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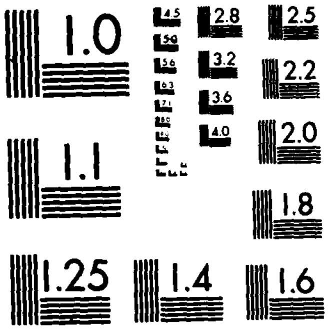

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H. W. H. Lee, M. Gehrtz, E. Marinero, and W. E. Moerner

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TWO-COLOR, PHOTON-GATED SPECTRAL HOLE-BURNING IN AN ORGANIC MATERIAL

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ABSTRACT: We report the first observation of two-color, photon-gated spectral hole-burning in an organic system: carbazole in boric acid glass. This novel hole-burning mechanism involves stepwise biphotonic photoionization of carbazole at 1.4K. The quantum yield for photoionization increases exponentially with the energy of the second photon.

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INTRODUCTION

In the ten years since the first observation of persistent spectral hole-burning or photochemical hole-burning (PHB), a wealth of information has been obtained [1] [2] about dephasing, impurity-host interactions, solid-state photochemistry, and the properties of the amorphous state. This research has been stimulated by the novel scientific phenomena involved as well as by the possible applications of PHB for frequency domain optical storage[3]. In virtually every case, the photoinduced change in the absorbing center has been monophotonic in nature, and recent modeling studies[4] have outlined several serious limitations of single-photon mechanisms for optical storage applications (such as destructive reading) that arise from the lack of a threshold in the photoreaction. For this reason as well as for scientific reasons, hole-burning mechanisms in which the hole-burning and hole-detection processes are uncoupled are of great interest.

Possible nonlinear photochemical hole-burning under one-color irradiation has been reported for s-tetrazine and dimethyl-s-tetrazine in molecular crystals[5] and for tetracene in an ether/isopropyl alcohol glass[6], but these measurements used a single wavelength for excitation and thus did not show a clear decoupling of the hole-burning and detection processes. What would be desirable is two-color, photon-gated hole-burning which requires two distinct wavelengths for hole formation: the first (λ_1) to achieve site-selection within the inhomogeneously broadened absorption line, and the second (λ_2, the gating light) to produce photochemistry [7] [8] . Since hole detection simply probes the remaining ground state distribution, a hole then appears in the spectral region near λ_1. Unique to photon-gated hole-burning is the ability to observe the hole with light of the first wavelength without producing additional photochemistry. This property not only permits nondestructive reading, but it also allows more accurate high resolution hole-burning studies to be performed without concern for distortion of previously burned holes during hole detection.

In recent measurements, two-color, photon-gated hole-burning has been observed in an inorganic system composed of rare earth ions in an alkaline earth fluoride crystal[9]. In this paper, we report the first observation of two-color, photon-gated spectral hole-burning in an organic material, which indicates that photon gating may be a fairly general phenomenon. The system consists of carbazole molecules in a boric acid glass matrix maintained at liquid helium temperatures. In contrast to room temperature two-photon holography experiments[10] on carbazole in poly(methylmethacrylate) (PMMA) in which N-H homolytic bond breaking was suggested as the mechanism, carbazole in boric acid at liquid helium temperatures undergoes biphotonic photoionization hole-burning. It is known that aromatics in boric acid glasses undergo both monophotonic and biphotonic photoionization at room temperature in liquid solutions [11] [12] or in rigid glass matrices at 77 K [11] [12] [13] . In these previous investigations, the photoionization was monitored and detected by observing the ESR signal of the ejected electron, or by observing the recombination luminescence of the photoproducts. Here, we demonstrate the observation of biphotonic photoionization at a much lower temperature (1.4K) and in addition detect the photochemistry in transmission by monitoring the narrowband drop in absorption at the λ_1 excitation wavelength. By monitoring the parameters of the hole-burning process including product spectra, dependence of the quantum yield of hole burning on λ_2 (action spectrum), and gating ratio, we verify that the photoionization occurs in a stepwise fashion with initial singlet excitation followed by triplet excitation to a reactive level. This new mechanism for hole-burning should be illustrative of a broader class of organic materials that should show two-color, photon-gated hole-burning.

EXPERIMENTAL

The samples were prepared by mixing zone-refined and sublimed carbazole with MCB reagent grade or Aldrich gold label ortho-boric acid (H_2BO_3) in a concentration near 7 x 10^{-4} mole/mole. This mixture was heated in air between quartz plates for a few minutes to remove H_2O and then cooled slowly to room temperature yielding carbazole dissolved in clear meta-boric acid glass (HBO_2)[14]. We find that two-color holes are produced more easily in the reagent grade boric acid compared to the gold label grade, indicating that some impurity in the reagent grade material may be acting as an electron trap (see discussion of mechanism below). The resulting OD of the samples at the electronic singlet-singlet absorption origin at 335 nm was approximately 1.0 for a 0.2 mm thick sample. The samples were maintained at 1.4K during the experiments by immersion in superfluid liquid helium.

Figure 1 shows the relevant energy levels and excitation wavelengths. The site-selection wavelength, λ_1, was chosen near the $S_0 \rightarrow S_1$ origin at 335 nm, and was generated by frequency doubling a Molectron DL-II pulsed dye laser pumped by a Molectron UV-14 N_2 laser. The laser was operated at 24 Hz with roughly 11 μJ per pulse in a 0.01 nm linewidth. For some experiments, a cw Ar^+ ion laser line at 334 nm was also utilized for λ_1. The second excitation wavelength, λ_2, was chosen near $T_1 \rightarrow T_n$ transitions of carbazole and was generated by the cw output of a Spectra-Physics Ar^+ ion laser, a Coherent Kr^+ ion laser, or by the focused radiation from a 100 W Hg arc lamp filtered by various Oriel interference filters. The right side of the figure shows the principal peaks in the T-T absorption spectrum of carbazole [15]. Both excitation sources were focused to 2 mm spot diameters and overlapped at the sample. Holes were detected in transmission with an RCA 1P28A phototube and a 75 W Xe arc lamp dispersed by a Spex 0.75 m monochromator with 20 μm slits. Photoproducts were detected with a cooled RCA C31034 phototube.

RESULTS AND DISCUSSION

The demonstration of the 2-color nature of the hole burning is summarized in Figure 2. We used seven different irradiation conditions for illustration. The figure shows the transmission spectrum of a portion of the 0-0 $S_0 \rightarrow S_1$ absorption origin of carbazole in boric acid. To spectrally separate the results of the various irradiations, we incremented λ_1 in 0.1 nm steps. The figure shows the transmission spectrum after all the irradiations were completed. (On this expanded scale, the inhomogeneously broadened line was featureless before the irradiations.) Starting at the left edge of the figure, the sample was irradiated with only λ_1=335.1 nm from the pulsed laser for 1 min; no observable hole was produced. Then λ_1 was tuned to 335.2 nm (to select an unburned spectral region) and the sample was simultaneously irradiated with λ_1 and λ_2 for 1 min with 0.25 mW of power at λ_2. This produced the spectral hole labelled "$\lambda_1 + \lambda_2$ (a)". For this figure, λ_2 was provided by the cw uv output of the Ar^+ ion laser at 351 and 363 nm. The hole labeled "$\lambda_1 + \lambda_2$ (b)" corresponds to identical conditions except that the power at λ_2 was increased to 1.25 mW; the resulting 2-color hole is correspondingly larger. This hole appears to be 3% deep in relative transmission change, although its actual depth and width may be obscured by the monochromator resolution of 0.02 nm. We note that an extremely small fraction of the total number of carbazole molecules photoreacted to form this spectral hole.

To show that longer one-color irradiations produce shallow spectral holes, at the wavelength labeled "λ_1, 1 min" (335.4 nm) the sample was irradiated for 1 min with λ_1 only; again no observable hole was produced. The locations labeled "λ_1, 2 min" and "λ_1, 3 min" correspond to λ_1 irradiations for 2 min and 3 min, respectively. It is clear that for sufficient irradiation times (or sufficient irradiation energy), one-color holes are eventually produced. We believe that this effect is due to excited state absorption of λ_1 and that it may be reduced by adjusting the duty cycle and/or peak power of the λ_1 laser. The final hole labeled "λ_1 + λ_2 (c)" is another 2-color burn for 1 min with 2.5 mW at λ_2.

Since 1-color irradiation at λ_1 for 1 min produces unobservable holes and irradiation with λ_2 alone is at a wavelength beyond the onset of singlet absorption[16], these results provide definitive evidence for the 2-color, biphotonic nature of the hole-burning process that we observe. The gating ratio, or the ratio of the 2-color effect to the 1-color effect for our value of λ_1 energy and for 2.5 mW at λ_2 can be estimated to be greater than 10 from this figure (recall that the true area under the 2-color holes in Figure 2 was not determined because of limited spectrometer resolution). For higher powers at λ_2, this ratio increases, and we have easily observed gating ratios near 400 for 300 mW at λ_2. Higher powers at λ_2 (=351 nm) produce broad and deep holes in the absorption line, presumably due to heating or photochemical saturation broadening effects[2].

To understand the excited state dynamics of the hole burning process, various experiments were performed. We determined the hole burning action spectrum of λ_2 using a 100 W Hg arc lamp and Hg line interference filters at 334 nm, 365 nm, 405 nm, and 546 nm, single-line Ar^+ laser radiation at 472.7 nm, 488.0 nm and 514.5 nm, and single-line Kr^+ laser radiation at 406.7 nm. For λ_2=334 nm, no hole is produced and previously written holes are partially erased because λ_2 is competing with λ_1 (=335 nm), destroying the site-selection. We argue below that the hole-burning process is two-step, biphotonic photoionization, hence it is also possible that the electrons generated by λ_2 are reversing the photochemistry. 2-color PHB readily occurs for λ_2=365 nm or 405 nm with roughly equal total yields (estimated from the area of the holes in transmission), whereas the total yield is successively and drastically reduced for λ_2 = 472.7 nm, 488.0 nm, and 514.5 nm in a manner that qualitatively mimics the T_1 - T_n absorption of carbazole in cyclohexane at 25 °C [15]. This strongly suggests that the lowest triplet state, T_1, is the intermediate in the biphotonic process. The action spectrum of λ_2 will be discussed in more detail below.

We considered the possibility that the process leading to 2-color PHB might be identical to the N-H bond-breaking mechanism for room temperature 2-photon holography for carbazole in PMMA suggested by Schmitt and Burland [10]. To do so, we attempted to burn 2-color holes for carbazole in PMMA hosts at 1.4K using apparatus identical to that which yielded 2-color PHB for carbazole in boric acid. Even at total irradiation energies 10 times larger than required to observe 2-color PHB in the boric acid host, no 2-color or 1-color PHB was observed for the PMMA host. This suggests that the photoreaction responsible for 2-color PHB is not N-H homolytic bond scission and subsequent reaction of the carbazyl radical with the host matrix. It is reasonable that thermal barriers quench this reaction at liquid helium temperatures.

To determine the photoreaction that occurs, a spectrum of the photoproduct was obtained by acquiring a transmission spectrum before and after two-color hole burning. In order to make the product spectrum easier to detect, the two-color hole-burning was performed with 780 mW at λ_2 (351-363 nm) for 5 minutes to make a deep hole. The log of the ratio of the two transmission spectra yielded the spectrum of the photoproduct as shown in Figure 3. The three strong peaks from 650 to 850 nm are readily identified with the known spectrum for the carbazole radical cation[17]. It is obvious from the figure that the carbazole radical cation is the predominant photoproduct, clearly establishing that photoionization is responsible for the biphotonic hole burning. The peaks near 400 nm and 500-600 nm result from the carbazyl radical[18], indicating that N-H homolytic bond breaking occurs to a minor extent. The negative change in optical density near 335 nm is just the two-color hole itself.

It is reasonable that photoionization should occur in this system at low temperatures. Boric acid hosts are known to depress the ionization potential of a solute molecule by 2.3 eV due to the high dielectric constant and screening of the ion-electron pair potential [11]. This would lower the ionization potential of carbazole [12]from I_G = 7.57 eV to I_{BA} = 5.27 eV as indicated in Figure 1, and thus photoionization from T_1 (3.05 ev) would be energetically possible for photons of wavelength less than 559 nm.

Furthermore, our analysis of the 2-color PHB process is consistent with a previous report[12] of one-color biphotonic photoionization for carbazole in ethanol glasses at 77K. In that study, even though $\lambda_1=\lambda_2$, it was argued that the second photon is absorbed from T_1 after intersystem crossing from S_1. In addition, the quantum yield of photoionization was shown to increase exponentially with the energy of the second photon. That our system behaves similarly is demonstrated in Figure 4 where we have plotted the estimated quantum yield of hole burning, Φ, normalized to the estimated quantum yield at 514 nm, Φ_0, versus the energy at λ_2, E_2. A prerequisite in determining the exact quantum yield is knowledge of the excited state-excited state absorption spectrum for the intermediate level. Figure 4 was plotted assuming T_1 as the intermediate state. In other words, the quantum yield at each value of λ_2 was estimated by dividing the area of the two-color hole by the T-T absorption at that wavelength[10]. This approximation is valid so long as the holes are shallow and constant in width, and these conditions were maintained for the measurements of the quantum yields. The straight line result yields further evidence for T_1 as the intermediate state in the hole burning process. The physical basis for this exponentially increasing quantum yield is not known at present[12], but it may be expected to contain information about the distribution of reaction barrier heights, or equivalently in this case, the distribution of barriers for electron tunnelling away from the excited molecule. We note that the barriers for the reverse reaction must be fairly high: holes burned at 1.4 K remain after temperature cycling to 77 K for several hours, although the holes are shallower and broadened somewhat.

If S_1 (3.69 ev) were the intermediate state, then photoionization should be possible with λ_2 less than 783 nm. The $T_1 \rightarrow T_n$ and $S_1 \rightarrow S_n$ absorption peaks are well-separated (420 nm and 615 nm respectively; see Reference [19]) and allow interaction with only one transition. Using λ_1 as before and λ_2 at 647.1 nm from a Kr^+ laser, no two color holes were observed. This again implicates T_1 as the intermediate state.

Thus we conclude that the mechanism for the observed 2-color PHB is in fact excitation from S_0 to S_1 with λ_1, intersystem crossing to T_1, and excitation from T_1 to an autoionizing or other photoreacting level near the unperturbed $T_1 \rightarrow T_n$ absorption maximum with λ_2. The long (7.6 s) triplet lifetime and high triplet yield (0.55) of carbazole [20] facilitate this process by producing large triplet populations. The photoejected electron may tunnel over a distribution of barrier heights and presumably becomes trapped at electrophilic sites in the boric acid glass matrix. Experiments are in progress to fully understand the novel 2-color PHB described here, and to attempt to observe 2-color PHB in other aromatic molecules. The results reported here open up a new class of materials for 2-color PHB while at the same time demonstrate a new high resolution, sensitive technique for the study of biphotonic solid state photoreactions in rigid matrices. As is the case for hole-burning in general, Stark and Zeeman effect experiments may now be performed within the inhomogeneously broadened line on the carbazole/boric acid system. Photon-gated, or two-color processes represent a new and unusual class of mechanisms for PHB because hole-burning occurs only with two wavelengths present, whereas nondestructive reading can be performed with only one wavelength.

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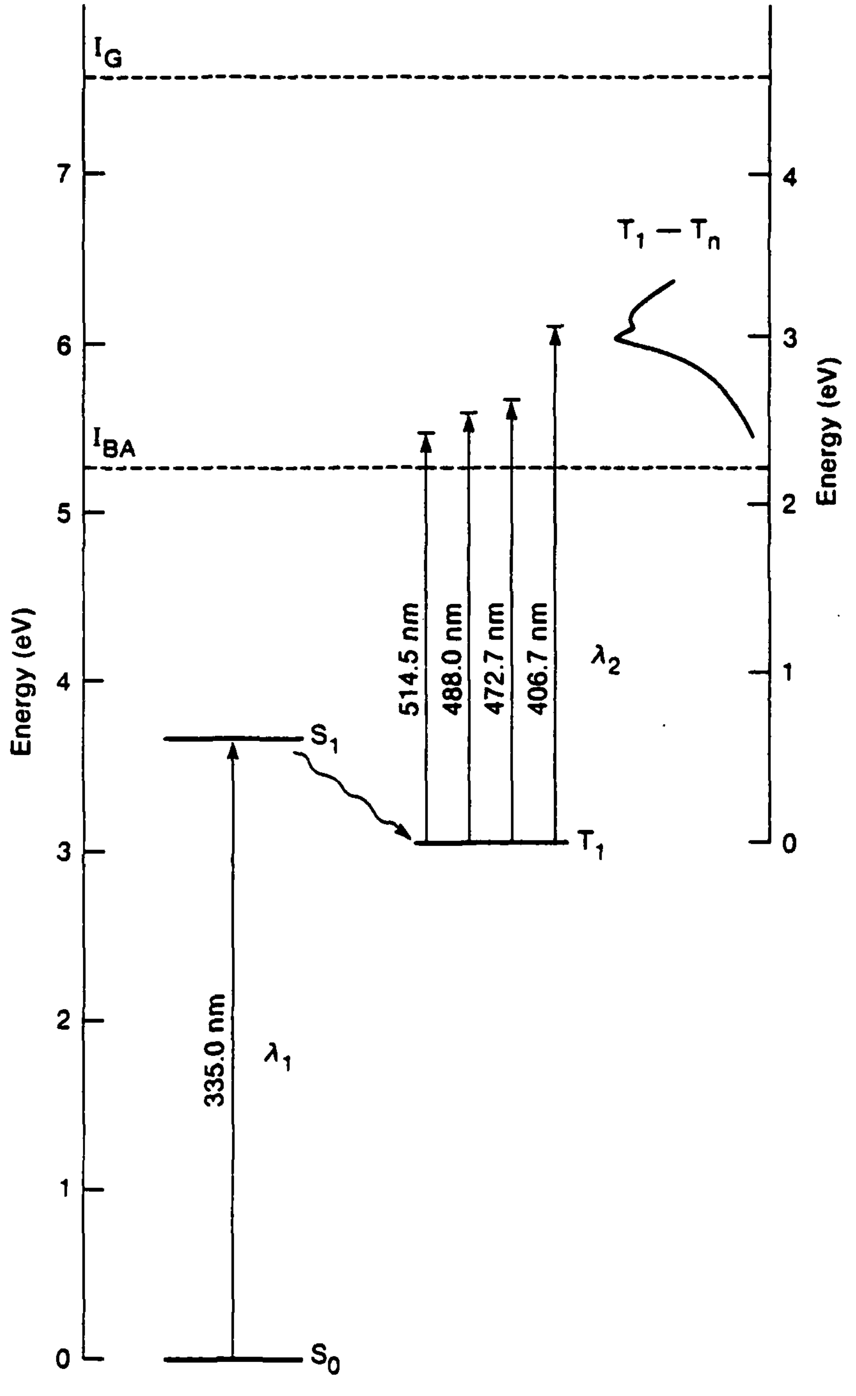

Figure 1. Schematic energy level structure of carbazole. The left axis shows energy measured from S_0, and the right axis measures energy from T_1. The definition of λ_1 is indicated, and the vertical lines originating from T_1 indicate various λ_2 excitation wavelengths. The T-T absorption spectrum of carbazole is illustrated using the right axis, after Reference [15]. The ionization energy for carbazole, I_G, and the approximate value, I_{BA}, in boric acid are indicated on the left axis.

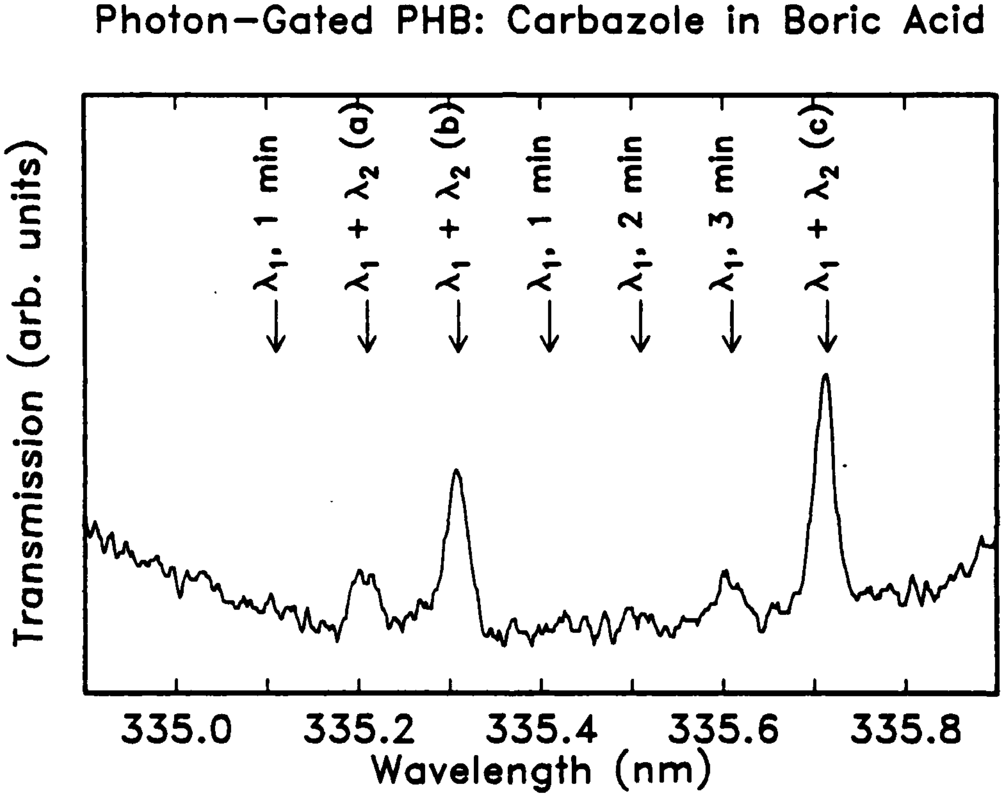

Figure 2. Transmission spectrum of carbazole in boric acid at 1.4K in the region of the λ_1 irradiation wavelengths. The various indicated irradiations are described in the text.

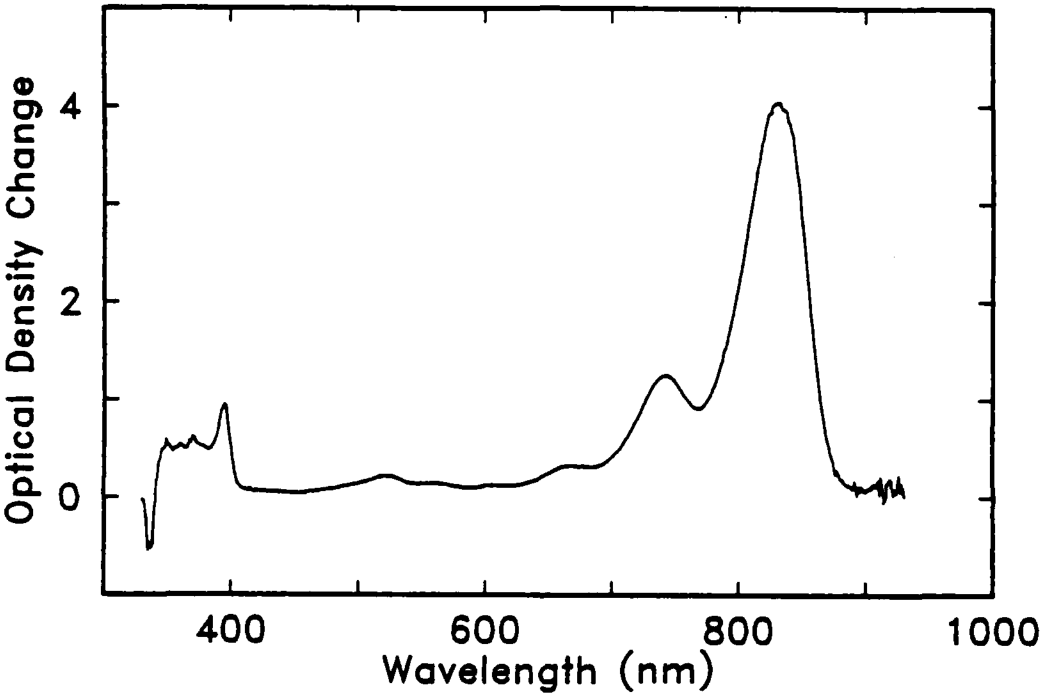

Figure 3. Product spectrum. The figure shows the change in optical density after two-color hole-burning, as described in the text.

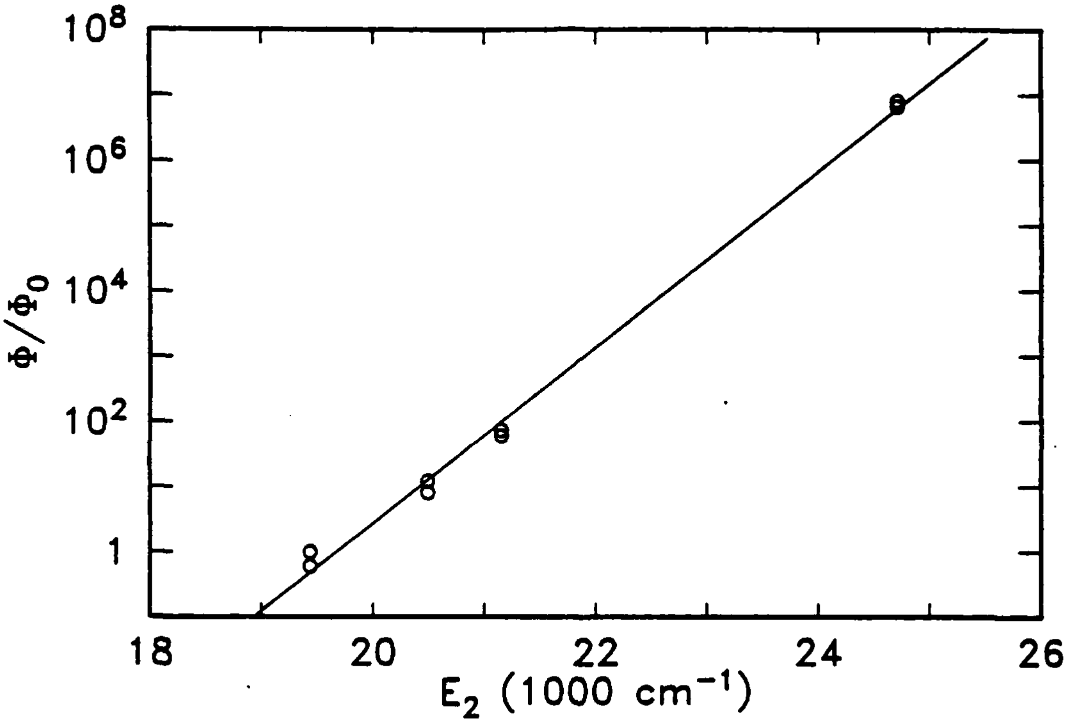

Figure 4. Relative quantum efficiency, Φ/Φ_0, versus photon energy at λ_2, E_2.

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