A MODEL FOR ISOTOPE SEPARATION VIA MOLECULAR MULTIPHOTON PHOTODISSOCIATION

Shaul MUKAMEL* and Joshua JORTNER

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

Multiphoton photofragmentation of an "isolated" molecule on the lowest potential surface is considered in terms of a truncated anharmonic oscillator driven by a pulsed, intense laser field. Intramolecular vibrational relaxation and indirect photodissociation are accounted for by assignment of decay widths to the appropriate levels. The effective-hamiltonian formalism is applied to derive explicit expressions for the photofragmentation yield and for the isotopic separation factor.

Recent experimental studies by Ambartzumian et al. [1–3] and by Robinson et al. [4,5] have established that multiphoton photodissociation of a variety of molecules, e.g., SiF_4, BCl_3, SF_6, C_2H_4, CH_3OH, etc., can be induced by a high-power pulsed CO_2 laser (output 1–2 J per pulse, pulse duration ≈ 100 ns, pulse frequency 2–5 Hz, power 1–10 GW cm^{-2}). These multiphoton photofragmentation processes are distinct from trivial effects of laser heating, i.e., increase of the translational energy of the reactants, and constitute a new class of interesting photophysical phenomena. Several experimental facts should be noted [1–5]. First, the photodissociation yield exhibits a sharp power dependence, the power threshold for an observable effect being ≈ 5 MW cm^{-2}. These observations are compatible with a multiphoton process of high order, i.e., ≈ 25 and ≈ 31 photon process for the photofragmentation of SF_6 and BCl_3, respectively**, and also with power-broadening effects. Second, time scaling‡ of the photofragmentation process supports the notion of a laser induced reaction. Third, photodissociation can occur either to ground state or electronically excited fragments, depending on the nature of the molecule. Fourth, for a variety of systems, multiphoton photodissociation was observed to occur in a "collision-free" molecule, unaffected by V–V scrambling processes. Fifth, the multiphoton fragmentation was found to be highly isotopically selective. Enrichment factors for photodissociation of $^{32}SF_6$ (in $^{32}SF_6/^{34}SF_6$ mixtures) of ≈ 35 were reported at moderately low pressures (1 torr SF_6/H_2 mixture).

In this note we advance a quantum mechanical model for multiphoton photofragmentation in intense fields of an "isolated", collision-free molecule on the electronic ground state potential surface, with special emphasis on the isotopic selectivity of this process. We shall attempt to incorporate anharmonicity effects, power-broadening phenomena, as well as intramolecular nonreactive vibrational relaxation and nonradiative decomposition, i.e., predissociation. The present approach is more general and more informative than previous work by Goodman et al. [6–8], on coherent and incoherent excitation processes of a harmonic oscillator as well as the classical model

---

* Also at Applied Optics Department, Soreq Nuclear Research Centre, Yavne, Israel.
** The number of photons, N_p, required for bond rupture is inferred from the simple relation $N_p = D_e/\hbar\omega$, where D_e is the dissociation energy ($D_e \approx 24000$ cm^{-1} for $SF_6 \rightarrow SF_5 + F$ and $D_e \approx 30000$ cm^{-1} for $BCl_3 \rightarrow BCl_2 + Cl$, while $\hbar\omega \approx 950$ cm^{-1} is the energy of a photon emitted by the CO_2 laser).

‡ Time scaling of the multiphoton photofragmentation process implies that the yield and the isotope separation factor vary linearly (see refs. [2,4]) with the number of laser shots.

for the excitation of an anharmonic oscillator recently advanced by Bloembergen [9].

The molecular energy level scheme is portrayed in fig. 1. The molecule is optically pumped with the laser frequency $\hbar\omega$, being near-resonance with a certain vibrational mode (ν_3 in the case of SF_6) which will be characterized by the vibrational quantum number υ. The following three energy regions, in the order of increasing energy (fig. 1), can be distinguished:

Region I. Low energy range where the density $\rho_B(E)$ of background states corresponding to other vibrational modes is low.

Region II. Intermediate energy range where the levels (υ) of the vibrational ladder are quasidegenerate with a background manifold of vibrational states which correspond to other modes[#]. The physical situation is reminiscent of interstate coupling between two electronic configurations in polyatomic molecules. In the present case the condition for strong coupling

$$V_A(E)\rho_B(E) \gg 1, \qquad (1)$$

where $V_A(E)$ is the (high-order) anharmonic coupling, marks the onset of region II.

[#] No complete theory of IVR in an isolated molecule is available at present. Nordholm and Rice [10] have considered the problem of quasiperiodic intramolecular nuclear motion and ergodicity in a small system, which does not obey relation (9) and does not exhibit practical irreversibility. A simple-minded model for IVR may be advanced in the spirit of the coarse graining model used for intramolecular electronic relaxation [11]. Consider a (zero-order) vibrational state coupled to a background manifold of vibrational levels which in turn are coupled among themselves. If both diagonal and off-diagonal anharmonicity terms are all equal and the level spacing in the manifold, ρ_B^{-1}, is uniform, then this naive model leads (unpublished results) to the following conclusions: first, for times considerably shorter than the recurrence time $t_r \equiv \hbar\rho_B$ the decay is exponential. Second, the time evolution on this time scale is given by $\exp(-2t/t_r)$, the IVR decay time is just t_r, being independent on the magnitude of the anharmonic coupling. If for a moment this model is taken seriously than for $\rho_B > 10^8$ 1/cm^{-1} which is the onset of IVR, $t_r \gtrsim 10^{-3}$ s and IVR rate is exceedingly low. This model is unrealistic as phase coherence is artificially introduced into this "uniform" model (for a similar problem related to intercontinuum coupling see ref. [12]). In view of the discussion of Heller and Rice we believe that eq. (4) provides a reasonable guess for the IVR rate.
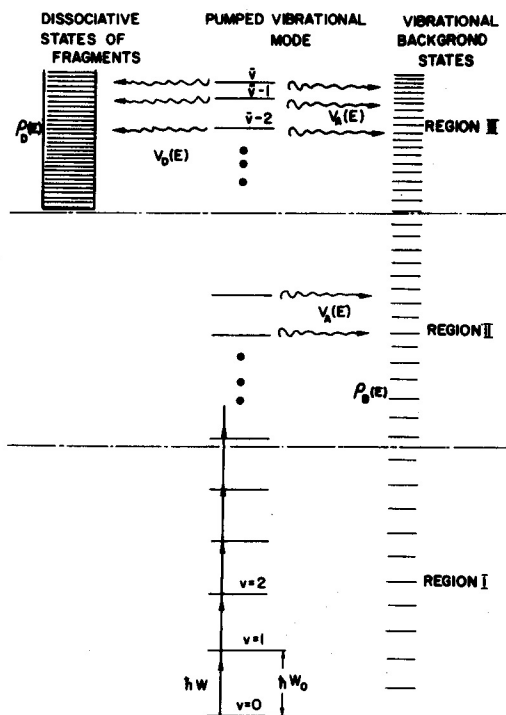

Fig. 1. A molecular energy level scheme for a multiphoton fragmentation. Three energy regions are exhibited: region I—low ρ_B, power broadening; region II—high ρ_B, scrambled levels and vibrational relaxation; region III—reactive region.

One has now to distinguish between the effect of coupling between (zero-order) levels and intramolecular vibrational relaxation. Consider the case where the level spacing $[\rho_B(E)]^{-1}$ in region II exceeds the width of these levels, γ_B (which for the isolated molecule originates from infrared decay), i.e.,

$$\gamma_B(E)\rho_B(E) < 1. \qquad (2)$$

When relations (1) and (2) are obeyed level scrambling will take place and the intensity of the $\upsilon \to \upsilon + 1$ transition will be spread over the energy range which is very roughly given by $W_B(E) \approx 2\pi|V_A(E)|^2\rho_B(E)$, as in the case for interstate coupling in small molecules [13]. It is important to realize that no intramolecular vibrational relaxation (IVR) occurs when condition (2) holds. At high energies, when

$$\gamma_B(E)\rho_B(E) > 1 \qquad (3)$$

overlap of the (zero-order) background levels is exhibited, and the manifold acts as an effective dissipa-

tive continuum for IVR. The IVR rate from a zero-order level $|v\rangle$ located at $\approx E$ is then

$$\Gamma_v^{VR} \approx 2\pi |V_A(E)|^2 \rho_B(E). \tag{4}$$

Taking $\gamma_B \approx 10^{-7} - 10^{-8}$ cm^{-1} (corresponding to IR decay time of $10^{-3} - 10^{-4}$ s) then from the available level density data [14,15] for SF$_6$, we assert that condition (3) for the onset of legitimate IVR, sets in at $E \approx 10^4$ cm^{-1} above the ground state where $\rho_B \approx 10^{-8}$ cm. Thus in region II one has to account, in principle, for the level spread parameter $W_B(E)$ at lower E when condition (2) holds and for the IVR relaxation width, eq. (4) at higher E, when condition (3) is satisfied.

Region III. The high energy reactive region where a dissociative channel opens up. Here rotational predissociation, or vibrational predissociation (or electronic predissociation when the ground state and an electronically excited potential hypersurfaces intersect) will occur. The reactive intramolecular decay will be handled by considering the $|v\rangle$ levels in region III as metastable decaying resonances in the spirit of the unimolecular reaction theory of Mies and Krauss [16]. Neglecting interference effects between these resonances, we shall characterize each $|v\rangle$ state in that region by a decay width Γ_v^D,

$$\Gamma_v^D = 2\pi |V_D(E)|^2 \rho_D(E), \tag{5}$$

where $V_D(E)$ and $\rho_D(E)$ (fig. 1) correspond to the coupling and the density of states in the dissociative continuum, respectively, at the energy $E \approx E_v$.

Turning now to this model molecule, pumped by an intense CO$_2$ laser, we note that in region I power-broadening (i.e., dynamical Stark level shifts) [17] effects will be exhibited. To assess the role of level coupling and subsequent IVR in range II, we would like to point out that a recent penetrating analysis by Rice and Nordholm [10] and by Zare et al. [18] of experimental data regarding intramolecular vibrational energy redistribution in isolated polyatomic molecules, such as single vibronic level fluorescence [19], mass spectrometry [20], infrared chemiluminescence [21] and optical excitation in molecular beams [18], indicate that at least in some cases, IVR is slow on the time scale of the lifetimes (or the reaction times). At the present stage of our study we shall assume that Γ_v^D always exceeds the level spread in the low energy range of region II, that is that the level spread

$W_B(E)$ will be disregarded, while for states $|v\rangle$ in the higher E range of region II, the IVR rate is lower than the dissociative rate of states $|v'\rangle$ in region III, i.e., $\Gamma_v^{VR} \ll \Gamma_{v'}^D$, while for region III $\Gamma_v^{VR} \ll \Gamma_{v'}^D$.

Our model for multiphoton molecular photofragmentation rests on the following explicit assumptions:

(a) The molecular levels in near-resonance with the laser energy $\hbar\omega$, constitute a truncated anharmonic oscillator, being represented, in first order approximation for such a system, by the energy levels

$$E_v = \omega_0 v - \omega_0 x v^2, \quad v = 0, 1, 2, ..., \bar{v}. \tag{6}$$

ω_0 is the oscillator frequency and $\omega_0 x$ the anharmonicity constant.

(b) This "optically active" mode is characterized by $M = \bar{v} + 1$ discrete (zero-order) levels.

(c) Rotational effects will be disregarded at present.

(d) The higher levels in region II and the levels in region III are characterized by IVR widths Γ_v^{VR}.

(e) To the highest $\bar{v}$th, level we assign a predissociative level width $\Gamma_{\bar{v}}^D$, the total width of this level is $\Gamma_{\bar{v}} = \Gamma_{\bar{v}}^D + \Gamma_{\bar{v}}^{VR}$.

(f) As we have asserted that the predissociative width overwhelms the IVR process, it is reasonable to assert that $\Gamma_{\bar{v}}^D \gg \Gamma_{\bar{v}}^{VR}, \Gamma_{v'}^{VR}$ for all v and $\Gamma_{\bar{v}} = \Gamma_{\bar{v}}^D$ being the dominant width involved in the problem‡.

(g) An intense electromagnetic field is tuned on the time scale $0 \leqslant t \leqslant T$. The field is specified in terms of a state $|n\rangle$ containing n photons of frequency ω in a single mode. The off-resonance energy for the $0-1$ molecular transition is

$$\Delta = \omega_0 - \omega. \tag{7}$$

(h) The zero-order states of the entire system $|v, n\rangle$ (i.e., the "dressed" molecular states) are characterized by the energy levels

$$E(v, n) = n\omega + v\omega_0 - \omega_0 x v^2. \tag{8}$$

Consider a group of near-resonant "dressed" molecular states corresponding to the sequence $|v, n-v\rangle$, i.e.,

‡ Numerical calculations based on the theory advanced in the present paper reveal that as long as the (finite) widths Γ_v^{VR} (for the relevant v states in region II and for all the states in range III) are small relative to $\Gamma_{\bar{v}}^D$, the photofragmentation yield is unaffected by changing Γ_v^{VR}. This result is reasonable as the strong electromagnetic interaction scrambles the widths of the "dressed" molecular states.

$$E(v, n-v) = n\omega + \Delta v - \omega_0 x v^2, \quad v = 0, 1, 2, ..., \bar{v}. \tag{8a}$$

The energetic spread of these states for a given value of the off-resonance energy Δ is given by

$$\delta(\Delta) = \Delta(\bar{v} - v_m) - \omega_0 x(\bar{v}^2 - v_m^2), \tag{9}$$

where

$$v_m = \Delta/2\omega_0 x, \quad 0 < \Delta/2\omega_0 x < v; \\ = 0, \qquad \text{else.} \tag{9a}$$

(i) Radiative coupling is taken only between adjacent levels, and we take for the matrix elements of the radiation—matter interaction H_{int} those corresponding to a harmonic oscillator

$$\langle v'n'|H_{int}|vn\rangle \\ = \mu E \delta_{n',n\pm1}[(v+1)^{1/2}\delta_{v',v+1} + v^{1/2}\delta_{v,v-1}], \tag{10}$$

where μ is the dipole matrix element for the $0 \to 1$ transition, E corresponds to the amplitude of the electromagnetic field and we take $n \gg 1$.

(j) Spontaneous infrared emission $v \to v-1$ will be neglected.

Table 1
Typical energetic data for SF_6 pumped by an intense pulsed CO_2 laser

Parameter			Ref.
frequency	$\omega_0(\nu_3)$	948	[22]
dissociation energy	D_e	24000 cm^{-1}	a)
anharmonicity	$\omega_0 x$	1–10 cm^{-1}	[15]
number of vibrational states in ν_3	M	≈ 50	b)
isotope shift	S	17 cm^{-1}	[9]
spread of P, Q, R branches		10 cm^{-1}	[24]
Rabi frequency	μE	1–10 cm^{-1}	c)
pulse duration	T	100 ns	c)
laser frequency	$\hbar\omega$	944–960 cm^{-1}	c)

a) Estimated from thermochemical data [23].
b) Estimated from the rough relation for a truncated anharmonic oscillator $\omega_0 x \approx \omega_0^2/4D_e$ and $\bar{v} = \omega_0/2\omega_0 x$.
c) Typical values in the experiments (μ is taken to be ≈ 0.1 D).

(k) The "dressed" molecular states in the energy range δ, eq. (9), are radiatively coupled according to eq. (10). Furthermore, off-resonance coupling occurs between zero-order states (e.g., $|x, n-x\rangle$ couples with $|x \pm 1, n-x \pm 1\rangle$). The latter off-resonance coupling occurs between states separated by $D \approx 2\omega_0$. As $\delta/2\omega_0 \approx 0.01-0.05$ for typical values (see table 1) of Δ, ω_0 and $x_0\omega_0$, we invoke the rotating wave approximation [25] (RWA) neglecting the off-resonance coupling.

We now proceed to consider the time evolution of a system of M discrete "dressed" molecular states $|0,n\rangle, |1,n-1\rangle,..., |\bar{v}, n-\bar{v}\rangle$, some of which are coupled to an intramolecular IVR quasicontinuum and to a dissociative continuum. The intramolecular relaxation and decomposition processes are specified by assigning to the highest levels the IVR widths Γ_v^{VR}, while the $\bar{v}$th level is characterized by a width $\Gamma_{\bar{v}} = \Gamma_{\bar{v}}^{VR} + \Gamma_{\bar{v}}^D$. This problem can be readily handled by the effective hamiltonian formalism [26–28], which focuses attention on the time evolution within the subspace of the Hilbert space spanned by the M discrete (zero-order) levels. The effective hamiltonian, H_{eff}, for the problem at hand is

$$H_{eff} = \begin{pmatrix} \overbrace{E_0 \quad \mu E}^{\text{region I}} & \overbrace{\qquad}^{\text{region II}} & \overbrace{\qquad}^{\text{region III}} \\ \mu E \quad E_1 \quad \mu E\sqrt{2} & & \\ & \mu E\sqrt{v} \quad E_v - \tfrac{1}{2}i\Gamma_v^{VR} \quad \mu E\sqrt{v+1} & \\ & & \mu E\sqrt{v} \quad E_{\bar{v}} - \tfrac{1}{2}i\Gamma_{\bar{v}} \end{pmatrix} \tag{11}$$

for the time $0 \leqslant t \leqslant T$. For $t > T$, when the field is switched off, we have to set $\mu E = 0$ in eq. (11). The initial state of the system is $|0,n\rangle$ and the probability amplitude for the population of the dissociative state $|\bar{v}\rangle$, i.e., the state $|\bar{v}, n-\bar{v}\rangle$, at time t is

$$C_{\bar{v}}(t) = \langle 0,n|U(t,0)|0,n\rangle \\ = -(2\pi i)^{-1} \int dE\, e^{-iEt} \langle 0,n|(E-H_{eff})^{-1}|0,n\rangle, \tag{12}$$

where $U(t,0)$ is the time-evolution operator. This amplitude, eq. (12), can be expressed in terms of the (complex) eigenvalues $\Lambda_j = \epsilon_j - \tfrac{1}{2}i\gamma_j$ and the (non-orthogonal) eigenvectors $\{|j\rangle\}$ of the effective hamiltonian [29], eq. (11), resulting in

$$C_{\bar{v}}(t) = 0, \qquad\qquad\qquad t < 0;$$

$$= \sum_j \langle\bar{v}|j\rangle\langle 0|j\rangle \exp\left(-i\epsilon_j t - \tfrac{1}{2}\gamma_j t\right), \quad 0 \leqslant t \leqslant T;$$

$$= C_{\bar{v}}(T)\exp\left(-iE_{\bar{v}}t - \tfrac{1}{2}\Gamma_{\bar{v}}t\right), \qquad t > T. \quad (13)$$

The probability for photofragmentation, $P_D(t)$, is finally given by

$$P_D(t) = \Gamma_{\bar{v}}^D \int_0^t |C_{\bar{v}}(\tau)|^2 \, d\tau, \qquad 0 \leqslant t \leqslant T; \tag{14a}$$

$$= P_D(T) + \exp[-\Gamma_{\bar{v}}^D(t-T)]\,|C_{\bar{v}}(T)|^2 \quad t > T. \tag{14b}$$

Eqs. (13) and (14) constitute the solution for multiphoton photofragmentation in the model system considered herein.

Numerical simulations of multiphoton dissociation of the molecular system were conducted using the following physically feasible (see table 1) energetic parameters: $M = 10$, 15 and 20, $\omega_0 x = 1-5$ cm^{-1}, $\Delta = -50 - +50$ cm^{-1}. For the decay widths we have assumed that IVR is slow (relative to the decay width) and accordingly set $\Gamma_v^{VR} = 0$ for the relevant levels in region II and in region III, while $\Gamma_{\bar{v}}^D$ was varied in the range $10^{-5}-10^{-1}$ cm^{-1}. The pulse duration was taken in the region $T = 10-10^4$ ns, while the Rabi frequency $\omega_R = \mu E/\hbar$ was chosen in the range $\omega_R = 1-10$ cm^{-1} corresponding to experimentally accessible intense pulses (for a laser power of $\approx 10^6$ V/cm $\approx$ 1 GW cm^{-2} and a transition dipole $\mu \approx 0.10$ D we have $\mu E = 10$ cm^{-1}). Preliminary numerical simulations performed to probe the effects of $\Gamma_{\bar{v}}^D$ and of T, indicate that when

$$\Gamma_{\bar{v}}^D T \gg 1, \tag{15}$$

the dominating contribution to photofragmentation occurs during the pulse ($t \leqslant T$) and $P_D \propto \Gamma_{\bar{v}}^D$, as expected. Typical numerical results which provide information concerning field effects and anharmonicity effects are portrayed in figs. 2 and 3. At low fields P_D increases rapidly with ω_R (as expected for a multiphonon process), while for

$$\omega_R > \delta(\Delta) \tag{16}$$

saturation occurs, as is evident from fig. 2. The P_D versus Δ curves (fig. 3) are characterized by a maximum at the off-resonance energy
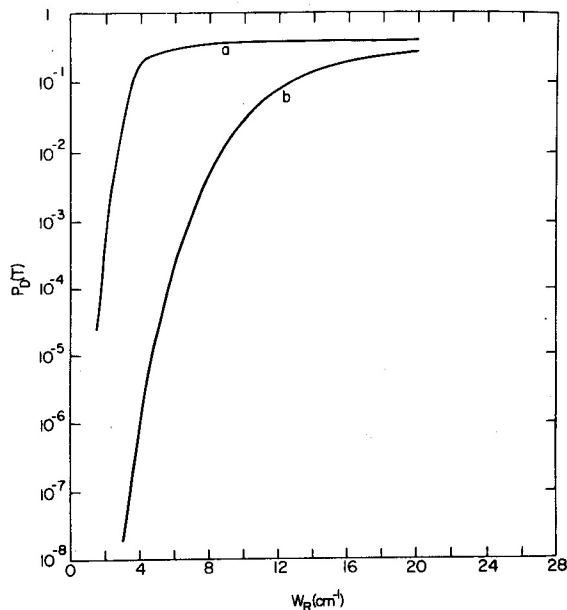

Fig. 2. The photofragmentation probability, $P_D(T)$, versus the Rabi frequency ω_R. $M = 10$; $T = 5000$ (1/cm^{-1}); $\Gamma_{\bar{v}}^D = 10^{-3}$ cm^{-1}, $\omega_0 x = 1$ cm^{-1}. (a) $\Delta = \bar{\Delta}$ (maximum dissociation probability, ignoring the resonances); (b) $\Delta = 0$.

$$\bar{\Delta} \approx \omega_0 x \bar{v}, \tag{17}$$

which exhibits only a very weak dependence on ω_R. The maximum efficiency is exhibited when the lowest $v = 0$ and the highest $v = \bar{v}$ (zero-order) levels are resonant. As $\bar{\Delta} > 0$, anharmonicity effects should be compensated by tuning the laser source below the 0-1
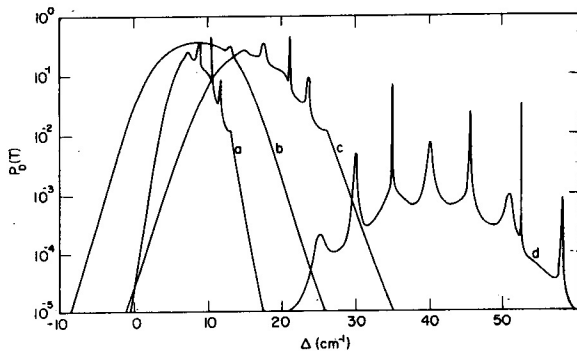

Fig. 3. The photofragmentation probability, $P_D(T)$, versus the off-resonance frequency Δ. $M = 10$; $T = 5000$ (1/cm^{-1}); $\Gamma_{\bar{v}}^D = 10^{-3}$ cm^{-1}. (a) $\omega_R = 5$ cm^{-1}, $\omega_0 x = 1$ cm^{-1}; (b) $\omega_R = 10$ cm^{-1}, $\omega_0 x = 1$ cm^{-1}; (c) $\omega_R = 10$ cm^{-1}, $\omega_0 x = 2$ cm^{-1}; (d) $\omega_R = 10$ cm^{-1}, $\omega_0 x = 5$ cm^{-1}.

molecular transition, in accordance with Bloembergen's classical argument [9]. Furthermore, we find that the P_D versus Δ curve is characterized by several regularly spaced resonances, which are prominent at moderately low fields, i.e. $\omega_R < \delta$, while when $\omega_R \gg \delta$ the resonances merge into a broad background. These resonances are exhibited whenever $v = \Delta/\omega_0 x$, i.e., the dressed $v = 0$ and another dressed level v are quasi-degenerate. Unfortunately, rotational effects, which were disregarded herein, may result in the smearing out of these resonances.

The implications and applications of these results to isotope separation via multiphoton molecular photodissociation should be noted:

(1) The most effective photofragmentation process will be induced at off-resonance energies satisfying eq. (17). For SF_6 we estimate $\bar{\Delta} \approx 30-100 \text{ cm}^{-1}$. As $\bar{\Delta} > 0$, photofragmentation will be induced below the ν_3 vibrational–rotational band whose total energetic spread at room temperature is $\approx 10 \text{ cm}^{-1}$.

(2) To obtain efficient photofragmentation, the laser power should obey relation (16), i.e., $\omega_R > \delta \cdot (\bar{\Delta})$ whereupon

$$\omega_R \gtrsim \bar{v}^2/4\omega_0 x. \qquad (18)$$

For SF_6 taking $\omega_0 x \approx 1-10 \text{ cm}^{-1}$, $\omega_R \approx 10 \text{ cm}^{-1}$ which is just in the accessible power range of lasers recently utilized.

(3) Laser powers higher than those given by eq. (18) will result in additional broadening of the P_D versus Δ distribution, ruining the isotopic selectivity.

(4) Vibrational isotope shifts, S, of a few wavenumbers (e.g., $S = 17 \text{ cm}^{-1}$ for $^{32}SF_6 - ^{34}SF_6$) are ample to obtain a dramatic isotopic selectivity of the photofragmentation process. When the isotopic molecular species characterized by the lower molecular frequency ω_0 is excited with $\omega < \omega_0$, we have $\Delta > 0$ for both isotopic species, whereupon the optimal isotopic separation factor is just

$$\beta = P_D(\bar{\Delta})/P_D(\bar{\Delta} + S). \qquad (19)$$

As evident from fig. 3, for fields obeying condition (16), appreciable isotope separation will occur for $S \gtrsim 5 \text{ cm}^{-1}$, e.g. for $S = 17 \text{ cm}^{-1}$ the enrichment factor is $\beta \approx 10^3 - 10^4$.

Finally, we would like to note that for octahedral molecules containing a heavy central atom, moderate values of the isotope shift, e.g., $S \approx 0.5 \text{ cm}^{-1}$, may

be encountered in some cases of physical interest. Multiphoton photofragmentation induced by a single intense pulse will not be isotopically selective, as for fields sufficient to overcome anharmonicity effects and cause saturation effects, β eq. (19), will be then close to unity, as evident from fig. 3. In this case we may attempt to conduct isotopically selective multiphoton photodissociation induced by two moderately intense laser sources of frequencies ω_1 and ω_2, ω_1 being tuned near-resonance with the lower v levels, while ω_2 being tuned closely to the higher v levels in the vibrational ladder of the optically pumped mode.

References

[1] R.V. Ambartzumian, V.S. Letokhov, E.A. Ryabov and N.V. Chekalin, JETP Letters 20 (1975) 273.

[2] R.V. Ambartzumian, Yu.A. Gorkhov, V.S. Letokhov and G.N. Makarov, JETP Letters 21 (1975) 171.

[3] R.V. Ambartzumian, N.V. Chekalin, V.S. Letokhov and E.A. Ryabov, Chem. Phys. Letters 36 (1975) 301.

[4] J.L. Lyman, R.J. Jensen, J. Rink, C.P. Robinson and S.D. Rockwood, Appl. Phys. Letters 27 (1975) 87.

[5] C.P. Robinson, in: Laser spectroscopy, eds. S. Haroche, J.C. Paybay-Peyroula, T.W. Hansch and S.E. Harris (Springer, Berlin, 1975) p. 275.

[6] M.F. Goodman and E. Thiele, Phys. Rev. A5 (1972) 1355.

[7] J. Stone, E. Thiele and M.F. Goodman, J. Chem. Phys. 59 (1973) 2909; 63 (1975) 2936

[8] M.F. Goodman, J. Stone and E. Thiele, J. Chem. Phys. 59 (1973) 2919; 63 (1975) 2929.

[9] N. Bloembergen, in: Laser spectroscopy, eds. S. Haroche, J.C. Paybay-Peyroula, T.W. Hansch and S.E. Harris (Springer, Berlin, 1975) p. 450.

[10] S. Nordholm and S.A. Rice, J. Chem. Phys. 61 (1974) 203, 768.

[11] M. Bixon and J. Jortner, J. Chem. Phys. 48 (1968) 715.

[12] E.J. Heller and S.A. Rice, J. Chem. Phys. 61 (1974) 936.

[13] J. Jortner and S. Mukamel, in: MTP International Review of Science, Vol. 13, ed. A.D. Buckingham (Butterworths, London, 1972).

[14] D. Jackson, Report LA-6025-MS (1975).

[15] C. Cantrell, private communication

[16] F.H. Mies and M. Krauss, J. Chem. Phys. 45 (1966) 4455.

[17] M. Sargent, M. Scully and W. Lamb, Laser physics (Addison-Wesley, Reading, 1974).

[18] R.K. Sander, B. Soep and R.N. Zare, Observation of Radiationless Processes in a Molecular Beam, J. Chem. Phys., to be published.

[19] M.H. Hui and S.A. Rice, J. Chem. Phys. 61 (1974) 833; J.C. Hemminger and E.K.C. Lee, J. Chem. Phys. 56 (1972) 5284.

[20] A. Lee, R. Le Roy, F. Herman, R. Wolfgang and J.C. Tully, Chem. Phys. Letters 12 (1972) 569; S.E. Butrill, J. Chem. Phys. 61 (1974) 619.

[21] J.G. Moehlmann, J.T. Gleaves, J.W. Hudgens and J.D. McDonald, J. Chem. Phys. 60 (1974) 2040.

[22] G. Herzberg, Electronic spectra of polyatomic molecules (Van Nostrand, Princeton, 1966).

[23] G. Pilcher, in: MTP International Review of Science, Vol. 10, ed. H.A. Skinner (Butterworth, London, 1972).

[24] I. Burak, A.V. Nowak, J.I. Steinfeld and D.G. Sutton, J. Chem. Phys. 51 (1969) 2275; J.I. Steinfeld, I. Burak, D.G. Sutton and A.V. Nowak, J. Chem. Phys. 52 (1970) 5421.

[25] W. Louisell, Radiation and noise in quantum electronics (McGraw-Hill, New York, 1964).

[26] L. Mower, Phys. Rev. 142 (1966) 799.

[27] C. Cohen Tannoudji, in: Cargese Lectures in Physics, Vol. 2 (Gordon and Breach, London, 1967).

[28] S. Haroche, Ann. Phys. (Paris) 6 (1971) 189.

[29] J. Jortner and S. Mukamel, in: The world of quantum chemistry, eds. R. Daudel and B. Pullman (Reidel, Dordrecht, 1973).