

KINETICS OF TWO-STEP SELECTIVE PHOTODISSOCIATION OF MOLECULES BY LASER RADIATION

V. S. LETOKHOV and A. A. MAKAROV

Institute of Spectroscopy, Academy of Sciences U.S.S.R., Moscow (U.S.S.R.)

(Received June 13, 1973)

SUMMARY

Two-step photodissociation of molecules is considered. Spatial radiation absorption is taken into account. Appropriate estimations and numerical calculations are presented. Conclusions are drawn about two-step photodissociation efficiency and quantum yield.

INTRODUCTION

The method of two-step photodissociation of molecules by laser radiation for selective destruction of molecular bonds was first proposed in ref. 1*. Some radiation of frequency ω_1 is in resonance with a rotation-vibration transition and provides vibrational excitation of molecules. Radiation of another frequency ω_2 provides photodissociation of vibrationally excited molecules but its energy is insufficient for photodissociation of molecules from the ground state (Fig. 1).

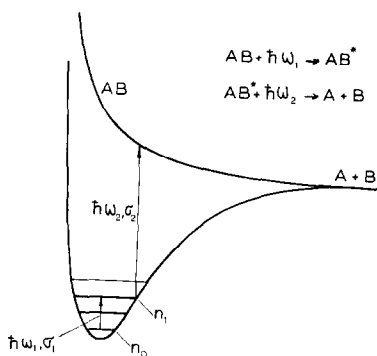


Fig. 1. Schematic diagram of two-step photodissociation (n_0 , n_1 are the ground and excited states populations; σ_1 , σ_2 are the absorption cross-sections of exciting and dissociating laser radiations).

*Earlier this method was mentioned with respect to two-step ionization of atoms².

Practically ω_1 lies in the infra-red region of the spectrum and ω_2 in the ultra-violet, but exceptions are possible, for example when exciting molecular overtones³ or when dissociating molecules with weak bonds.

Experimentally, two-step photodissociation was studied in ammonia molecules⁴. It was shown that in the predissociation spectrum of the NH_3 molecule excited into the first vibrational level of the symmetrical vibrational mode ν_2 , a new absorption band appeared in the long-wave range with respect to the boundary of the non-excited molecule predissociation spectrum. In further work by the same authors⁵ selective photodissociation of $^{15}\text{NH}_3$ in presence of $^{14}\text{NH}_3$ followed by selective chemical reaction was carried out by the two-step photodissociation method and isotope separation was achieved in the reaction products.

One can see from the results of the work⁵ that the two-step photodissociation method is of interest due to possibility of the dissociation of "fixed" molecules contrary to the usual gas mixture flash photolysis. So the method gives in principle a universal way for achieving selective chemical processes. Selectivity of the method is limited in the main only by the thermal population of the upper level. Therefore the requirement

$$\exp\left\{\frac{-h\omega_1}{kT}\right\} \ll 1 \quad (1)$$

must be satisfied.

The efficiency of the two-step photodissociation method for photochemistry is defined by the possibility of producing considerable relative concentrations of two-step photodissociation products during the laser pulse. Besides, it is an advantage to work under such conditions that high yields of products may be reached together with near to maximum quantum yield of two-step photodissociation; that is, with small infra-red and ultra-violet radiation losses. The maximum quantum yield of two-step photodissociation is equal to 0.5 and may be reached with total absorption of laser radiation. Hence it is necessary to irradiate a great deal of substance so that the whole radiation be absorbed.

We shall find below some relations between infra-red and ultra-violet laser pulse parameters which simultaneously assure considerable yield of two-step photodissociation products and small losses of laser radiation energy.

BASIC EQUATIONS

Let us consider the two-step dissociation of molecules under conditions of quick rotational relaxation and slow vibrational relaxation with respect to the laser pulse duration. This means that the laser pulse duration has to satisfy the requirements:

$$\tau_p \ll \tau_{\text{vib}} \quad (2)$$

$$\text{but } \tau_p \gg \tau_{\text{rot}} \quad (3)$$

It should be noted that the requirement (2) results because two-step photodissociation selectivity demands forbidding in essence vibrational energy transfer to molecules in a mixture which it is not desirable to excite. The requirement (3) results from the fact that infra-red radiation is in resonance with only one rotation-vibration transition of the molecule and so intensive rotational relaxation has to take place during the laser pulse in order to obtain a considerable yield of dissociation products. It must be clear that it is possible to satisfy simultaneously the requirements (2) and (3) since rotational relaxation is usually several orders of magnitude quicker than vibration-translation relaxation, and the role of vibration-vibration exchange processes may be diminished if the mixture is diluted with buffer gas.

If the requirements (2) and (3) are fulfilled, the process may be described in terms of the total populations of ground and vibrationally excited states, only stimulated radiation processes being taken into account:

$$\left. \begin{aligned} \frac{\partial N_0}{\partial t} &= -W_{\text{ir}}(N_0 - N_1) \\ \frac{\partial N_1}{\partial t} &= W_{\text{ir}}(N_0 - N_1) - W_{\text{uv}} N_1 \end{aligned} \right\} \quad (4)$$

where W_{ir} is the rate of the stimulated transitions between ground and excited vibrational states and W_{uv} is the rate of photodissociation of excited molecules, W_{ir} and W_{uv} being defined as:

$$W_{\text{ir}} = \sigma_{\text{ir}} P_{\text{ir}}, \quad W_{\text{uv}} = \sigma_{\text{uv}} P_{\text{uv}} \quad (5)$$

where σ_{ir} is absorption cross-section for the vibrational transition, σ_{uv} is photodissociation cross-section from the excited state, and P_{ir} , P_{uv} are the intensities of the exciting and dissociating pulses correspondingly (expressed in photon $\text{cm}^{-1} \text{s}^{-1}$).

Consideration of the absorption of both pulses along their spreading direction produces the equations:

$$\left. \begin{aligned} \frac{\partial P_{\text{ir}}}{\partial z} &= -\sigma_{\text{ir}} P_{\text{ir}}(N_0 - N_1) \\ \frac{\partial P_{\text{uv}}}{\partial z} &= -\sigma_{\text{uv}} P_{\text{uv}} N_1 \end{aligned} \right\} \quad (6)$$

Let P_{ir} and P_{uv} start at the instant $t = 0$ and remain constant at the working medium edge ($z = 0$). Then eqns. (4) and (6) together with initial and boundary conditions

$$N_0|_{t=0} = N_0^0, \quad N_1|_{t=0} = 0, \quad P_{\text{ir}}|_{z=0} = P_{\text{ir}}^0, \quad P_{\text{uv}}|_{z=0} = P_{\text{uv}}^0 \quad (7)$$

represent the complete description of the process. It should be noted that the initial conditions for N_0 and N_1 follow from the demands of process selectivity (see the requirement (1) in the Introduction) and usually conform to the real physical conditions. If a CO_2 laser is used to excite molecular vibrations (for example the ν_2 vibration of NH_3) and if the gas temperature is equal to 300 K, the thermal population of the upper level is about 1%.

CHOICE OF OPTIMUM PARAMETERS FOR THE TWO-STEP PHOTODISSOCIATION PROCESS

Let us reduce the set of eqns. (4), (6) and the initial and boundary conditions (7) to a more convenient form, making a change of variables and functions according to:

$$T = W_{\text{ir}}^0 t, \quad n_0 = \frac{N_0}{N_0^0}, \quad n_1 = \frac{N_1}{N_0^0} \quad (8)$$

$$L = \sigma_{\text{ir}} N_0^0 z, \quad W_{\text{ir}} = \frac{P_{\text{ir}}}{P_{\text{ir}}^0}, \quad W_{\text{uv}} = \frac{P_{\text{uv}} \sigma_{\text{uv}}}{P_{\text{ir}}^0 \sigma_{\text{ir}}}$$

For the new functions n_0 , n_1 , w_{ir} , w_{uv} , depending on the new variables T , L , eqns. (4), (6) and (7) take the form:

$$\left. \begin{aligned} \frac{\partial n_0}{\partial T} &= -w_{\text{ir}}(n_0 - n_1), n_0|_{T=0} = 1; \\ \frac{\partial n_1}{\partial T} &= w_{\text{ir}}(n_0 - n_1) - w_{\text{uv}} n_1, n_1|_{T=0} = 0; \\ \frac{\partial w_{\text{ir}}}{\partial L} &= -w_{\text{ir}}(n_0 - n_1), w_{\text{ir}}|_{L=0} = 1; \\ \frac{\partial w_{\text{uv}}}{\partial L} &= -S w_{\text{uv}} n_1, w_{\text{uv}}|_{L=0} = \alpha; \end{aligned} \right\} \quad (9)$$

where $S = \sigma_{\text{uv}}/\sigma_{\text{ir}}$, $\alpha = S(P_{\text{uv}}^0/P_{\text{ir}}^0)$.

Attention should be paid to the fact that concrete schemes of two-step photodissociation correspond to various value of S . If exciting molecular vibrational overtones, the situation when $S \gg 1$ is realized, since the absorption cross-section of such transitions is usually considerably less than that of photodissociation. In most cases, when a resonance vibrational transitions of molecule is excited, the situation with $S \ll 1$ is realized because of the great value of the resonance absorption cross-section. We shall discuss below these two important cases. But in some systems the situation with $S \sim 1$ can be realized. For these cases the results obtained for $S \ll 1$ are valid.

Ultimately in the solution of eqn. (7) we are interested in the absolute number of gas molecules which have been dissociated by the fixed moment in the definite volume; that is, the quantity being described by the function:

$$N_d(L, T) = L \int_0^L [n_0(T, x) + n_1(T, x)] dx \quad (10)$$

The following expression may be obtained for $N_d(L, T)$:

$$N_d(L, T) = \frac{1}{S} \int_0^T [a - w_{uv}(L, \tau)] d\tau \quad (11)$$

This means that the number of dissociated molecules is equal to the number of ultra-violet photons absorbed in the volume, and, if

$$\int_0^T w_{uv}(L, \tau) d\tau \ll aT \quad (12)$$

then

$$N_d(L, T) \simeq \frac{aT}{S} \quad (13)$$

In the region of parameters a , T , L , where the condition (12) is valid, the quantum yield of two-step photodissociation is about $(1 + (S/a)^{-1})^{-1}$ so it increases with increase of a . It is impossible to find the exact analytical solution of eqn. (9) but good estimates may be obtained. These estimates show that the condition (12) is not fulfilled when $a = S$ but if T and L are chosen appropriately it can be satisfied when a is sufficiently close to S . Such choice of parameters appears to correspond to the near-to-maximum two-step photodissociation quantum yield.

Taking into account this preliminary remark, let us consider in detail the question applicability of condition (12). It is possible to show that w_{uv} as a function of time decreases monotonically from the beginning, reaching a minimum at the instant T_1 , and then increases monotonically, going to a when $T \rightarrow \infty$ (Fig. 2). In the region of decrease if $S(1 - e^{-L}) > a$ then:

$$w_{uv} \lesssim a \exp\{-[S(1 - e^{-L}) - a]T\} \quad (14)$$

It is clear that if T_1 is subjected to the relation:

$$T_1 \gg [S(1 - e^{-L}) - a]^{-1} \quad (15)$$

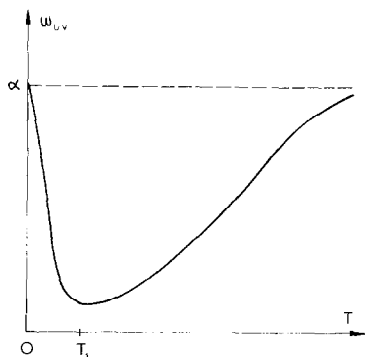


Fig. 2. Qualitative dependence of w_{uv} on T for fixed L .

the condition (12) is valid at least for $T = T_1$. T_1 may be estimated from the relations:

$$T_1 \approx \frac{1}{2} \left(1 - \frac{\alpha}{2S} \right)^{1/2} \ln \left[\frac{2S}{\alpha} (e^L - 1) + \left(\frac{\alpha}{S} - 3 \right) e^L + 2 \right] \quad \text{if } S \gg 1 \quad (16)$$

$$\left(2 - \frac{\alpha}{S} \right)^{1/2} \ln \left[\left(1 - \frac{\alpha}{S} \right) e^L \right] < T_1 < \ln \left[\frac{1}{\alpha} \left(1 - \frac{\alpha}{S} \right) e^L \right] \quad \text{if } S \gg 1 \quad (17)$$

On the contrary, the incorrectness of eqn. (15), where T_1 has been calculated with eqns. (16) or (17), shows up the inapplicability of eqn. (12).

The condition (12) by itself appears to be sufficient for total use of the ultra-violet laser pulse energy. As to losses of infra-red radiation, these may be estimated from the relations:

$$\frac{\varepsilon^{ir_{out}}}{\varepsilon^{ir_{in}}} \leq \frac{1}{2T} \ln [1 + e^{-L} (e^{2T} - 1)] = \eta^{ir_+} \quad (18)$$

$$\frac{\varepsilon^{ir_{out}}}{\varepsilon^{ir_{in}}} \geq \frac{1}{T} \ln [1 + e^{-L} (e^T - 1)] = \eta^{ir_-} \quad (19)$$

Appropriate calculations which allow a conclusion to be drawn about applicability of eqn. (12) are presented in Table 1. In this Table values of N_0/L , η^{ir_+} , η^{ir_-} , corresponding to T_1 (calculated), are listed.

From these data one can estimate the efficiency and the quantum yield of the two-step photodissociation method.

TABLE I

CHOICE OF TWO-STEP PHOTODISSOCIATION PARAMETERS

S	L	α	T_1	$\frac{N_a(T_1)}{L}$	$\eta^{ir+}(T_1)(\%)$	$\eta^{ir-}(T_1)(\%)$
100	1	40	0.79	0.316	55.7	45.6
100	1	63.2	0*			
100	2	50	1.27	0.318	37.8	24.4
100	2	71.6	0*			
100	3	70	1.81	0.433	28.7	12.7
100	3	96.9	0*			
100	5	80	3.15	0.504	24.5	4.4
100	5	99.3	0*			
1	20	0.5	20	0.500	50	5
1	100	0.9	100	0.900	50	1
10^{-2}	2×10^3	0.5×10^{-2}	2×10^3	0.500	50	0.05
10^{-2}	10^4	0.9×10^{-2}	10^4	0.900	50	0.01

* T_1 being equal to zero nominally points out the inapplicability of the condition (12) for the value of α presented.

CONCLUSION

The two-step photodissociation method presents the possibility of satisfying simultaneously such requirements as: (1) producing considerable relative concentrations of two-step photodissociation products (at least $\sim 50\%$); (2) producing considerable absolute concentrations of two-step photodissociation products (there are no restrictions in principle and choice of substance is mainly connected with the laser pulse energy available); (3) practically total use of radiation.

It should be noted that the analysis made in this work is also valid in the case when the first radiation excites a stable electronic molecular state and the other one provides photodissociation of the electronically excited molecules. In such a case the situation with $S \ll 1$ is realized because the absorption cross-sections for electronic transitions is usually considerably more than those for photodissociation.

REFERENCES

- 1 R. V. Ambartzumian and V. S. Letokhov, *Quantum Electron.*, QE-7 (1971) 305; *Appl. Optics*, 11 (1972) 354.
- 2 R. V. Ambartzumian, V. I. Kalinin and V. S. Letokhov, *JETP Lett.*, 13 (1971) 305.
- 3 R. V. Ambartzumian, V. M. Apatin and V. S. Letokhov, *JETP Lett.*, 15 (1972) 336.
- 4 R. V. Ambartzumian, V. S. Letokhov, G. N. Makarov and A. A. Puzetzky, *JETP Lett.*, 15 (1972) 709.
- 5 R. V. Ambartzumian, V. S. Letokhov, G. N. Makarov and A. A. Puzetzky *JETP Lett.*, 17 (1973) 91.