

Dye Laser Probing of Primary C₂ Radicals Formed by IR Intense Field Photolysis of Ethylene

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Abstract. The C₂-radicals in the lower electronic state $a^3\Pi_u$ have been studied by the method of laser-excited luminescence of products of ethylene IR photolysis. The dependence of C₂-radical concentration on IR field power density and its time evolution have been investigated. The threshold characteristics of C₂-radical occurrence and the ratio between excited and unexcited radicals have been determined. Different mechanisms for their formation are being discussed.

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Dissociation of ethylene molecules in the intense IR field of a pulsed CO₂-laser was first observed in [1]. The characteristics of visible luminescence made it possible to identify the primary products of IR photolysis, that is, C₂-radicals. Rough estimates showed that the portion of electron-excited radicals was small, just $10^{-5} + 10^{-7}$ of the total number of molecules. Since the probability of dissociation of ethylene molecules in intense IR fields is very high [4], it is clear that electron-excited radicals are not the main primary products of IR photolysis.

In the present paper, using the method of laser excitation of radical fluorescence, it is shown that the C₂-radical in the lower electronic state $a^3\Pi_u$, in contrast to UV photolysis, is one of the main primary products of ethylene dissociation. The threshold characteristics for the occurrence of C₂-radical and the time variation of its concentration have been measured. The ratio between excited and unexcited radicals has been determined. Possible mechanisms for their occurrence are being discussed.

1. Experiment

The block diagram of the experimental set-up is given in Fig. 1. The radiation of a pulsed TEA CO₂-

laser, the pulse energy being up to 1 J and the pulse half-width 150 ns, was focused by the Ge-lens 7 ($f = 35$ mm) into the glass cell 1 filled with ethylene. If the IR field power density is above threshold, in the focal area molecular dissociation takes place and is accompanied by visible luminescence of excited C₂-radicals. To register the radicals formed in the lower electronic state, the radiation of the tunable dye laser with its frequency adjusted to the frequency of the transition $a^3\Pi_u \rightarrow d^3\Pi_g$ of the C₂-radical was focused through a side window. The luminescence of

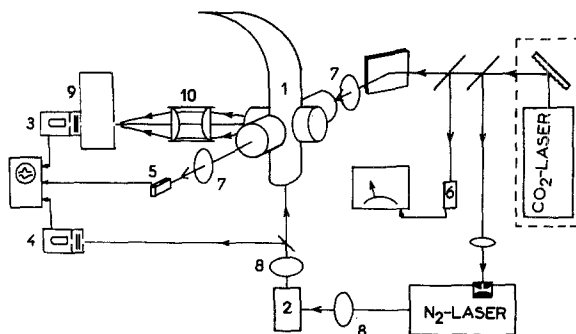


Fig. 1. Block diagram of the experimental set-up (1: cell with ethylene, 2: dye laser, 3, 4: photomultiplier, 5: photon drag detector, 6: thermopile, 7: Ge-lenses, 8: cylindrical lenses)

the radicals excited in this way as well as that of electron-excited dissociation products were observed through another side window of the cell. For this purpose the luminous area was reflected by the condenser onto the entrance slit of the MDR-2 monochromator. To eliminate the effect of luminous volume increase due to increasing power of the IR field, the entrance slit of the monochromator cut out only the central part of the luminous area. The vertical dimension of the slit was restricted with a diaphragm of 1 mm in diameter. Upon passing through the monochromator, the luminescence signal was registered by a photomultiplier and the C-8-2 type oscillograph.

The dye laser pumped by a nitrogen laser could generate pulses of 50 μJ and 7.5 ns duration in the range 4800 to 5400 \AA .

The N_2 -laser spark gap was triggered by CO_2 -laser radiation that provided pulse synchronization of both lasers. By changing the gas pressure in the spark gap at constant voltage we could vary the delay time of dye laser pulse from the CO_2 -laser pulse between 100 ns and 5 μs .

The pulse energies of both lasers were recorded by the photomultiplier and photon drag detector. The CO_2 -laser frequency of 951 cm^{-1} used in the experiment coincided with the Q -branch of the V_7 vibration mode of ethylene.

2. Experimental Results

As the dye laser frequency is tuned to the frequency of the transition (0, 0) of the band $a^3\Pi_u \rightarrow d^3\Pi_g$ (Swan band with the intensity maximum at the wavelength of 5165 \AA), luminescence grows drastically; namely, the signal amplitude increases 40 to 100 times (Fig. 2). Luminescence can be observed not only at the vibrational-rotational transitions excited by laser but also within the whole band (0-0). Therefore the monochromator exit slit was set so that it could transmit almost all radiation of the band under study. This corresponded to a spectral width of transition of about 80 \AA .

The experiments have shown that the intensity of laser-induced luminescence remains constant as the dye laser pulse energy increases, i.e. the pulse energy is sufficient to saturate the absorption of the transition (0, 0) of the band $a^3\Pi_u \rightarrow d^3\Pi_g$. Since under these conditions the luminescence intensity is proportional to the concentration of C_2 -radicals in the state $a^3\Pi_u$ at the instant of excitation, we carried out measurements under saturation conditions.

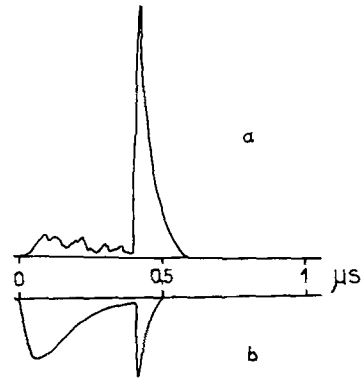


Fig. 2. a) Oscillogram of C_2^* -radical luminescence pulse. (First ordinary luminescence, and then luminescence excited by dye laser radiation.) b) Oscillogram of pulses of CO_2 -laser (first) and dye laser (thereafter) $P_{\text{C}_2\text{H}_4} = 2_{\text{torr}}$

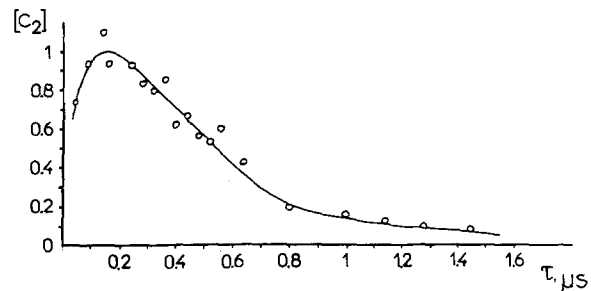


Fig. 3. Time dependence of concentration of C_2 -radicals in the $a^3\Pi_u$ state $P_{\text{C}_2\text{H}_4} = 2_{\text{torr}}$

Figure 3 presents the results of measurements of radical concentrations taken at various instances of time. The instant $t=0$ corresponds to the beginning of the CO_2 -laser pulse. It can be seen that the radical concentration decreases with a characteristic time of 500 ns. Because of a gross error in luminescence intensity measurement we could not ascertain how the actual decay deviated from an exponential one.

As seen from Fig. 2, the time characteristics of ordinary luminescence and that excited by a dye laser differ essentially. In the first case the time characteristic of the luminescence pulse is determined mainly by dissociation of ethylene molecules while in the second one it depends on the decay time of the excited state of the C_2 -radical. This has enabled us to determine the lifetime of the excited state $d^3\Pi_g$ of the C_2 -radical depending on the gas pressure in the cell.

The rate of excited state deactivation is given by the equation

$$dN^*/dt = -N^*/\tau_{\text{rad}} - \alpha PN^* \quad (1)$$

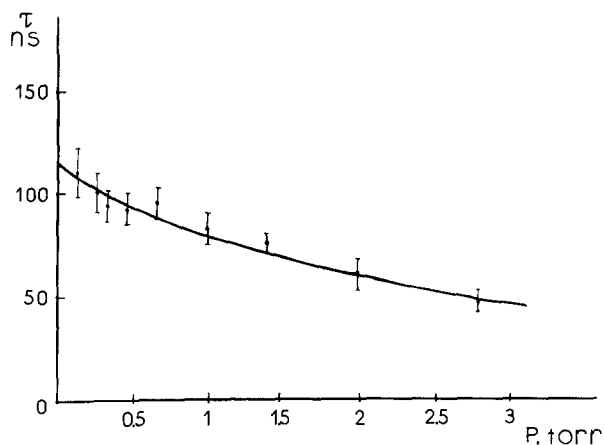


Fig. 4. Dependence of lifetime of C₂-radicals in the $d^3\Pi_g$ state on ethylene pressure

where N^* is the concentration of excited radicals, τ_{rad} is the radiative lifetime, α is the constant of quenching, and P is the pressure. The collisional radical lifetime is related to τ_{rad} and α as

$$\tau = \tau_{\text{rad}} / (1 + \alpha P \tau_{\text{rad}}). \quad (2)$$

From the experimental curve $\tau(p)$ (Fig. 4), τ_{rad} and α have evaluated

$$\tau_{\text{rad}} = (115 \pm 10) \text{ ns}, \quad \alpha = 4 \cdot 10^{-3} \text{ torr}^{-1} \text{ ns}^{-1}.$$

The value obtained for τ_{rad} correlated very well with the value $(120 \pm 10) \text{ ns}$ measured by the same method in a discharge [2].

The high intensity of laser-excited luminescence as compared to that of the ordinary one has made it possible to investigate the concentration of radicals in the $a^3\Pi_u$ state according to the power density of the IR field, and to evaluate the threshold of their formation (Fig. 5). At high intensities of the IR field $[C_2] \sim I_{\text{las}}^{2.5}$. At intensities below $2.5 \cdot 10^8 \text{ W/cm}^2$ their concentration falls off sharply, faster than $I_{\text{las}}^{1.4}$. More precise evaluation of the approach to threshold is difficult because of the spatial inhomogeneity of laser beam varying from pulse to pulse, and its associated variability of experimental results on approach to the threshold.

3. Estimation of C₂- and C₂*-Concentrations

According to the data obtained the radical concentration in the lower state $a^3\Pi_u$ -[C₂] is much higher than that in the excited state $d^3\Pi_g$ -[C₂*]. Comparing

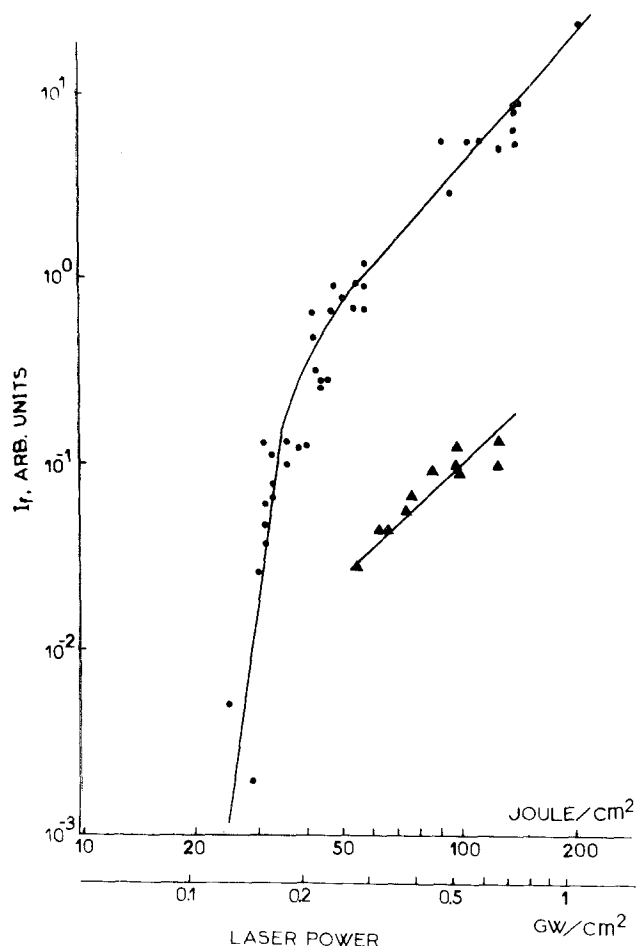


Fig. 5. Dependence of C₂*-radical luminescence intensity on IR field power density. (● Luminescence excited by dye laser radiation, ▲ ordinary luminescence) $P_{C_2H_4} = 2 \text{ torr}$

the intensity of spontaneous luminescence in IR photolysis I_2 with that of laser-excited luminescence I_1 we may get a quantitative estimate for the concentration ratio.

If the absorption of a transition excited by a dye laser is under saturation, I_1 equals

$$I_1 = \frac{h\nu}{\tau_{\text{rad}}} \cdot A \cdot [C_2] \cdot \frac{1}{2} \cdot \frac{Z_{\text{exc}}(a^3\Pi_u)}{Z_{\text{total}}(a^3\Pi_u)}, \quad (3)$$

where A is a geometrical factor; the factor 1/2 arise from the fact that in strong saturation one half of all molecules, which can absorb the dye laser radiation, is in the upper state; $Z_{\text{exc}}(a^3\Pi_u)$ is the number of rotational states involved in absorption; $Z_{\text{total}}(a^3\Pi_u)$ is the number of populated vibrational-rotational states of the electron state $a^3\Pi_u$.

Since in our experiments we excited the rotational sublevels with $J=12, 13, 14$ of the transition $(0, 0)$, we can easily find that $Z_{exc}(a^3\Pi_u)=81$. Assuming that the distribution over vibrational-rotational levels is Boltzmann's distribution with the characteristic temperature T we have for $Z_{total}(a^3\Pi_u)$

$$Z_{total}(a^3\Pi_u) = \sum_{J,v} (2J+1) \cdot \exp\left(-\frac{BJ(J+1) + \omega(v+\frac{1}{2})}{\kappa T}\right), \quad (4)$$

where B is the rotational constant which is 1.8 cm^{-1} , ω is the vibrational constant which equals 1641 cm^{-1} . If $B \ll \kappa T \ll \omega$, we have

$$Z_{total}(a^3\Pi_u) = \sum_{J=0}^{J_{max}} (2J+1) \simeq J_{max} + J_{max}(J_{max}+1), \quad (5)$$

where J_{max} may be determined from the relation

$$B \cdot J_{max}(J_{max}+1) = \kappa T_{rot}. \quad (6)$$

When

$$J_{max} \gg 1, \quad Z_{total}(a^3\Pi_u) = \frac{\kappa T_{rot}}{B}.$$

Hence,

$$I_1 = \frac{h\nu}{\tau_{rad}} \cdot A \cdot [C_2] \cdot \frac{81}{2} \frac{B}{\kappa T_{rot}}. \quad (7)$$

For the intensity I_2 we have

$$I_2 = \frac{h\nu}{\tau_{rad}} \cdot A \cdot [C_2^*] \frac{Z_{observ}(d^3\Pi_g)}{Z_{total}(d^3\Pi_g)}, \quad (8)$$

where $Z_{observ}(d^3\Pi_g)$ is the number of vibrational-rotational sublevels of the state $d^3\Pi_g$ in which fluorescence is registered, $Z_{total}(d^3\Pi_g)$ is the total number of populated vibrational-rotational sublevels of the $d^3\Pi_g$ state.

Since in our experiment we registered almost all fluorescent radiation of C_2^* -radical,

$$Z_{observ}(d^3\Pi_g) = Z_{total}(d^3\Pi_g). \quad (9)$$

From this it follows that

$$I_2 = \frac{h\nu}{\tau_{rad}} \cdot A \cdot [C_2^*] \quad (10)$$

or

$$\frac{[C_2]}{[C_2^*]} = \frac{I_1}{I_2} \cdot \frac{2}{81} \frac{\kappa T_{rot}}{B}. \quad (11)$$

substituting the constants and considering that $I_1/I_2 \simeq 10^2$ we have

$$[C_2]/[C_2^*] \simeq T_{rot}. \quad (12)$$

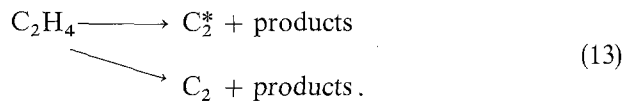
The results obtained do not enable us to determine exactly T_{rot} and hence $[C_2]/[C_2^*]$. But taking into account the fact that the states at least up to $J=14$ are populated, we have for the ratio $[C_2]/[C_2^*]$ the value of not less than $5 \cdot 10^2$.

To evaluate $[C_2]$, absolute calibration of the recording system was done using a dye laser pulse with a known energy. Measuring the pulse energy of laser-excited luminescence and taking into account the quantum yield of luminescence, which at a given pressure is equal τ_{rad}/τ , we can evaluate $[C_2]$ at the instant of excitation.

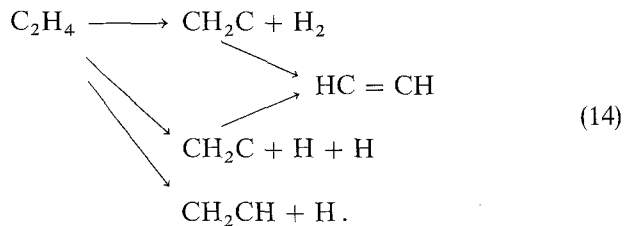
According to the estimates under the conditions specified above and at the IR field power density of 10^9 W/cm^2 the concentration of radicals $[C_2]$ in the states $a^3\Pi_u$ reaches 10^{+14} cm^3 . The ethylene pressure being 2 torr, this accounts for 0.15% of the total number of molecules in cm^3 . The density being $5 \cdot 10^9 \text{ W/cm}^2$, the radical concentration makes up to 10% of the number of C_2H_4 molecules.

4. Discussion

The results obtained show that the concentration of radicals in lower electron states is very high. Thus, the C_2 -radical is the main primary product of IR photolysis which follows the scheme



This scheme, as indicated in [1], differs greatly from that of UV photolysis [6]



From this it follows that the mechanisms of photolysis by photons of high (UV) and low (IR) energies differ essentially, although the final product in the both cases is acetylene.

The fact that the lifetime of excited C_2 -radicals is much shorter than the time of luminescence allows the study into the kinetics and mechanism of their formation. The experiments on observation of lumin-

escence excited by laser pulses of various duration (from 60 ns to 3–4 μs on base) show that the length of the luminescence pulse equals that of the laser pulse. This suggests that a fairly intense IR field is necessary for the formation of C₂-radicals, irrespective of whether they arise directly under the action of the field or from molecular collisions in the field. In the second case, like for molecules of dichlorethylene [5], a leading role plays the “tail” of the laser pulse.

There is another possibility for the formation of electron-excited radicals from secondary processes, for instance, during collisions of unexcited radicals with one another or with vibrationally excited molecules of ethylene. Since the dissociation fragments may have a large storage of kinetic energy, the probability of such excitation throughout a laser pulse may be rather high. It is clear, however, that luminescence pulse decay would be determined by the cooling time of radicals rather than by the laser pulse duration. Such a mechanism therefore is improbable.

The high sensitivity of the method of laser-excited luminescence has enabled us for the first time to measure precisely the threshold of occurrence of primary dissociation products. For the C₂-radical this threshold lies in the range of 150 ÷ 250 Mw/cm².

The values of threshold obtained are several times smaller than those determined by final products of dissociation [4]. This is associated with both the uncertainty in determining the threshold by dissociation products and the uncertainty in the volume of the dissociation zone. The correlation between threshold values by radical luminescence and by laser-induced luminescence is rather satisfactory (Fig. 5), though in the first case the threshold is determined only by the sensitivity of recording system.

The experiment has also enabled us to clarify the character of approach to threshold. Since the laser radiation was multimode, the character of change of [C₂], as the incident energy approached its threshold values, depended mainly on the number of modes in which it exceeded the threshold due to fluctuations on the value of incident energy. Therefore the relation [C₂] ~ I_{las}^{1.4} may substantially differ from the real one which must depend on I_{las} much stronger.

To have the character of approach to threshold determined more precisely, the TEM₀₀ mode of CO₂-laser radiation must be used.

Conclusion

1) The method of laser-excited luminescence has been used to study the products of IR photolysis of ethylene, that is C₂-radicals in the lower electronic state. It has been proved that the concentration of these radicals is 5 · 10² times higher than the number of excited C₂*-radicals and according to energy density may range from 0.1 to 10% of the total number of ethylene molecules. Thus it has been ascertained that the C₂-radical is the main product of IR photolysis.

2) The dependence of C₂-radical concentration on IR field energy density has been measured, the threshold of its formation has been determined, the character of approach to threshold is being estimated.

Hence, the estimate for the threshold of formation of various primary IR photolysis products has demonstrated a high sensitivity of the method of laser-excited luminescence. In virtue of high frequency selectivity the method possesses great possibility to evaluate isotopic selectivity of dissociation in isotope separation. It enables us not only to evaluate the selectivity of yield of main primary products and to eliminate the complicated problem of taking account of secondary processes, but also to choose optimum acceptors for the resultant radicals and conditions under which the primary selectivity would be maintained in final products.

References

1. R. V. Ambartzumian, N. V. Chekalin, V. S. Letokhov, E. A. Ryabov: Chem. Phys. Lett. **36**, 301 (1975)
2. T. Tatarczyk, E. H. Fink, K. H. Becker: Chem. Phys. Lett. **40**, 126 (1976)
3. V. N. Bagratashvili, I. N. Knyazev, V. S. Letokhov, V. V. Lobko: Opt. Comm. (in press)
4. V. N. Bagratashvili, I. N. Knyazev, Yu. R. Kolomiisky, V. S. Letokhov, V. V. Lobko, E. A. Ryabov: Kvantovay elektronika (in press)
5. R. V. Ambartzumian, N. V. Chekalin, V. S. Dolzhikov, V. S. Letokhov, V. N. Lokhman: J. Photochem. **6**, 55 (1976)