

TRANS-CIS ISOMERIZATION OF C₂H₂Cl₂ MOLECULES, SELECTIVE DISSOCIATION AND THE ROLE OF THERMAL PROCESSES IN AN INTENSE I.R. LASER FIELD

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Summary

The interaction between *trans*-dichloroethylene molecules and a strong i.r. field of TEA CO₂ laser has been studied. When the power density is above 5×10^8 W/cm², three processes can be observed: (1) selective isomerization, *i.e.* *trans*-C₂H₂Cl₂ → *cis*-C₂H₂Cl₂ reaction; (2) selective molecular dissociation giving unexcited fragments; the end product of this reaction is acetylene; (3) dissociation giving electron-excited fragments, or CH* and C₂* radicals.

The characteristic times of the three processes are different. The dependence of dissociation and isomerization efficiency on wavelength and laser energy has been determined, which makes it possible to choose optimum conditions to realize each of the processes. The effect of different buffer gases on the processes of molecular excitation and de-excitation in a strong field has been investigated. It is shown that the addition of a buffer increases by one order the energy absorbed in the gas which is probably connected to the acceleration of rotational and intramolecular relaxation in a strong field. The mechanisms of the processes as well as possibilities of using isomerization reactions for laser isotope separation are being discussed.

Introduction

The effect of isotopically-selective molecular dissociation in an intense i.r. field was discovered previously [1]. It had been preceded by studies in visible luminescence of molecular gases under the action of a high-power pulse of CO₂-laser. From these studies it was concluded that the effect of molecular dissociation occurred due to interaction with a strong resonant i.r. field without molecular collisions [2, 3]. Selective dissociation was successfully employed to separate the isotopes of boron, sulphur and other elements [4] which stimulated more comprehensive investigation of multi-photon absorption of i.r. radiation and dissociation of polyatomic molecules [5 - 7].

At the same time interest was aroused in other (non-dissociation) molecular processes taking place during multiphoton absorption of i.r. radiation by polyatomic molecules. Specifically, if a molecule interacting with the field can exist in some isomeric forms, multiphoton excitation of vibrations in a strong field may result in its structural changes that is isomerization. Were this effect discovered there would be a better understanding of the mechanism of multiphoton absorption of i.r. radiation by polyatomic molecules. Besides, the realization of selective molecular isomerization in a strong i.r. field is important for widening the scope of isotope separation under i.r. radiation since: (1) isomerization results in stable molecules and there is no need to bind fragments and to preserve selectivity in secondary processes which is very complicated in the general case; (2) the energy of isomerization is much smaller than that of dissociation which enables separation with smaller consumption of energy.

On the other hand, because of small isomerization energy this process is more sensitive to thermal heating than dissociation. This fact makes it possible to use isomerization to study the role of thermal processes that are one of the main factors limiting selectivity of molecular processes in strong fields.

The purpose of this paper is to describe the results of our experiments on the action of powerful TEA CO₂ laser radiation on dichloroethylene existing in three isomeric forms (*cis*, *trans* and asymmetrical). Molecular *trans*-configuration absorbs CO₂-laser radiation and selective reactions such as *trans*-C₂H₂Cl₂ → *cis*-C₂H₂Cl₂ may occur.

The experiments have shown that in strong enough fields ($>5 \times 10^8$ W/cm²) the following processes come about: (1) selective dissociation of *trans*-C₂H₂Cl₂ molecules giving electronically excited and unexcited fragments and products, the characteristic times of these processes being different; (2) molecular transitions from one configuration to another (*trans*-*cis* transitions).

The results of our experiments have enabled us to estimate the role of thermal and radiative processes and to discuss potential mechanisms of isomerization and dissociation and their relation to strong fields. The experiments have demonstrated the strong influence of buffer gases on the processes of multiphoton absorption of i.r. radiation by molecular vibrations as well.

Experimental

The experiment consisted in laser excitation of the ν_6 mode of *trans*-C₂H₂Cl₂ molecule whose R-branch of absorption band coincided with the operation range of CO₂ laser*. The laser radiation was focused by a NaCl

*The *cis*-C₂H₂Cl₂ molecule has no linear absorption in these wavelengths, but it can absorb the laser energy in a strong field. The experiments have shown, that *cis*-C₂H₂Cl₂ molecule can also dissociate and pass to the *trans*-form in a strong field. However, the efficiency of such process is considerably smaller than that for *trans*-molecules.

lens ($f = 8$ cm) on to a glass cell filled with a mixture of *trans*-C₂H₂Cl₂ and *cis*-C₂H₂Cl₂ isomers. The cross-section of focal spot under these conditions was 3×10^{-3} cm². The content of *cis*-isomer in the mixture varied from 10 to 40%.

The experiments on isomerization and dissociation were conducted at two pressures of dichloroethylene, 0.4 and 1.0 Torr. A great difference between the i.r. spectra of *trans*- and *cis*-isomers of dichloroethylene made it possible to analyze their relative content as well as to detect the formation of new products by i.r. absorption spectra. For recording spectra an "IKS-24" spectrometer was used. The number of dissociated molecules was determined both from dissociation products and by reduction of the amount of dichloroethylene in the cell.

The CO₂ laser with selection of rotational-vibrational lines employed in the experiments had the following parameters: pulse energy of up to 2 J, pulse half-height duration of 100 ns, repetition rate from 1.5 to 3.0 Hz. The rear front of pulse was shortened by mixture choice but the energy of the tail of pulse made up about 60% of the total pulse energy. Experiments were carried out also on a "shortened" laser pulse that had a symmetric form and duration of 60 ns on half-height and of 250 ns on base. The laser energy was controlled and was held constant during irradiation. The laser tuning range was 9.2 + 10.9 μ m. Isomerization was carried out at two laser frequencies, $\nu_1 = 935$ cm⁻¹, $\nu_2 = 980$ cm⁻¹.

The experimental setup to observe the kinetics and time-resolved spectra of luminescence is described in previous papers [5, 6]. The measurements of absorbed energy by means of an optical-acoustic cell followed the method given in ref. [8].

Experiments on isomerization and dissociation

Figure 1 shows the i.r. spectra of dichloroethylene and of its dissociation products recorded in the frequency range 700 + 950 cm⁻¹ with the initial *trans*:*cis* isomer ratio 0.6:0.4 and different irradiation times. One can see here an increase in the amplitude of the peaks corresponding to the *cis*-isomer and a decrease of the peaks belonged to *trans*-dichloroethylene which points to the fact that a part of the *trans*-isomer transforms to the *cis*-form. In the region of 730 cm⁻¹ a new peak develops which corresponds to the main final product of i.r. photolysis, *i.e.* acetylene.

Figure 2 shows time-histories of relative concentrations of *trans*- and *cis*-C₂H₂Cl₂ (in case of the laser frequency of 980 cm⁻¹) obtained from i.r. absorption spectra. Analogous curves are obtained in case of laser frequency at 935 cm⁻¹. Although at the start of the irradiation the quantity of *cis*-isomer rises, the process of *trans*-*cis* transformation does not come to an end. After the maximum concentration of ~ 0.5 (with respect to the initial mixture) is attained, the amount of *cis*-isomer in the mixture drops gradually. But the *cis*-*trans* ratio grows constantly and at the end of radiation mounts

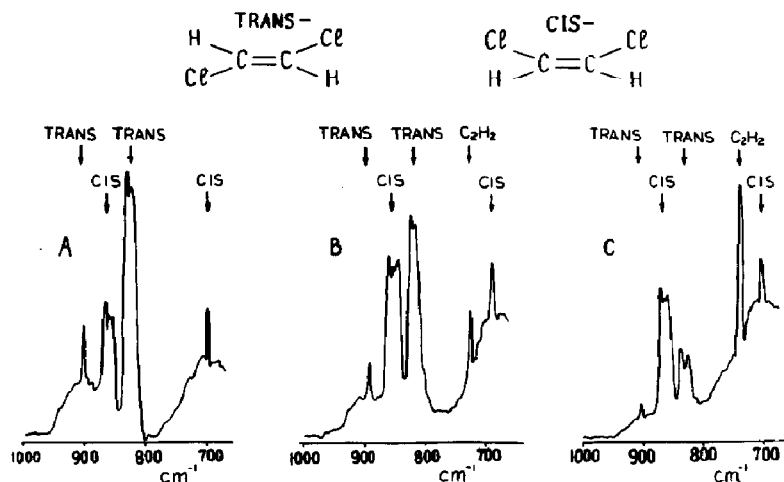


Fig. 1. I.r. absorption spectrum of dichloroethylene and its dissociation products: (A) before irradiation; (B) after being irradiated by 1.5×10^4 pulses; (C) irradiated by 4.5×10^4 pulses. ($\nu_{\text{las}} = 934.9 \text{ cm}^{-1}$, energy density in focus is 250 J/cm^2).

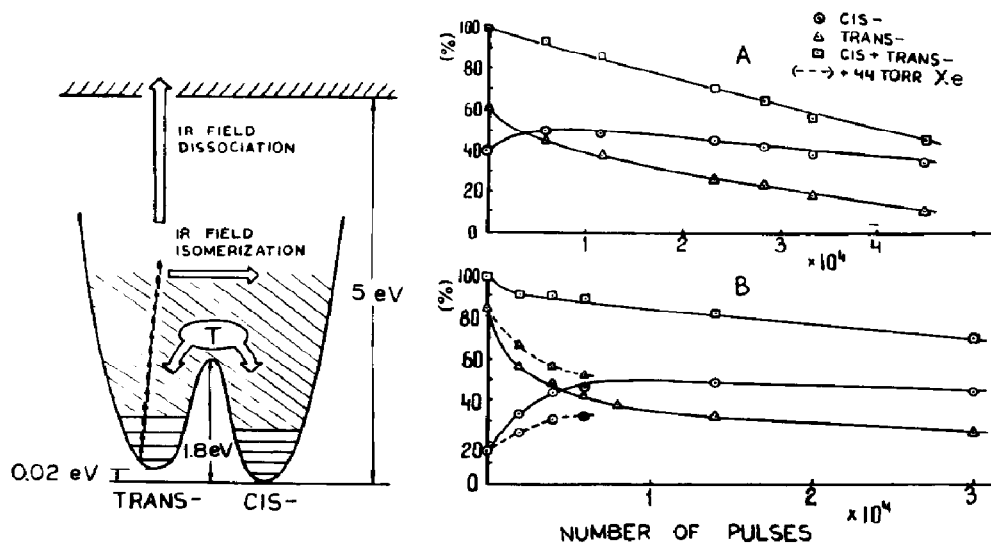


Fig. 2. Left side shows schematically main processes: dissociation and isomerization in a strong i.r. field as well as thermal isomerization. On right side relationships between relative concentrations of *trans*- and *cis*-dichloroethylene isomers and number of laser pulses are shown: (A) $\nu_{\text{las}} = 934.9 \text{ cm}^{-1}$, gas cell volume is 60 cm^3 , initial dichloroethylene pressure is 0.4 Torr, energy density on focus is 100 J/cm^2 ; lens with $f = 20 \text{ cm}$; (B) $\nu_{\text{las}} = 980.9 \text{ cm}^{-1}$, gas cell volume is 24 cm^3 , energy density on focus is 250 J/cm^2 . Lens with $f = 8 \text{ cm}$, initial dichloroethylene pressure is 1 Torr (—) and buffer gas (Xe) pressure is 44 Torr (---).

up to values from 2 to 3, the initial ratio being 0.67 (A) and 0.18 (B). The mixture in this case is enriched with *cis*-isomer all the time. This Figure gives also the time history of the total number of dissociated molecules. It is seen

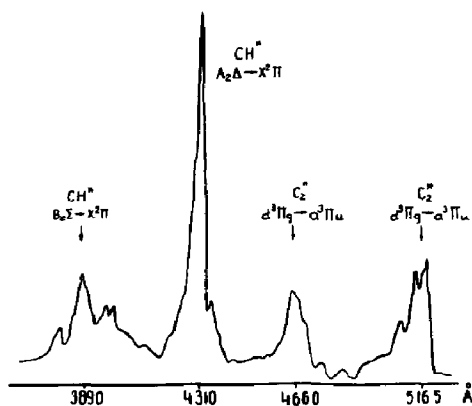


Fig. 3. Luminescence spectrum of electron-excited products of *trans*-C₂H₂Cl₂ dissociation by an intense i.r. field of TEA CO₂ laser.

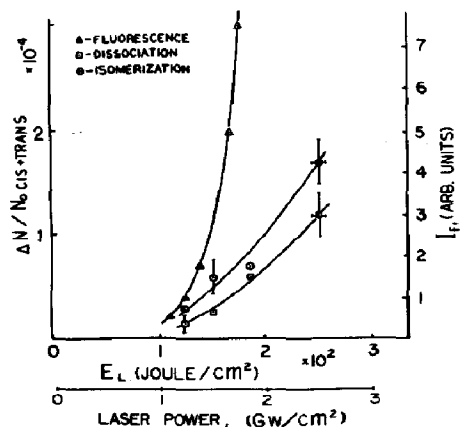
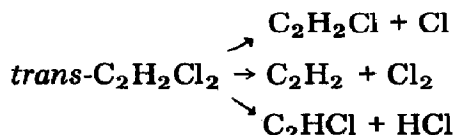


Fig. 4. Dependence of dissociation, isomerization and intensity of luminescence on energy density and laser radiation power. ($\nu_{\text{laser}} = 980.9 \text{ cm}^{-1}$; C₂H₂Cl₂ pressure = 1 Torr; luminescence is detected in the whole luminous volume.)

that *trans*-C₂H₂Cl₂ molecules dissociate for the most part.

During u.v. photolysis of dichloroethylene dissociation is possible in three ways [9]:



In the all cases unexcited products are formed, and mainly acetylene is the final one as during i.r. photolysis. The problem on dissociation channels during i.r. photolysis can be solved when studying the composition of radicals that are initial i.r. photolysis products. In case of dichloroethylene dissociation is followed by visible luminescence, or, in contrast to u.v. photolysis, electronically-excited radicals are formed. From the luminescence spectrum these radicals are identified as CH* and C₂* (Fig. 3). Excited radicals appear at the delay stage of luminescence at the tail of laser pulse after the strong field disappears.

To check how the tail of laser pulse acts on the processes under study, we have carried out experiments on a "shortened" laser pulse without tail (its base length was 250 ns). It turned out that neither luminescence nor isomerization could be observed at the same power density of i.r. field, and only dissociation takes place giving unexcited products.

When the "tailed" laser pulse was used, all the three processes occur in the same range of laser energies (Fig. 4) and stop at energy densities of below $50 + 100 \text{ J/cm}^2$.

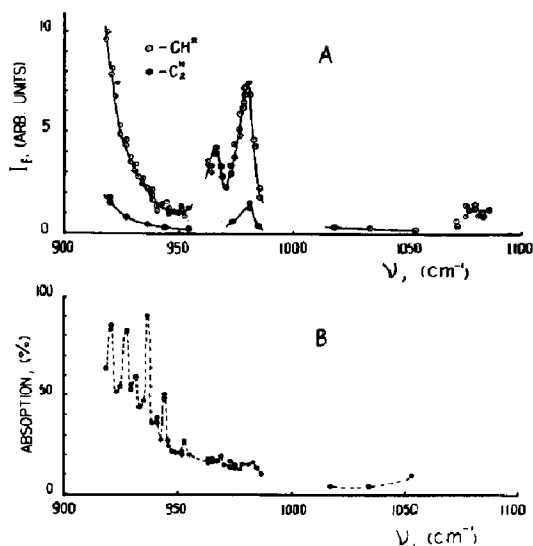


Fig. 5. (A) Luminescence intensity of electron-excited radicals CH^* and C_2^* depending on irradiation frequency ($\text{C}_2\text{H}_2\text{Cl}_2$ pressure = 1 Torr). (B) Linear absorption of $\text{C}_2\text{H}_2\text{Cl}_2$ in a weak unfocused beam 10^{-3} J/cm^2 at different lines of CO_2 laser ($\text{C}_2\text{H}_2\text{Cl}_2$ pressure is 10 Torr. Cell length is 50 cm).

Electron-excited fragments

The formation of electron-excited dissociation fragments is followed by visible luminescence, and this makes it possible to investigate the kinetics of their production under different conditions. The observation of luminescence time dependence has shown that under all experimental conditions (different pressures, excitation wavelengths, densities of incident energy) the luminescence pulse of electron-excited fragments has *no instantaneous stage* that exists during dissociation of other molecules of similar structure (C_2H_4 , $\text{C}_2\text{F}_3\text{Cl}$) [6], though (it will be seen from Fig. 10) the delay of luminescence maximum about laser pulse becomes very small as the pressure increases.

The centre of the excited ν_6 mode of *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$ molecule lies in the region of 895 cm^{-1} , so that the minimum laser frequency (918 cm^{-1}) falls within the edge of the R-branch. Luminescence was observed not only in excitation of the R-branch of the ν_6 mode but also beyond it in the whole range of laser tuning up to 1090 cm^{-1} . Figure 5 shows the relationship between luminescence intensity of CH^* and C_2^* radicals and excitation frequency. It shows for comparison linear absorption at the laser generation frequencies. It is apparent that the absorbed energy varies by several times during transitions from line to line, while the luminescence intensity therewith remains practically constant. The luminescence peaks observed at the excitation frequencies 966 cm^{-1} , 980 cm^{-1} and in the region of 1080 cm^{-1} are not evidently associated with the excitation of the ν_6 mode, and since there are no other basic frequencies in this region, the observed processes (iso-

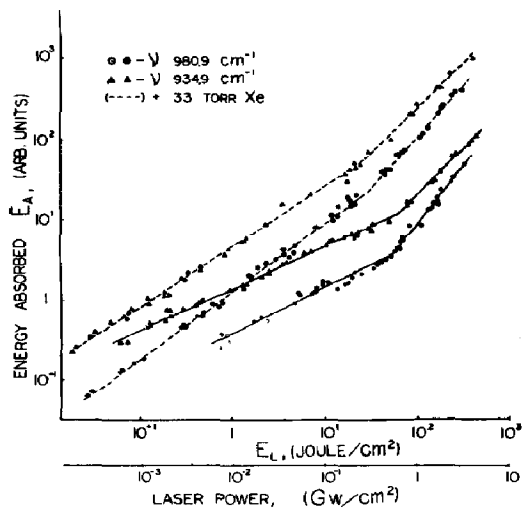


Fig. 6. Dependence of absorbed energy in $C_2H_2Cl_2$ on energy density and laser radiation power in the lens focus. Pressure is 1 Torr. Below the salient point $E_{abs} \sim (E_{incid})^{0.5}$, above the salient point $E_{abs} \sim E_{incid}$.

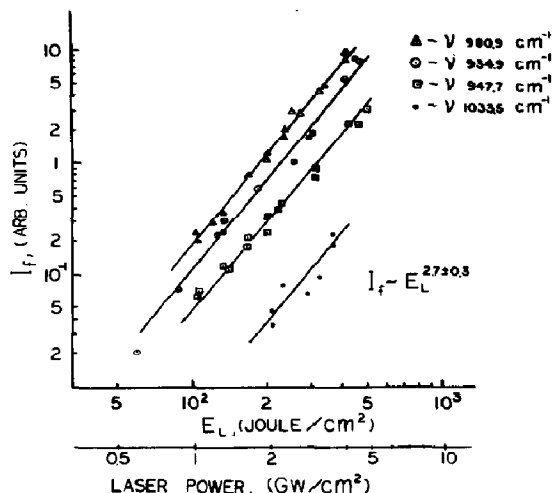


Fig. 7. Dependence of luminescence intensity on energy density and radiation power. Luminescence is detected from the central region of focal volume. $C_2H_2Cl_2$ pressure is 1 Torr.

merization and dissociation) must be related to multiphoton excitation of combination frequencies in a strong field as in the case with CCl_4 and SF_6 [10].

To evaluate the excitation efficiency of dichloroethylene molecules at different laser frequencies we directly measured the absorbed energy at different levels of incident energy and power density in the optical-acoustic gas cell (see Fig. 6). The measurements show that: (1) the energy absorbed in a strong field is of the same order when exciting both the fundamental band and combination vibrational band; (2) the absorbed energy is non-linearly dependent on radiation power. E_{abs} as a function of E_{las} in $-\log$ scale have the form of two different slope straight lines, which fractured in the region of power density 500 MW/cm^2 , energy density 50 J/cm^2 ; (3) luminescence intensity at different excitation frequencies is *not proportional* to absorbed energy. So though at all the studied frequencies of excitation channels of molecular transformation are the same their relative role is different. To relate luminescence intensity to absorbed energy at an excitation frequency $I_{lum}(E_{incid})$ dependences were measured at different excitation frequencies (Fig. 7). Comparison between Fig. 6 and Fig. 7 shows that at one and the same frequency luminescence intensity grows quicker than absorbed energy even without taking into account the fact that luminescence observation is conducted from small part of focal volume and energy is measured in the whole focal volume.

Discussion of basic processes

Isomerization

There are several potential mechanisms which can be responsible for the transition $trans\text{-C}_2\text{H}_2\text{Cl}_2 \rightarrow cis\text{-C}_2\text{H}_2\text{Cl}_2$ (see left side of Fig. 2): (1) multi-photon excitation of high vibrational levels of $trans\text{-C}_2\text{H}_2\text{Cl}_2$ molecules, with the result that a molecule can take another isomeric form either through the mode which is excited or after intramolecular redistribution of energy over vibrational degrees of freedom and its accumulation on a degree of freedom that is responsible for isomerization. In both cases the process is shifted towards cis -isomer formation, *i.e.*, the process of isomerization is selective; (2) different isomeric configurations may be formed under recombination of the radicals resulting from dissociation of $trans\text{-C}_2\text{H}_2\text{Cl}_2$. This mechanism leads also to accumulation of cis -isomer in the mixture; (3) thermal isomerization is possible too when increasing temperatures in the focal region, as the absorbed energy is thermalized, secures a sufficiently high rate of $trans\text{-C}_2\text{H}_2\text{Cl}_2 \rightleftharpoons cis\text{-C}_2\text{H}_2\text{Cl}_2$ reactions. Such a process is non-selective, and a strong field is needed only to ensure absorption of a high enough energy.

The fact that minimum energies and intensities, at which dissociation and isomerization take place, are very close favours the selective mechanisms of isomerization. At the same time the height of potential barrier for $trans$ - cis transition makes up 1.8 eV [11], and dissociation energy equals 5.0 - 8.0 eV depending on resultant products which eliminates practically the contribution of thermal mechanisms to this process.

Experiments with "shortened" laser pulses also favour selective mechanisms because in this case the conditions for thermal reaction are no worse than in experiments on common pulses. Nevertheless there is no isomerization. It seems at first sight that in the case of selective mechanisms the cis -isomer must accumulate in the mixture at all times but it is not confirmed by experiments. It should be kept in mind, however, that the experimental conditions change greatly during irradiation. The number of $trans\text{-C}_2\text{H}_2\text{Cl}_2$ molecules absorbing energy decreases but, in return, an excess number of $cis\text{-C}_2\text{H}_2\text{Cl}_2$ and acetylene molecules appears which acting as buffer gases may affect the processes of energy absorption and relaxation. Moreover, the $cis\text{-C}_2\text{H}_2\text{Cl}_2$ molecules have small absorption of CO_2 laser radiation and so they dissociate also.

When considering the possibility of the thermal mechanism of isomerization we should first of all answer the following questions: (1) what is the maximum temperature that may be established in the reaction zone ? ; (2) how long does this temperature exist in the zone ? ; (3) are this temperature and time sufficient for the reaction to proceed to a observed rate ?

The maximum temperature can be evaluated thus. As a result of V - T relaxation, the vibrational energy of field-excited molecules transforms to heat and in $3\tau_{V-T}$ time equilibrium is reached between different degrees of freedom. In this time the excited molecules, because of diffusion and migration of vibrational energy, take a volume V which is bigger than that of focused

field. According to our experimental evaluations the intense i.r. field volume equals about $4.5 \times 10^{-3} \text{ cm}^3$.

The process of energy migration neglected, it is possible to evaluate the volume increase by diffusion from the formula:

$$\langle \tau^2 \rangle = 2Dt_{\text{th}} \quad (1)$$

where D is the diffusion coefficient, t_{th} is the thermalization time of absorbed energy, $t_{\text{th}} \approx 3\tau_{V-T}$. The value τ_{V-T} has not been directly measured in dichloroethylene. To evaluate it one can use the Lambert and Salter empirical formula dependence for hydrogenous molecules [13] and take into account the fact that the lowest vibrational frequency in dichloroethylene equals 230 cm^{-1} . In this case $\tau_{V-T} \approx 2 \text{ mc s Torr}$. τ_{V-T} can be evaluated from luminescence signal duration provided that the lifetimes of luminescent radicals CH^* and C_2^* do not exceed 500 ns even in the absence of collisions. From this it follows that τ_{V-T} is no less than 2 - 3 mc s Torr.

By the use of formula (1) with a diffusion coefficient $D = 50 \text{ cm}^2/\text{s}$ Torr and the value of absorbed energy $E_{\text{abs}} \approx 2.0 \times 10^{-5} \text{ J}$ determined from Fig. 6 we have $\Delta T_{\text{max}} < 350 \text{ }^\circ\text{C}$, *i.e.* the temperature in the reaction zone is no higher than 650 K. The thermal reaction time at this temperature $\tau_{\text{th}} \approx 10^3 \text{ s}$ [11] and the cooling time of reaction volume is $10^{-4} - 10^{-5} \text{ s}$. This suggests that thermal mechanism of isomerization is unlikely.

Dissociation

The experiments show that dissociation may be realized in two different channels with different characteristic times and mechanisms. The first channel, molecular dissociation into unexcited products, can be observed both with short and long laser pulses. Hence we may conclude that the characteristic time of this process is comparable to the duration of a short laser pulse (250 ns). A necessary and sufficient requirement for the existence of this dissociation channel is a high power i.r. field (power about 10^9 W/cm^2 and energy density about 10^2 J/cm^2).

The second channel is connected with the formation of electron-excited particles, and a strong field is also necessary for its existence. But our experiments with short pulses show that this is not sufficient. It is of importance that a field (not necessarily so strong as in laser pulse maximum) whose energy may be absorbed by molecules should exist in a certain time τ_{relax} that depends on gas pressure. In our case such a field is formed by the tail of laser pulse.

It follows from the obtained results that the relation between different molecular processes in a strong field does not remain constant. It depends on both pulse duration, its intensity and laser frequency. By changing these parameters we may choose optimum conditions for one or another process, *i.e.* control these processes.

To study this problem in more detail and to clear up the role of vibration-excited molecules in the processes considered we have experimented on buffer gases.

Experiments on buffer gases

The effect of buffer gases is many-sided. First, addition of a buffer gas increases the heat capacity of a system which, all other experimental conditions being constant, leads to a decrease in the maximum temperature and thus to an abrupt suppression of thermal processes. In this case only buffer gas thermal capacity is essential. Secondly, buffer gases influence vibrational, translational and rotational relaxation, that is they influence the efficiency of multiphoton excitation and all following processes. In this case the influence depends on the nature of a buffer gas.

In our experiments we studied the effect of buffer gases (Xe, He, H₂, N₂) as well as of a pure dichloroethylene gas on dissociation and isomerization reactions. The experiments have given the following results.

1. As a buffer is added, the absorbed energy increases. The addition of 33 Torr Xe increases the absorbed energy by more than 10 times which practically compensates for growing thermal capacity (Fig. 6). So in this case the addition of buffer gases has no pronounced effect on the course of thermal processes.

It should be noted that such action of buffers (enhancement of absorbed energy) is conditioned *by intense field* to a great extent. As is seen from Fig. 6, the "enhancement effect" disappears in weak laser fields.

2. Buffer gases suppress partly the process of isomerization (Fig. 8). It can be seen that the effect of suppression differs for various gases with the same thermal capacity (compare H₂ and N₂, Xe and He) and then it differs for various gas mixtures "buffer gas + dichloroethylene" with the thermal capacity being constant.

3. Buffer gases have *no significant effect* on dissociation product yield (Fig. 2).

4. At low pressures of C₂H₂Cl₂ (0.3 Torr) all buffer gases increase almost by one order the yield of excited products of dissociation (Fig. 9A).

At a C₂H₂Cl₂ pressure of 1 Torr there is no strong enhancement of intensity and individual features of buffer gases show up. When the pressure of a buffer is over 10 Torr, its deactivating action begins to show itself. As in the case of isomerization, hydrogen has the most deactivating effect (Fig. 9B).

5. Luminescence intensity of electron-excited dissociation products is pressure dependent (Fig. 10) being quadratic at low (<1 Torr) and linear at high pressures of dichloroethylene.

It follows from our experiments that the main effect of buffer gases consists in deactivation of vibrationally excited molecules, decrease of vibrational excitation time at the expense of a reduction in τ_{V-T} . Here as well as in many other systems [12, 13] individual features of buffer gas molecules show themselves. Hydrogen has the most deactivating effect, next are nitrogen, helium and last xenon.

The experimental data show that, as the buffer gas pressure is increased, first of all isomerization reaction is suppressed and then the yield of electron-

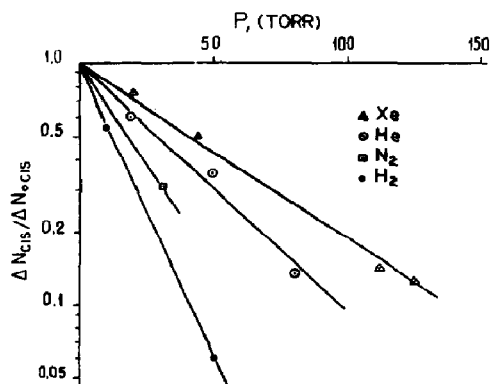


Fig. 8. Dependence of isomerization efficiency on buffer pressure ($\nu_{\text{las}} = 980.9 \text{ cm}^{-1}$; $\text{C}_2\text{H}_2\text{Cl}_2$ pressure is 1 Torr).

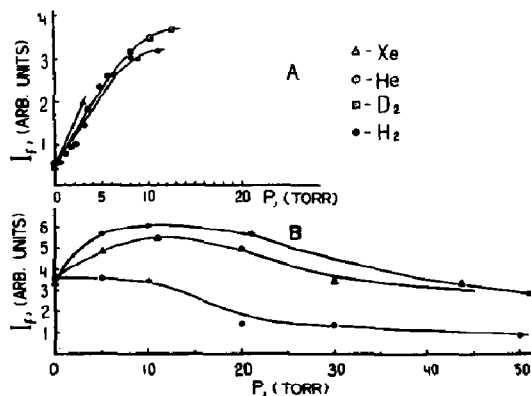


Fig. 9. Effect of buffer gases in luminescence intensity at energy density on focus about 800 J/cm^2 : (A) $\text{C}_2\text{H}_2\text{Cl}_2$ pressure is 0.3 Torr, $\nu_{\text{las}} = 934.9 \text{ cm}^{-1}$. (B) $\text{C}_2\text{H}_2\text{Cl}_2$ pressure is 1 Torr, $\nu_{\text{las}} = 980.9 \text{ cm}^{-1}$.

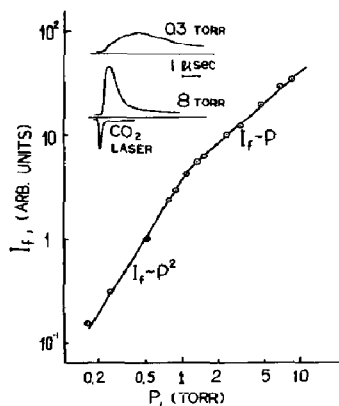


Fig. 10. Dependence of luminescence intensity on $\text{C}_2\text{H}_2\text{Cl}_2$ pressure ($\nu_{\text{las}} = 935 \text{ cm}^{-1}$, energy density on focus is 800 J/cm^2) and shape of luminescence pulses at different pressures of $\text{C}_2\text{H}_2\text{Cl}_2$ (Torr).

excited dissociation products drops. The yield of ground state products is independent of buffer pressure in the whole studied range (up to 50 Torr).

The results obtained together with the information about the effect of laser pulse duration on processes under investigation enable us to conclude that dissociation into unexcited products comes about very rapidly, under pulse action, which means that it is collisionless. The characteristic times of the rest processes are much longer and increase in the following sequence:

$$\tau_{\text{diss}} < \tau_{\text{lum}} < \tau_{\text{isom}} \quad (2)$$

Discussion

Electron-excited fragments with time delay about laser pulse resulting from dissociation enable us to suppose that the mechanism of their origin is the following: electron-excited radicals may be formed by dissociation of molecules being in excited electronic states. In this case, with appropriate arrangement of electron terms, a molecule having stored rather high vibrational energy in the field may pass into an excited electron state. Then the molecule absorbs the field energy again and reaches the high vibrational levels of excited electron state up to dissociation. The exchange process vibrational and electron energies $V - E$ realized during collisions and calling for some selection rules to be met determines in this case the time delay of excited fragments.

The process $V - E$ may be, in principle, responsible for the course of isomerization reaction.

It is not excluded either that the occurrence of excited radicals can result from secondary processes. There may be, for example, reactions during collisions between primary products of dissociation and vibrationally excited molecules of dichloroethylene.

The linear dependence of I_{lum} on dichloroethylene pressure (Fig. 10) is indicative of the mechanism of electronic excitation, but to draw final conclusions necessitates additional experiments.

Conclusions

Trans-cis isomerization of dichloroethylene molecules observed in an intense i.r. field is non-thermal by nature.

In intense fields ($>5 \times 10^8$ W/cm²) with sufficiently high energy densities (>50 J/cm²) three processes can be observed at the same time: (1) selective dissociation of *trans*-C₂H₂Cl₂ giving unexcited fragments; (2) selective dissociation giving electron-excited radicals, CH* and C₂*; (3) selective isomerization of *trans*-C₂H₂Cl₂ → *cis*-C₂H₂Cl₂.

The characteristic times of all these three processes are different.

Dissociation into unexcited fragments occurs mainly in the time of strong field existence (100 ns) and corresponds to a non-collisional process. Addition of buffer gases (up to 120 Torr) does not affect substantially this process.

Dissociation giving electron - excited fragments occurs in 3 - 4 mc s (at a pressure of 1 Torr), the time delay of yield maximum about laser pulse being 1 mc s. For this process to be observed, a strong field and a sufficient energy in the tail of laser pulse are necessary. The deactivating effect of buffer gases on this process begins to show itself at pressures above 10 Torr.

Isomerization of trans-C₂H₂Cl₂ → cis-C₂H₂Cl₂ can also be observed with a strong field and a high enough energy in the tail of pulse. The suppressing action of buffer gases on this process shows itself at smaller pressures and is

pronounced more distinctly. From this it follows that this process needs the longest life time of vibrational excitation.

It has been illustrated that under pulsed excitation of the gas in the focal region the temperature in this region depends on time of vibrational-translational relaxation, and the maximum temperature for $C_2H_2Cl_2$ with $\tau_{V-T} \approx 2 \times 10^{-6}$ s is no higher than 650 K.

The efficiency of dissociation and isomerization does not depend on the value of linear gas absorption at the laser frequency, and it may be the same both when exciting combination and basic frequencies.

It has been shown that the relative role of different channels of dissociation (excited and unexcited fragments) depends on laser frequency and energy which makes possible selective excitation of these channels.

Addition of buffer gases increases the energy absorbed in the gas, and the effect depends on the i.r. field magnitude. With power densities of $> 5 \times 10^8$ W/cm² the absorbed energy is increased by more than one order.

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