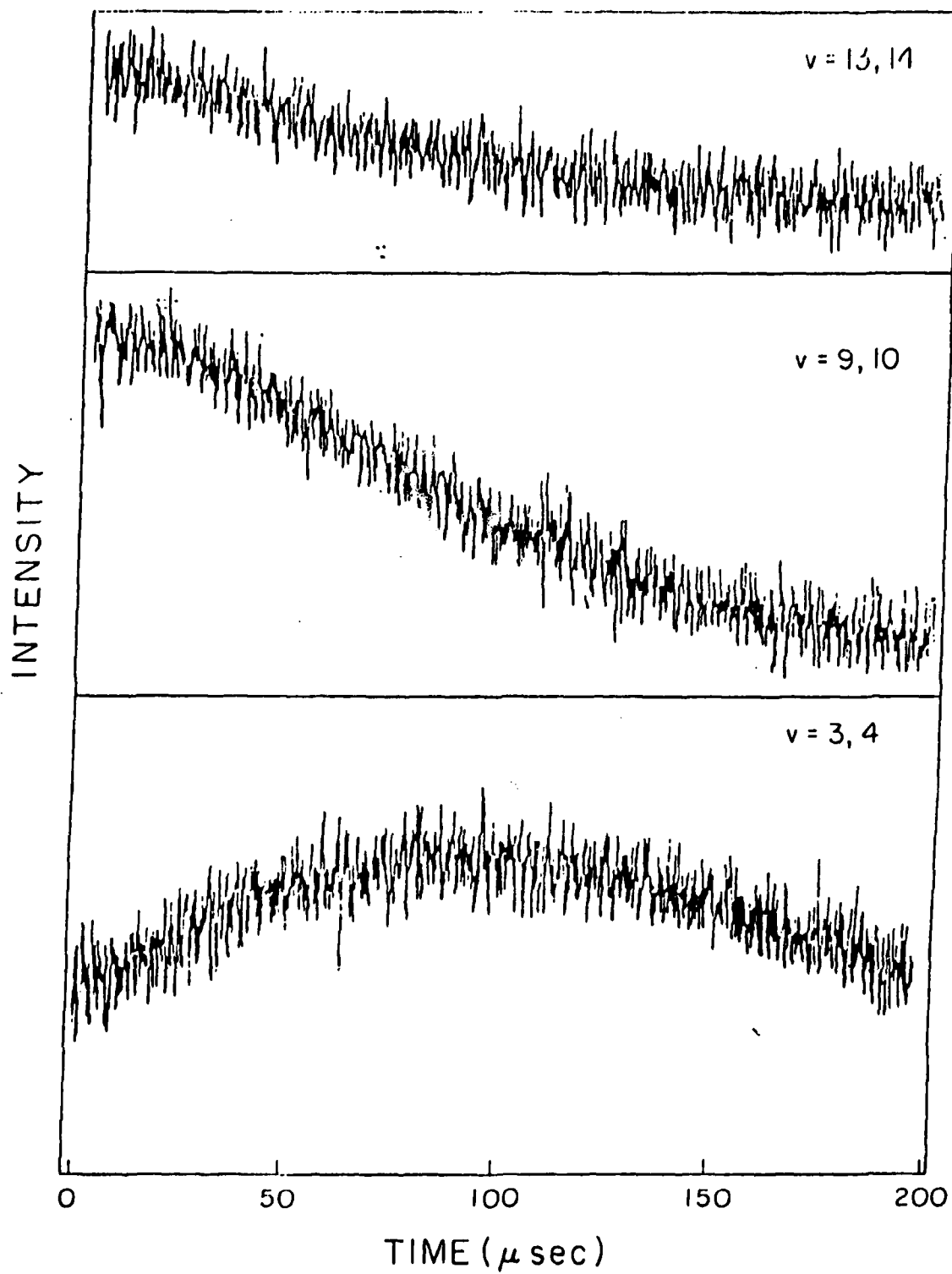


Figure 3

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