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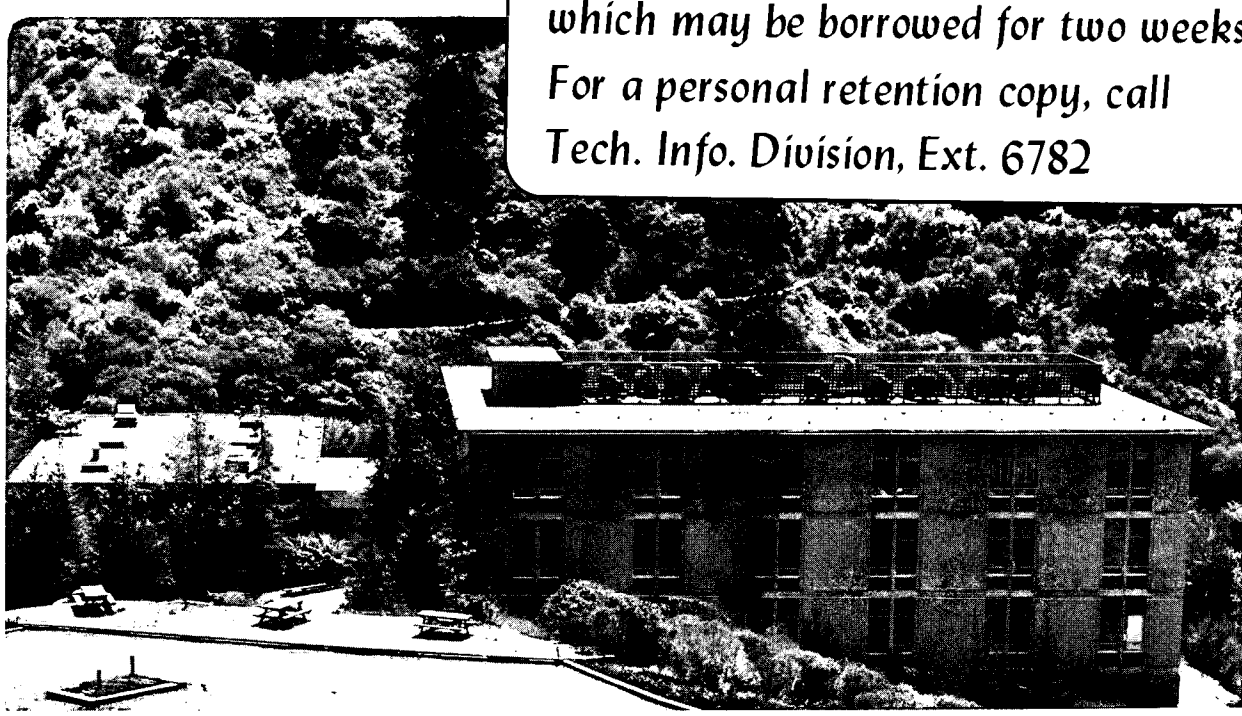

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DISSOCIATIVE IONIZATION OF WATER INDUCED BY SINGLE-PHOTON VIBRATIONAL EXCITATION

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ABSTRACT

Vibrational photochemistry of pure liquid water to produce H^+ and OH^- ions has been initiated by pulsed, single photon excitation of overtone and combination transitions. The quantum yield at 283 ± 1 K varies from 2×10^{-9} to 4×10^{-5} for wavenumbers between 7605 cm^{-1} and 18,140 cm^{-1}. The quantum yield rises through the low frequency side of an absorption band and is relatively constant through the band center and high frequency wing. The threshold for dielectric breakdown at 297 K is 20 GW cm^{-2} for excitation at 7605 cm^{-1}.

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INTRODUCTION

Conventional studies of unimolecular reactions in solution rely on thermal activation of reactants. Thus only averaged rate information for molecules with a broad, low temperature Boltzmann energy distribution in a large range of local environments is obtained. Detailed rate information is not available for molecules with a particular energy, with a particular local molecular structure, or with initial excitation energy in a particular vibrational mode.

Recently, single-photon overtone excitation using lasers has provided activated molecules with a high total energy and an energy spread less than or equal to the room temperature Boltzmann distribution.[1-4] If dye lasers are used as the excitation source, rates as a function of internal energy can be obtained by simply tuning the laser. The bond selective nature of overtone excitation, possibly enabling deposition of energy in a single bond, has also sparked a search for mode specific rate effects in unimolecular reactions.[2-4,5] If the pumped mode is closely coupled to the reaction coordinate, then the reaction rate would be higher immediately following excitation, before inter and/or intramolecular energy transfer is complete. In gas phase unimolecular reactions, the relatively large reaction yield from intramolecularly relaxed molecules can obscure an initially nonstatistical rate. In solution, initial non-statistical effects can be exposed if intermolecular energy transfer is rapid enough to quench the population of reacting, intramolecularly relaxed

molecules.[5] The combination of low cross section for high overtone excitations and low quantum yields resulting from rapid intermolecular relaxation makes detection of products difficult.

The proton transfer

$$H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq), \quad \Delta H_{283} = 14.5 \text{ kcal/mole}$$

has a low ΔH due to effective solvation and dielectric shielding of product ions in liquid water. Excitation with an intense, pulsed laser produces an observable transient increase in the solution conductivity. One signal component is proportional to the reaction induced change in ion concentration.[1] In an earlier paper, quantum yield measurements were made with a single laser pulse. The quantum yield, ϕ, increased with increasing photon energy for four fixed wavelengths in the vibrational overtone region.[1] As a laser is tuned from the low to the high frequency side of an absorption band, the absorbing molecule's surrounding local structure changes and the extent of hydrogen bonding decreases. Both "pure" O-H stretch and combination stretch + bend overtones are present in the H_2O absorption spectrum. It is possible that similarity of O-H stretching to the proton transfer reaction coordinate would result in an enhancement of the quantum yield for excitation of pure stretch bands compared to stretch + bend combinations. This work gives Φ as a detailed function of excitation frequency, and demonstrates that the observed conductivity increase follows from reaction induced by single photon vibrational excitation.

EXPERIMENTAL

The methods for water purification, conductance monitoring of the reaction, and data analysis were similar to those already reported.[1] Minor differences will be reported in a future paper. An acousto-optically modelocked iodine laser[6,7] with 0.1 to 2 J pulses 2 ns long, focussed with a 1 m focal length mirror, was used to investigate the H_2O dielectric breakdown threshold. Single shot quantum yield measurements at 7605 cm^{-1} were made with the laser oscillator operating multimode to produce 3 μs, 1 J pulses with an intensity of 3 MW cm^{-2}. A Quanta Ray neodymium YAG pumped dye laser was Stokes shifted in a 400 psi hydrogen Raman cell or used directly to produce 0.3 to 10 mJ, 6 - 10 ns pulses between 8120 cm^{-1} and 18140 cm^{-1}. The intensity ranged between 1.5 and 50 MW cm^{-2}. A Tektronix R7912 transient digitizer with PDP-11/10 computer was used to signal average from 800 to 1600 laser shots.

RESULTS AND DISCUSSION

Conductivity vs time data are shown in Fig. 1. The baseline conductivity step increase comes from the higher ionic mobility and the shift of the ionic equilibrium concentration induced by the bulk solution temperature increase of from 2 to 600 x 10^{-5} K following photon absorption. The initial conductivity jump comes from the thermally induced ionic mobility increase and from ions produced by vibrational photochemistry. The quantum yield is determined from the number of photochemically produced ions calculated from the initial jump, and from the number of photons absorbed as calculated from the baseline step.[1] The major contribution to quantum yield uncertainty comes from baseline step uncertainty at 16670 cm^{-1} (A) where weak absorption produces a small temperature increase. The initial jump comes predominantly from the thermal ionic mobility increase at 8440 cm^{-1} (C) where quantum yields for vibrational photochemistry are low. Uncertainty in the temperature dependent mobility and concentrations of ionic contaminants results in a large uncertainty in the photochemical contribution to the initial conductivity jump in (C). Quantum yield uncertainty is lower around 11740 cm^{-1} (B) where both baseline steps and initial jumps are easily measured.

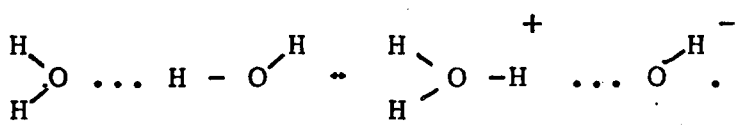
Figure 2 shows the initial transient voltage as a function of laser energy at 12500 cm^{-1} and 16670 cm^{-1}. The unit slope of these graphs signifies that the transient voltage is induced by a single photon process.

The iodine laser was used to find the breakdown threshold of about 20 GW cm^{-2} at 7605 cm^{-1}. Dielectric breakdown is marked by a large increase in the signal voltage as shown in Fig. 3 and by light emission from the focal volume for intensities just above the threshold for voltage increase. All quantum yield measurements were performed with intensities less than 100 MW cm^{-2}, well below the threshold for breakdown.

Figure 4 shows the photoionization quantum yield as a function of excitation wavenumber, $\tilde{\nu}$. The departure from a smooth increase of Φ with $\tilde{\nu}$ is outside the limits of experimental error. The most striking feature of Fig. 4 is that superimposed on the trend of increasing ϕ with increasing $\tilde{\nu}$ noted in ref. 1 is a pattern which correlates with the absorption spectrum. The quantum yield rises rapidly on the low frequency side of a band and is relatively constant through the band center and high frequency wing. Broad O-H stretch absorption lines are decomposable into four inhomogeneous, Gaussian components with high frequency components attributed to non-hydrogen bonded OH groups and low frequency components attributed to hydrogen bonded OH groups.[11] Thus the quantum yield per unit of input energy is higher for excitation of hydrogen bonded groups than for excitation of non-hydrogen bonded groups. This would result naturally if the vibrationally excited hydrogen atom forms a hydrogen bond, with a consequent loss of energy comparable to the vibrational linewidth, more rapidly than it loses vibrational quanta.

No qualitative difference in behavior is seen between bands involving pure stretching excitation and those involving combination with bending vibrations. The small hump in the quantum yield at the $3\nu_s + \nu_b$ overtone shows that excitation of the bend is effective in causing ionization, though perhaps not as much as an equal energy of stretching excitation. Fermi resonance between stretch and bend vibrations may degrade the purity of O-H stretch excitation.

The simplest representation of the primary reaction step in the photoionization is a proton transfer within a hydrogen bond to form an ion pair:



In order to be detected conductometrically the H_3O^+ and OH^- ions must separate from the ion pair in an energetically unfavorable secondary process. Rapid intermolecular relaxation of activated molecules and ion pair recombination produces a low overall quantum yield of less than 10^{-4}. Derivation of rate constants for the primary reaction from quantum yields is difficult because vibrational relaxation rates for highly excited liquid water are not known. Theoretical chemists have attempted to dynamically model the properties of liquid water.[12-16] Inspite of its complexity, several approximate molecular dynamics simulations have been performed. Comparisons of these data with simulations of the relaxation and first stages of the reaction of vibrationally excited molecules should be illuminating. It

is hoped that this investigation might stimulate interest in and assist in the development of the more accurate models needed. The present data combined with data as a function of temperature and isotopic substitution should provide a basis for further qualitative mechanistic conclusions.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1. Transient conductivity signals at 16670 cm^{-1} (A), 11740 cm^{-1} (B), and 8440 cm^{-1} (C). The initial baseline for each signal is given by the dotted line (....). The conductivity jump extrapolated to the time of the laser pulse is shown with an arrow (→). The calculated jump for a quantum yield of zero is shown with an arrow (←).

Figure 2. Normalized initial transient voltage ($\Delta V/\Delta V_m$) as a function of normalized pulse energy (E/E_m). □ - data at 16670 cm^{-1} where ΔV_m is 0.525 ± 0.015 volts and E_m is 11.5 ± 0.1 mJ. Δ - data at 12500 cm^{-1} where ΔV_m is 0.144 ± .008 volts and E_m is 2.02 ± 0.05 mJ. The solid lines represent the behavior expected for a single photon process. 10 mJ corresponds to an intensity of 50 ± 25 MW cm^{-2} and a fluence of 0.4 ± 0.2 J cm^{-2}.

Figure 3. Initial transient voltage signal (ΔV) as a function of pulse energy (E) and power density (I) for 7605 cm^{-1} photolysis of H_2O at 297 K.

Figure 4. Log_{10} quantum yield for photoionization of water at 283 ± 1 K as a function of photon energy. A line is drawn through experimental points with estimated errors from this study (●). The point (■) was taken with the iodine laser. The absorption spectrum of water is shown as the dependence of log_{10} of the natural absorption coefficient ($I/I_o = \exp(\alpha\ell)$) on wavenumber. Band assignments are shown (refs. 8 - 10) with subscripts b and s representing bending and stretching modes respectively.

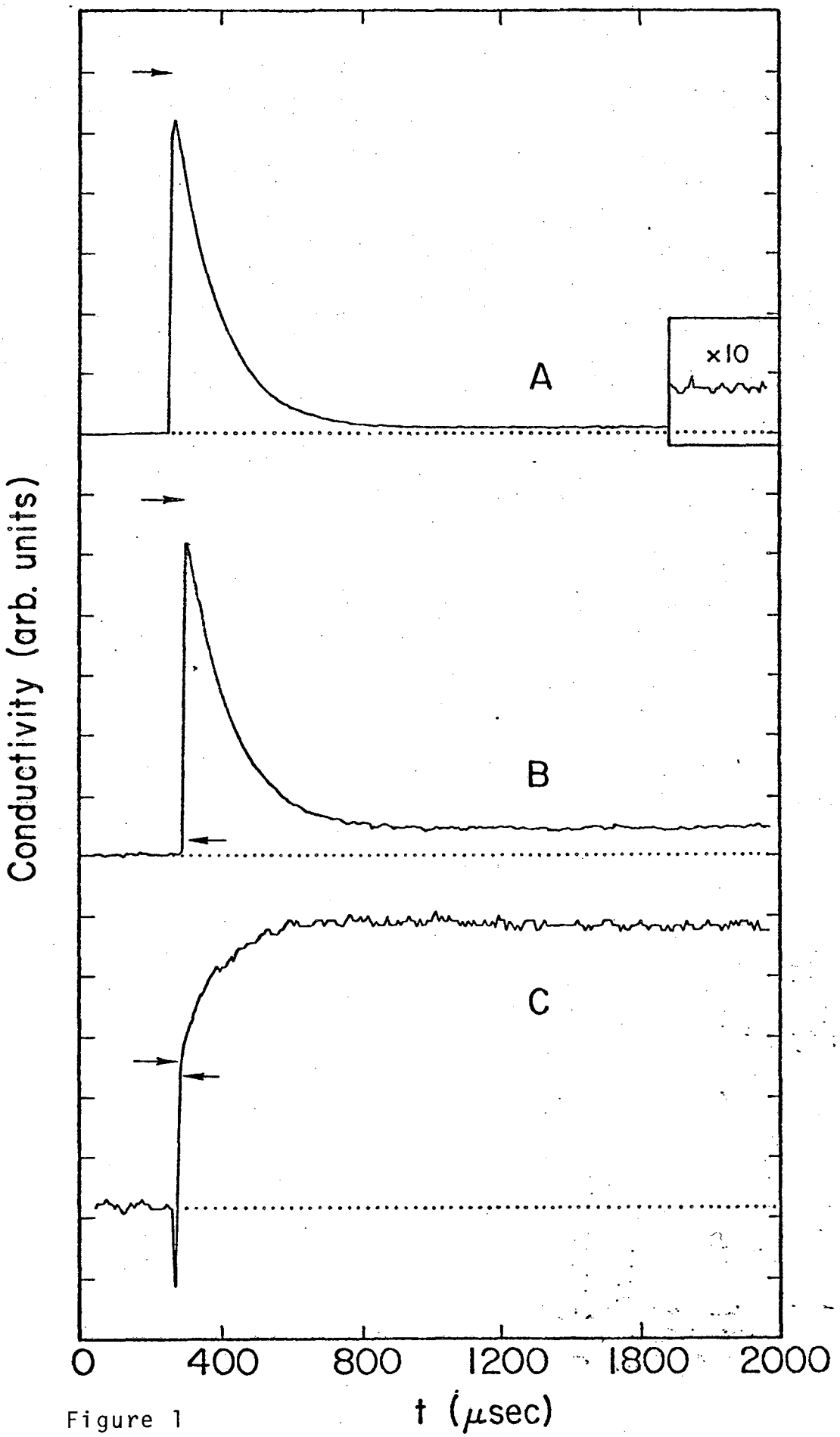

Figure 1

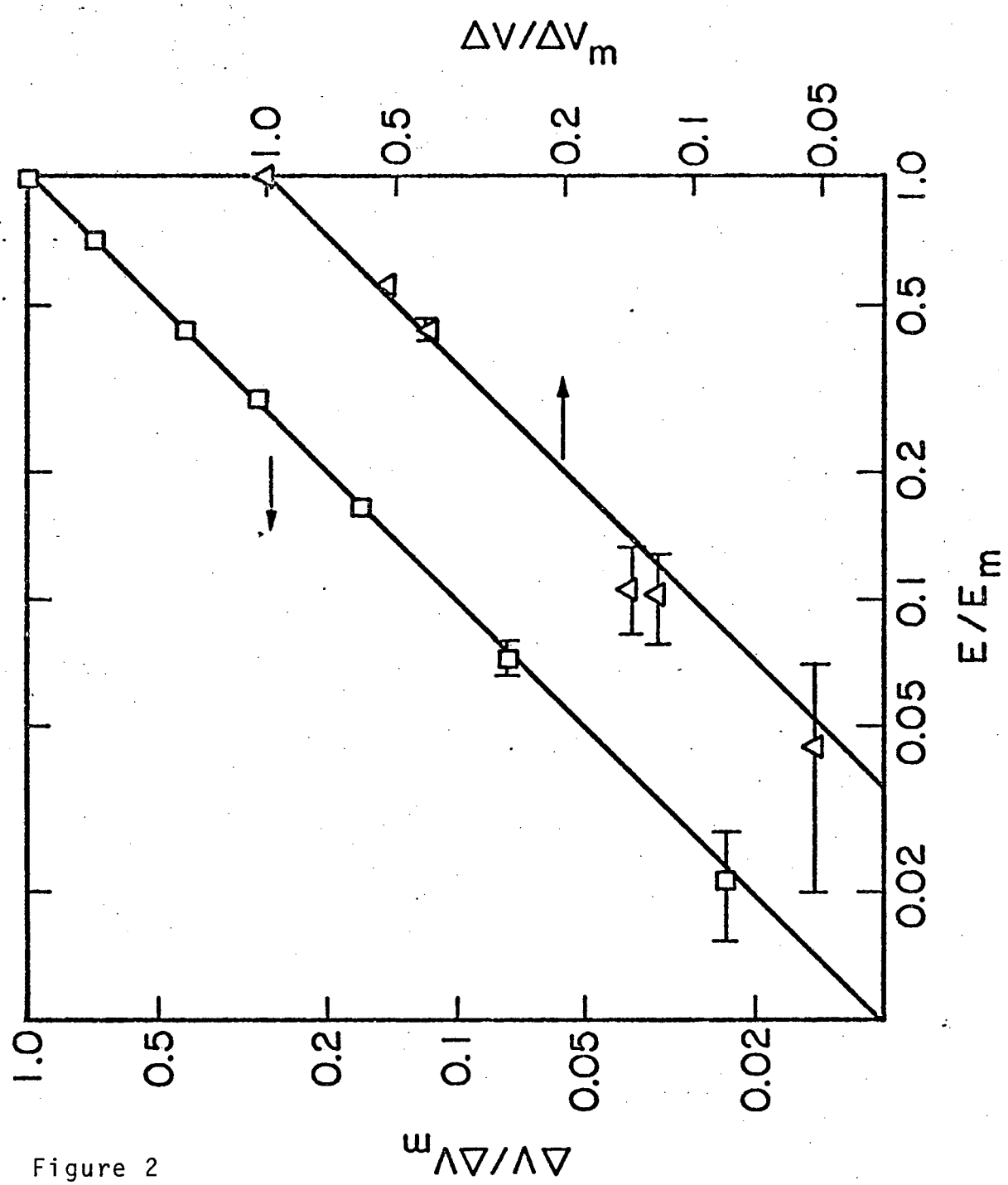

Figure 2

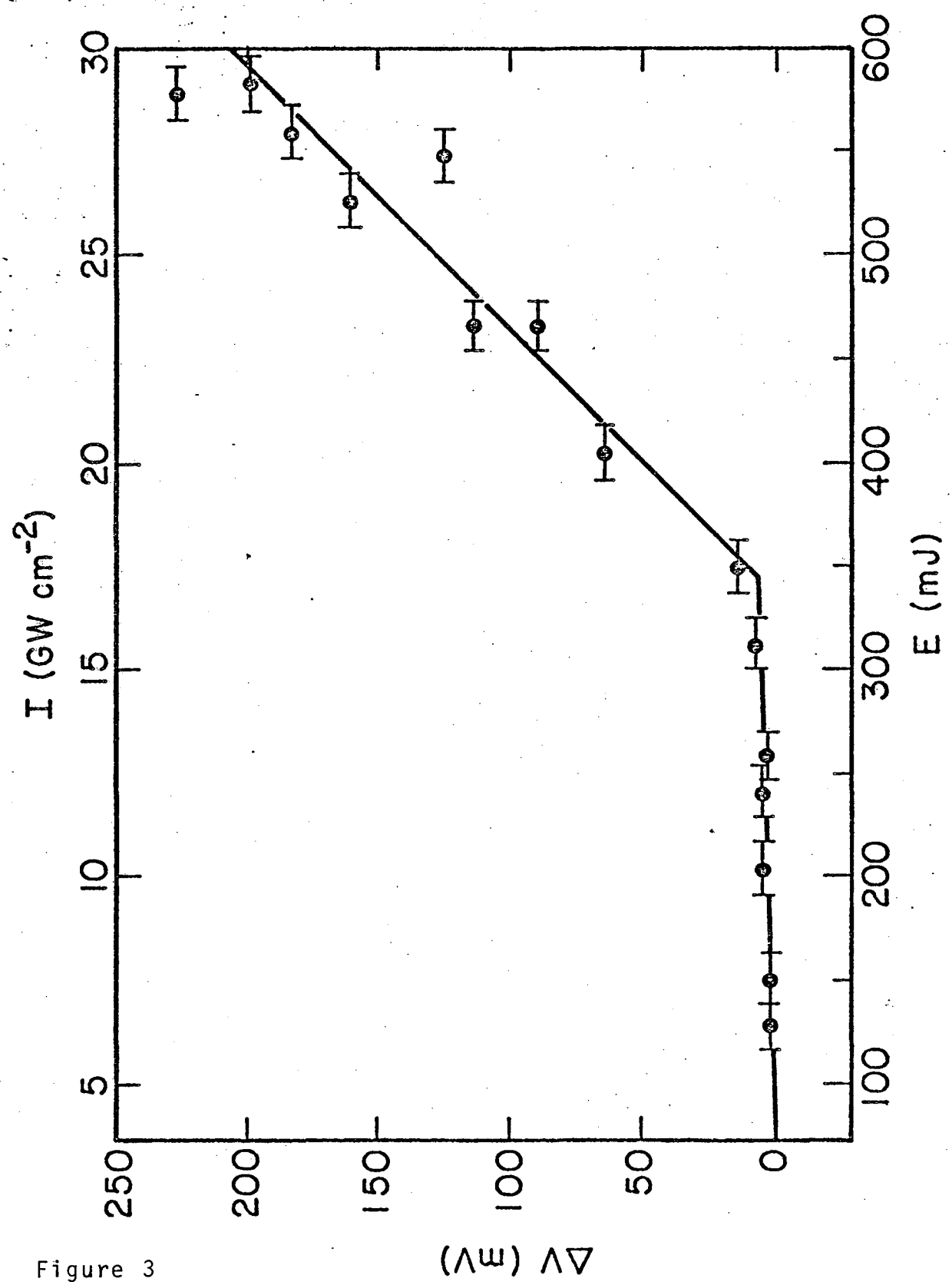
I (GW cm^{-2})
5
10
15
20
25
30
E (mJ)
100
200
300
400
500
600
ΔV (mV)
0
50
100
150
200
250

Figure 3

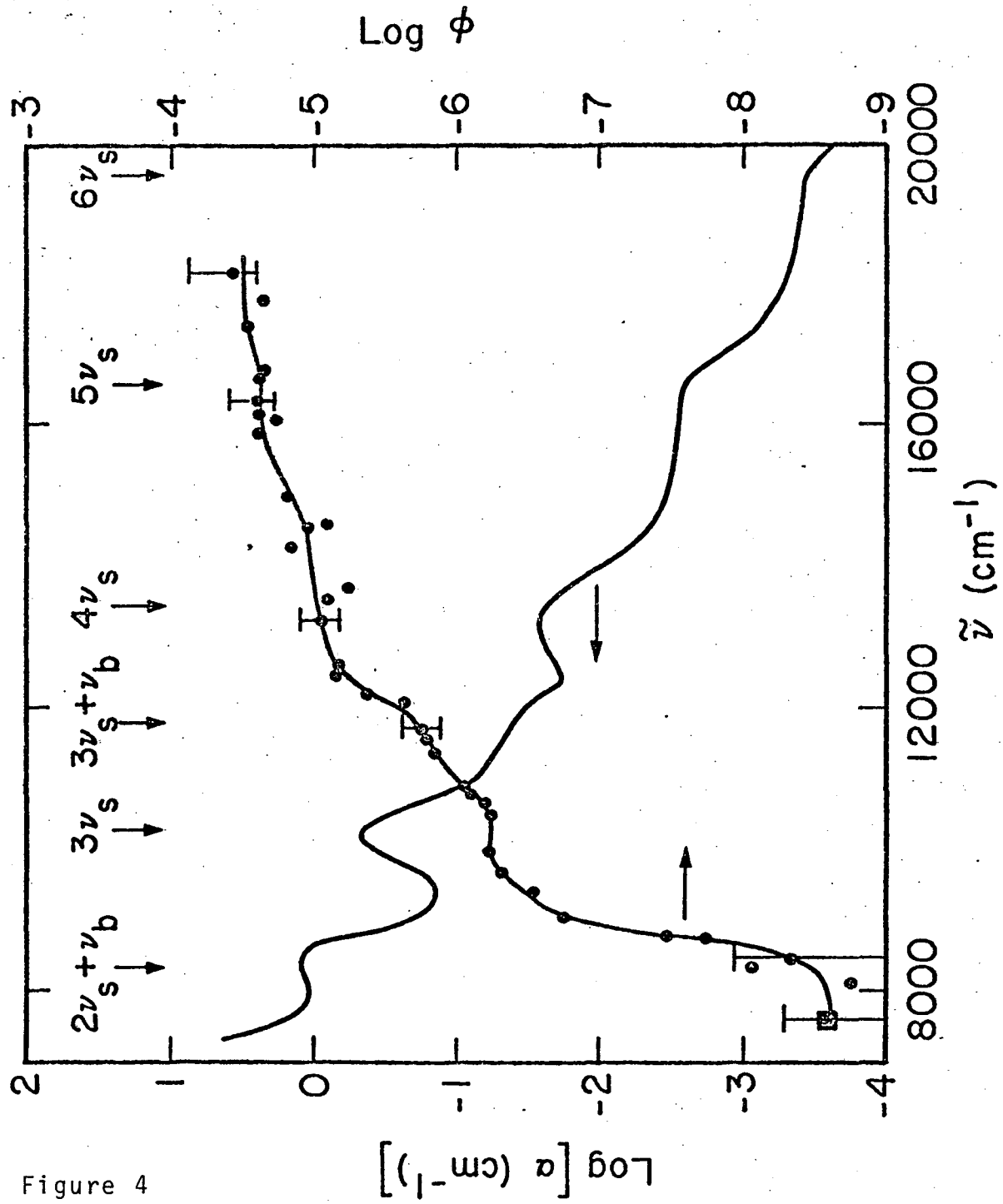
Log ϕ
-3
-4
-5
-6
-7
-8
-9
$6\nu_s$
$5\nu_s$
$4\nu_s$
$3\nu_s+\nu_b$
$3\nu_s$
$2\nu_s+\nu_b$
2
1
0
-1
-2
-3
-4
Log [α (cm^{-1})]
8000
12000
16000
20000
$\tilde{\nu}$ (cm^{-1})

Figure 4

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