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OPTICAL PROBING OF A PHOTODISSOCIATIVE LASER

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It was repeatedly suggested[1-3] that photodissociation of perfluoroalkyl iodides in the working cell of a pulsed laser operating at the iodine transition of $\lambda = 1.315\ \mu$ may result in a rapid heating of the gas up to temperatures where the controlling process is thermal dissociation of molecules forming unexcited iodine atoms (pyrolysis). The present paper reports on an attempt to observe this phenomenon experimentally by optical probing of the active medium in the absorption band of the working gas. The obtained time dependences of the optical density are complicated by thermal deformation of the band masking the onset of pyrolysis. The time dependences of temperature T(t) and CF_3I molecule concentration $\Delta n(t)$ are calculated for experimental values of pumping pulse parameters, assuming that heat exchange is sufficiently fast and is mainly due to vibrational-vibrational relaxation (equilibrium approximation). The onset of pyrolysis is indicated by a sharp increase in the slope of the $\Delta n_{\text{diff}}(t)$ curve. Termination of generation is observed about the same time (slightly earlier). If a sufficient quantity of buffer gas (argon) is introduced, the "pyrolytic" temperature is not reached within a pulse period and generation damps out slowly. The suggested method of analyzing the thermal regime of the laser is in agreement with the observed laser emission when buffer gas (argon) is introduced into the cell and also when C_3F_7I vapor is used as the working gas.

A beam of light passing through the active medium of a photodissociative laser (PDL) in the absorption band of the working gas in principle carries information about three different phenomena occurring in the active medium: (1) variation of concentration of working gas molecules (photodissociation, pyrolysis, etc.); (2) heating of the active medium resulting in deformation of the working gas absorption band contour; and (3) new products capable of absorption in this region of the spectrum.

The present research was attempted in the expectation to obtain at least qualitative data on the effectiveness of the above factors for the case of a PDL using perfluoroalkyl iodides (CF_3I and C_3F_7I)[1-3]. A PDL of this type is known to be mainly suitable for pulsed operation, since the lower laser level which is the ground state of iodine atoms ($5^2P_{3/2}$) is practically free of "leakage" (recombination of iodine atoms can be neglected) and the working gas molecules are expended irreversibly. Nevertheless the low value of radiative probability for the laser transition ($A = 7.7\ \text{sec}^{-1}$) makes this problem insignificant if the nonradiative mechanisms for populating the lower laser level are not too effective. In the case of perfluoroalkyl iodides the following two mechanisms are the most destructive to generation[2,3]:

1. Pyrolyisis of working gas molecules when heating is sufficiently rapid ("rocking" and breaking of the C-I bond):

$$RJ \rightleftarrows (RJ)^* \rightarrow R + J \quad (R = CF_3,\ C_2F_5 \text{ etc.}). \tag{1}$$

The temperature dependence of the rate of process (1) is determined by the factor $\exp(-E_{\text{act}}/RT)$ where the activation energy E_{act} seems to be close to the thermal effect ΔH of the reaction and equals 50–60 kcal/mole (in the case of CF_8I, $\Delta H = 57$ kcal/mole[4,5]).

2. Recombination mechanism accumulating molecular iodine, a strong quenching agent of $I(^2P_{1/2})$ atoms, investigated in detail in[3]. (The efficiency of this mechanism drops sharply with increasing temperature[6,7].)

The evaluation of the effect of these mechanisms can be aided by comparing the PDL energy output with the depletion of working gas molecules for the same period of time.

Optical probing along the laser axis is difficult in view of the high pump light absorption cross sections. In the present experiment the laser was probed in a transverse direction along the laser cell diameter as shown in Fig. 1. The uniformity of diameter-averaged probing results and laser-output energy values was achieved by placing a rectangular diaphragm, limiting the generation region, inside the resonator (Fig. 1).

EXPERIMENTAL TECHNIQUE

The experimental setup included a laser with an 8-lamp illuminator and plane dielectric mirrors, a synchronized source of the probe radiation, and the recording equipment (photomultipliers, oscilloscopes, and a calorimeter). A capacitor bank was used to power the pump lamps. The discharge time measured at 0.35 amplitude was of the order of 120 μ sec, the emission brightness temperature T_{brt} was ~10,300°K at maximum, and the reflector efficiency

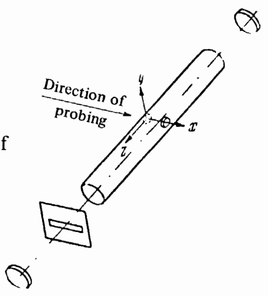

FIG. 1. Diagram of optical probing of of a PDL cell.

$\eta = P_{cell}/P_{lamp} = 0.35$ (P_{cell} is the light flux incident on the cell and P_{lamp} is the light flux emerging through the surface of all lamps). For the sake of convenience in computing losses the windows at the cell end faces were inclined ~15°. Quartz windows ~10 mm in diameter were fused to the lateral surface of the cell along its diameter and opposite corresponding holes in the reflector to probe the active medium. The probing radiation penetrated the active medium and was focused at the input slit of a DMR-4 monochromator (the experiments were performed with both magnification and reduction of the image). The probing radiation in the form of a flat-top pulse up to 200–400 μsec long was also recorded with an FÉU-18A photomultiplier on the screen of an OK-17M oscilloscope (Fig. 2). A 20–40 Å pass bandwidth of the monochromator was used (the width of the absorption bands of the working gases is ~400 Å at room temperature).

DISCUSSION OF RESULTS

Optical probing in various regions of the working gas absorption band should yield completely identical plots of the time dependence of RI molecule concentration, provided the vibrational temperature corresponding to the vibrations of the C - I bond does not vary in time during the PDL pumping process, or the process does not accumulate products capable of a sufficiently strong absorption in the same spectral region as the working gas molecules (RI).

We used the experimental data to compute the effective molecular concentration losses Δn_{eff} for various time instants:

$$\Delta n_{\text{eff}}(t, \lambda) = \frac{1}{\sigma_\lambda^0 d} \ln \frac{I(d, t, \lambda)}{I(d, 0, \lambda)}, \qquad (2)$$

where σ_λ^0 is the absorption cross section of the probing radiation of wavelength λ at the initial (room) temperature (the measurements were performed with an SF-4 spectrophotometer[1]), and I(d, 0, λ) and I(d, t, λ) are the intensities of the probing radiation in the direction of the x axis (Fig. 1) at the exit from the active medium (i.e. at x = d, where d is the cell diameter) corrected for the time dependence of the radiation source itself. The time is reckoned from the beginning of pumping. The time dependence of pumping is given in Fig. 4 b below.

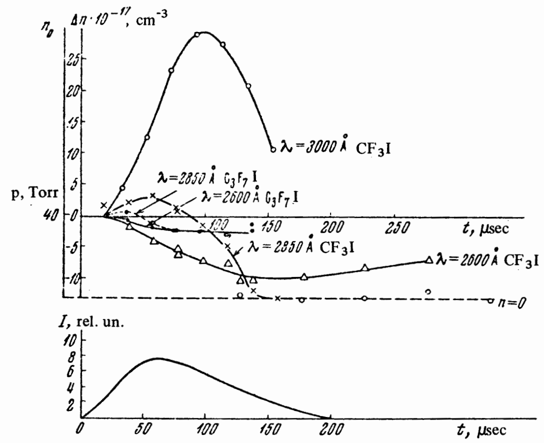

FIG. 2. The function Δn_{eff} (t, λ) for CF_3I and C_3F_7I at an initial pressure of 40 Torr. (In the computation of Δn_{eff} it was difficult to take into account the small variation of this quantity in the time interval from 0 to 20 μsec; it is therefore not reflected in the above curves).

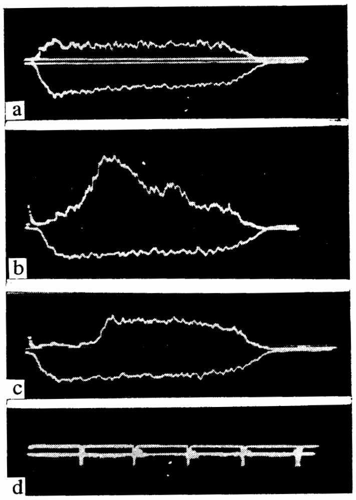

FIG. 3. Oscillograms of the probing signal at initial CF_3I vapor pressure of 40 Torr and wavelengths of 2600 Å (b) and 2850 Å (c); a – time dependence of the EV-45 source itself with a supplementary line; d – timing marks at 100 μsec intervals. The negative pulse is a reference channel signal. The pumping and probing pulses are started simultaneously.

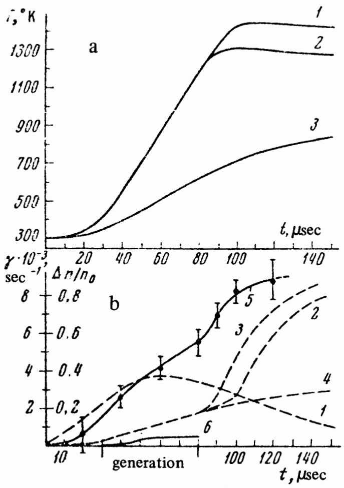

FIG. 4. Time dependences illustrating the decomposition of the working gas (CF_3I) and the thermal regime in the PDL. a – curves 1–3 are plots of T(t) in "equilibrium" approximation: without addition of argon and with the value of A equal to 10^{13} sec^{-1} (1) and 10^{14} sec^{-1} (2), and for a ratio of Ar to CF_3I of 10:1 (3). b – curve 1 is a plot of γ(t) computed taking reflector efficiency into account from measurements of brightness temperature of pump lamps and CF_3I absorption cross section at room temperature (in the case of an optically thin medium γ(t) seems to be weakly dependent on temperature); curves 2 and 3 are computed functions $\Delta n_{diff}(t)/n_0$ for A = 10^{13} sec^{-1} (2) and A = 10^{14} sec^{-1} (3); curve 4 is the function $\Delta n_{diff}(t)/n_0$ for argon to CF_3I ratio of 10:1 (purely photodissociative decomposition of CF_3I); curve 5 is the function $\Delta n_{eff}(t, \lambda_{max}^0)/n_0$ for an initial CF_3I pressure of 20 Torr and λ = 2600 Å; curve 6 is the function $\Delta n_{gen}(t)/n_0$ obtained from the same experiment as curve 5.

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[1] The measured absorption spectra of CF_3I and C_3F_7I molecules are in agreement with the data in [8,9].

The experiment showed that the functions $\Delta n_{\mathrm{eff}}(t)$ differ quite sharply in various regions of the absorption band of the CF_3I molecule. Less distinct is the difference in the function $\Delta n_{\mathrm{eff}}(t)$ for various wavelengths in the case of the C_3F_7I. Figure 2 shows the experimental functions $\Delta n_{\mathrm{eff}}(t)$ for the central region (2600 Å) and for the long-wave wing (2850 and 3000 Å) of the absorption bands of CF_3I and C_3F_7I molecules. The accumulation of absorbing products accompanying photodissociation of RI molecules is not a probable cause of the lack of any similarity between the curves. Both the radicals and molecules of the C_2F_6 type formed in secondary processes and I_2 molecules at near-room temperatures show a negligible absorption in the spectral range of 2300–3000 Å. Even with heating to 1000–1500°K their absorption in this range can barely rise enough to explain the behavior of the curves in the time interval from $t = 0$ to $t \sim 100$–$150\ \mu$sec.

At the same time the probing of CF_3I, beginning with approximately 100–150 μsec, revealed a gradual and sometimes even fairly sharp increase of the optical density of the active medium at $\lambda \leq 2600$ Å (Fig. 3). The nature of this absorption is not clear. It may possibly be due to the accumulation of "hot" C_2F_6 molecules.

Let us consider how realistic is our model of the thermal deformation curves of the absorption band contour.

The "hot" particles in the active laser medium are basically due to two processes: photodissociation of the working gas molecules supplying the "hot" radicals and recombination of the radicals forming "hot" $R_2(R - CF_3, C_3F_7)$ molecules. Owing to the quasi-stationary concentration of the radicals reached in a few μsec under laser conditions in view of the constant recombination rate of 3.9×10^{-11} cm^3-sec[10,11], there is on the average one act of recombination of radicals for every two acts of dissociation of the working gas molecules. In the case of CF_3I molecules for example, computation of the energy emitted by these two processes during the time interval of a single dissociation act yields a value of ~76 kcal/mole (of this about 28 kcal/mole is due to photodissociation and 48 kcal/mole to recombination of radicals[12]). Other possible processes can emit much less energy in this time; their rates and (or) thermal effects are low.

In terms of decreasing thermal contribution, the next process appears to be that of quenching excited iodine atoms[13-15]; this competes with the generation process and accelerates as the latter attenuates (in contrast to all other relatively weak processes, such as iodine atom recombination[6,7,16] or interaction of radicals with iodine molecules of this type $CF_3 + I_2 \rightarrow CF_3I + I$[17,18], that slow down on heating). The rapid energy transfer from the "hot" molecules (R and R_2) to the working gas molecules proceeds via vibrational-vibrational relaxation since the frequencies of the majority of RI type molecules of the working gas (excluding the frequencies of vibrations involving the C-I bond) are close to the frequencies of the corresponding vibrations of particles R and R_2[19,20].

A convenient and apparently adequate approximation to the thermal regime of perfluoroalkyl iodide PDL is a model with an equilibrium energy distribution among the vibrational degrees of freedom of working gas molecules. These quickly acquire the bulk of thermal energy and determine the temperature of the active medium. It seems that a significant disruption of the equilibrium can occur only under conditions of low working gas pressure (of the order of 10 Torr), absence of buffering impurities, and very strong pumping. In this approximation the thermal regime of the laser can be described by the following system of equations, taking only the basic processes into account:

$$\frac{dn}{dt} = -n\left[\gamma(t) + A\exp\left(-\frac{E_{\mathrm{act}}}{RT}\right)\right] \tag{3}$$

$$\frac{dT}{dt} = n\left[\Theta'\gamma(t) + \Theta'' A\exp\left(-\frac{E_{\mathrm{act}}}{RT}\right)\right] \tag{4}$$

where n and T are the concentration and temperature respectively of the working gas, $\gamma(t)$ is the probability of photodissociation of a working gas molecule per second forming an excited iodine atom (convolution of absorption cross section spectrum and spectral density of pumping photon flux), A is a coefficient of the exponential term in the constant-rate expression of process (1), R is the universal gas constant, $\Theta' = \Theta_2 + \frac{1}{2}\Theta_3 + \kappa\Theta_4$, $\Theta'' = \Theta_1 + \frac{1}{2}\Theta_3$,

$$\Theta = \Delta H \Big/ \sum_k (c_v)_k n_k, \tag{5}$$

Θ is the mean variation of active medium temperature due to a single elementary act in pyrolytic (Θ_1) and photodissociation (Θ_2) processes of initial molecules, recombination of radicals (Θ_3), and quenching of excited iodine atoms (Θ_4), ΔH is the corresponding thermal effect in cal/mole, $(c_V)_k$ is the molar heat capacity of the kth species of the active medium particles, and n_k is their concentration. Under conditions typical of this type of PDL the termination of generation usually occurs with a relatively low degree of decomposition of the working gas and thus no excessive error can result from limiting the summation in (5) to the working and buffer gas molecules in their initial concentrations and from neglecting the function $c_V(T)$. The quantity κ is the relative (per a single act of dissociation) yield of the quenching process. In a PDL κ grows monotonically in time (from zero at $t = 0$ to values $\kappa \geq 1$ after suppression of generation), the faster the lower the resonator Q. On the whole the term $\kappa\Theta_4$ is a small correction for the "generation" stage of the pumping pulse. The function $\kappa(t)$ can be neglected at this stage, setting $\kappa = 0.5$.

Under the experimental conditions involving pure iodine trifluoromethane, the relations $\Delta n_{\mathrm{diff}}(t)$ and $T(t)$ shown in Fig. 4 were computed by numerical integration of (3) and (4). The necessary values of the function $\gamma(t)$ were determined from measurements of the brightness temperature of the pulse lamps, efficiency of the reflector (taking the diameters of the cell and lamps into account), the CF_3I absorption spectrum at room temperature, and oscilloscopic data determining the time dependence. The active medium was assumed to be optically thin. The following values were used: heat capacity $c_V = 17$ cal/mole, activation energy $E_{\mathrm{act}} = \Delta H = 57$ kcal/mole, and coefficient $A = 10^{13}$ and 10^{14} sec^{-1}[4].

It follows from the curves T(t) (Fig. 4) that within an "equilibrium" approximation the temperature of the working gas molecules rises quickly enough to produce a significant thermal deformation of the CF_3I absorption band in several tens of μsec. We must only remember here that the frequency of valence vibration of the C-I bond is 283 cm^{-1} (ν_3) and the frequency of the twice degenerate "rocking" of this bond is 265 cm^{-1} (ν_6)[19], i.e., both frequencies are sufficiently low. In particular the sharply pronounced "reverse" course of the Δn_{eff} curve for λ = 3000 Å and t from 0 to 80 μsec can be attributed to the rapid rise in the contribution from the high vibrational levels to the absorption band.

In the case of CF_3I the center of the absorption band lies at $\lambda = \lambda^0_{max}$ = 2600 Å at the initial temperature $T_0 \sim 300°K$. It is obvious that the corresponding value of the absorption cross section $\sigma(\lambda^0_{max}, T_0)$ is almost completely determined by the contribution from the ground and the first excited levels of frequencies ν_3 and ν_6. However as the temperature rises to 1000—1500°K some contribution to absorption at $\lambda = \lambda^0_{max}$ can come from even higher vibrational levels basically of the same frequencies. At the present time it is not possible to obtain a theoretical evaluation of the function $\sigma(\lambda^0_{max}, T)$. Experimental determination under stationary conditions is unfeasible due to the rapid thermal dissociation of the molecules. Comparing the time-dependent functions $\Delta n_{eff}(t, \lambda^0_{max})$ and $\Delta n_{diff}(t)$ shown in Fig. 4 b we can assume that the quantity $\sigma(\lambda^0_{max}, T)$ decreases with increasing temperature (in contrast to $\sigma(\lambda, T)$ at λ = 3000 Å, for example) since

$$\frac{\sigma(\lambda^0_{max}, T)}{\sigma(\lambda^0_{max}, T_0)} = \frac{n_0 - \Delta n_{\text{eff}}(\lambda^0_{max}, T)}{n_0 - \Delta n_{\text{diff}}} < 1$$

(n_0 is the initial concentration of CF_3I molecules).

This result is understandable if the contribution of excited vibrational levels to the quantity $\sigma(\lambda^0_{max}, T)$ cannot compensate for the reduction of this quantity due to a rapid depletion of the lower and first excited levels at ν_3 and ν_6. On the other hand a correction to $\Delta n_{eff}(\lambda^0_{max}, T)$ eliminating the thermal contribution and computed by taking the population variation of only the lower levels into account turned out to be too large. Consequently the absorption from excited vibrational levels at $\lambda = \lambda^0_{max}$ is not weak.

The instant of sharp increase in the rate of pyrolysis is hardly noticeable in the curves $\Delta n_{eff}(t, \lambda^0_{max})$ (Fig. 4 b). This can be attributed to the compensation of two opposed phenomena. If Δn_{temp} denotes the contribution to Δn_{eff} from temperature change, we have

$$\Delta n_{\text{eff}} = \Delta n_{\text{temp}} + \Delta n_{\text{diff}}$$

The sharp increase of the pyrolysis rate is accompanied by a rise in Δn_{diff}, but at the same time the rise of Δn_{temp} ceases because of the simultaneous cessation of T increase (since $\Theta'' < 0$ in the case of CF_3I). The conclusion that the thermal model of iodide PDL based on (3) and (4) is qualitatively correct is further confirmed by experiments in which Ar was added to the working gas. The addition of Ar in the ratio of 10 : 1 prevents the onset of critical temperature $T_{cr} = E_{act}/R \ln(A/2\gamma)$ (determined by the condition that generation terminates only due to pyrolysis), as follows from Fig. 4, and pyrolysis does not occur. According to the above the experimental function $\Delta n^*_{eff}(t, \lambda^0_{max})$ is now somewhat less steep. However the behavior of generation changes significantly. In the case of pure iodine trifluoromethane generation terminates sharply at t ~ 70—90 μsec, i.e., before T_{cr} is reached (see Fig. 4). The number of molecules per 1 cm^3 dissociated at that time with the formation of iodine atoms that underwent stimulated emission (Δn_{gen}) amounts to at most 30—40% of the total number of dissociated molecules (Fig. 4 b, curve 6). The number of such molecules was determined from the total energy according to the formula

$$\Delta n_{\text{gen}} = \frac{3}{2} \frac{E_{\text{gen}}}{k h\nu V}$$

where E_{gen} is the PDL energy output, $h\nu$ is the photon energy of laser emission, k is the ratio of useful emission losses (absorption in the calorimeter) to total losses, the coefficient $3/2$ is determined by the statistical weight of the laser levels, and V is the volume of the generating region of the active medium.

According to Fig. 5 (CF_3I) and Fig. 6 (C_3F_7I), the addition of argon delays the onset of generation (apparently because of the additional broadening of the line contour). However attenuation is also much slower in this case so that the energy output increases, especially in CF_3I (for an initial CF_3I pressure of 20 Torr), and seems to be limited by the recombination mecha-

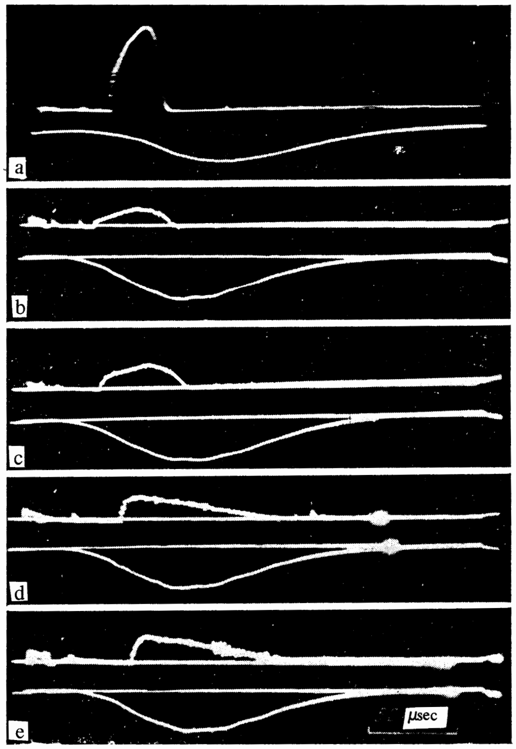

FIG. 5. Oscillograms of CF_3I PDL emission (20 Torr) for various argon pressures: a – 0, b – 55, c – 100, d – 500, e – 700 Torr. In the case of oscillograms b, c, d, and e the sensitivity of the receiver is the same and is lower than in the case of oscillogram a. The second beam recorded the pumping pulse; its maximum corresponds to T_{brt} = 10,300°.

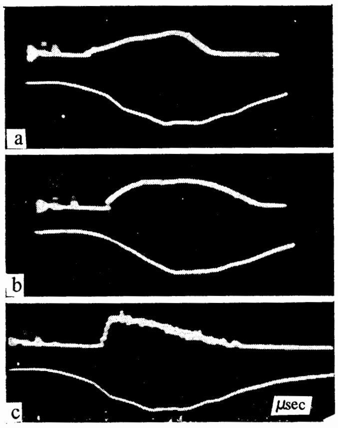

FIG. 6. Oscillograms of C_3F_7I PDL emission (20 Torr) for argon pressures of 0 (a), 100 (b), and 500 (c) Torr. Pumping parameters are the same as in Fig. 5.

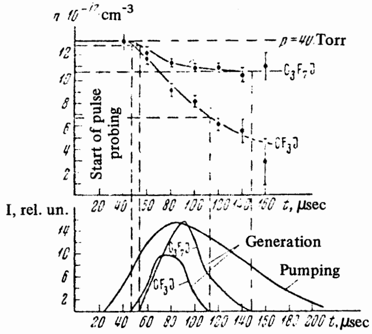

FIG. 7. The function $\Delta n_{\text{eff}}(t, \lambda^0_{\text{max}})$ (initial pressure of CF_3I and C_3F_7I is 40 Torr, $\lambda^0_{\text{max}} \approx 2600$ Å).

nism of generation quenching. The addition of argon in a C_3F_7I PDL has a weaker effect (Fig. 6).

The difference in the photolysis kinetics of CF_3I and C_3F_7I molecules is clearly apparent when an optically thick medium is used. Figure 7 shows the time dependence of the values of Δn_{eff} averaged over the cell diameter for CF_3I and C_3F_7I molecules when the optical density is sufficiently high and the energy absorbed within the cell is almost the same in both cases. We can conclude with an accuracy defined by the difference in thermal deformation of the absorption bands that there is a significant difference in the degree of pyrolytic decomposition of these molecules. A lower degree of working gas decomposition averaged over the cell diameter (or a smaller extent of "wear" of the active medium) in the case of C_3F_7I can be due to the larger (by a factor of two approximately) thermal capacity of these molecules which respond to the pyrolytic effect at a higher degree of dissociation of the working gas. This is probably the reason (as well as the higher photon absorption cross section) why C_3F_7I has a higher energy yield than CF_3I as shown by Pollack[21].

We take this opportunity to thank S. B. Kormer for a very stimulating discussion about the problems considered in this paper.

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