

Experimental Study of Laser-Induced Thermal Ignition in O₂/O₃ Mixtures

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Abstract. O₂/O₃ mixtures are ignited by absorption of laser pulses of a TEA CO₂ laser along the axis of a cylindrical cell. The dependence of the radial propagation of the O₃ decomposition, detected by uv absorption of the ozone, on laser fluence and on O₃ concentration is investigated. Oscillations of the signals are identified to be the first radial acoustic mode of the cell. For mixtures of 0.35 bar and 0.70 bar total pressure and O₃ percentages within 20–50%, the ignition limit is in the order of 0.1–0.2 J/cm³ (absorbed energy density). These values are in reasonable agreement with the results of the corresponding numerical simulations.

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Gas-phase reactions, for instance explosions, may be initiated by exposure of the combustible gas mixtures to laser pulses. One method utilizes laser generated discharges [1–4]. A detailed modelling of these ignition processes has to take into account the system of chemical reactions, the hydrodynamics and the plasma. By avoiding laser sparks the modelling is reduced to the solution of the conservation equations for mass, momentum, energy, and the mass fractions of each of the chemical species. In suitable experiments energy is deposited in a gas mixture by absorption of laser light in one of its components [5–10].

At present, numerical simulations of laser-induced ignition processes are tested for an ozone decomposition flame because of its small system of chemical reactions [11]. The calculations are carried out in one spatial dimension, i.e. in spherical or cylindrical symmetry. For the corresponding experiment the cylindrical symmetry was chosen, because it seems to be realized by simpler means than the spherical one.

Ozone has strong absorption bands in the range of the (00⁰1)–(02⁰0) emission of a CO₂ laser [12, 13]. Thus there is no need of additional absorbers in the gas mixture and the gas may be heated by absorption of slightly focused CO₂ laser pulses at the axis of a cylindrical vessel filled with a given O₂/O₃ mixture.

Provided that sufficient energy is deposited and the heating is homogeneous, O₃ decomposition starts into the radial direction uniformly over the whole axis. Because of its strong uv absorption [14, 15] O₃ is detectable by absorption of the light of a HgXe high pressure lamp.

1. Experiment

O₃ decomposition is initiated by pulses of a Lumonics TEA 801–A CO₂ laser, operating at the 9P20 line at $\lambda = 9.552 \mu\text{m}$ in multimode oscillation. The pulse consists of a leading spike of 0.2 μs half width (FWHM) containing about 50% of the energy and a decaying tail of approximately 3 μs duration. The laser light is focused with a concave spherical mirror along the axis of a glass cell that is fitted with KCl windows (Fig. 1). The cell axis forms an angle of about 5° with the optical axis of the laser. Therefore the beam profile shows optical aberrations at the beam waist and has more an elliptic shape than a spherical one. A circle, isohedral to the real profile has a mean diameter of $1.5 \pm 0.2 \text{ mm}$ along the cell axis. With pulse energies up to 0.7 J mean fluences of about 40 J/cm² were reached at the beam waist. Owing to multimode operation of the laser, the fluence is fairly constant over the whole

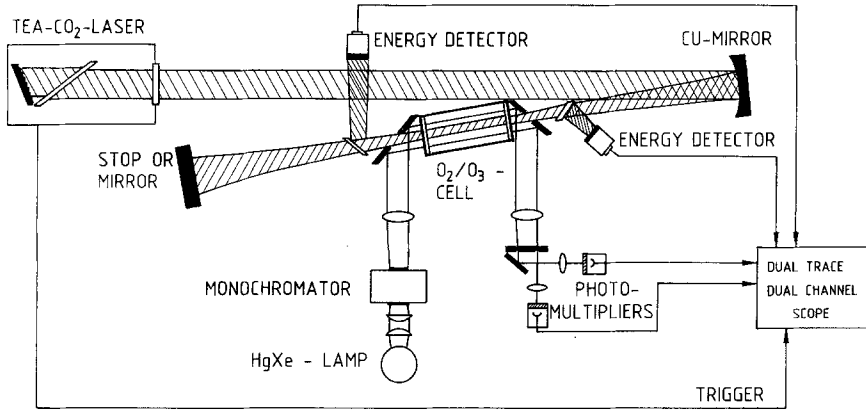


Fig. 1. Experimental setup

profile, neglecting statistical variations. A part of the laser radiation is coupled out in front of and behind the cell, and measured by two pyroelectric energy detectors. With regard to the reflectivity of the beam splitters and cell windows and the polarization of the laser light the absorbed energy is calculated.

The radial moving of the flame front is observed by uv absorption of O_3 at $\lambda = 312.6$ nm. For all mixtures under investigation the relative light intensity at this wavelength is in the range of some percent to 100% during O_3 decomposition, and therefore measurable without further improvement of the S/N - ratio. To that end a grating monochromator separates light of $\lambda = 312.6$ nm from the radiation of a HgXe lamp. The exit slit is imaged to the middle of the cell perpendicular to the cell axis. A double pin hole determines two traces parallel to the axis with a radial resolution of 1.5 ± 0.5 mm. The light intensity of the two beams is detected by photomultipliers (1P28A) and recorded by a dual trace oscilloscope (Tektronix 7623 A). If the two beams are chosen at different radii r_1 and r_2 , the radial propagation of the O_3 decomposition may be observed.

Ozone was produced by a silent discharge in a commercial ozonizer and adsorbed in silica gel at -77°C [16]. The total pressure of the O_2/O_3 mixtures was measured with a capacitance manometer (Baratron 221 A), the partial pressure of ozone by uv absorption at $\lambda = 312.6$ nm.

Preliminary investigations of the radial moving of the O_3 decomposition flame at varying O_3 percentages and laser fluences and of the ignition limit of O_2/O_3 mixtures at the total pressures $p_{\text{tot}} = 0.35$ bar and 0.70 bar, respectively, are reported.

2. Results and Discussion

2.1. The Propagation of the Decomposition Flame

Figure 2 shows a set of results for the ignition of O_2/O_3 mixtures of 23% O_3 at the total pressure $p_{\text{tot}} = 0.35$ bar.

The laser fluence varies between 3 and 37 J/cm^2 . Given is the transmitted light intensity ($\lambda = 312.6$ nm) following the laser pulse, and recorded simultaneously at two radial positions $r_1 = 6.2$ mm and $r_2 = 12.4$ mm. After the pulse a slight reduction of intensity is observed followed by an increase to the maximum value I_0 first at r_1 and subsequently at r_2 . On these signals periodic oscillations are superimposed with a greater amplitude for $I(r_1)$ than for $I(r_2)$. Probably these oscillations are due to acoustic resonances of the cell (Sect. 2.2).

Provided the deflagration occurs in cylindrical symmetry, the relation between I and the O_3 concentration $c(r)$ as well as the temperature T is

$$\log(I(v, T)/I_0) = -\varepsilon(v, T) \cdot c(r) \cdot L \quad (1)$$

L : cell length, v : wave number of the transmitted light, where

$$\varepsilon(v, T) = \varepsilon_a(v, T) + \varepsilon_b(v, T) \quad (2)$$

is an empirical Sulzer-Wieland expression for the molar absorptivity of ozone [15]. The two terms on the right-hand side of (2) are detailed in [15]. At $\lambda = 312.6$ nm $\varepsilon(v, T)$ rises strongly with increasing temperature.

For comparison with the experimental result in Fig. 2 ($F = 21 \text{ J/cm}^2$), the time development of the O_3 decomposition has been calculated with the computer program of Warnatz et al. [11] for the same mixture and absorbed energy. The shape of the theoretical source term has been assumed to be a Gaussian profile in the radial coordinate and a rectangular profile in time with a duration of $1 \mu\text{s}$. The results at the radius $r_1 = 6.2$ mm for the temperature T , the local O_3 concentration c and the relative transmitted light intensity I/I_0 , calculated by means of (1) and (2) are given in Fig. 3. The curves are smooth since the program utilizes the imposition of uniform spatial pressure dependence. Therefore acoustic resonances and other spatial pressure variations are not simulated.

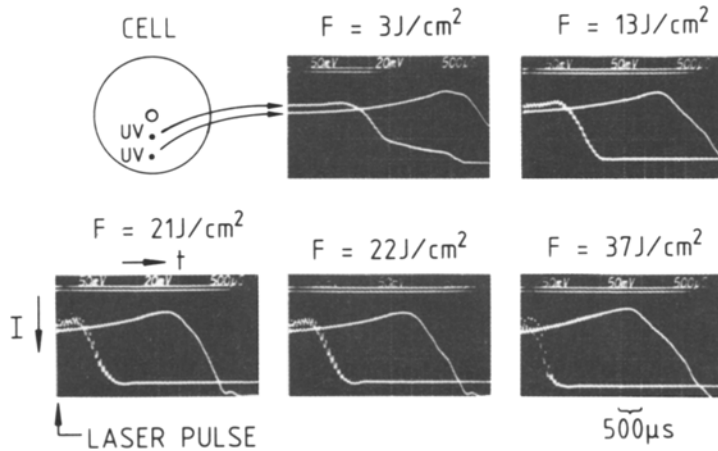


Fig. 2. Time dependence of transmitted uv intensity at $r_1=6.2$ mm and $r_2=12.4$ mm following CO₂ laser pulses of different fluences F ; O₂/O₃ mixture with $p_{tot}=0.35$ bar and $\approx 23\%$ O₃

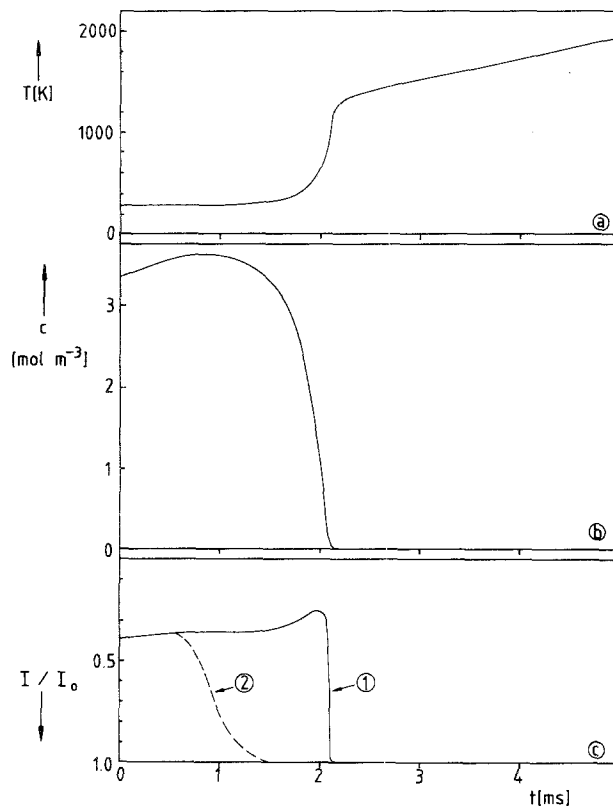


Fig. 3a-c. Numerical simulation of the O₃ decomposition, same mixture as in Fig. 2 ($F=21$ J/cm²); values at $r=6.2$ mm for (a) temperature T , (b) O₃ concentration c , (c) 1: transmitted light intensity I/I_0 , 2: smoothed I/I_0 from Fig. 2 ($F=21$ J/cm²)

At $t \approx 2$ ms, Fig. 3c shows an intensity dip and a steep increase to final intensity (curve 1), that are caused by the rise of $\epsilon(\nu, T)$ due to increasing temperature and by the decomposition of ozone. There are two differences between the theoretical and the smoothed experimental signal function (curve 2). First, the increase of the experimental signal is not as steep as that of the theoretical one, and second, it occurs at $t \approx 1$ ms, that

is, the propagation of the experimental flame to $r_1=6.2$ mm is faster by a factor of about two than that of the theoretical flame. Possibly accelerating effects of the spatial pressure fluctuations and the corresponding temperature variations on the velocity of the flame may contribute to this difference. The gentle increase of the experimental signals may be attributed to the radial dimension of the detection beams (diameter ≈ 1.5 mm) and possibly to a flame front that doesn't move exactly into the radial direction due to inhomogeneous ignition along the cell axis. In that case the location of the flame front depends on the longitudinal coordinate z and is given by $r+r'(z)$ with the mean radius r and a deviation term $r'(z)$. Referring to the time dependence of the experimental signals the following observations can be summarized:

(i) In all cases there is a time difference $\Delta t_b = t_3 - t_2 > 0$ between the end of the increase of $I(r_1)$ at t_2 and the intensity minimum $I_{min}(r_2)$ at t_3 . With the time difference Δt_c (observation iii) and Δt_b the upper limit of the deviation term $r'(z)$ of the flame front is estimated for all investigated mixtures to be 3 mm over the cell length of 61 mm.

(ii) The time difference $\Delta t_a = t_1 - t_0$ between the laser pulse at t_0 and the intensity minimum $I_{min}(r_1)$ at t_1 decreases for a constant O₂/O₃ mixture with increasing laser fluence F or absorbed energy density (Fig. 2). Furthermore, Δt_a decreases at constant F and p_{tot} with increasing O₃ percentage.

(iii) The time difference $\Delta t_c = t_3 - t_1$ between the minima of intensity at r_1 and r_2 seems to be independent of the laser fluence and the absorbed energy density (Fig. 2), and decreases with increasing O₃ percentage (Fig. 4).

Observation (ii) verifies qualitatively the existence of an induction period for the O₃ deflagration decreasing with increasing concentration of the reacting molecules and increasing temperature, that is, absorbed energy density in our case. From observation (iii) one

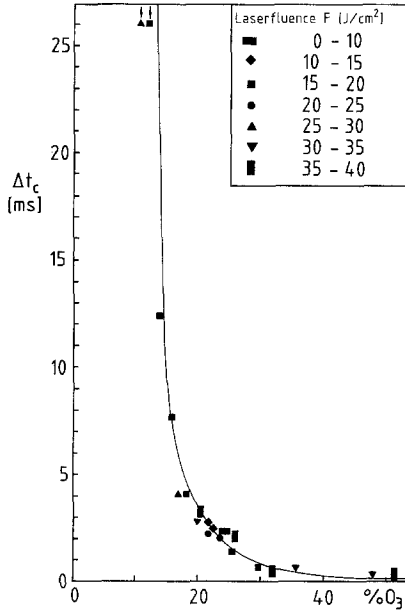


Fig. 4. Duration Δt_c (see text) of radial propagation of O_3 decomposition between r_1 and r_2 ; $p_{tot}=0.35$ bar

can conclude that the propagation of the decomposition flame outside the irradiated volume ($r > 4r_i$, r_i : radius of the irradiated volume) is not influenced by the ignition process itself but depends only on the composition of the mixture.

2.2. The Oscillations of Transmitted Light Intensity

In all cases oscillations of the transmitted light intensity have been observed during the period after the laser pulse where light was absorbed by the ozone not yet decomposed. For a given mixture the amplitude of the oscillations rises with increasing laser fluence, i.e. absorbed energy density (Fig. 2). Within the accuracy of measurement the period is $T_{exp}=83 \pm 3 \mu s$ during the time interval of intensity increase independent of the laser fluence and the composition of the investigated gas mixtures. Generally the oscillation of $I(r_1=6.2 \text{ mm})$ has an amplitude greater than that of $I(r_2=12.4 \text{ mm})$ and there is a phase displacement between them of exactly π . Obviously, the oscillations are caused by acoustic resonant modes of the cylindrical gas volume. Fig. 5 shows the onset of the oscillations after the laser pulse. The first dip of $I(r_1)$ has its minimum at $22 \mu s$ whereas the first dip of $I(r_2)$ has a double structure with minima at 42 and $70 \mu s$. These values are in good agreement with the duration of sound propagation that is calculated from the sound velocity of an ideal gas [17]

$$c = \Delta r / \Delta t = [(c_p/c_v) \cdot (RT/M)]^{1/2} \quad (3)$$

with the specific heats c_p and c_v , and the molar mass M ,

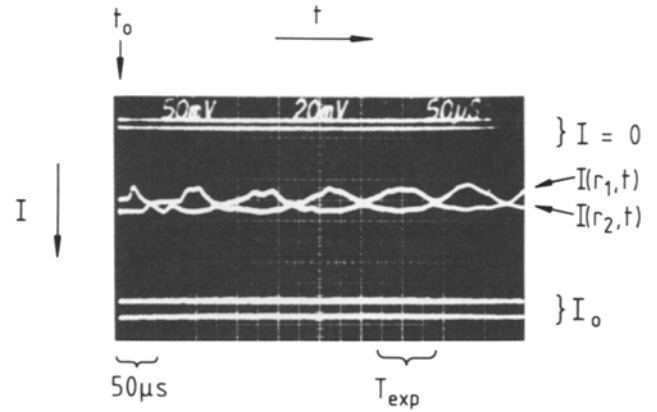


Fig. 5. Time dependence of transmitted uv intensity at $r_1=6.2 \text{ mm}$ (upper signals) and $r_2=12.4 \text{ mm}$ (lower signals) following laser pulse at t_0 ($F=34 \text{ J/cm}^2$); O_2/O_3 mixture with $p_{tot}=0.35$ bar and 21% O_3

of the given mixture. The temperature is assumed to be $T=300 \text{ K}$ since heating of the gas outside the irradiated volume by means of heat conduction is not efficient at the time scale under consideration. The results are: $\Delta t=20 \mu s$ for $\Delta r=6.2 \text{ mm}$, $\Delta t=40 \mu s$ for $\Delta r=12.4 \text{ mm}$ and $\Delta t=69 \mu s$ for $\Delta r=21.6 \text{ mm}$. The latter value corresponds to the sound propagation to $r_2=12.4 \text{ mm}$ with one reflection at the wall of the cell.

The agreement of the experimental time intervals, consisting of the duration of the molecular relaxation and the propagation of the sound wave, with the time intervals calculated only for sound propagation indicates a fast relaxation of deposited energy occurring possibly at higher molecular states with a duration of at most a few μs .

Since the cell and approximately the laser profile are of cylindrical symmetry, the pressure fluctuations p' are assumed to show no azimuthal but only radial and longitudinal dependence: $p'(r, z)$. Neglecting heat conduction, dissipation of energy via viscous effects and assuming only small fluctuations $p' \ll p_{tot}$, the solution of the conservation equations is [18]

$$p'(r, z, t) = \sum_{m,i} \{ A_{m,i} \cdot J_0(x_i r/r_c) \cdot \cos(m\pi z/L) \cdot \sum_u B_{m,i,u} [\cos(2\pi t/T_{m,i}) - \exp(-k_u t) - 2\pi \sin(2\pi t/T_{m,i}) / (T_{m,i} \cdot k_u)] \} \quad (4)$$

The spatial dependence is given in the radial direction by the Bessel functions $J_0(x_i r/r_c)$ with r_c being the cell radius and x_i the roots of the first-order Bessel function, and in the longitudinal direction by the trigonometric factors $\cos(m\pi z/L)$ with L being the cell length. The time dependence consists of exponentials, that are governed by the rate constants k_u of relaxation

of the upper molecular levels, and of trigonometric terms with the temporal period [18]

$$T_{m,i} = 2\pi \{c[(x_i/r_c)^2 + (m\pi/L)^2]^{1/2}\}^{-1}. \quad (5)$$

The temporal and spatial dependence of the pressure is $p(r, z, t) = p_{\text{tot}} + p'(r, z, t)$ and that of the partial pressure of ozone $x \cdot p(r, z, t)$ whereby x , the local mole fraction of the reacting ozone is assumed to be independent of the longitudinal coordinate z . With this the relative transmitted light intensity I/I_0 is given by

$$\log(I/I_0) = -\alpha x \left[p_{\text{tot}} L + \int_0^L p'(r, z, t) dz \right] \quad (6)$$

with α being the absorptivity of ozone. Because of the $\cos(m\pi z/L)$ term in (4) the integral in (6) cancels for all $m \neq 0$ and temporal oscillations of the transmitted intensity are observable only for the acoustic modes (m, i) with $m=0, i=1, 2, \dots$. With (3 and 5) the corresponding periods for all investigated gas mixtures are calculated to be in the range: $T_{0,1} = 91 \pm 3 \mu\text{s}$, $T_{0,2} = 49 \pm 2 \mu\text{s}$, $T_{0,3} = 34 \pm 1 \mu\text{s}$, etc. for $T = 300 \text{ K}$. The observed mean period $T_{\text{exp}} = 83 \pm 3 \mu\text{s}$ agrees reasonably with $T_{0,1}$, the first radial mode but is a little smaller possibly because of perturbations due to the flame propagation (e.g., the $T_{m,i}$ decrease with increasing temperature). Further reasons may be slow relaxations of the thermally occupied vibrational levels giving smaller dynamic heat capacities or the incorrectness of the assumptions leading to (4). For instance, the upper limit of the amplitude of the pressure fluctuations p' , deduced from Fig. 5 with the molar absorptivity $\varepsilon(v, T = 300 \text{ K})$, is 0.03 bar or about 10% of $p_{\text{tot}} = 0.35 \text{ bar}$, so that the assumption $p' \ll p_{\text{tot}}$ may be incorrect.

The spatial dependence of the first radial mode is given by the Bessel function $J_0(x_1 r/r_c)$. For r_1 and r_2 the amplitude of this mode is proportional to $J_0(x_1 r_1/r_c) = 0.57 > 0$ and $J_0(x_1 r_2/r_c) = -0.19 < 0$, respectively. This accounts for the higher amplitude of the oscillations of $I(r_1)$ compared to those of $I(r_2)$ and the phase displacement of exactly π between them.

2.3. Absorption of Laser Pulses

The portion of the laser energy absorbed in the O₂/O₃ mixture has been measured at small laser fluences for the investigation of the ignition limit and at higher fluences in the experiments dealing with the propagation of the ozone decomposition flame. The mean absorptivity α (base 10) of O₃ for the laser pulse is

$$\alpha = -[p(\text{O}_3) \cdot L]^{-1} \log(F_{\text{out}}/F_{\text{in}}), \quad (7)$$

where F_{in} and F_{out} are the incoming and outgoing fluences, respectively, and $p(\text{O}_3)$ is the partial pressure

of ozone. The result of the measurements is a dependence of α on the fluence F_{in} , the total pressure p_{tot} and possibly the O₃ partial pressure $p(\text{O}_3)$. For $p_{\text{tot}} = 0.70 \text{ bar}$ and $F_{\text{in}} \lesssim 2 \text{ J/cm}^2$ the absorptivity is $\approx 0.7 \text{ atm}^{-1} \text{ cm}^{-1}$ and it decreases to $\approx 0.2 \text{ atm}^{-1} \text{ cm}^{-1}$ at $F_{\text{in}} = 40 \text{ J/cm}^2$. For $p_{\text{tot}} = 0.35 \text{ bar}$ and small fluences α is smaller by a factor of two compared to $p_{\text{tot}} = 0.70 \text{ bar}$ but has about the same order at $F_{\text{in}} = 40 \text{ J/cm}^2$. At both total pressures there is some evidence for a slight decrease of α with increasing O₃ percentage but this is partially obscured by the jitter of the results. The observed absorption coefficients are smaller than that of O₃ diluted in air at $p_{\text{tot}} = 1 \text{ bar}$ and $T = 300 \text{ K}$, measured with a cw-CO₂ laser presumably in the low intensity limit [19]. For the 9P20 line this value has been given by several authors to be in the range of $1.3 - 2.2 \text{ atm}^{-1} \text{ cm}^{-1}$ [19].

Additionally the absorbed energies were converted to the average number of photons absorbed by an ozone molecule in the irradiated volume during the laser pulse. This number rises with increasing fluences and at higher fluences the corresponding energy may be greater than the dissociation limit. However, following the theory of collisionless multiphoton dissociation of O₃ [20], a dissociation of O₃ at the 9P20 line of the CO₂ laser is unlikely using fluences such as those in this experiment [21].

This is assumed to be the case in the collision regime, too, since additional effects of collision broadened linewidths (e.g. $0.083 \text{ cm}^{-1} \text{ atm}^{-1}$ for air-broadened O₃-lines [22]) should be small compared to the intensity broadening, being greater than 0.5 cm^{-1} in this experiment [21]. Moreover there are relaxations by collisions with other molecules acting against the multi-photon absorption.

Excluding the dissociation, a fast relaxation process has to take place during the laser pulse to account for the high number of absorbed photons/molecule.

This relaxation process probably occurs at higher vibrational ozone levels by collisions with O₃ and O₂ molecules, respectively, since the relaxation of the $v=1$ levels of O₃ is relatively slow [23, 24] and therefore not efficient during a laser pulse of $\approx 1 \mu\text{s}$ duration. On the other hand, it is known that the probability of relaxation (for example, the $V-T$ processes) is proportional to the vibrational quantum number v and to $\exp(-B\omega^{2/3})$ with ω being the frequency difference of neighbouring vibrational levels [25]. Thus for higher v 's and due to the anharmonicity the probability should be enlarged. Furthermore, if vibrational excitation approaches the barrier of a bimolecular reaction the vibrational $V-T$ relaxation can be dramatically enhanced due to chemical affinity [25].

An experimental verification of a fast deactivation of vibrationally highly excited triatomic molecules is given by first direct measurements in the case of CS_2 and SO_2 [26]. For all investigated bath gases the average energy $\langle \Delta E \rangle$ transferred per collision from the highly excited molecules to the bath gas is roughly proportional to E^2 (E : average vibrational excitation energy). Thus, by similarity, for O_3 an increase of the deactivation rate of high vibrational levels may be possible.

An influence of the collision partners on the relaxation of O_3 may be concluded from the measured pressure dependence of the molecular absorptivity of ozone. The higher values of α observed at the greater total pressure $p_{\text{tot}}=0.70$ bar may be interpreted as molecular relaxation to absorbing O_3 energy levels being more efficient at higher pressures of the collision partner O_2 . The decrease of α with increasing fluence can be caused by multi-photon absorption (MPA) or saturation processes. MPA typically takes place in greater molecules, whereas triatomic molecules are chiefly affected by saturation effects [27]. In both cases an overall decrease of α with increasing fluence is observed [27].

2.4. The Ignition Limit

The ignition limit of gas mixtures of $p_{\text{tot}}=0.35$ and 0.70 bar having varying O_3 percentage has been investigated in the following manner. Beginning with small fluences a given mixture is irradiated with up to 4 pulses and, provided no ignition occurred, the fluence is raised by removing partial reflectors from the beam or raising the laser high voltage. Figure 6 shows the absorbed energy densities, being average values along the cell axis. These values are calculated from absorbed energies for the fluence setting leading to ignition and the trial just before that does not lead to ignition. For an ozone percentage $20\% < x < 50\%$ the measured ignition limit is in the range of $0.1 - 0.2 \text{ J/cm}^3$ and of the same order as the theoretical results of Warnatz et al. [11]. Below $x=20\%$ the ignition limit increases and reaches about 1 J/cm^3 at $x=10\%$. In this range the flame velocity of stationary ozone decomposition flames vanishes [28] since the O_3 percentage is not sufficient to sustain a propagating flame. The increase of the ignition limit possibly reflects a "forced decomposition", i.e. heating the irradiated gas volume to a temperature higher than the ignition temperature for $x > 20\%$ overbalances the deficiency in O_3 percentage and the resulting O-atom concentration suffices to decompose the O_3 in the whole gas volume. Below $x=10\%$ no O_3 decomposition takes place at laser fluences up to 40 J/cm^2 , possibly since these fluences don't suffice to induce a forced decomposition. How-

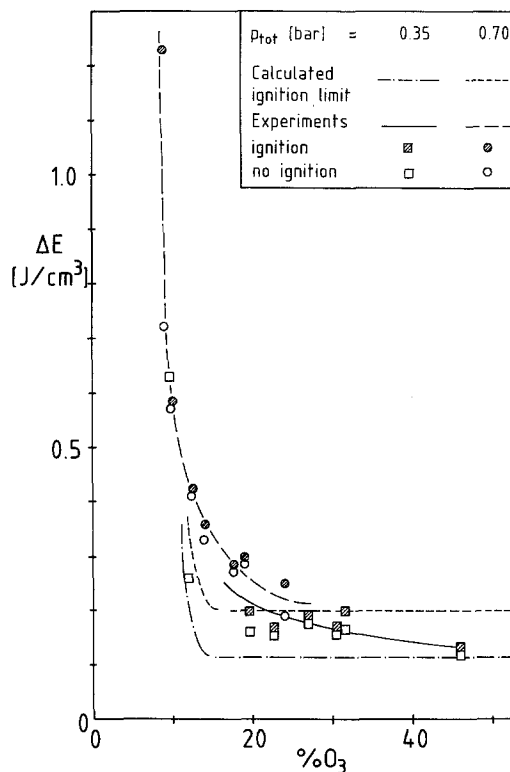


Fig. 6. Ignition limits for mixtures ($p_{\text{tot}}=0.35$ bar and 0.70 bar) compared with calculated ignition limits [11]

ever, in some cases a partial decomposition has been observed, i.e. the decomposition of ozone starts but then dies away and only leads to a reduced O_3 concentration in the cell.

3. Conclusions

It has been demonstrated that O_3 decomposition may be initiated by the multimode pulses of a TEA CO_2 laser in a reproducible way. After ignition the flame moves roughly into the radial direction and its propagation has been observed by uv absorption of O_3 at two different radii. Two typical features of the ignition processes are verified: a) there is an induction period, and b) the flame speed in the gas volume not irradiated is independent of the energy of the ignition source. Furthermore, oscillations of the uv signals are identified to be the first radial acoustic mode of the cell containing O_2/O_3 mixtures.

The fluence dependence of the absorptivity of O_3 indicates that the absorption of the laser light at fluences $> 1 \text{ J/cm}^2$ is a strongly non-linear process, possibly due to multi-photon absorption and saturation.

The ignition limit of O_2/O_3 mixtures has been measured and is in reasonably agreement with the results of

the theoretical calculations of Warnatz et al. [11] for O₃ percentages 20% < x < 50%.

Further experiments have to elucidate the nonlinear absorption behaviour of the ozone in order to evaluate the extent of inhomogeneous ignition along the cell length. Clearing up this feature is essential for quantitative temperature and concentration measurements by high-resolution absorption spectroscopy and for comparison with detailed numerical simulations of ignition processes thus far carried out in one spatial dimension.

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