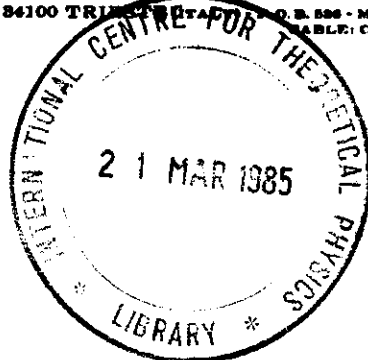




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WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS
(21 January - 22 March 1985)

Topical Meeting on Multiphoton Processes

CHEMICAL APPLICATIONS OF INFRARED MULTIPHOTON EXCITATION

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CHEMICAL APPLICATIONS OF INFRARED MULTIPHOTON EXCITATION

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Excitation of molecular vibrations in a strong infrared field allows different approaches to non linear laser chemistry which can be classified using the different times required for relaxation of the vibrational energy stored in the molecule:

γ_{VV}^{in} = time required for the intramolecular transfer of vibrational energy to the different vibrational modes of the same molecule.

γ_{VV} = time required for intermolecular transfer of vibrational energy between different molecules of the mixture.

γ_{VT} = time of relaxation of the vibrational energy to rotational and translational degrees of freedom, i.e. the time required to reach thermal equilibrium in the system.

one has: $\gamma_{VV}^{in} \ll \gamma_{VV} \ll \gamma_{VT}$

A simplified classification can be based on a comparison of these times with the multiphoton excitation rate w_{exc} . On this basis one can visualize four different approaches to non linear laser chemistry.

$$-I) w_{exc} \gg (\gamma_{VV}^{in})^{-1}$$

Mode (or bond) selective excitation is possible in this case; a given mode or functional group in a polyatomic molecule has a higher vibrational "temperature" than the other modes and no vibrational equilibrium is therefore established even inside the molecule. is

in the range of 10^{-12} s.

$$\text{-II) } (\gamma_{VV}^{IN})^{-1} \gg \tau_{exc} \gg (\gamma_{VV})^{-1}$$

Selective vibrational excitation of different species in a mixture is possible and there is no overall equilibrium in the system.

Molecules interacting with the ir field do possess internal vibrational equilibrium but are characterized by a vibrational "Temperature" higher than the other species in the system, while translational and rotational temperatures remain unchanged for all molecules.

Selective molecular ir photochemistry under these conditions is the best developed field in non linear laser chemistry. Laser isotope separation falls into this class. depends on pressure and are in the range of 10^{-6} s torr.

$$\text{-III) } (\gamma_{VV})^{-1} \gg \tau_{exc} \gg (\gamma_{VV})^{-1}$$

Vibrational equilibrium is established i.e. all molecules reach the same vibrational temperature but vibrational excitation does not yet relax to heat ($T_V, T_{R,T}$). Photochemical reactions are essentially non-selective and those with sufficiently small activation energy will take place in times are in the range 10^{-3} s torr.

$$\text{-IV) } (\gamma_{VV})^{-1} \gg \tau_{exc}$$

Thermal equilibrium is present and $T_V = T_R = T_T$. Experiments under these conditions are of interest when special requirements are to be met e.g. rapid and/or localized heating, no interaction with the walls.

Examples under condition I) are treated elsewhere in this meeting.

Examples under conditions II), III) and IV) have been considered in other invited talks concerned with various problems some of which are also relevant to developments of new technologies.

Additional examples of non linear laser chemistry falling under conditions II), III) and IV) will be considered in this talk:

- 1) Laser induced reactions under collisionless conditions.
- 2) Radical reactions induced by ir multiphoton dissociation.
- 3) Photosensitized organic reactions induced by ir multiphoton excitation.

1) Laser-induced reactions under collisionless conditions.

Infrared laser chemistry under collisionless conditions is restricted to unimolecular processes of dissociation or isomerisation. Yet this field is one of the most intensively pursued in non linear laser chemistry. In fact new and rapidly developing techniques are providing rather formidable tools to one of the strategic goals of modern chemistry: understanding chemical reactivity from first principles. These techniques parallel the theoretical progress and provide more and more stringent tests. Lectures in this meeting have competently dealt with these problems. Collisions play the important role of expanding the domain of non linear laser chemistry and some of the possibilities of ir multiphoton excitation in a collisional regime will be examined in this talk. Laser-induced collisionless reactions are however so important that a rapid overview is necessary.

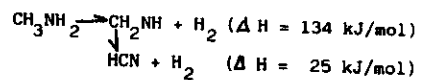
Some of the questions that may be addressed experimentally are:

Do the product-states from unimolecular reactions reflect a statistical redistribution of energy in the excited parent molecule? Do either the product-state distributions or the unimolecular decay rates show any mode or site specificity? Time and state resolved experiments are necessary to answer the questions which explore the details of the decay dynamics.

Let us start from a crossed ir laser and molecular beam study of the ir

multiphoton dissociation of C_2F_5Cl .⁽¹⁾ This molecule dissociates according to two different channels: Cl atom elimination at 347 kJ/mol and C-C bond rupture at 405 kJ/mol. According to RKKM theory rate constants for dissociation into these channels can be calculated as shown in figure 1.1. Figure 1.2. summarizes the experimental results. In molecular beam experiments the angular and velocity distribution of the products can be measured and compared with theoretical distributions of product translational energy. The statistical RKKM theory appears to be an acceptable one for this dissociation process.

The situation is however different in the case of CH_3NH_2 . The most favourable channel for dissociation of this molecule is:



The CH_2NH radical also absorbs laser radiation and has a very small dissociation energy into HCN and H_2 . A different channel is possible, $CH_3NH_2 \rightarrow CH_3 + NH_2$ ($\Delta H = 343 \text{ kJ/mol}$), but requires almost three times more energy than the first one. The infrared multiphoton dissociation under collisionless conditions (pressures in the range of 10^{-2} torr) has been independently investigated in two laboratories (2 a, b) using a laser induced fluorescence (LIF) technique to monitor the NH_2 radical formed.

The results are very similar and show that the main reaction channel is the more energetic one. HCN has only been observed at much higher pressures. One appreciates that a straightforward application of RKKM theory to this case would lead to opposite conclusions.

A more stringent comparison between experimental results and the predictions of statistical theories of the dynamics of dissociation processes has been attempted⁽³⁾ based on the analysis of the energy distribution in the $CN(X^2\Sigma^+)$ fragment formed in the IRMPD of CF_3CN . Rotational and vibrational distributions of this radical have been

measured by LIF. The rotational distribution is Boltzmann with $T_{rot} = 1200 \text{ K}$ and vibrational distributions correspond to a vibrational temperature $T_{vib} = 2400 \text{ K}$. Phase space theory and the statistical adiabatic channel theory have been utilized to calculate the internal energy distributions of CN. RKKM theory does not explicitly consider the ways into which the available energy is partitioned amongst the degrees of freedom of the dissociation fragments. This analysis has shown that the adiabatic channel theory is able to reproduce the observed temperatures while phase space theory inevitably leads to $T_{vib} = T_{rot}$. The experimental data are also consistent with a simple model which assumes that fragment rotational and translational excitations derive from parent R,T motions combined with the kinetic energies of the vibrations of the parent molecules which are converted to product R,T excitations.

IRMPD of CH_2CHCN yields C_2 and CN radicals which can both be monitored by LIF. The time dependence of their concentration and of their rotational temperatures have been determined⁽⁴⁾ (figure 1.3) and shows the presence of laser intensity effects, in the final stages of pumping, reflecting the competition between dissociation into these fragments and up-pumping of the parent molecule.

Closely related to IRMPE is the newly developed technique of vibrational overtone excitation: the pump laser is a tunable dye laser which explores the one-photon excitation spectrum of an overtone vibration or of a combination band. By this technique a precise energy increment can be introduced into a single vibrational mode of the molecule.

The unimolecular decay can then be followed by LIF analysis of the fragments, which can be both time and state resolved, or by conventional product analysis. Figure 1.4 illustrate the method in its application to H_2O_2 decomposition.⁽⁵⁾ Figure 1.5 shows an overtone vibrational excitation spectrum, and figure 1.6 typical rotational state distributions of product OH radical as obtained from LIF analysis at low pressure (10^{-1} torr).

Vibrational overtone excitation using a cw dye laser at higher (15-60 torr) pressures, i.e. in a collisional regime, has been utilized in reference to investigate the isomerisation reactions reported in figure 1.7.

The photoisomerisation kinetics can be described by $A \xrightarrow[k_d[M]]{k_a(h\nu)} A^* \xrightarrow{k(E)} B$ and the steady-state rate constant for the forward reaction is given by $k = k_a k(E) / [k(E) + k_d[M]]$; k^{-1} plotted against $[M]$, or pressure, yields a straight line (Stern-Volmer plot). The table in figure 1.8 illustrate the results. The magnitude of the increase of $k(E)$ with frequency and the absolute magnitude of these constants are in nearly quantitative agreement with RKKM predictions. The important result is that these constants are independent of the type of CH overtone excited be it methylenic, olefinic, etc. Collisions are very important in these experiments in that photoactivated molecules are quenched by collisions at a rate $k_d[M]$. Pressure therefore controls the collisional time scale, the shortest observed being 100 ps. The results are consistent with the idea that energy randomization occurs on a ps scale in large molecules at high excitation levels. There appear to be exceptions, however, to this apparently general conclusion. One of them comes from the study of vibrational overtone decomposition of $(CH_3)_3C-CO-OH(CH_3)_3COH$ pumped to the 5-0,6-0 overtones of O-H stretching.⁽⁷⁾ A classical, or purely statistical, kinetic scheme of this radical reaction, again carried on under collisional conditions in the presence of buffer gases (SF_6 , Ar), predicts linear Stern-Volmer plots. The situation is however quite different (figure 1.9) with clear saturation of the rate constant with pressure. A different kinetic scheme is necessary to account for this behaviour which includes the possibility of non purely statistical behaviour. Calculations based on RKKM theory in which one assumes partial localisation of excitation energy in a "part molecule" could reproduce the experimental observation. The same agreement can however be obtained on the assumption of dissociation from a low-lying excited electronic state which can be reached thanks to the

relatively high level of vibrational excitation.

IRMPE and VOE are complementary methods of vibrational excitation in the ground electronic state of the molecule. The main difference between these two methods is that VOE prepares a rather narrow distribution of excited molecules while IRMPE distributions can be fairly wide. Direct comparisons of these excitation methods have recently been attempted.⁽⁸⁾ We should finally mention a promising technique in the study of IRMPE. (figure 1.10) The 118 nm radiation from a VUV laser is used to photoionize the molecules of a molecular beam at the focus of a pulsed CO_2 laser. These ions are mass-analysed by a quadrupole or a time of flight mass spectrometer. The optical chopper truncates the CO_2 laser pulse at variable times thus providing a variable dose of ir photons to the beam molecules. The evolution of the mass spectrum with chopper time allows detailed informations to be collected on excitation and dissociation pathways.⁽⁹⁾

These are but a few examples taken from a rapidly growing body of experimental information. We think they can provide a general impression of the type and direction of experimental efforts in laser studies of molecular dynamics in the ground electronic state of the molecule.

2) Radical reactions induced by ir multiphoton dissociation. ⁽¹⁰⁾

When a mixture of BCl_3 and H_2 is heated to sufficiently high temperatures a mixture of B_2H_6 , higher boranes, HCl and a few percent of BCl_2H is obtained. However, when the same mixture is laser irradiated in the absorption region of BCl_3 only BCl_2H and HCl are formed. Again if a mixture of CF_3Br and I_2 is heated, CF_3I is formed in small quantities because the thermal stability of this compound is smaller than that of CF_3Br . When CF_3Br is laser irradiated in the presence of excess I_2 CF_3I is formed with almost 100% yield. These early examples of ir laser induced radical reactions emphasize some important features of these

processes: 1) non thermal character of the reaction 2) high yields of desirable products i.e. high selectivity 3) high photochemical yields 4) possibilities for the synthesis of compounds less stable than the initial ones. Synthetic routes to new compounds or with higher yields of desirable products are therefore opened. Two cases will be examined which illustrate in more detail the requirements for optimal processes of laser chemical synthesis.

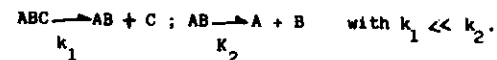
Synthesis of $(CF_3)_3CI$. This molecule was synthesized by irradiating a mixture of $(CF_3)_3CBr$ and I_2 with TEA CO_2 laser pulses. The primary act is: $(CF_3)_3CBr + n_1 h \longrightarrow (CF_3)_3C\cdot + Br$ followed by $(CF_3)_3C\cdot + I_2 \longrightarrow (CF_3)_3CI + I\cdot$.

The primary radical $(CF_3)_3C\cdot$ can undergo further decomposition in a successive channel $(CF_3)_3C\cdot + n_2 h \longrightarrow CF_3\cdot + (CF_3)_2C\cdot$ while a possible parallel channel is $(CF_3)_3CBr + n_3 h \longrightarrow (CF_3)_2CBr + CF_3\cdot$. These two channels produce the radical $CF_3\cdot$ which is undesired because it reacts to produce the secondary product CF_3I . The dissociation yield β and the relative yield of desired product β_1/β have been investigated as a function of fluence, wavelength and pulse duration and the results are reported in figures 2.1, 2.2, 2.3. The contribution of the parallel channel is probably small because it involves the detachment of a CF_3 radical and, according to RKKM theory, the probability of this process is one order of magnitude smaller than the detachment of a Br atom in the primary act. The main contribution to the formation of undesired CF_3I then comes from the successive channel. The observed decrease of β_1/β as a function of pulse duration is attributed to collisional energy transfer from the highly excited $(CF_3)_3CBr$ molecule to the primary $(CF_3)_3C\cdot$ radical which then begins to absorb energy from the laser; the probability of its further decay in the successive channel therefore increases with increasing pulse duration. In fact the increase in pulse duration corresponds to a change toward a thermal regime where the primary selectivity is lost. These results give clear indication of the possibility of optimizing this radical synthesis by proper selection

of fluence, wavelength and pulse duration.

Synthesis with combined laser and thermal excitation.

It is not necessary that all the energy needed to dissociate a molecule should be provided by multiphoton absorption. A considerable part of it could be stored as thermal energy. An example of combined thermal and laser excitation is provided by the synthesis of CF_3I from $CF_3Br + I_2$. This mixture can be preheated to different temperatures by exposure to CW CO_2 laser radiation of variable intensity followed by pulsed ir MP dissociation. The results are reported in figures 2.4 and 2.5. The increase in dissociation yields with increasing initial temperature is quite evident. The dependence of the yield on laser frequency at 3000 K is significant when compared to the linear absorption spectrum of CF_3Br . Such broadening and shift of the frequency dependence of β at high temperatures, related to vibrational anharmonicity, is of practical interest; it allows ir MP dissociation of molecules whose absorption bands are somewhat shifted from the spectral range of pulsed ir lasers. A comparison of laser and thermal initiation of gas phase radical reaction is illustrated in figure 2.6 which refers to a reaction sequence

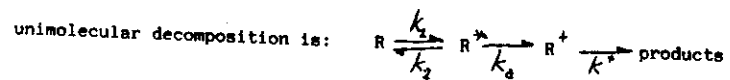


It should be mentioned that preparation of radicals by IRMPD of parent molecules is presently improving the possibilities of kinetic studies of reactions of these free radicals with stable molecules.⁽¹¹⁾ When IRMPD produces radicals with excess internal energy one can also determine the influence of vibrational excitation of the radicals on the rates of their reactions.⁽¹²⁾

3) Photosensitized organic reactions induced by ir multiphoton excitation.

Photosensitization represents a method for carrying out a photochemical process when a molecule can not be raised to the desired excited state by direct absorption of light. Pulsed ir laser-induced processes are made possible, for molecules which do not appreciably absorb in the 9-11 μm region of the CO_2 laser, by the addition of a sensitizer (NH_3 , SiF_4 , SF_6 , C_6F_6) which, on the contrary, strongly absorbs in this spectral region. The multiphoton excitation of the sensitizer is transferred, via collisional processes, to the desired molecule which then reacts or dissociates. It will be shown that these sensitized reactions fall under conditions III or IV depending on experimental parameters. The unimolecular decomposition reactions reported in fig. 3.1 have been investigated in the presence of a large excess of SF_6 in the pressure region 10-30 torr. (13) The decomposition of cyclohexene has also been studied in the presence of different sensitizers: SiF_4 , SF_6 , C_6F_6 . (14)

The absorbed energy per mol of sensitizer S, is a function of time determined by the laser pulse shape and by the spectral characteristics of S. Sensitizer molecules with vibrational energy $E_S(t)$ transfer to the reactant R, via vibrational-vibrational processes, an amount of energy per mol of R and per collision $\alpha_v = \alpha_v^C E_S(t)$. The general scheme for a



with R energized molecule and R activated complex. Under conditions of these experiments the process of energization $R \rightarrow R^*$ is assumed to be dominated by the v-v transfer process from excited S molecules. As a consequence of this transfer of energy the vibrational energy per mol of R, $E_R(t)$ will increase with time and R will decompose to products at a rate corresponding to its vibrational energy, according to RRKM theory.

The instantaneous energy balance for one mole of R is:

$$dE_R(t)/dt = Z n x_S \alpha_v^C E_S(t) - E_R(t) [k_1 + k_2] \quad 3.1)$$

with $Z \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $n \text{ cm}^{-3}$, and x_S mole fraction of S; $k_1 = k_1(t) = A_1 \exp(-E_1 / R T[E_R(t)])$ is the time dependent rate constant as given by the Arrhenius equation and where $T[E_R(t)]$ is the temperature corresponding to the reactant vibrational energy $E_R(t)$ which can be calculated according to standard methods.

Calculation of $k_1(t)$ during the laser pulse is therefore reduced to the evaluation of $E_R(t)$. This can be done by proper integration of equation 3.1 Figure 3.2 reports the logarithmic plots of the average rate constant \bar{k}_1 multiplied by the pulse duration t_p (1.6 μs) as a function of the inverse total energy absorbed during the pulse $E_A(t_p)$. Fitting of the integrated form of eq. 3.1 to these data yields the lines of figure 3.2. This allows the evaluation of the v-v transfer quantity and of k_2 , the rate of collisional deactivation of R.

When multiphoton absorption takes place at sufficiently high pressures deexcitation of the sensitizer by v-t processes becomes important and a fraction of the energy absorbed by S is lost to the thermal bath whose temperature will increase with time. In the presence of collisional v-t deactivation the vibrational energy of the sensitizer $E_S(t)$ is characterized by a pressure dependent maximum occurring at a pressure dependent time $t_{\text{max}} \geq t_p$. From these considerations and from the experimental pressure dependence of $\bar{k}_1 t_p$ (figure 3.2) it is possible to evaluate both the temperature at the end of the pulse and the v-t transfer parameter d_T . Values of d_v , α_p and α_m^R (as derived from k_2) for typical conditions are reported in figure 3.3. The average vibrational energy transferred (per collision and per mole of R) from S to the vibrational manifold of R is larger by at least a factor of five than the corresponding vibrational energy lost by S to the translational and rotational degrees of freedom of the molecules, α_{tr} .

This accounts for the fact that transfer of vibrational energy between the excited sensitizer and the reactant is sufficiently fast to cause appreciable decomposition during the laser pulse while the gas temperature remains sufficiently low to prevent any thermal contribution to the reaction. As a matter of fact a large contribution to gas heating comes from the collisional deactivation of R, as indicated by the large values of $\chi_p^R \approx 0.7 \chi_v$. ($400 \text{ K} \leq T_T \leq 1000 \text{ K}$)

These sensitized reactions do therefore appear to occur under non-equilibrium conditions corresponding to case III above.

Sensitized reactions which would fall under conditions IV have however also been reported. (15)

Conditions for a thermal regime of the reaction are different. In this case there should be no appreciable decomposition of the reactants before extensive thermalization of the absorbed laser energy has occurred and the system should be allowed to remain at a sufficiently high temperature for a sufficiently long time. ($10 \mu\text{s}$).

These conditions can be attained but require proper selection of pressure, composition and specific heat of the gas mixture. E.g. in ref (15) mixtures SF_6/R_1 at 7 torr were irradiated in the presence of ≈ 100 torr CO_2 .

This laser powered homogeneous pyrolysis has proven extremely valuable in the determination of kinetic parameters by the comparative rate method for reactions where the traditional heating by a hot walled vessel is inappropriate because of surface sensitivity and where the use of shock-tube techniques is made difficult by low volatility of the reactant.

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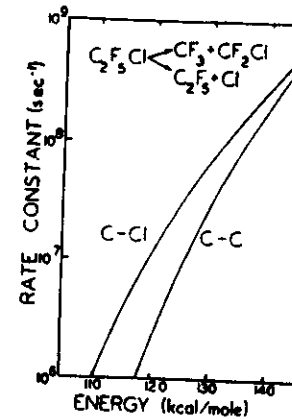


Fig. 1 RRKM rate constants for dissociation of C_2F_5Cl as a function of total energy in the molecule.

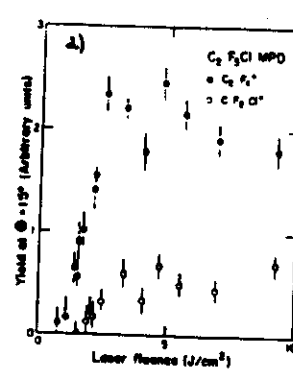


Fig. 2a Yield of $C_2F_5^+$ (from C_2F_5) and CF_2Cl^+ (from CF_2Cl) vs. laser energy fluence at $\theta = 15^\circ$ in the laboratory.

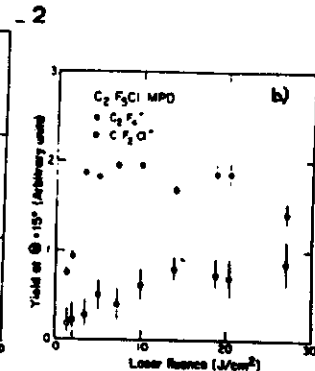


Fig. 2b Yield of $C_2F_5^+$ (from C_2F_5) and CF_2Cl^+ (from CF_2Cl) vs. laser energy fluence at $\theta = 15^\circ$ in the laboratory.

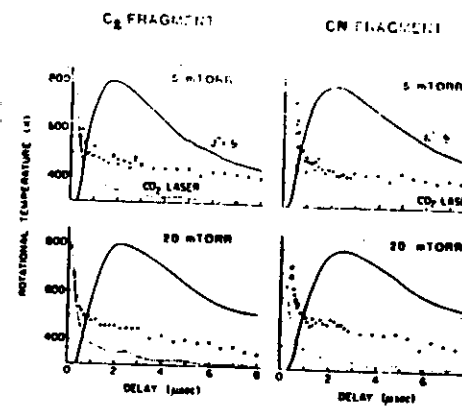
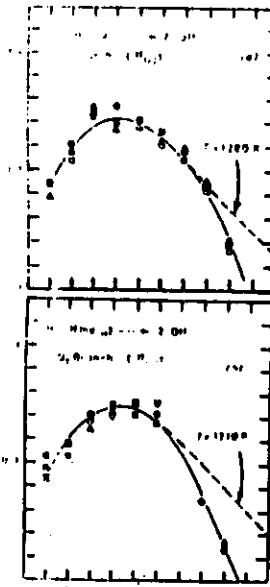
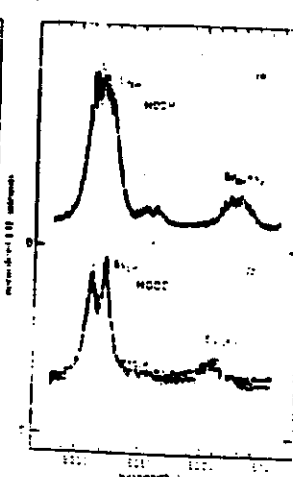
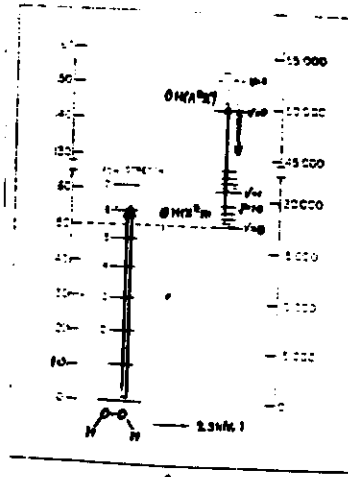
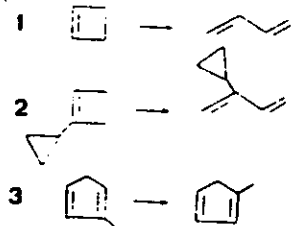


FIG. 3 Rotational temperature of the $C_2F_5^+$ ion as a function of the delay from the start of the photolysis pulse under various pressure conditions. The $C_2F_5^+$ ion is produced by the laser pulse profile shown in Fig. 1. The solid line with the intensity label is the fit to the data. Rotational temperatures of the $C_2F_5^+$ ion are shown in Fig. 3. For the same pressure conditions are included for comparison.



1) Reactions under collisionless conditions

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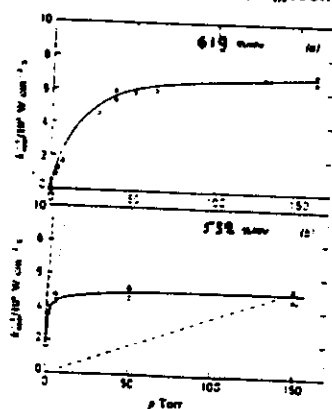


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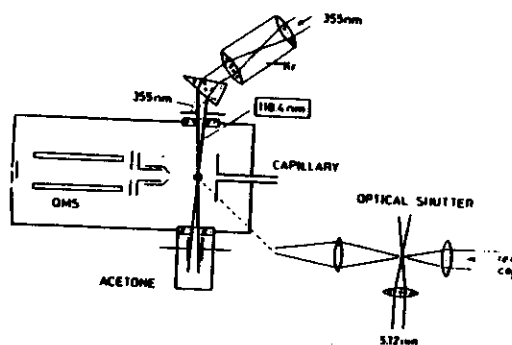
Table 1. Isomerization rate constants

molecule	frequency cm ⁻¹	spectroscopic assignment	k(E) 10 ⁻¹¹ s ⁻¹
cyclobutene 1	13 245	combination band	3.5 ± 0.8
	13 420	0-5 methylene	4.3 ± 0.8
	13 446	0-5 methylene	4.0 ± 0.5
	13 500	0-5 methylene	3.5 ± 0.7
	14 094	0-5 olefinic	9.1 ± 1.4
	14 120	0-5 olefinic	7.4 ± 1.6
cyclopropylcyclobutene 2	15 446	0-5 cyclobutenyl CH ₂	0.027 ± 0.008
	16 470	0-6 cyclopropyl CH ₂	0.10 ± 0.04
2-methylcyclopentadiene 3	13 221	0-6 methylene	1.3 ± 0.3
	13 396	0-3 methyl out-of-plane	1.8 ± 0.6
	13 596	0-5 methyl in-plane	4.3 ± 0.9
	14 209	0-3 methine	0.1 ± 0.2

UNIMOLECULAR DECOMPOSITION OF (CH₃)₂COOH



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2) Radical reactions

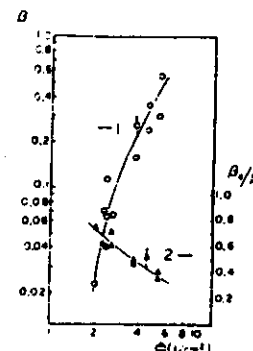


Figure 1. Dependences of yield β (curve 1) and relative yield of desired product β_d/β (curve 2) for MPD of (CF₃)₂CBr molecule as a function of CO₂-laser energy fluence Φ. p_{CH₂Br} = 0.9 torr; p₀ = 12 torr.

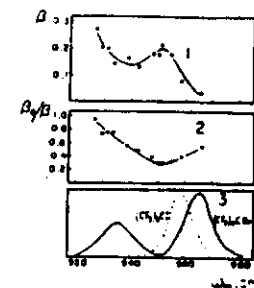


Figure 2. Dependences of β (curve 1) and β_d/β (curve 2) for MPD of (CF₃)₂CBr molecule as a function of IR laser frequency ω. Curves 3—linear IR absorption spectra for (CF₃)₂CBr and (CF₃)₂Cl molecules. p_{CH₂Br} = 0.9 torr; p₀ = 12 torr.

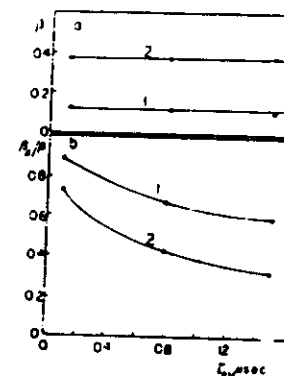


Figure 3. Dependences of β (a) and β_d/β (b) for MPD of (CF₃)₂CBr as a function of laser pulse duration. Curves 1. Φ = 2.8 J/cm². Curves 2. Φ = 5.0 J/cm².

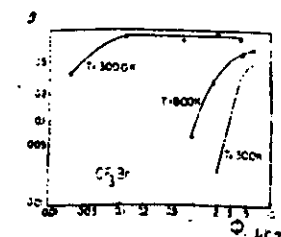


Figure 4. Dependences of yield of MPD for CF₃Br as a function of fluence at various temperatures.

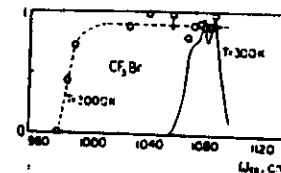


Figure 5. Dependence of yield of MPD for CF₃Br at T₀ = 3000 K (dashed curve) as a function of laser wavelength. Solid curve: CF₃Br linear absorption spectrum of T₀ = 300 K.

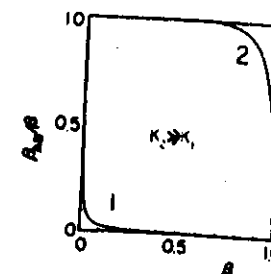


Figure 6. Dependences of the relative yield of radical AB β_d/β on the total yield β of dissociation of the molecule ABC in reactions 11 and 12 of successive dissociations. Curve 1: thermal initiation. Curve 2: IR MP initiation of reactions. Parameters, resembling those of reaction sequences 4 and 7, were used in the calculations.

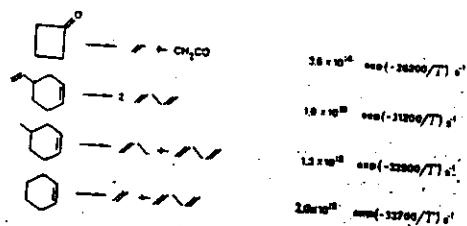


Figure 1

Values of k_1 , k_2 and k_3 (s⁻¹) (total pressure: 30 Torr)

Sensitizer	k_1 (s ⁻¹)	k_2	k_3	k_4
2.8×10^{-4} exp(-26200/T) s ⁻¹				
1.0×10^{-3} exp(-31200/T) s ⁻¹				
1.3×10^{-3} exp(-32300/T) s ⁻¹				
2.0×10^{-3} exp(-32700/T) s ⁻¹				
27_4	200	5.7	1.80	0.3
	200	2.7	0.45	1.0
C_6F_6	200	3.2	0.70	2.1
$54P_6$	200	1.0	10.021	1.3

Figure 3

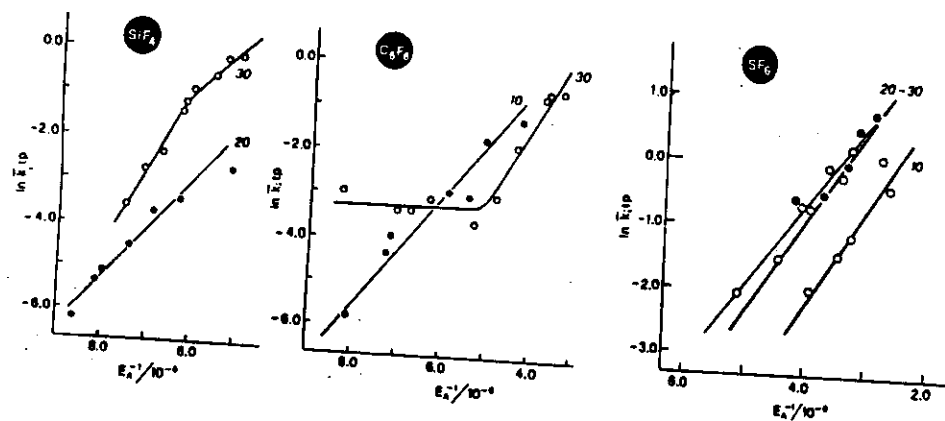


Figure 2