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MOLECULAR BEAM STUDIES ON MULTIPHOTON
DISSOCIATION OF POLYATOMIC MOLECULES

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The possibility that an isolated molecule placed in the intense field of an infrared laser can absorb many photons (enough to dissociate) in a very short span, is first suggested in 1971 by Isenor and Richardson¹ based on their experimental observation of prompt luminescence. This infrared multiphoton dissociation process was subsequently shown to be isotopically selective in the dissociation of SF₆, BCl₃ and other molecules in 1975 by Ambartzumian et al.² and Lyman et al.,³ in a series of experiments, and has now become one of the most extensively pursued subjects in recent years. The process has been shown to be quite efficient, and the physical principles and phenomena involved in multiphoton absorption by isolated molecules have been elucidated through many experimental and theoretical investigations.^{4,5} However, there are many questions on the dynamics of excitation and decomposition which remain to be answered; especially, the extent of vibrational

excitation and the degree of intramolecular relaxation before molecular decomposition, i.e., the question of whether the excitation energy is completely randomized such that a simple RRKM theory⁶ can be used for the description of decomposition dynamics.

Actually, a considerable amount of interest and excitement was generated with the suggestion that multiphoton dissociation is a very unusual method for energizing molecules, one that offered the potential for vibrational mode control of unimolecular reactions. For the present situation, this means deciding the dissociative outcome of a reaction by not only controlling how much energy is supplied to each molecule, but also, loosely speaking, by directing which vibrational modes the energy is to go into and producing dissociation products different from those of thermal activation. Initial evidence tended to support this hypothesis. The first reported primary product analysis for the multiphoton dissociation of SF_6 indicated that this molecule dissociated directly to SF_4 and F_2 ,⁷ bypassing the lower energy SF_5 and F fragmentation channel. Results of gas cell experiments with $CFCl_3$ were interpreted to evidence direct dissociation to $CFCl$ and Cl_2 .⁸ In addition, the observation of C_2 and CN from CH_3CN and CH_3NH_2 ⁹ and prompt luminescence for a number of molecules¹⁰ under conditions which were supposedly collision-free suggested explosive dissociation of very highly excited molecules.

If indeed such phenomena are a direct consequence of mode-specific vibrational pumping, the implications, both fundamental and applied, would be very important. The measurements of such unusual dynamical

effects could significantly aid in the fundamental understanding of energy flow in highly excited polyatomic molecules. Also, in a practical sense, a technique for controlling the path of a chemical reaction, bypassing, say, an undesired low-energy channel, could prove to be of considerable utility for synthetic applications.

For these reasons we were attracted to a study of the multiphoton dissociation of SF_6 and other molecules under the collisionless molecular beam conditions used routinely in our laboratory. A molecular beam experiment on CO_2 laser-induced photodissociation of SF_6 was performed previously by Brunner et al.,¹¹ in which the influence on the molecular beam of SF_6 itself by the CO_2 laser was studied using the mass spectrometer detector. In our experiments, using a rotatable mass spectrometer, direct identification of fragment species as well as the measurements of angular and velocity distributions of dissociated products were performed under various laser excitation conditions. The results of our experiments, mainly derived from the dissociation pattern and the relation between the shape as well as the magnitude of translational energy distributions, are unambiguously consistent with a far more orderly picture of the excitation and dissociation process than that suggested by many earlier experiments and theoretical constructs. Recent work of Bloembergen, Yablonovitch, and their coworkers¹² on the measurements of multiphoton absorption by SF_6 and their theoretical interpretation of the experimental observations are in close agreement with our conclusion that although the initial excitation is selective, nearly complete energy randomization must take place in the molecular vibrational degrees of freedom before decomposition.

A schematic diagram of the apparatus used in our study is shown in Fig. 1. It consists of a nozzle source for the propagation of a supersonic beam of SF_6 through three regions of differential pumping into a main chamber crossed by a focused CO_2 laser beam at the scattering center. The laser energy density at this intersection was varied by both moving the lens to defocus the light and by using external attenuators.

The products of reaction were detected by means of a triple-differentially-pumped quadrupole mass spectrometer contained within the main chamber. The mass spectrometer was rotatable about the vertical axis through the scattering center. This feature combined with internal defining slits made the detection system angularly resolved to within 0.5° .

The experiments were performed in two modes of operation. To simply obtain the product angular distribution, the laser trigger pulse was used to start a gate and delay timing circuit that regulated the detection electronics. An initial delay of generally 300-400 μsec between the firing of the laser and the enabling of the detector was used to allow for the flight time of the fragments traveling over a distance of 17.5 cm. Then, a gate of approximately 500 μsec was opened to insure that all fragments arriving at the detector were counted. A subsequent gate of equal duration provided a background count for the determination of net signal. Signal-to-noise in this mode at optimum angle ran as high as four to one. Alternative time-of-flight measurements were made at several angles by using the laser pulse to define

a time origin in starting a 256-channel multiscaler. Channel widths of 8 μ sec generally provided adequate velocity resolution and enough of the time-of-flight spectrum to establish a baseline. The resolution of time-of-flight measurements is approximately 10% FWHM, mainly due to the finite width caused by the ionizer. These angular and time-of-flight data were converted to velocity space and transformed into the center of mass to provide the recoil energy distribution for the multiphoton dissociation of SF_6 .

For all the polyatomic molecules we have investigated so far, the molecules are seen to decompose through the channel that requires the least amount of energy, without exception. For example, CF_3Br and CF_3I dissociate solely into $CF_3 + Br$ and $CF_3 + I$. The high energy channels such as $CF_2Br + F$ or $CF_2 + BrF$ have not been observed. Contrary to the earlier suggestion that CCl_3F dissociates into $CClF + Cl_2$,⁸ the only channel which was detected in our collisionless molecular beam experiment was $CCl_2F + Cl$. No F_2 was detected in the decomposition of SF_6 . These observations are in agreement with what one would expect from a statistical theory of unimolecular decomposition. A situation exists in which the intramolecular energy transfer is faster than the chemical decomposition such that an isolated molecule serves as its own heat bath for thermal decomposition. These results also suggest that some of the observations made previously in cell experiments, even at pressures below 1 Torr, might not be entirely "collisionless."

The translational energy distributions of fragments for those systems mentioned above have one common feature; namely, the average

kinetic energy released is relatively low, no more than several kcal/mole, and the shape of distributions are strongly peaked at zero kinetic energy. This is also a feature one would expect from a statistical unimolecular decomposition. This is true because of the fact that if the excitation energy is completely randomized, the probability of a molecule decomposing into product molecules with specific translational and internal energies will depend on the phase space volume available. Hence, for polyatomic molecules with many vibrational degrees of freedom, (since the state density for the internal degrees of freedom is a steeply increasing function of energy, whereas that for translation is not), the statistical theory characteristically predicts a recoil energy distribution that is peaked near zero, i.e., most of the excess energy is stored as internal excitation of fragments, and correspondingly large amounts of translational energy release are improbable. The average recoil energy of the fragments is a function of laser energy, the number of vibrational degrees of freedom, and density of state associated with those vibrational degrees of freedom. If the statistical theory is applied to CF_3Br and SF_6 , observed translational energy distributions correspond respectively to an average absorption of 1-3, and 6-10 excess CO_2 laser photons beyond dissociation energies of CF_3Br and SF_6 . Although these numbers seem to suggest a vast difference in the ability of molecules to absorb excess photons beyond dissociation energy, they actually represent very similar degrees of excitation in terms of the lifetime of excited molecules. For both CF_3Br and SF_6 molecules, the range of excitations correspond to dissociation states with a lifetime ranging from 10^{-7} to 10^{-9} sec, which

is not entirely unrelated to the typical laser pulse width of 5×10^{-8} sec.

Although the multiphoton dissociation of SF_6 molecules has attracted more attention than any other polyatomic molecule, its detailed experimental study is difficult because its dissociation mechanism is complicated, and as a consequence, our previous experimental results require further clarification. The complications that we have observed are partly due to the unusual fragmentation pattern of sulfur polyfluoride compounds in the ionization chamber of our mass spectrometer and partly due to the fact that the SF_5 fragment can further decompose into $SF_4 + F$ in the intense CO_2 laser field. Both SF_6 and SF_4 are known to completely decompose in the ionization process to give SF_5^+ and SF_3^+ ions respectively, as major mass peaks in the mass spectrometer. It appears that the SF_5 radical as well only produces a negligible fraction of the parent SF_5^+ in the ionization process. Our preliminary observation¹³ of SF_5^+ was found to be heavily contaminated by SF_6 molecules that were scattered into the detector by molecules released from the wall of the vacuum chamber by the laser radiation. When the experimental conditions were improved to eliminate this background scattering, the most prominent peaks in the mass spectrometer were found to be SF_3^+ and SF_2^+ . When the laser energy was low, namely, around 10 joule/cm^2 or below, the laboratory angular distributions of SF_3^+ and SF_2^+ were found to be identical as shown in Fig. 2. Irrespective of the laboratory scattering angles, the ratios of SF_3^+ to SF_2^+ were found to be approximately 4, which is between the value of 6 and 2 given by SF_6 and SF_4

ionization¹⁴ and is believed to be from a single parent molecule of SF₅. When the energy of the laser pulse was increased, the angular distributions of SF₃⁺ and SF₂⁺ started to deviate from each other at wide angles as the angular distributions broadened and the ratios of SF₃⁺ to SF₂⁺ at wide angles approached ~2 which is the value given for ionization of SF₄. Thus, we conclude that the signals observed at the wide angles were exclusively due to SF₄. These observations suggest that at higher laser energies, the SF₅ radicals produced during the laser pulse were further decomposed into SF₄ + F with additional recoil energy resulting from absorption of additional photons. This is supported by the facts that the production of F atoms in SF₆ dissociations have been observed from the secondary chemiluminescent F + H₂ reaction in other laboratories¹⁵ and the F₂ fragments were not detected in spite of an exhaustive search in our experiments. We therefore conclude that SF₆ → SF₄ + F₂ is not a significant channel in the multiphoton decomposition of SF₆.

The observation that SF₆ molecules decompose in a time scale comparable to the laser pulse width is most interesting, since it provides further verification of the statistical model. Preliminary analysis of the time-of-flight velocity spectra of the fragments, as shown in Fig. 3 as a typical example, indicate that the level of excitation which yields the observed translational energies according to the statistical theory is approximately 6-10 excess photons absorbed beyond dissociation energy. This level of excitation gives the typical lifetime of excited SF₆ of 10⁻⁷ to 10⁻⁹ sec which is comparable to the laser pulse width of 5 x 10⁻⁸

sec. Extensive data have been collected on many other aspects of multi-photon dissociation of SF_6 molecules in our molecular beam studies, including, the dependences of dissociation on the laser frequency, the laser energy and the rotational and vibrational temperatures of SF_6 molecules. These experimental results will be presented in other publications in the near future.

As an aid to interpreting our experiments we have developed a very simple mathematical model for the pumping and dissociation process. Proceeding from Bloembergen and Yablonovitch's observation^{12b} that observation in the quasi-continuum occurs sequentially with decreasing cross section, and our experimental findings that the dissociation process can be treated statistically, we constructed the corresponding ordinary master equation. It describes the pumping process in completely linear terms as absorption versus stimulated emission over a series of evenly spaced levels; irreversible reactive transitions to products are included above the dissociation threshold. This model does not consider the possibility of coherent processes that may occur in the first few transitions. The linear approximation, however, should be a good one for most of the powers of interest (above a few $Mw\ cm^{-2}$) where in a real system any discrete initial bottleneck is easily overcome.

In our application we determined the physical parameters for this model in a purely empirical fashion. We assumed, as the results of Bloembergen and Yablonovitch indicate, that the absorption cross section decreases exponentially with increasing molecular energization (expressed hereafter as I , the number of photons absorbed). We thus assumed a cross section function of the form

$$\log \sigma_I = mI + b . \quad (1)$$

The parameters for equation (1) were determined by fitting the results of our calculation to experimental data. We found that the rate of pumping in the early stages of absorption was a sensitive function of the cross section intercept. Thus, the comparison of our calculated results for this rate to the photoacoustic data of Bloembergen and Yablonovitch served to determine a value for b ($-18.361, \sigma_1 = 4 \times 10^{-19} \text{ cm}^2$). The slope of the cross section function was found by fitting our experimental measurements of the fractional yield versus incident energy fluence. The result, $m = -0.03656$ gives a cross section at $I = 40$, well into the reactive manifold, of $1.5 \times 10^{-20} \text{ cm}^2$. So determined, the cross section function was combined with the desired laser intensity to calculate coefficients for absorption, then weighted by the state density ratio between successive levels to produce those for stimulated emission.

We believe that this calibration procedure has produced a reasonably realistic model for multiphoton absorption and dissociation. The detailed picture of this process that it presents is quite interesting. Instantaneous level populations frozen at several times during a laser pulse of typical power (200 MW) and duration (100 ns) are shown in Fig. 4. We note immediately that at this intensity multiphoton pumping to the dissociative threshold requires a time on the order of tens of nanoseconds. It is conceivable that, at moderate levels of excitation in the dissociative manifold, unimolecular reaction could successfully compete with further pumping and the excitation process would become

lifetime limited. We see such an indication here in the high energy tails of the distributions for 50 and 100 ns (the dissociative threshold occurs in this model at a level of 30 photons). We observe the phenomenon experimentally as a product angular distribution that at low powers initially broadens with increasing power but then stabilizes to further power increases.

The dynamical basis for a second experimental result is also rather clearly indicated by this calculation. In the example shown in Fig. 4 the laser pulse width is 100 ns. The apparent shrinkage in the population distribution is due to a reaction that has occurred while the laser was on. Once the pulse is over, disregarding spontaneous emission and assuming a collision free environment, all the population above an energization level of 29 photons, will dissociate. The partitioning between dissociation during the laser pulse and after can be controlled in this model by appropriately choosing the laser pulse width and power. This important result is directly supported by our observation of the secondary absorption and subsequent dissociation of the newly formed SF_5 . We have obtained experimental evidence that closely relates the onset of the secondary channel to the power densities predicted by the model calculation. In sum, then, all of the available experimental evidence indicates that this simple model for multiphoton dissociation is quite adequate for providing some phenomenological understanding and suggests many more detailed future experimental inquiries.

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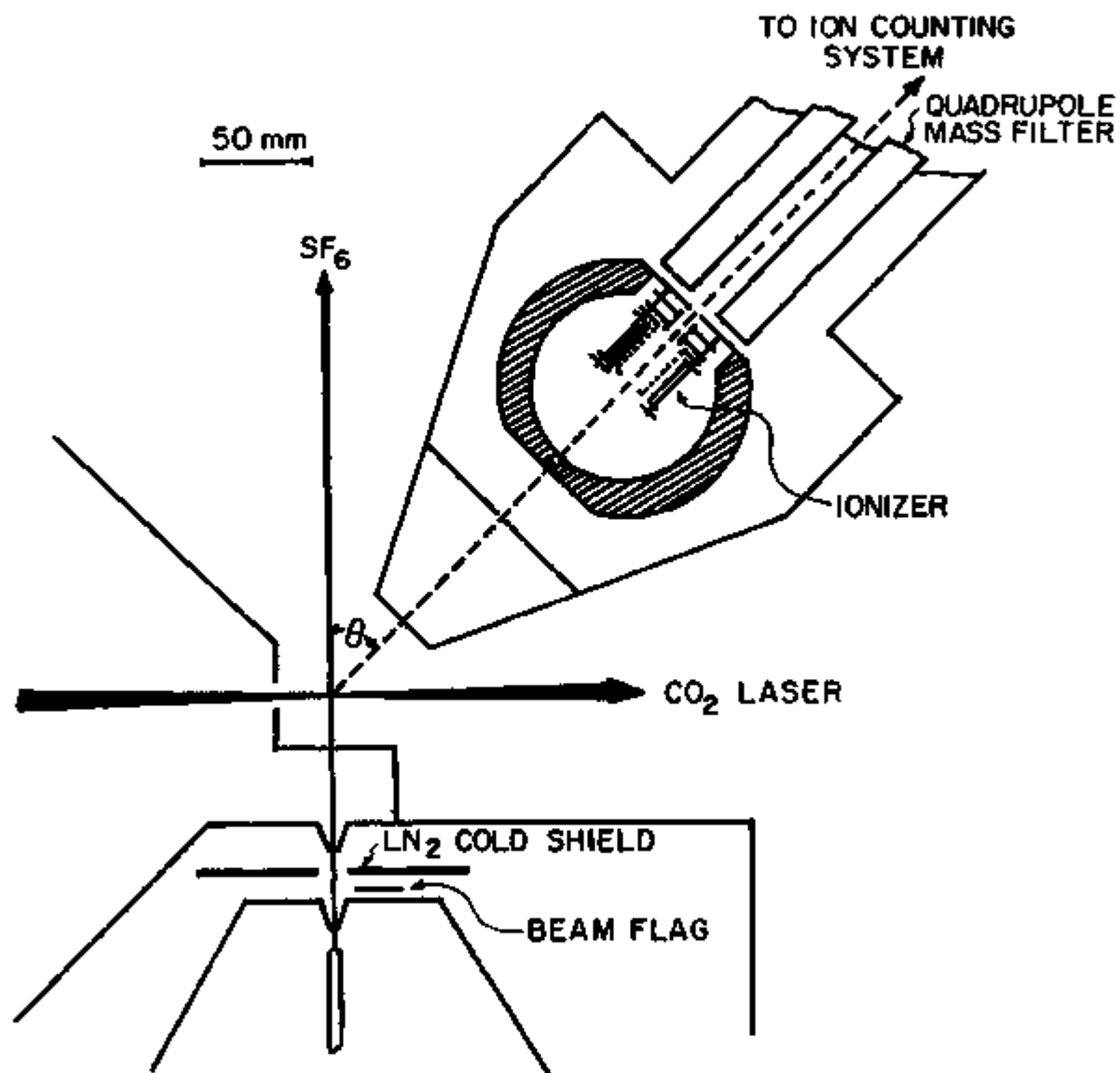
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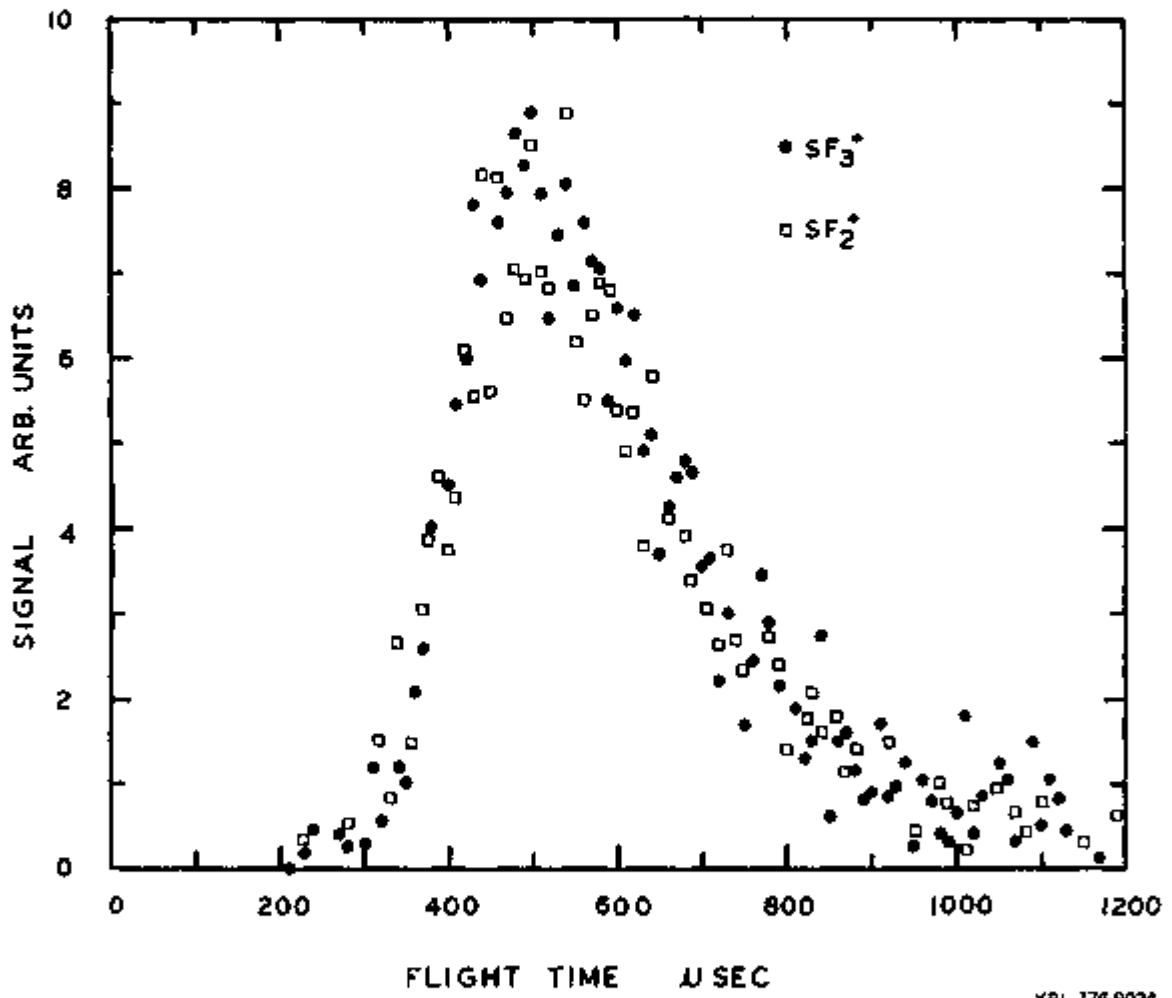
FIGURE CAPTIONS

- Fig. 1. Schematic diagram of the molecular beam apparatus used for the study of multiphoton dissociation.
- Fig. 2. Angular distributions of SF_3^+ and SF_2^+ at higher and lower laser intensity: lower intensity, X, SF_3^+ ; +, SF_2^+ ; higher intensity, \square , SF_3^+ ; \circ , SF_2^+ .
- Fig. 3. Time of flight spectra for SF_3^+ and SF_2^+ formed in the ionizer from the multiphoton dissociative product SF_5^+ : \bullet , SF_3^+ ; \square , SF_2^+ .
- Fig. 4. Calculated excited state population distributions for various times during a typical laser pulse (200 MW cm^{-2} , 100 ns).



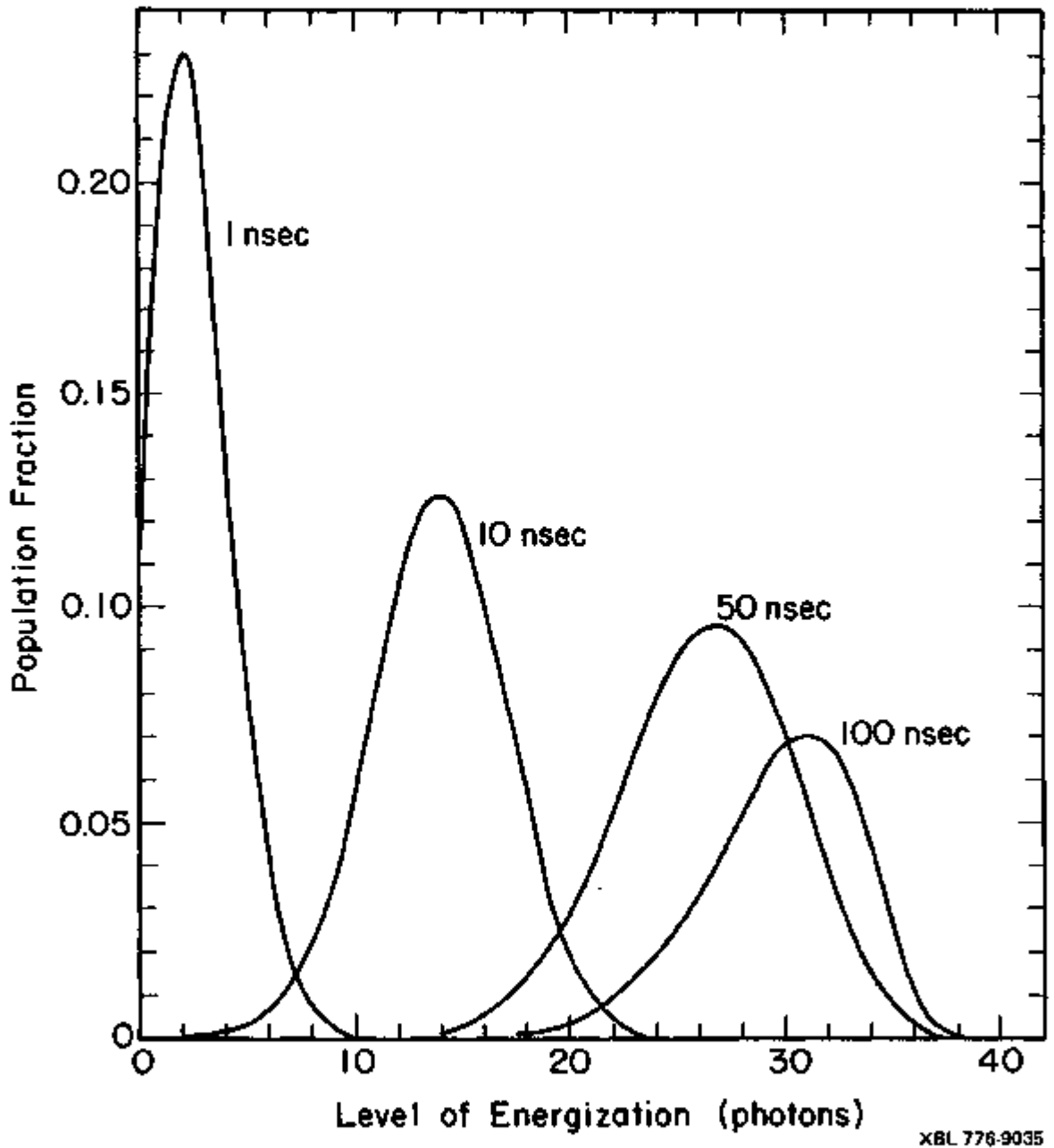
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Fig. 1



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Fig. 3



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Fig. 4

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