Effect of intense UV flashes from laser discharges in gases: observation of a fast-rising photodissociation halo leading a shock wave

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The photodissociation of gases near intense laser sparks have been studied experimentally. The power and flux density of UV light have been estimated. It is shown on the basis of the results that the "kern" of the breakdown is an intense source of UV light, in fact, a source with a record-high flux density. It is also shown that over a short time, on the order of the length of the laser pulse, a new physical effect is observed: a fast-rising halo of intense photoionization of the gas. This halo leads the shock wave and generates its own shock wave. It is shown that there is a bleaching of the media for UV light because of intense photodissociation and photoionization. Chlorofluorocarbons are used as examples to demonstrate the fate of polyatomic impurities in a background gas subjected to UV light. Some new possibilities for removing harmful pollutants from the atmosphere by means of new sources of UV light (excimer lamps and the radiation from lasers, laser sparks, and laser plumes) are discussed. An analogy is drawn between the effect of the "kerns" of laser sparks and that of the streamers of microwave discharges.

A fast-rising halo of photoionization of a gas by a UV flash from a laser spark in a gas or from a plume at a target has been observed previously.[1,2] The time of appearance of the halo ($\simeq$10 ns) and its dimensions, $\simeq$(2–3) cm at an electron density level $n_e \simeq 10^{13}$ electrons/cm^3 at pressures of about 1 atm, have been determined from the cutoff of a microwave beam. Over such short times the shock wave has extremely small dimensions—on the order of a fraction of a millimeter. These studies were carried out at laser energies of a few joules in diatomic and monatomic gases. The observation of a halo has played a major role in the development of our understanding of the generation of currents and fields in laser plasmas.

In the present study we have observed a new effect: a fast-rising halo of a photodissociation of molecules. This effect was observed at a far higher power level, during laser breakdown in polyatomic gases. We show that there is a record-high UV flux density, which leads to intense photodissociation, a bleaching of the medium (associated with a destruction of molecules), and the excitation of a new shock wave, which leads the main shock wave.

1. DESCRIPTION OF THE EXPERIMENT

The experimental layout is shown in Fig. 1. We used a neodymium laser (1) based on a GOS-1000 laser with Q switching by saturable LiF. This laser produces a giant pulse with a length at half-width of 30–40 ns and with an energy $Q_l \simeq 80$ J (i.e., the output

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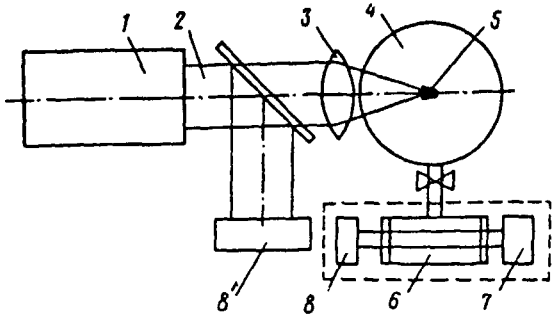

FIG. 1. Schematic diagram of the apparatus used to measure the photodissociating effect of a UV flash from a laser discharge. 1—Intense pulsed neodymium laser; 2—laser beam; 3—lens with a focal length of 8 cm; 4—glass vessel holding the test gas; 5—laser breakdown; 6—measurement flask with IR-transparent windows; 7—spectrophotometer; 8, 8′—radiation detectors (detector 8′ is used to measure the incident power).

power is $\simeq 2$ GW). The beam from this laser (2) is focused by a lens (3) with a focal length $\simeq 8$ cm inside a spherical glass vessel (4) with a volume of 1.2 liters, filled with Freon-12 (CF_2Cl_2) or a mixture of the latter with air at various partial and total pressures. (Freon was selected as the polyatomic gas not only because it models the behavior of other polyatomic gases and impurities well, and not only because its destruction is easily diagnosed, but also because of the need to remove chlorofluorocarbons from the atmosphere[3] in order to protect the ozone layer.) At the center of the vessel, at the focus of the lens, a laser breakdown is arranged. Before and after a train of laser shots ($\simeq 30$ shots at intervals of 10 min), we drew a sample of the gas from the vessel into an evacuated measurement flask (6) with IR-transparent windows. This measurement flask was in the beam of a spectrophotometer (7) tuned to the Freon absorption line at 670 cm^{-1}. In addition, a photometer (a) measured the Freon concentration on the basis of the absorption. We also measured the generation of radicals and their derivatives. To measure the energy of the laser pulse, we tapped part of the energy by means of a glass plate and sent it to a photometer (8′). The beam was slightly collimated in order to improve the uniformity of the distribution. The beam energy inside the flask was $Q_l \simeq 60$ J, where we are allowing for reflection from the lens and the wall of the flask.

The measurements showed that $\simeq 6\%$ of the Freon was destroyed in the train of 30 shots in the vessel. In other words, a Freon volume $\simeq 2$ cm^3 was destroyed per shot. Correspondingly, there was an expenditure of 6 eV per mole of Freon. These figures refer to pure Freon and to standard gas pressures, at which the absorption of the laser light in the discharge is very high.

The laser discharge was photographed from the side by a camera with an open shutter (Fig. 2) with various filters. With very dense filters we were able to discern a central "kern," which is the initial zone of energy evolution. This kern was a cone of length $l_0 \simeq 1$ cm and base diameter $2a_0 \simeq 5$ mm; i.e., the volume of the initial zone of energy evolution was $V_0 \simeq \pi a_0^2 l_0/3 \simeq 6 \times 10^{-2}$ cm^3. The length of the kern is

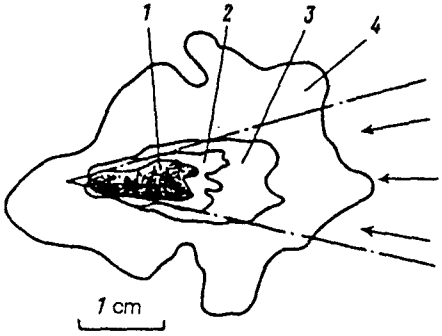

FIG. 2. Time-lapse photographs of the laser spark with various neutral filters in front of the camera. The transmission Tr is referred to $\lambda=500$ nm. 1—$Tr=3\times10^{-5}$, the "kern" of the breakdown has become visible; 2—$Tr=5\times10^{-4}$; 3—$Tr=10^{-3}$; 4—$Tr=5\times10^{-2}$.

$$l_0 \simeq \int_0^{\tau} v_{\mathrm{ld}} dt \approx \left(\frac{2I}{\rho_0}\right)^{1/3}_{\mathrm{avg}} \tau$$

(v_{ld} is the velocity of the laser detonation wave,[4] I_0 is the laser flux density, and ρ_0 is the gas density). In other words, this length is equal to the distance traversed by the laser detonation wave over the duration of the laser pulse, τ. The time scale of the transverse expansion exceeds the duration of the energy evolution, as is shown below. We worked from these data to estimate the energy, power, and flux density of the UV light. The results show that, even during the laser pulse, these properties are so high that they cause many new effects, including the observed destruction volumes.

2. ESTIMATE OF THE UV FLASH AND THE KERN TEMPERATURE

The high energy evolution density $q_{\mathrm{avg}} \simeq Q_l/V_0 \simeq (60\ \mathrm{J})/(6\times10^{-2}\ \mathrm{cm}^3) \simeq 10^3$ J/cm^3 shows that the matter in the kern is in an extremely dissociated state (for comparison, the energy density of the gas under standard conditions is $p_0 \simeq 1$ atm $\simeq 0.1$ J/cm^3). We can estimate the temperature by taking into account the energy expended on dissociation and ionization, and we can estimate the flash of UV light over a time comparable to the length of the laser pulse (i.e., before the expansion of the plasma).

The balance equation for the expenditure of energy is

$$\left\{\sum \epsilon_{\mathrm{d}} + \sum \epsilon_{\mathrm{ioniz}} + (k_i + k_e)\frac{3}{2}kT\right\} N_L \simeq q,$$

where N_L is the Loschmidt number, $\Sigma\epsilon_{\mathrm{d}} \simeq k_a \epsilon_{\mathrm{d}} \simeq 30$ eV is the expenditure on complete dissociation of one molecule, $\Sigma\epsilon_{\mathrm{ioniz}} \simeq k_a\ \epsilon_{i1} \simeq 50$–$60$ eV is the expenditure on single ionization of the atoms of the molecule, $\Sigma\epsilon_{\mathrm{ioniz}} \simeq k_a(\epsilon_{i1} + \epsilon_{i2}) \simeq 200$ eV is the expenditure on double ionization of the atoms, k_i is the number of ions, and k_e is the number of electrons produced. In the former case we have $(k_i + k_e) \simeq 10$, and in the latter $(k_i + k_e) \simeq 15$. The quantity q determines, in terms of T, which case will be realized. To estimate T we adopt two values for the energy-evolution density q: $q_{\mathrm{avg}} \simeq Q_l/V_0$ and $q^* \sim I/v_{\mathrm{ld}} \simeq I^{2/3}\rho_0^{1/3} \simeq P_l^{2/3}\ \rho_0^{1/3}/\pi^{2/3}a^{4/3}$. We assume $a^* \simeq a_0/2$ to be the average cross-sectional radius of the kern cone. In our case we find $q^* \simeq 4q_{\mathrm{avg}}$. For the two scenarios we find temperatures $T = 10$–20 eV and respective degrees of ionization $k_e \simeq 1$ and $k_e \simeq 2$.

Although the initial temperatures are not very high, the initial pressures are at a record high level, because of the high densities of new particles.

The velocities of the lateral expansion, $v_\perp \simeq \sqrt{p/\rho_0} \simeq 2 \times 10^6$ cm/s, yield $\tau_\perp < 10^{-7}$ s as the time of the initial expansion. In other words, over the duration of the energy evolution the volume expands only slightly, and a stage of an intense UV flash precedes the beginning of the formation of the shock wave.

Let us estimate the initial, and most intense, flash of UV light.

The power of strictly the bremsstrahlung emission from a cubic centimeter of the volume is

$$w_{\text{brem}} \simeq n_e \frac{r_0}{c} \epsilon_e \nu_s \Delta\omega \simeq n_e \frac{r_0 \epsilon_e^2 \nu_s}{c\hbar}$$

in a frequency interval $\Delta\omega \simeq \epsilon/\hbar$. Here the rate of Coulomb collisions is

$$\nu_s \simeq Z_{\text{eff}}^2 n_i \frac{\pi e^4}{\epsilon_e^2} \ln \Lambda \times v_e,$$

where r_0 is the classical radius of an electron, Z_{eff} and n_i are the degree of ionization and density of the ions, $\ln\Lambda$ is the Coulomb logarithm, and e and v_e are the charge and the velocity of the electrons. For the temperatures and volumes of the present experiments, the total radiation power wV_0 is comparable to the laser power. Bremsstrahlung is not the only mechanism for a radiation loss, since recombination radiation and spectral emission may be predominant at our temperatures (see, for example, Ref. 5 for the similar elements C, O, etc.).

This estimate shows that the kern of laser discharges in dense gases sets records in terms of flux density and efficiency of the conversion of laser light into UV light. The energy loss due to radiation should probably also be taken into account in the balance equation for the plasma heating.

We wish to call attention to the record high-flux density of UV photons, $\dot{\eta} \simeq wa_0^2/2\hbar\omega a \simeq 10^{27}$ photons/(cm^2·s), even for $a \simeq 1$ cm. Accordingly, there is a rapid decay of molecules in a volume many times larger than the volume of the kern and the shock wave. (The probability for a photodissociation event is $x \simeq \dot{\eta}\tau\sigma_{\text{phd}} \simeq 10^2$ at $a \simeq 1$ cm.) During the application of such agents, however, the medium should become transparent because of intense dissociation and the disappearance of absorption centers. Under these bleaching conditions, the number of dissociating molecules is determined not from an exponential law but by equating the total number of photons to the number of dissociated molecules. This estimate yields a value for the volume of the photodissociation halo which is comparable to that found experimentally.

The actual emission process is more complicated. First, there is a stage of intense dissociation and ionization of the kern. This stage is followed by excitation of the surrounding gas, which involves recombination radiation with a decreasing degree of dissociation. Nonequilibrium processes are possible, e.g., a deviation of the electron tempera-

ture from the ion temperature before encountering the next level. The main point is that the photodissociation halo leads the main shock wave substantially and can create its own shock wave.

3. SHOCK WAVE FROM A PHOTODISSOCIATION HALO OR IONIZATION HALO

Interestingly, the intense flash of ionizing and dissociating UV light creates its own shock wave, which leads the main one. Even in the case of a single "photoaction" processes, not only does the number of particles increase but there is also an evolution of energy in the gas because the photon energy must be significantly greater than a threshold (for a sufficient increase in the cross section). This energy, a few electron volts, usually remains in the kinetic energy of an electron or a radical, so a pressure drop $\Delta p > n_a \Delta \epsilon_{\text{phd}} > 10^2$ atm arises in 10^{-7} s at distances $\simeq 1$ cm. In other words, it can easily be diagnosed and distinguished from the main part, which, at the same distances, has a comparable amplitude over a far longer time $t \sim a^2/(E_{10}/\pi\rho_0)^{1/2} \simeq 3 \times 10^{-6}$ s, where E_{10} is the energy evolution per unit length.

Under the influence of radiation, and in shock waves, there can also be a dissociation and structural conversions of polyatomic molecules (these conversions require less energy), because of an interaction of excited molecules, e.g., $\Phi^* + \Phi^* \rightarrow \Phi_0 + \Phi$, where Φ_0 represents stable compounds (e.g., CF_4, which poses no serious danger).

The effect of the kerns of laser breakdowns has an analog in microwave breakdowns, in which characteristic, thin, twisting streamers, reminiscent of fiery worm drives, are observed.[6] Their visible diameters are 1 mm. They are apparently formed by streamer breakdowns in the strong microwave fields, which are intensified at the edges of streamers. The high energy-evolution densities in such streamers lead to intense UV flashes, which resemble the effect of the laser-breakdown kerns.

4. FATE OF INDIVIDUAL POLYATOMIC MOLECULES (LOW-DENSITY CASE)

Practical applications[3] attract interest to the behavior of impurities at low densities, 10^9–10^{10} molecules/cm^3, in background gases (e.g., the actual impurities of the average concentration of chlorofluorocarbons in the atmosphere). We can estimate the lifetime of such molecules as they interact with excited background molecules produced by, for example, another discharge[3] or other radiation.

If the density of excited molecules, n_a^*, is given, then the probability for collisions of impurity molecules with them is $x \simeq n^* \sigma v \tau^*$, where τ^* is the lifetime of the excited molecules. With $\sigma \simeq 10^{-15}$ cm^2, $v_a = 3 \times 10^4$ cm/s, and $\tau^* \simeq$ ms, for example (for vibrational excitation), we find $x \simeq 1$ at $n^* \simeq 3 \times 10^{13}$ cm^{-3}. In other words, the effective density is quite low, corresponding to low densities of energy deposition in the background gas, 10^{-5} J/cm^3.

There can also be a preliminary excitation of impurity molecules by resonant light (e.g., vibrational or electronic excitation by laser light) and a subsequent destruction of the impurities by a UV flash, not intercepted by unexcited molecules of the background gas. This route may prove more effective than the resonant breakup of impurity molecules by intense laser light, which was recently suggested.[7]

The intense new sources of UV light (excimer lamps and lasers; open discharge sources using electrical, microwave, or laser (pulsed or cw) discharges; laser plumes; etc.) make it possible to act on impurities in a multifaceted and effective way. The fate of impurities is extremely important not only for purifying the atmosphere but also for studying new possibilities for initiating and observing molecular processes at high densities of radiation and applied shocks. Polyatomic molecules, which have large UV-adaptation cross sections and a multichannel excitation, are extremely sensitive to such agents. These agents lead to intense dissociation of these molecules and to new physical effects analogous to those described in the present paper.

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