Lawrence Berkeley National Laboratory
LBL Publications

Title
Is Multiphoton Dissociation of Molecules A Statistical Thermal Process?

Permalink
https://escholarship.org/uc/item/6t3381r0

Authors
Grant, E R
Schulz, P A
Sudbo, Aa S
et al.

Publication Date
1977-08-01

UC-34α

IS MULTIPHOTON DISSOCIATION OF MOLECULES A STATISTICAL THERMAL PROCESS?

E. R. Grant, P. A. Schulz, Aa. S. Sudbo,
Y. R. Shen, and Y. T. Lee

August 1977

LBL-6659 Rev.

DISCLAIMER
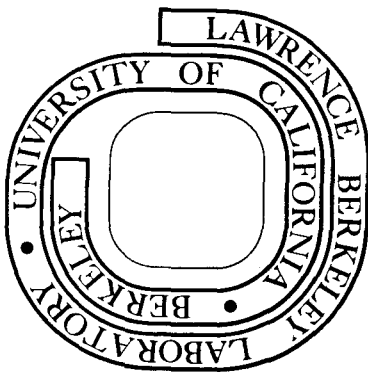
LBL-6659

IS MULTIPHOTON DISSOCIATION OF MOLECULES A STATISTICAL THERMAL PROCESS?

E. R. Grant,[*][‡] P. A. Schulz,[†] Aa. S. Sudbo,[†]

Y. R. Shen[†] and Y. T. Lee[*]

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

AUGUST 1977

ABSTRACT

We present here a phenomenological model calculation that exhibits
the realistic qualitative behavior of multiphoton excitation and
dissociation of polyatomic molecules. It is also used to show that
at least theoretically multiphoton excitation of molecules is not
equivalent to thermal heating.

[*]Also associated with Dept. of Chemistry, Univ. of California, Berkeley.

[†]Also associated with Dept. of Physics, Univ. of California, Berkeley.

[‡]Present address: Dept. of Chemistry, Cornell Univ., Ithaca, NY 14853

There is at present a lively discussion concerning the dynamics of infrared multiphoton dissociation (MPD) of polyatomic molecules.[1] Recent molecular beam experiments have convincingly shown that in the many molecules investigated, the excitation energy in a molecule is completely randomized in all its vibrational modes before it is decomposed, and a statistical theory can be used to adequately describe the dissociation dynamics.[2] But there is another very interesting question that is worth pursuing: namely, for an ensemble of isolated molecules under multiphoton excitation, what is the population distribution among the molecular energy levels. It has recently been proposed by Bloembergen and coworkers[3] that such a distribution can be considered as a thermal one characterized by an effective vibrational temperature which increases with laser pumping. One may however intuitively expect that there is a fundamental difference between monochromatic laser excitation and thermal heating. In thermal heating, which carries the assumption of adiabaticity, the molecules are always infinitesimally close to thermal equilibrium. However, this is not the case for laser excitation. We have recently developed a realistic model calculation of laser multiphoton excitation and dissociation of a molecule. This calculation describes the observed qualitiative behavior of MPD very well. In what follows, we present some of these results. We also show a comparison of the laser-excited distribution with the thermally heated distributions and state the reasons for their discrepancies.

In their recent experiment,[3] the Harvard group measured both the dissociation yield and the average number of infrared photons

absorbed per molecule under multiphoton excitation. In order to minimize the effect of molecular collisions, they used subnanosecond laser pulses for excitation. They then suggested that multiphoton laser excitation and dissociation could be considered as a statistical thermal process and their results could be interpreted by a simple theory describing such a process. They made the following assumptions in their theoretical calculation, (1) Multiphoton laser excitation is equivalent to thermal heating. (2) All the vibrational modes are degenerate. (3) The excitation energy in a molecule is randomized in all vibrational modes and the classical equipartition theorem is valid. (4) The dissociation rate is described by the quantum Kassel theory for unimolecular dissociation. Together with the thermal population distribution, it leads to the dissociation yield. (5) The thermal population distribution is not significantly perturbed by molecular dissociation.

Although their theoretical calculation is attractively simple, the assumptions are not easily justifiable. We present here a phenomenological model where many of the above assumptions can be eliminated. In our model calculation, we assume that the multiphoton excitation of a molecule can be described by stepwise incoherent one-photon transitions among a set of equally spaced energy levels; the degeneracy factor of each level is given by the corresponding molecular density of states which can be calculated. The excitation is then governed by the following set of rate equations:

$$dN_m/dt = C_{m-1}^a N_{m-1} + C_m^e N_{m+1} - (C_m^a + C_{m-1}^e) N_m - K_m N_m \qquad (1)$$

Here, N_m is the population in the mth excited level; K_m is the molecular dissociation rate from the mth level calculated from the RRKM statistical theory for unimolecular dissociation.[5] (For levels below the dissociation energy E_o we have $K_m = 0$) C_m^a and C_m^e are respectively the absorption rate from level m to $m + 1$ and the emission rate from $m + 1$ to m. For one-photon transitions, we can write

$$C_m^a = \sigma_m \frac{I}{h\nu} , \qquad C_m^e / C_m^a = g_m / g_{m+1} \qquad (2)$$

where σ_m is the absorption cross-section for m to $m + 1$ transition, $h\nu$ is the photon energy, I is the laser intensity, and g_m is the degeneracy factor for the mth level. In the above model, we have neglected the initial one-step multiphoton transition over the discrete states. This will have little effect on the results if the laser intensity is much higher than the threshold intensity to overcome the discrete state barrier, e.g., ~ 30 KW/cm^2 for SF$_6$.[6] We also believe that the coherent effect in the present multiphoton excitation process is not important as long as the exciting laser pulse is longer than 10 nsec.

For a given molecule with σ_m and $I(t)$ specified, the set of rate equations in Eq. (1) can be easily solved on a computer. We have performed such a calculation using SF$_6$ as an example. The frequencies of the vibrational modes of SF$_6$ are well known. To find the densities of states, we used exact count at low energies and the Whitten-Rabinovitch formula at higher energies.[5] The dissociation energy E_o was chosen to be 78 kcal/mole. The spacing between adjacent levels is 944 cm^{-1}. Because of anharmonic coupling among vibrational modes, the absorption

cross-section σ_m was expected to decrease with increase of m.[3] We

assumed that σ_m takes the form

$$\sigma_m = \exp[\alpha m + \beta] \tag{3}$$

where $\alpha = -.029$ and $\beta = -42.9$ for σ_m in cm^2. These values were

chosen so that our numerical results fit the experimentally observed

variation of the average number of photons absorbed[3] and the

dissociation yield[8] as a function of laser energy fluence.

Figure 1 shows the population distribution at various times

calculated with these parameters for a 100-nsec 200-MW/cm^2 rectangular

laser pulse excitation. Initially only the ground level is populated,

but the laser excitation, being a stochastic process, soon distributes

the population over many levels. As time goes on, the population

is continuously pumped up and the distribution curve shifts to higher

energies. Correspondingly, the average excitation energy, $\langle n \rangle h\nu$, also

increases with time. At t ~20 nsec, the high-energy tail of the

distribution curve clearly extends beyond the dissociation level. We

should then expect the onset of molecular dissociation. As the laser

excitation continuously drives the population distribution upward,

the dissociation yield increases rapidly. For those levels well

above E_o, the depletion of their population is dominated by the

dissociation rate. Consequently, the further up-excitation of the

population is restricted, the population at the high-energy tail is

heavily depleted by dissociation and the distribution curve becomes

asymmetric. The t = 80 nsec curve in Fig. 1 clearly exhibits this

feature.

Our model also allows us to calculate the dissociation yield as a function of time. More specifically, we can calculate the dissociation yield per unit time $Y_m(t) = K_m N_m(t)$ from each m level above E_o. In Fig. 2, we show the integrated dissociation yields from each level during and after the laser pulse respectively. The total dissociation yield is of course the sum of all. As shown in Fig. 2, most of the molecules dissociate during the laser pulse. (More than half dissociate before 2/3 of the laser pulse is over.) They dissociate mainly from those levels 6 hν – 11 hν above E_o. These results are fairly consistent with the experimental observations. In particular, we can now understand why SF_6 will undergo a two-step dissociation process if the exciting laser pulse is sufficiently long and intense.[2] In the primary dissociation of SF_6 into SF_5 and F, our molecular beam experiment[2] has shown that on the average less than hν of the total excess energy appears as recoil energy of the fragments; the rest is retained by SF_5 in its internal degrees of freedom. With the total excess energy $\geq$ 6 hν, this puts SF_5 in the excited quasi-continuum states. Then, if the laser field is still present for a sufficiently long time, the SF_5 fragments can readily absorb additional photons to exceed the threshold for subsequent dissociation into SF_4 + F. Apparently, this can happen for the case shown in Fig. 2.

We now turn to the question of how the laser-excited population distribution compares with a thermal distribution. This is shown in Fig. 3. The laser-excited distribution curve with <n> = 20 was

obtained from our model calculation at $t \simeq 20$ nsec. The thermal

distribution with $T = 2200°K$ has an average excitation energy

of $\langle n \rangle h\nu \cong 20$ $h\nu$, while the other with $T = 1800°K$ has its characteristic

temperature obtained from the equipartition theorem 15 $kT = 20$ $h\nu$. To

be more realistic, we have calculated the thermal distributions from

the Boltzmann function

$$P(n) \;=\; Ag_n \exp(-nh\nu/kT) \tag{4}$$

where A is a normalization constant and g_n is the realistic density

of states used in Eq. (2). The correspondence between T and $\langle n \rangle$ can be

easily calculated and is listed in Table I. We note that if we assume,

as did Bloembergen et al.,[3] that the equipartition theorem $\langle n \rangle h\nu =$

skT_e with $s = 15$ holds, then for a given $\langle n \rangle$, the "temperature" T_e

obtained is too low. In other words, the thermal distribution

characterized by T_e populates a significantly lower set of energy

states than the real distribution characterized by $\langle n \rangle$. An example

is shown in Fig. 3. The discrepancy here arises because the condition

$kT \gg h\nu_i$ cannot be satisfied by several of the 15 vibrational modes

of SF_6 so that the classical equipartition theorem is not valid.

The above discussion suggests that it is probably more meaningful

to compare the laser-excited distribution with the thermal distribution

characterized by the same excitation energy $\langle n \rangle h\nu$. One finds that the

thermal distribution is still broader and has a longer high-energy

tail. It is possible that a real laser pulse may somewhat broaden

the laser-excited distribution since in exciting the population over

the discrete state barrier, the leading edge of the laser pulse may have prepared a spread of population over a number of low-lying states in the quasi-continuum. However, the effect is expected to be not very significant in the case where the dissociation yield depends only on the laser energy fluence but not on the laser intensity. In fact, the thermal distribution can be approximated only if σ_m in the calculation remains constant or increases slightly with m. We can thus conclude that the thermal distribution is only a rather crude approximation to the laser-excited distribution. Experimentally, this can be verified by an accurate measurement of the dissociation yield as well as <n> versus the laser energy fluence. Recent studies on intramolecular isotope effect in CH_2DCH_2Cl by Benson and coworkers indicated that the excitation energy distribution is indeed narrow.[7] At large dissociation yield, the laser-excited distribution being strongly affected by the fast dissociation will certainly be different from the thermal distribution.

In summary, we have shown that our phenomenlogical model calculation gives a realistic description of multiphoton excitation and dissociation of polyatomic molecules. Furthermore, it is used to demonstrate that multiphoton laser excitation is not really equivalent to thermal heating.
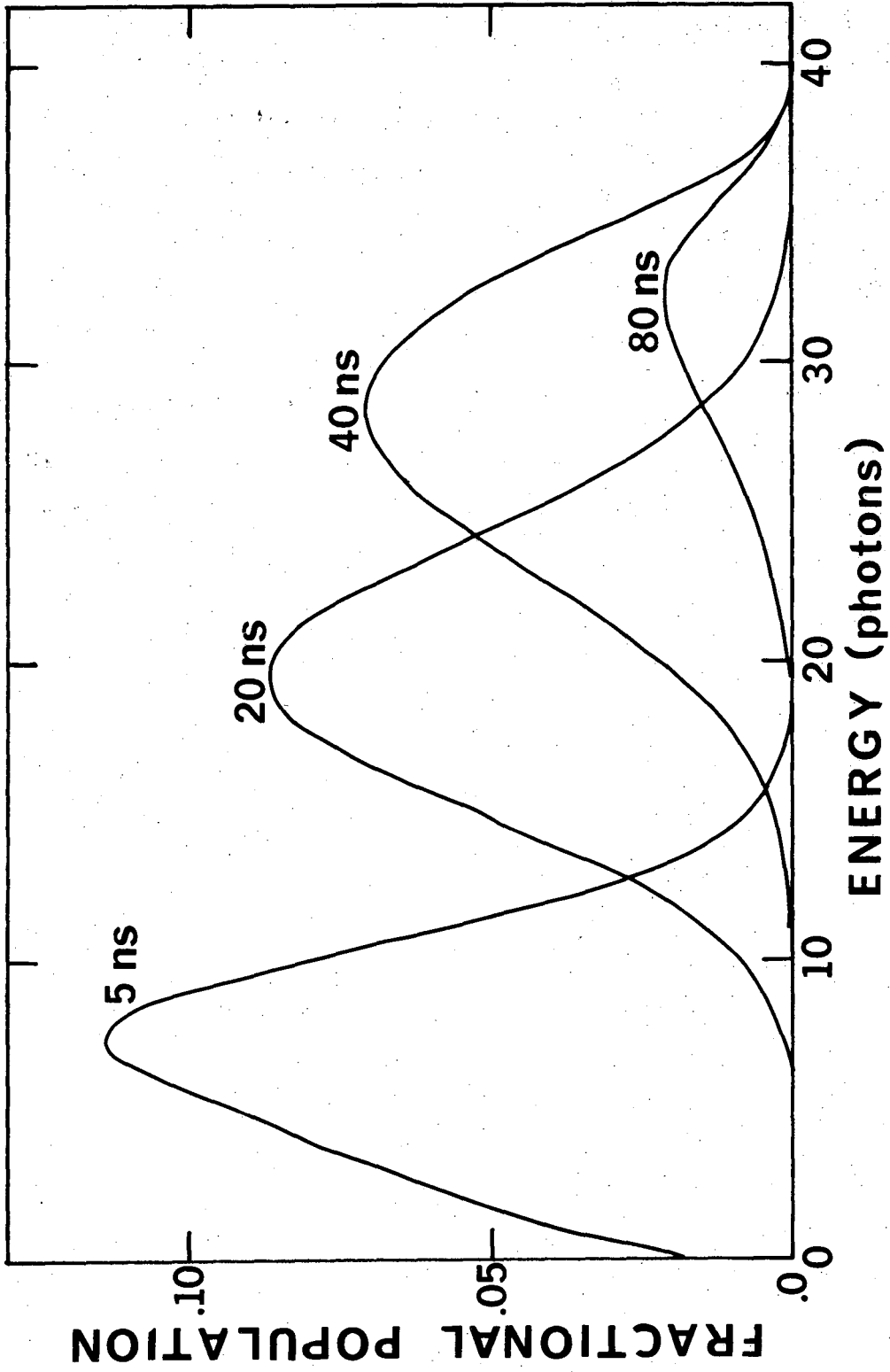
REFERENCES

1. See the papers presented in the Conference on Multiphoton Processes (Rochester, N.Y., June, 1977) (to be published).

2. M. J. Coggiola, P. A. Schulz, Y. T. Lee, and Y. R. Shen, Phys. Rev. Lett. $\underline{38}$, 17 (1977); E. R. Grant, M. J. Coggiola, Y. T. Lee, P. A. Schulz, Aa. S. Sudbo, and Y. R. Shen, Chem. Phys. Lett. (to be published).

3. J. G. Black, E. Yablonovitch, N. Bloembergen, and S. Mukamel, Phys. Rev. Lett. $\underline{38}$, 1131 (1977); Ref. 1; N. Bloembergen and E. Yablonovitch, Proc. Third Int. Conf. on Laser Spectroscopy (Jackson Lake Lodge, Wyoming, July, 1977) (to be published).

4. See, for example, P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions" (J. Wiley, New York, 1972).

5. R. V. Ambartzumian, N. P. Furzikov, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and A. A. Puretzky, Optics Comm. $\underline{18}$, 517 (1976); M. C. Gower, T. K. Gustafson, B. Fan, and T. K. Yee, Ref. 1.

6. N. Bloembergen, C. D. Cantrell, and D. M. Larsen, in "Tunable Lasers and Applications", edited by A. Mooradian, T. Jaeger, and P. Stokseth (Springer-Verlag, Berlin, 1976) p. 162.

7. A. J. Colussi, S. W. Benson and R. J. Hwang, submitted to Chem. Phys. Lett.

Table I.   Corresponding values of T, $\langle n \rangle$, s', and T_e, assuming thermal
distributions, s' = $\langle n \rangle h\nu/kT$, and T_e = $\langle n \rangle h\nu/ks$ with s = 15.

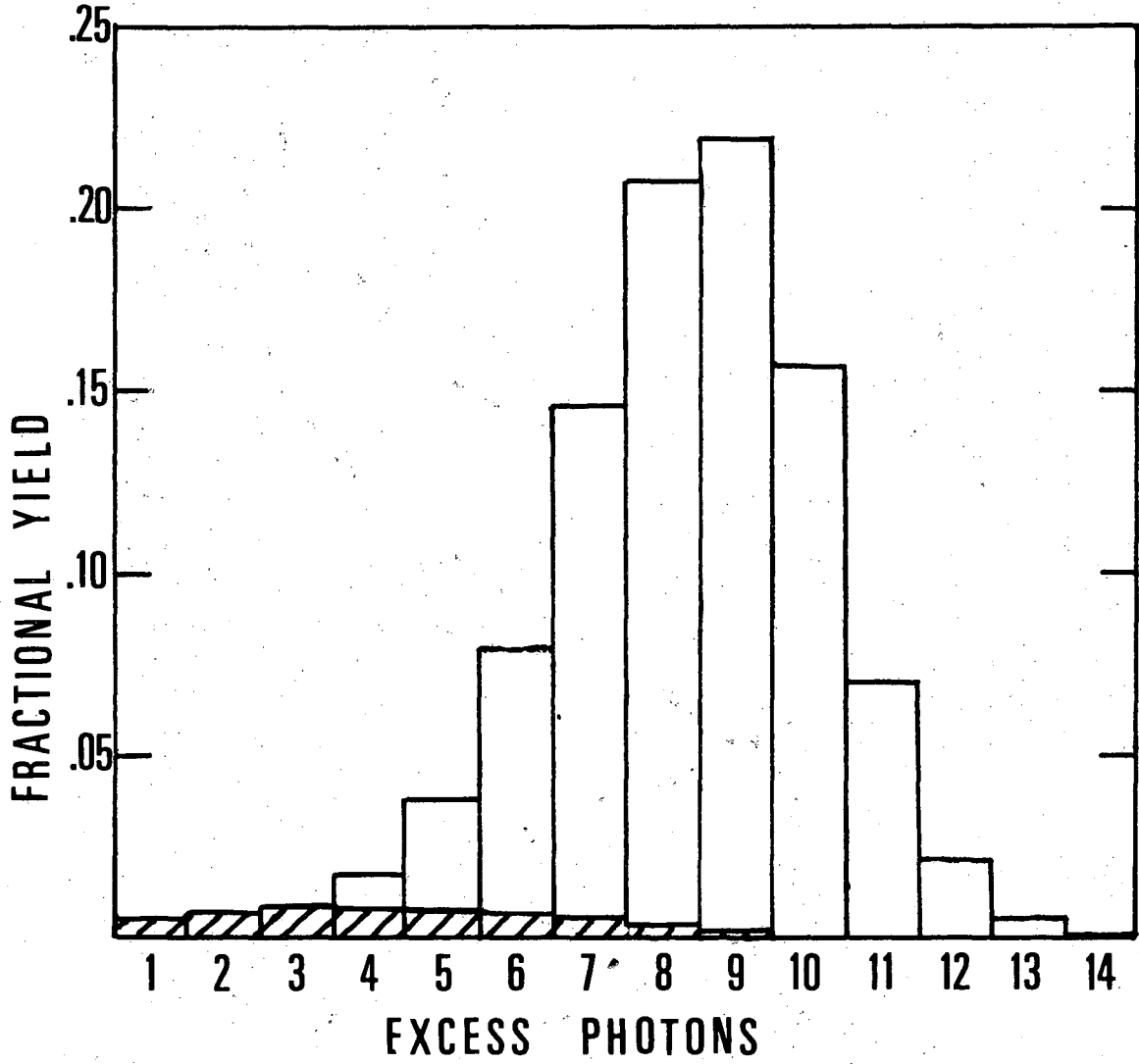| T(°K)	$\langle n \rangle$	Number of Effective Modes of s'	Effective Temperature T_e
1600	12.8	10.9	1160
1800	15.2	11.5	1377
2000	17.5	11.9	1585
2200	19.6	12.1	1776
2400	21.7	12.3	1966
2600	23.6	12.3	2138

FIGURE CAPTIONS

Fig. 1.   Population distribution at various times produced by a

100-nsec rectangular laser pulse excitation of 200 MW/cm^2.

Fig. 2.   Calculated dissociation yields from various levels above

the dissociation energy during the laser pulse (unshaded

region) and after the laser pulse (shaded region) for a

100-nsec, 200 MW/cm^2 laser pulse excitation.

Fig. 3.   Comparison of a laser-excited population distribution with

$\langle n \rangle$ = 20 with two thermal distributions, one with T = 2200 K

corresponding to $\langle n \rangle$ = 20 and the other with T = 1800 K
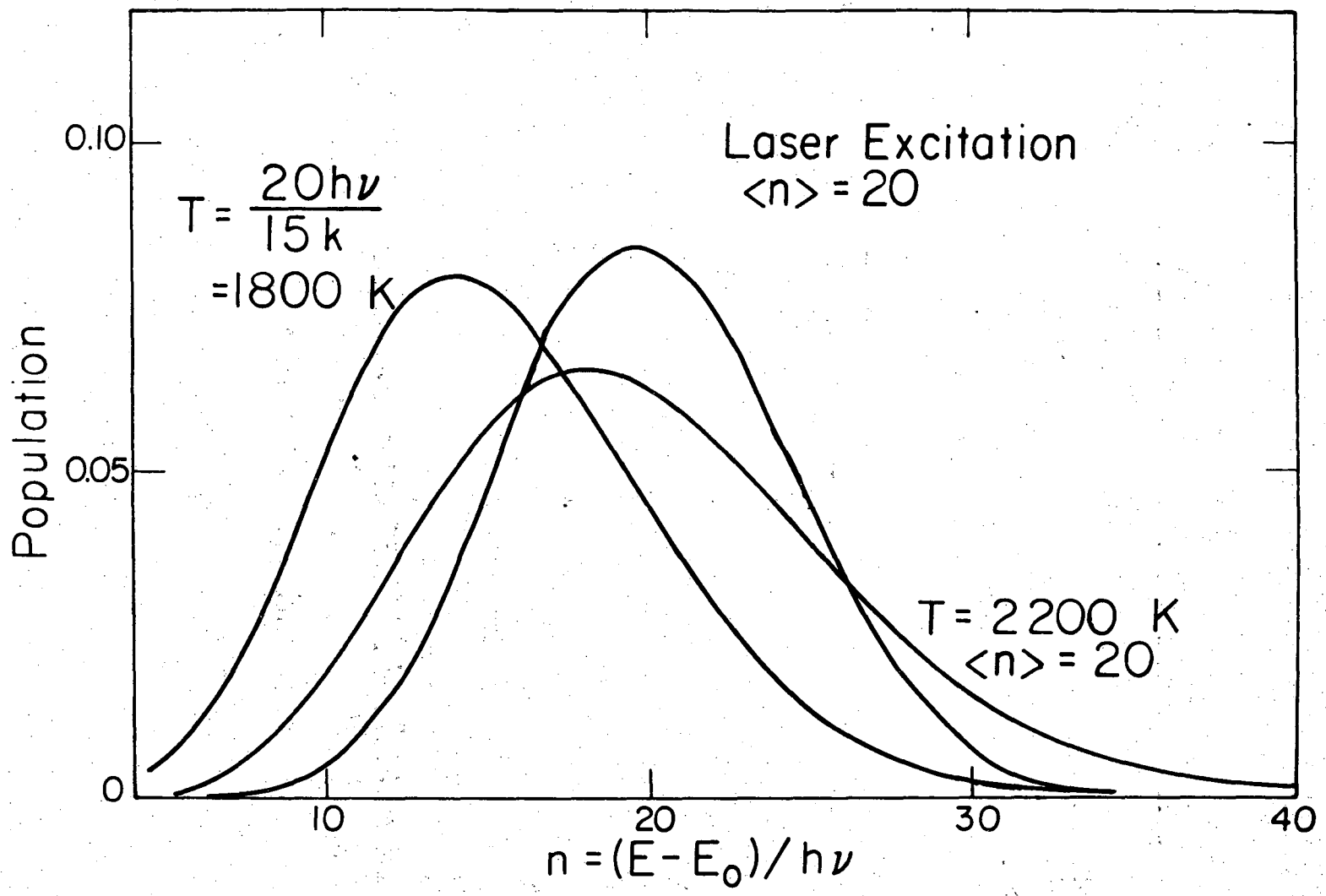
obtained from the equipartition theorem T = 20 hν/15k.

ENERGY (photons)

FRACTIONAL POPULATION

5 ns

20 ns

40 ns

80 ns

.10

.05

0.

0

10

20

30

40

XBL 779-2428

Fig. 1

XBL 778-9879

Fig. 2

Fig. 3

XBL777-5750A

-14-