Multiphoton induced isomerization: Dynamics and thermodynamics

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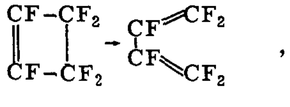
Irradiation of an equilibrium mixture of two or more isomers by a high power infrared laser can lead to quantitative formation of a single component that is not necessarily the thermodynamically preferred one. The case of a binary mixture in which only one isomer absorbs the laser light is quantitatively discussed. Light absorption populates levels above the isomerization energy threshold followed by collisional cooling to either reform the reactant or prepare the product. In the limit of weak collisions the branching ratio depends essentially on the phase space available to each isomer at the reaction threshold energy. It is shown that the entropic factor can be dominant under certain conditions and that excess foreign gas is essential for a quantitative transformation.

I. INTRODUCTION

An isolated molecule, irradiated by an intense laser beam, can absorb a large number of photons. In the case of infrared lasers this process of multiphoton excitation (MPE) is widely used to induce selective chemical reactions.[1] The unimolecular nature of MPE has been proved by working at very low pressures[1(c)] and by time resolved studies.[2] Collisions are not only unnecessary, but often detrimental to both selectivity and overall yield. This is primarily due to vibrational energy transfer to "cold" molecules (those that were not excited by the laser). Recently, it was shown that foreign gas addition can sometimes increase overall yields[3-5] without necessarily reducing the selectivity. One possible explanation[6-8] of this effect is rotational relaxation between the discrete energy levels of the so-called "region I."[9,10] This relaxation avoids bottlenecking due to hole burning in the early stages of the energy acquisition process, and leads to increased overall absorption.

In this paper we consider a laser induced process in which collisions with a cold, inert gas are not only beneficial, but actually essential to bring about a quantitative transformation.

The motivation for this work arises in part from the observation that collisions can increase the yield of isomerization reactions[5] and enhance isotopic selectivity.[11] These observations include the ring opening reaction



(1)

which will be used later to illustrate the results of the theory of Sec. II. Another example,[12] also involving a small ring compound, is that of cyclopropane isomerization to propylene. Here foreign gas addition was found to suppress unwanted side reactions, particularly such that are caused by excessive excitation of the reactant molecule or the primary products.

We consider an idealized isomerization reaction A ⇌ B, in which one isomer, say A, strongly absorbs the laser radiation while the other is essentially transparent. Those A molecules which were excited above the A→B activation barrier can rapidly isomerize. Collisions with the buffer gas are essential to reduce the energy of the newly formed B molecules, below the threshold for back reaction. Using thermodynamic and kinetic considerations, we show that the conversion of A to B can be driven to completion, even if at thermal equilibrium A is the predominant species. A statistical collision model leads to a simple formula for the branching ratio, determining whether an excited molecule will be deactivated back into A or transformed to B. The energy and entropy differences between the two isomeric forms and the reaction threshold energy appear explicitly in the expression for the branching ratio. Another expression relates the branching ratio to the degree of A→B conversion per laser pulse.

Our treatment does not include any specific model for the excitation process. A large number of models are available (see, for example, Refs. 13-16), mostly based on rate equations.

We show (subject to some simplifying assumptions) that the conversion per laser pulse depends basically on a single parameter, namely, the fraction of molecules excited beyond the energy threshold for reaction. The actual form of the distribution is unimportant. The treatment may be extended to include more than one reaction channel. In that case the species that has the lowest absorption coefficient at the laser frequency used can be made the dominant product, regardless of thermodynamic stability. In principle, this condition can be achieved for any system, although more than one laser source may be required.

II. EQUILIBRIUM THERMODYNAMICS AND KINETICS

Consider the isomerization reaction $A \rightleftharpoons B$ with the schematic energy profile displayed in Fig. 1 (compare Fig. 3 of Ref. 17). An energy profile of this type with $\Delta H^\circ = 11.7$ kcal/mole and barrier energy $E \simeq 47$ kcal/mole[18] characterizes Reaction (1). Assuming ideal gas behavior, the equilibrium constant of the isomerization reaction is given by[19]

$$K_{AB} = [B]_{eq}/[A]_{eq} = \exp(-\Delta G^\circ/RT)$$

$$= (q_B/q_A)\exp(-\Delta E_0/RT) , \tag{2}$$

where $\Delta G^\circ = G_B - G_A$ is the difference between the Gibbs'

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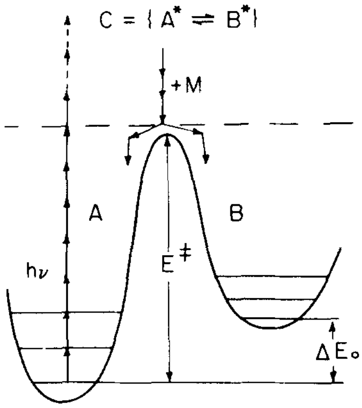

FIG. 1. Schematic illustration of the laser induced isomerization process A → B. An intense infrared laser pulse selectively excites the A isomer to beyond the reaction threshold energy $E^{\dagger}$, by multiphoton absorption. Above the barrier the isomerization is very fast and the two isomers can be regarded as representing adjacent regions in the phase space of the excited molecules $C = \{A^* \rightleftarrows B^*\}$. These molecules are deactivated to form either B or A by collisions with buffer gas molecules M which are present in excess in the reaction mixture. If the entropy change associated with the A → B process is positive $\Delta S° = S_B - S_A > 0$, the fraction of B molecules formed by deactivation is higher than their fraction at thermal equilibrium. Hence, the laser pumping–collisonal deactivation cycle leads to enrichment of the B isomer. Due to the slow back reactions B → A of the deactivated molecules, the process can be repeated many times before thermal equilibrium is re-established, leading to practically quantitative conversion of A to B.

free energies of 1 mole of pure B at temperature T and 1 mole of pure A at the same temperature. q_A and q_B are the molecular partition functions of A and B, respectively, with energies measured from their respective ground states. The exoergicity ΔE_0 is the difference between the ground state energies (per mole) of the two isomers.

Since there is no pressure change in isomerization reactions $\Delta H° = \Delta E°$ and $\Delta G° = \Delta A° = \Delta E° - T\Delta S°$, where $\Delta H°$, $\Delta E°$, $\Delta S°$, and $\Delta A°$ are the difference between the molar enthalpy, energy, entropy, and Helmholtz's free energy of B and A at temperature T, respectively. The standard energy change $\Delta E°$ involves two contributions $\Delta E° = \Delta E_0 + \overline{\Delta E°}$, where $\overline{\Delta E°} = \overline{E}_B - \overline{E}_A$ is the difference between the average energies of the two isomers measured from their respective ground state. Typically, $\Delta E_0 \gg RT$, whereas $\overline{\Delta E°} \lessdot RT$ so that $\Delta E° \simeq \Delta E_0$, which is independent of temperature.

A simple expression for K_{AB}, revealing its dependence on molecular parameters, is obtained in the classical rigid-rotor harmonic oscillator approximation. In this limit all degrees of freedom are separable so that $q = q_{tr} q_{rot} q_{vib}$. For nonlinear polyatomic molecules A and B one finds[19]

$$\Delta S° = R \ln(q_B/q_A) = R \ln[(\sigma_A/\sigma_B)(\overline{\nu}_A/\overline{\nu}_B)^s(\overline{I}_B/\overline{I}_A)^3] \quad , \quad (3)$$

where σ_A and σ_B are the symmetry numbers of A and B, respectively, and $\overline{\nu}_A$ and $\overline{\nu}_B$ are the geometric means of the s $(s = s_A = s_B)$ vibrational normal mode frequencies of A and B, respectively, and $\overline{I}_A$ and $\overline{I}_B$ are the geometric means of the moments of inertia. Also, in the classical limit $\overline{\Delta E°} = 0$; hence,

$$K_{AB} \simeq \exp(-\Delta E_0/RT + \Delta S°/R) \quad , \quad (4)$$

revealing the dominance of the energetic factor at low temperatures and the increasing importance of the entropic factor as T increases. In particular, $K_{AB} \to \exp(\Delta S°/R)$ as $T \to \infty$.

In most cases the energetically less stable isomer is preferred on entropic grounds as the weaker bonds result in lower vibrational frequencies, and the moments of inertia are typically larger. This is also the case for the ring opening process (1) where[18] $\Delta S° \simeq 9.6$ cal/mole deg. Since $\Delta E° \simeq 11.7$ kcal/mole, $K_{AB} = [B]_{eq}/[A]_{eq} \sim 10^{-7}$ at room temperature, and $K_{AB} \geq 1$ at $T > 1200$ °K.

If $E^{\ddagger}/RT \gg 1$ as is the case for Reaction (1) at ordinary temperatures, the forward and reverse rates of isomerization are quite small. For instance, at $T = 500$ °K, the rate constant for HFCB → HFB is $\sim 10^{-6}$ sec^{-1}. At higher temperatures, the large entropy increase tends to increase the equilibrium concentration of HFB. Also, the rate constant becomes much larger. Thus, for the system represented by Fig. 1, a possible process for converting A to B consists of initial heating of the mixture, followed by rapid cooling (i.e., with a rate exceeding the isomerization rate of molecules with energies below E'). High conversion yields can be obtained by removing the cold B isomer after this heating–cooling cycle, and repeating the cycle many times. This form of "distillation" is usually cumbersome and impractical using conventional heat sources. In contrast, MPE provides a simple way to selectively excite only the A isomer, whence the B isomer need not be physically removed after each cycle (laser shot). Cooling is assured if a large excess of a nonabsorbing gas is present. The parameters determining the efficiency of the laser pumping–collisional cooling mechanism are quantitatively discussed in the next section.

III. MODEL

Consider a cold equilibrium mixture of the A, B isomers, highly diluted by a monoatomic host gas M at temperature T. A suitable infrared laser source can be used to selectively excite the vibrational degrees of freedom of the A isomer. Following irradiation of the system by a short laser pulse of this kind, a fraction α of the A molecules will be excited above the reaction barrier $E^{\ddagger}$(Fig. 1). $\alpha = \alpha(\phi, P_M, T)$ will be a function of the laser pulse characteristics, in particular the fluence ϕ,[1] the "bath" (buffer gas) pressure P_M, and temperature T. In the next stage the excited molecules will be deactivated, predominantly by collisions with the host gas. Enrichment of B will be achieved if $r > K_{AB}(T)$, r being the branching ratio for the formation of B and A by collisional deactivation of excited molecules.

Our model is based on the following assumptions:

(1) A and B are the only stable isomers at the energies of interest.

(2) Only the A isomer absorbs the laser radiation and α is independent of its pressure.

(3) The translational and rotational energy distributions of all species remain thermal, at the heat bath temperature T at all times.

(4) The branching ratio r, between the fractions of excited molecules which after deactivation appear as A or B, can be calculated according to a statistical ("phase space," "prior") collisional model, as detailed below.

(5) The following time intervals are characteristic of the system: τ_l—the laser pulse duration; $\Delta t = f^{-1}$, where f is the laser's repetition rate; τ_{AB}—the mean time between A + B collisions; $\tau_{V-T} \sim (Z[M])^{-1}$ is the $V-T$ relaxation time due to collisions with M, where Z is the collision frequency; $\tau_{eq}(T)$ is $k_{AB}^{-1}(T)$, where $k_{AB}(T)$ is the thermal rate constant for the reaction $A \to B$.

We require (i) $\tau_l \ll \tau_{AB}$; this ensures no energy transfer from A to B during the excitation, and hence no absorption along the vibrational quasicontinuum of hot B molecules; (ii) $\tau_{V-T} \ll \Delta t$, ensuring that the excited molecules have sufficient time to cool down between successive laser pulses; (iii) $\tau_l \ll \Delta t \ll \tau_{eq}(T)$, which implies that many laser pulses can be absorbed by the system before thermal equilibrium is re-established.

(6) Above the activation barrier $E^\ddagger$ there is a very fast equilibrium between the A and B forms of the excited molecules, i.e., if A(E) and B(E) are excited isomers with the same total energy E (measured from a common origin), then, for $E > E^\ddagger$ we have at any instant of time

$$[B(E)]/[A(E)] = \rho_B(E)/\rho_A(E) \equiv K_{AB}(E) \quad , \tag{5}$$

where $\rho_A(E)$ and $\rho_B(E)$ are the vibrotational densities of states of A and B, respectively.

The last assumption is not essential for our model (see below). However, it was stated explicitly since it is almost invariably correct.[20] It will also simplify our expressions and derivations. This assumption is consistent with the point of view that the two isomers correspond to different regions in the phase space of one molecule.[19] At low energies ($E < E^\ddagger$), the two regions are practically separated and it is legitimate to regard A and B as distinct molecules. At high energies ($E > E^\ddagger$), the two regions are strongly coupled and even an isolated molecule can rapidly transform from one region to another. In accordance with this picture we shall regard A(E) and B(E) as distinct species only if $E < E^\ddagger$. Above $E^\ddagger$ we shall assume the existence of a single species $C(E) = [A(E) \rightleftharpoons B(E)]$ whose phase space volume is the sum of those of A and B (Fig. 1). [The last approximation neglects the overlap between the two regions, and the contribution of other possible forms, different from A or B, as in assumption (1).]

From assumptions (1), (2), and (5) it follows that after n laser pulses the concentration of the absorbing isomer $[A]_n$ is given by

$$[A]_n/[A]_0 = (1 - \alpha r_B)^n \quad , \tag{6}$$

where $[A]_0$ is the initial A concentration and $r_B = r/(1+r)$ is the fraction of excited molecule deactivated into B. Note that $r_A = 1 - r_B = 1/(1+r)$, $r = r_B/r_A$. The lhs of Eq. (6) is a measurable quantity. A simple model for r_B is derived below. Hence Eq. (6) provides a route for estimating α.

Setting a common energy origin for all species at the vibrational ground state of the more stable isomer (A, cf. Fig. 1) we shall use the notation C(E_C)—for an excited molecule, i.e., $E_C > E^\ddagger$; A(E_A)—for the A isomer, which "exists" only below $E^\ddagger$, namely, $0 \leq E_A \leq E^\ddagger$ and similarly B(E_B) for B with $\Delta E_0 \leq E_B \leq E^\ddagger$. The three possible outcomes of a collision between C(E_C) and a buffer gas atom are

$$C(E_C) + M \rightarrow \begin{array}{l} C(E_C') + M \quad , \\ A(E_A) + M \quad , \\ B(E_B) + M \quad . \end{array} \tag{7}$$

In the first product channel E_C' is either lower or higher than E_C. Clearly, by detailed balance, $E_C' < E_C$ is the (much) more probable outcome since E_C is higher than the average value of the vibrational energy at equilibrium at the heat bath temperature T.

Assigning rate constants (probabilities) to the three product channels of Eq. (7) is the first stage towards calculating r. To this end we shall employ a statistical (phase space, microcanonical) collision model according to which the rate constant into any product state is proportional to its phase space volume, or equivalently its prior microcanonical weight.[10,21] This model has been proven adequate for atom–polyatom collisions.[22] Like several other collision models,[23] the major qualitative result of the present model is that in atom–polyatom collisions only a small fraction of the vibrational energy of the polyatomic molecule is transferred into the relative translational motion and the rotational degrees of freedom. In other words, the atom is regarded as a "weak collider"[24–26]; most of the vibrational energy remains in the molecule. (The case of relaxation by polyatom–polyatom collisions and the "strong collision" limit are discussed in Sec. V.) More precisely, the model predicts that all final states with the same energy are equiprobable, or in classical terms, the energy is equipartitioned among all final degrees of freedom.

According to this model, for a collision with a given total energy $E = E_C + \epsilon$, where ϵ is the initial translational–rotational energy, the probability of, say, the second channel in Eq. (7), i.e., $P(E_A, E)$, is given by

$$P(E_A, E) \propto \Omega_A(E_A, E) = \rho_A(E_A)\bar{\rho}_A(E - E_A) \quad . \tag{8}$$

Here $\rho_A(E_A)$ denotes the vibrational state density of A(E_A) and $\bar{\rho}_A(E')(\epsilon' = E - E_A)$ is the density of rotational and (relative) translational states of the pair A + M. Thus $\Omega_A(E_A, E)$ is the joint density of states of the pair A + M when the vibrational energy of A is E_A and the sum of rotational and relative kinetic energies is $\epsilon' = E - E_A = E_C + \epsilon - E_A$, i.e., $\Omega_A(E_A, E)\, dE_A dE$ is the number of quantum states (the "phase space volume") of the pair A(E_A) + M for E_A and E within the small intervals dE_A and dE, respectively. The probabilities of the first and third product channels are defined similarly. The probabilities in Eq. (8) are related to the corresponding rate constants via $k(E_C \to E_A \mid E) = Z\Omega_A(E_A, E)$, where Z is the frequency of M + C collisions (per unit concentrations).

The overall probability that a $C(E_C)+M$ collision will end up as $I+M$ ($I = A, B, C$) is obtained by integrating $\Omega(E_I, E)$ over the accessible values of E_I, namely, for a collision with total energy E, the probability of the I + M channel is

$$P_I(E) = \Omega_I(E)/\Omega(E) \quad (I = A, B, C) \quad , \tag{9}$$

where

$$\Omega_I(E) = \int \Omega(E_I, E)\, dE_I \tag{10}$$

and

$$\Omega(E) = \Omega_A(E) + \Omega_B(E) + \Omega_C(E) \quad . \tag{11}$$

Hence, $P_C(E) = 1 - P_A(E) - P_B(E)$ is the probability that an excited molecule C is not deactivated below $E^\ddagger$.

Combining Eqs. (8) and (10), we find

$$\Omega_A(E) = \int_0^{E^\ddagger} \Omega_A(E_A, E)\, dE_A = \int_0^{E^\ddagger} \rho_A(x)\bar{\rho}_A(E-x)\, dx \quad , \tag{12}$$

$$\Omega_B(E) = \int_{\Delta E_0}^{E^\ddagger} \Omega_B(E_B, E)\, dE_B = \int_{\Delta E_0}^{E^\ddagger} \rho_B(y)\bar{\rho}_B(E-y)\, dy \quad , \tag{13}$$

$$\begin{aligned}\Omega_C(E) &= \int_{E^\ddagger}^{E} \Omega_C(E'_C, E)\, dE'_C = \int_{E^\ddagger}^{E} \rho_C(z)\bar{\rho}_C(E-z)\, dz \\ &= \int_{E^\ddagger}^{E} \rho_A(x)\bar{\rho}_A(E-x)\, dx + \int_{E^\ddagger}^{E} \rho_B(y)\bar{\rho}_B(E-y)\, dy \quad ,\end{aligned} \tag{14}$$

where the last equality in Eq. (14) expresses the assumption that the phase space volume of C is the sum of the phase space volumes corresponding to the A and B forms, at the same energy.

The rate constant corresponding to $M + C \rightarrow M + I$ ($= A$, B, C) at a given E_C and $\epsilon = E - E_C$ is $k(E_C \rightarrow I \mid E) = ZP_I(E) = Z\Omega_I(E)/\Omega(E)$. To calculate the branching fractions r_A and r_B [cf. Eq. (6)], we must average these rate constants over both the initial vibrational energy of the excited molecules $E_C > E^\ddagger$ and the initial translational–rotational energy ϵ. In addition, the effects of activating collisions, i.e., the backward processes in Eqs. (7), should be taken into account. Since the E_C distribution is changing in the course of relaxation, a rate equation description might appear appropriate. However, based on some obvious approximations we shall now argue that this rather complicated description is not at all necessary.

By definition, $E = E_C + \epsilon > E^\ddagger$. The translational–rotational energy distribution $P(\epsilon)$ is Boltzmann, i.e., $P(\epsilon) \propto \bar{\rho}(\epsilon)\exp(-\epsilon/RT)$, where T is the (cold) heat bath temperature. For collisions between atoms and nonlinear polyatomic molecules[10,21]

$$\bar{\rho}(\epsilon) = \bar{a}(\mu^{3/2}\bar{I}^3/\sigma)\epsilon^2 \quad , \tag{15}$$

where $\bar{a}$ is a constant, μ is the reduced collision mass, σ is the symmetry number, and $\bar{I}$ is the mean moment of inertia of the polyatomic molecule [cf. Eq. (3)]. $P(\epsilon)$ is maximal at $\hat{\epsilon} = 2RT$ and its width $\Delta\epsilon \sim 2RT$. Thus, for the cases that we are considering where (cf. Fig. 1) $E \sim E_C \gtrsim E^\ddagger \gg RT$ we can safely replace the averaging of E over ϵ by setting everywhere $E = E_C + \hat{\epsilon}(\simeq E_C)$. (A similar approximation is to replace ϵ by its average value $\langle\epsilon\rangle = 3RT$.)

In many multiphoton absorption experiments the fraction α of vibrationally excited molecules is small, and their number decreases with increasing excitation energy $E_C > E^\ddagger$. Thus, the average of $P_I(E)$ over all $E = E_C + \epsilon \simeq E_C + \hat{\epsilon}$ is well represented by $P_I(E^\ddagger + \hat{\epsilon})$. Nonetheless, even if a substantial amount of molecules is excited to energies well above $E^\ddagger$, the microcanonical prior model predicts that for computing r, one can replace the E averaging of $P(E)$ by setting $E \cong E^\ddagger + \hat{\epsilon}$. The properties of $P(E_I, E)$ leading to this result are outlined in the Appendix.

The major conclusion of this analysis is [cf. Eq. (A5)] that the average vibrational energy transfer per collision from an excited molecule is very small, i.e., $\langle\Delta E_C\rangle = E_C - \langle E'_C\rangle \ll E_C$. A related result is that $P_A(E)$ and $P_B(E)$ are negligible for practically all $E_C > E^\ddagger$ ($E_C \simeq E - \hat{\epsilon}$). Only when $E_C \simeq E^\ddagger$ can the excited molecule C be deactivated in one collision into A or B. Thus, if there are excited molecules with vibrational energy substantially above $E^\ddagger$, they must collide several times before reaching a point where one further collision will take them either to the A or to the B side of the activation barrier. From then on further collisions will continue to lower the vibrational energy content of the nascent A, B molecules until vibrational (but not chemical) equilibrium at the ambient temperature is reached. It should be noted that since the energy transfer per collision is small, the newly formed A and B molecules are still energy rich and might overcome the barrier again. Clearly, however, the probability of such activating collisions is lower than the deactivation probability. Furthermore, the small fraction of collisionally activated molecules will have the same fate as those originally formed by laser excitation, i.e., eventually all molecules will appear as either A or B isomers. According to this picture the branching ratio will be

$$r = \frac{P_B(E^\ddagger)}{P_A(E^\ddagger)} = \frac{\Omega_B(E^\ddagger)}{\Omega_A(E^\ddagger)} \quad . \tag{16}$$

Given the vibrational and translational–rotational densities of states we can evaluate r using the definitions (12) and (13). A simple expression involving the more important thermodynamic and spectroscopic factors governing r can be obtained using the classical expressions for the vibrational densities of states[17,26–28]

$$\rho_A^{cl}(E_A) = (a/\bar{\nu}_A^s)E_A^{s-1} \quad , \tag{17}$$

$$\rho_B^{cl}(E_B) = (a/\bar{\nu}_B^s)(E_B - \Delta E_0)^{s-1} \quad , \tag{18}$$

where $a = 1/(s-1)!h^s$, $\bar{\nu}_A$ is the geometric mean of ν_{iA} [cf. Eq. (3)], and "cl" = classical. Using these expressions and Eq. (15) in Eqs. (12) and (13), we find

$$\Omega_A^{cl}(E) = \gamma_A(E^\ddagger)^{s+2} \quad , \tag{19}$$

$$\Omega_B^{cl}(E) = \gamma_B(E^\ddagger - \Delta E_0)^{s+2} \quad , \tag{20}$$

where $\gamma_A = a\bar{a}\mu_A^{3/2}(\bar{I}_A)^3/\sigma_A(\bar{\nu}_A)^s$, etc. Since $\mu_A = \mu_B$, we get

$$r \simeq \left(\frac{\sigma_A}{\sigma_B}\right)\left(\frac{\bar{I}_B}{\bar{I}_A}\right)^3\left(\frac{\bar{\nu}_A}{\bar{\nu}_B}\right)^s\left(1 - \frac{\Delta E_0}{E^\ddagger}\right)^{s+2} \tag{21a}$$

or, using the classical expression (3),

$$r \simeq \exp(\Delta S^\circ_{\rm cl}/R)\left(1-\frac{\Delta E_0}{E^\ddagger}\right)^{s+2} \tag{21b}$$

More reliable estimates of r can be obtained by using more accurate procedures for calculating vibrational densities of states. A frequently used correction is obtained by replacing the number of classical vibrations s in Eqs. (17) and (18) by the "effective number" s' of classical vibrations. This parameter is sometimes estimated from the experimental value of vibrational heat capacity (at the appropriate temperature) via $C^{\rm exp}_{v,\rm vib} = s'R$ [see, for example, Ref. 17].

Our last result reveals that the branching ratio r, like the equilibrium constant $K_{\rm AB}(T)$, is a product of energetic and entropic factors. For an isomerization reaction of the type depicted in Fig. 1, e.g., Reaction (1), $\Delta S^\circ > 0$ and the entropic factor favors the B isomer while the energetic factor favors the A isomer, in analogy to the behavior of the equilibrium constant $K_{\rm AB}(T)$ [cf. Eq. (4)]. The structural–dynamical properties of the isomerization reaction enter the expression of r via the barrier height $E^\ddagger$. The higher is $E^\ddagger/\Delta E_0$ the less important is the influence of the energetic factor.

It is interesting to note that r can be brought more closely into the form of an equilibrium constant like K. Using the approximation $(1+x)^n \simeq \exp(nx)$, we find that

$$r = \exp(\Delta S^\circ_{\rm cl}/R - \Delta E_0/RT^\ddagger) \ , \tag{22}$$

with $T^\ddagger \simeq E^\ddagger/(s+2)R$.

It was mentioned above that efficient laser induced isomerization A → B can only be achieved if $r > K_{\rm AB}(T)$. Noting from Eqs. (22) and (4) that r can be identified as $K_{\rm AB}(T^\ddagger)$, and that $K_{\rm AB}(T)$ increases with T (for $\Delta S^\circ > 0$), the requirement for efficient conversion can be stated as

$$T^\ddagger \simeq E^\ddagger/(s+2)R > T \quad . \tag{23}$$

The nature of the temperature $T^\ddagger$ which may be termed the effective reaction temperature is revealed by the following considerations: By Eq. (16) r is the "equilibrium constant" for the reaction $\mathrm{A}+\mathrm{M} \rightleftarrows \mathrm{B}+\mathrm{M}$ for a microcanonical ensemble consisting of $[\mathrm{A}+\mathrm{M} \rightleftarrows \mathrm{B}+\mathrm{M}]$ pairs with a total energy $E^\ddagger$ (excluding the center of mass kinetic energy). It is well known that the microcanonical ensemble yields the same thermodynamic results as the canonical ensembles, provided the microcanonical energy E is identified with the average canonical energy $\langle E \rangle$ associated with the ensemble's temperature T.[19] This property holds only for macroscopic systems. The $\{\mathrm{A},\mathrm{B}\}+\mathrm{M}$ system is not really a macroscopic one, but if the number of degrees of freedom is large (e.g., for $s \geqslant 30$), the passage to a canonical description is a good approximation. In our case we can thus define a tenperature $T^\ddagger$, for which the average energy of the $\{\mathrm{A},\mathrm{B}\}+\mathrm{M}$ pairs is $E^\ddagger$. The branching ratio r assumes the role of a usual equilibrium constant

$$r = \frac{\Omega_{\rm B}(E^\ddagger)}{\Omega_{\rm A}(E^\ddagger)} = \exp(-\Delta G^\circ/RT) = \exp(\Delta S^\circ/R - \Delta H^\circ/RT^\ddagger) \ , \tag{24}$$

where ΔG°, ΔS°, and ΔH° are the free energy, entropy, and enthalpy changes for the $\mathrm{A}+\mathrm{M} \rightarrow \mathrm{B}+\mathrm{M}$ reaction at temperature $T^\ddagger$. Thus, one can use the experimentally available quantities to compute r. Unfortunately, experimental results are usually available only for $T < T^\ddagger$ and extrapolation methods[17] are required.

IV. EXAMPLES

The number of detailed studies on multiphoton induced isomerization reactions is rather limited.[5,11,12,29–31] The emphasis has usually been on the unimolecular characteristics, orbital symmetry considerations, and nonthermal features. In agreement with the conclusions of Sec. II, the thermodynamically less favored species can be formed preferentially. This trend was found in the case of hexafluorocyclobutene,[5] *cis*-3,4-dichlorobutene,[30] isomeric hexadienes,[31] and vinylcyclopropane.[29] In some of these cases it is indicated that molecules acquire energy from the laser field in considerable excess over the threshold energy. In the absence of foreign gas addition this appears to lead to reduced yields due to back reactions and secondary processes.

Addition of foreign gases simplifies the reaction scheme, in the sense that secondary products, i.e., those that cannot be obtained by a single thermal step, are eliminated. Formation of pentadiene in the case of vinylcyclopropane[29] and of *t*-1,3-hexadiene from *t*,*t*-2,4-hexadiene,[32] are recently reported examples. This observation can be understood as due to less extensive excitation of the parent molecule, so that only the lowest reaction channel is significant. Furthermore, vibrationally excited primary products can absorb laser excitation, unless they are quickly relaxed (quasicontinuum absorption).

The only example available to us at the moment for quantitative estimates is the ring opening of hexafluorocyclobutene (HFCB) [cf. Reaction (1)[5]]. It is reported that even under prolonged irradiation of pure HFCB, complete conversion to HFB could not be accomplished. Addition of excess helium, however, dramatically increased the conversion efficiency. This result is in line with our model. Moreover, available thermodynamic data allow us to estimate r for the reaction, and hence, by Eq. (6), the excitation factor α. Using $\Delta E_0 = 11.7$ kcal/mole, $E^\ddagger = 47.0$ kcal/mole, $\Delta S^\circ = 9.6$ cal/mole deg,[18] and (the classical value) $s = 24$, we get $r \simeq 0.07$. Recall that this is a lower limit to r, based on the assumption that all vibrations are classical. From Ref. 5 we find that the number of pulses n required to attain 90% conversion is 2200 at 400 mJ/pulse and 14 400 at 270 mJ/pulse. This leads, by Eq. (6), to $\alpha = 1.5\times10^{-2}$ at the higher fluence level, and to $\alpha = 2.4\times10^{-3}$ at the lower fluence level. These values appear reasonable in view of the experimental conditions employed. The increase in up-pumping efficiency with increased fluence is compatible with reported yield vs fluence curves.[1] The use of ΔS° obtained from thermal studies appears to be justified in this case. Available thermodynamic data, as well as calculations based on group additivity properties,[17] indicate that ΔS° of this reaction does not appreciably change with temperature. The use of the classical value of s appears also to be a good approximation, as the highest vibrational frequency involved[33] is about 1800 cm^{-1}. At the equivalent temperature of $E^{\ddagger}$ (~1200 °K) this mode is essentially classical.

V. DISCUSSION AND SUMMARY

The purpose of this paper was to focus attention on some basic aspects of laser induced chemistry. In this section we survey the underlying assumptions of the model of Sec. III and evaluate its applicability to experimental results.

Considerable effort has been invested in the elucidation of the mechanism by which an isolated molecule acquires energy from the laser field.[1,2] A closely related problem is whether MPE leads to the same distribution of excited states as thermal activation, or, for instance, to mode selective excitation which may allow mode selective chemistry.[12,34] Our model completely ignores this aspect of MPE, as well as the problem of coherent versus incoherent excitation.[35] We only assumed that molecules activated to beyond the threshold energy can react, and that the final product distribution is determined by statistical considerations. The justification for this procedure is twofold. Most of the MPE reactions reported to date can be analyzed in terms of statistical rate theories.[1,36] Secondly, even when specific behavior is indicated,[12,37] collisions with an inert gas tend to lead to conventional kinetics. As our analysis applies only in cases where frequent collisions occur, no peculiarities should be introduced. The requirements concerning the relative time scales [assumption (5) in Sec. III] are readily attainable in practice. In a typical MPE experiment, $\tau_l \sim 10^{-7}$ sec, $\Delta t \sim 1$ sec, and $\tau_{\mathrm{BA}} > 10^4$ sec. Addition of ~100 Torr of an inert gas places τ_{V-T} well below 10^{-3} sec, thus ensuring the required relaxation of the newly formed product between laser pulses.

Two of the model's assumptions are not essential, and were introduced primarily in order to keep the algebra simple. These are the vanishing absorption coefficiencies of species B at the laser frequency, and the existence of only one reaction channel. If we allow for uppumping of B, the net overall conversion efficiency per pulse will be given by

$$[\mathrm{A}]_i \alpha_{\mathrm{A}} r_{\mathrm{B}} - [\mathrm{B}]_i \alpha_{\mathrm{B}} r_{\mathrm{A}} \quad , \tag{25}$$

where $[\mathrm{A}]_i$ and $[\mathrm{B}]_i$ are the concentrations of A and B, respectively, before the pulse. From Eq. (25) it is clear that in the limit of very large n, the composition of the mixture will approach the ratio [cf. Eq. (6)]

$$[\mathrm{B}]_n/[\mathrm{A}]_n = (\alpha_{\mathrm{A}}/\alpha_{\mathrm{B}}) r \ . \tag{26}$$

In other words, the reaction cannot be driven to completion under these conditions. In the case of more than one reaction channel, absorption by all possible products must be considered. A case in hand is the hexadiene system.[31,32] It is obvious that the species with the smallest absorption coefficient will be the most abundant. In practice, a combination of two laser sources using two different frequencies may be used to drive the reaction in a predetermined direction.

Unlike isotope separation and similar reactions where different atomic compositions are involved, the case of isomerization is unique in that the laser can be used to completely transform one species to the other, without "wasting" material. The process may be likened to fractional distillation, in which one component is constantly removed from the column. In some industrial cracking processes, the distillation may be controlled in such a way as to produce primarily a particular boiling point fraction. Laser induced isomerization can be similarly termed preparative distillation, as the laser heating is extensive enough to convert the absorbing molecule to another one, before leaving the system. Thus, MPE induced isomerization may prove to be a promising test case for practical laser chemistry.

Finally, we wish to point out that the treatment of Sec. III can be extended to include the case of "strong colliders." In the framework of the microcanonical model, M is a strong collider if it has many degrees of freedom, e.g., a polyatomic molecule. The same reasoning applied in the derivation of Eq. (21) leads now to

$$r \simeq \exp(\Delta S^\circ/R)\left(1 - \frac{\Delta E_0}{E^{\ddagger} + \langle E' \rangle}\right)^{s+\bar{s}+(7/2)} \quad , \tag{27}$$

where $s, \Delta S^\circ$, ΔE°, and $E^{\ddagger}$ have the same meaning as in Eq. (21), $\bar{s}$ is the number of degrees of freedom of M, and $\langle E' \rangle = \langle E_{\mathrm{M}} \rangle + (9/2)RT$ is the sum of the average vibrational energy of M, the rotational energies of M and A(B) and the relative kinetic energies, all corresponding to the (cold) heat bath temperature T. Also, like in the passage from Eq. (21) to (22) we can rewrite r as

$$r \simeq \exp(\Delta S^\circ/R - \Delta E_0/\tilde{T}) \quad , \tag{28}$$

where $\tilde{T}$, the effective temperature, is defined by

$$\tilde{T} = (E + \langle E' \rangle)/[s + \bar{s} + (7/2)] \ . \tag{29}$$

We note that $\tilde{T} < T^{\ddagger}$ [cf. Eq. (23)] and that $\langle E' \rangle \leqslant [\bar{s} + (9/2)]RT$. Thus, strong colliders reduce the branching ratio r, and hence the efficiency of the laser induced conversion process. A qualitative statistical explanation to this behavoir is that the strong collider deactivates the excited molecules into regions (of A and B) where the vibrational densities of states are low, like those of cold molecules. Hence, the branching ratio r [cf. Eq. (16)] is determined primarily by the ratio of densities of states of cold A and B molecules.

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APPENDIX: PROPERTIES OF $\Omega_I(E)$ AND $P_I(E)$

Examining Eqs. (12)-(14) we note that Eq. (12) and the first term in Eq. (14) are two integrals of the same function $\rho_A(x)\bar{\rho}_A(E-x)$ covering, respectively, the regions $0 \leq x \leq E^\ddagger$ and $E^\ddagger < x \leq E$. Similarly the y integrals cover the ranges $\Delta E_0 \leq y \leq E^\ddagger$ and $E^\ddagger < y \leq E$. The sum of the two x integrals is proportional to the probability that after a C+M collision the molecule will appear in the form of A; either as stable A isomers $(0 \leq x \leq E^\ddagger)$ or in the A region of the C-phase space $(E^\ddagger < x < E)$. If the first x integral (12) gives the major contribution to the sum, a stable A is more probable and *vice versa*. Similar interpretation holds for the y integrals. Both types of integrals can be evaluated in a closed form using the classical expressions for the translational–rotational density of states, (15), and the vibrational densities of states:

$$\rho_A(x) = (a/\bar{\nu}_A^s)x^{s-1} \quad , \tag{A1}$$

$$\rho_B(y) = (a/\bar{\nu}_B^s)(y - \Delta E_0)^{s-1} \quad , \tag{A2}$$

Rather than comparing the explicit, but somewhat cumbersome expressions for the four x and y integrals we shall now follow an approximate but simpler analysis, in order to compare their relative contributions.

Both $\rho_A(x)\bar{\rho}_A(E-x)$ and $\rho_B(y)\bar{\rho}_B(E-y)$ obtain rather sharp maxima at the most probable values $\hat{x}$ and $\hat{y}$, respectively. Hence, the major contribution to the integrals comes from narrow ranges Δx and Δy around (mainly above) $\hat{x}$ and $\hat{y}$, respectively. If $\hat{x} < E^\ddagger$, then $\Omega_A(E) > \Omega_C(E)$ and the excited molecule will be deactivated into A rather than remaining excited. Similarly, if $\Delta E_0 < \hat{y} < E^\ddagger$, then $\Omega_B(E) > \Omega_C(E)$. Using Eqs. (15), (A1), and (A2), we find

$$\hat{x} = [(s-1)/(s+1)]E \quad , \tag{A3}$$

$$\hat{y} = [(s-1)/(s+1)E - [2/(s+1)]\Delta E_0 \quad . \tag{A4}$$

Setting $E = E_C + \hat{\epsilon}$, we find that $\Omega_A(E) \ll \Omega_C(E)$ unless

$$E_C < [(s+1)/(s-1)]E^\ddagger - \hat{\epsilon} \simeq E^\ddagger \tag{A5}$$

Similarly, $\Omega_B(E) \ll \Omega_C(E)$ unless

$$E_C < [(s+1)/(s-1)]E^\ddagger + [2/(s-1)]\Delta E_0 - \hat{\epsilon} \simeq E^\ddagger \quad . \tag{A6}$$

[The influence of the second term in the rhs of Eq. (A6) should not be overestimated: first because it is considerably smaller than the first term; second, a more careful analysis would reveal that since $\rho_B(y)$ increases more slowly than $\rho_A(x)$, the requirement $\hat{y} < E^\ddagger$ is more stringent than $\hat{x} < E^\ddagger$.]

The implications of Eq. (A5) and (A6) are quite obvious: Direct (single collision) deactivation of $C(E_C)$ into either A or B is improbable unless E_C is just above $E^\ddagger$, i.e., $E_C \gtrsim E^\ddagger$. Equivalently, if E_C is substantially above $E^\ddagger$, a single collision will only remove (on the average) a small amount of vibrational energy from C, leaving it with $E_C' \quad E^\ddagger$. In fact, it is not too difficult to show that the average vibrational energy transfer per collision, predicted by the microcanonical–prior model, is

$$\Delta E_C = E_C - \langle E_C' \rangle \simeq \frac{3}{(s+3)}(E_C + \hat{\epsilon}) \ll E_C \quad . \tag{A7}$$

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