Intracavity laser spectrometer for studying radicals

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An intracavity spectrometer with an additional channel for recording emission spectra is presented. The spectrometer is capable of recording weak absorption spectra of radicals in plasma with high threshold sensitivity, as well as monitoring the molecular composition of a gas mixture using visible and UV emission spectra with time resolution of 25 ns.

Introduction

Few-atom carbonic radicals (CH, CH_2, C_2, C_3, HCO and OH) play a significant part in the processes of radiation absorption in the upper atmospheric layers, as well as in physics of combustion, problems of environmental protection, and astrophysics.[1] Intense study of spectra of the radicals in recent years has led to considerable advance in understanding of the radical structure. Nevertheless, plasmochemistry of carbonic compounds is poorly developed by now. The mechanisms of formation and destruction of such molecules in plasma, cross sections and constants of reactions are unknown. Problems often arise in identification of spectra and assignment of spectral lines to one or another radical. For example, more than 10000 lines were recorded in the spectrum of CH_2, but only 477 of them were assigned.[2]

Many radicals have metastable electronic states, the optical transition to which from the ground state is possible after absorption of near-IR quanta. These states can be detected by highly sensitive laser spectrometers employing neodymium glass lasers, color-center lasers, and sapphire-titanium crystal lasers.

To record absorption spectra of radicals, it is worth using the method of broadband intracavity laser spectroscopy. This method consists in quenching of laser radiation at the frequencies of the absorption lines of a substance placed inside the laser cavity.[3] In this case, the spectrum of laser radiation has pronounced dips at the frequencies of the absorption lines and can be recorded with the ordinary spectral instrumentation. In the intracavity laser spectroscopy, the laser plays the part of a nonlinear detector of weak absorption. The laser imitates a multipass absorbing cell, but with significantly longer effective length L_{eff} of the absorbing layer than in the ordinary multipass cell, whose length is limited by radiation losses on mirrors. In the case of the broadband intracavity laser spectroscopy, L_{eff} is proportional to the quasicontinuous lasing duration t in the vicinity of some absorption line under study. The intracavity spectroscopy method is characterized by very high

sensitivity to the absorption ($10^{-7}–10^{-9}$ cm^{-1}). As a result, very weak absorption by, for example, radicals being intermediate products of chemical reactions can be recorded. The small size of the absorbing layer allows different ways of the radicals generation: in electric discharge, in plasma of laser jet, and in gas-phase chemical reactions.

The time characteristics of lasers used in intracavity spectrometers ($\tau \sim 10^{-5}–10^{-3}$ s) correspond to lifetimes of excited states of many short-living molecules. Therefore, nonstationary absorption in plasma and gas-phase reactions can be efficiently used for studying radicals. The main difficulty arising in the use of an intracavity spectrometer for recording weak spectra of short-living molecules is synchronization of the spectrometer with appearance of the radical of interest in plasma. This difficulty can be overcome by using an additional high-sensitive channel for detection of the radical by its emission, even if with low spectral resolution.

In this paper, we report an intracavity spectrometer developed for studying the structure of radicals and kinetic processes of their formation and destruction.

1. Description of the experimental setup

For generation of radicals we used two sources of low-temperature plasma (PS): stationary electric discharge in a hollow cathode and longitudinal pulsed discharge excited in a quartz tube by a vacuum-tube current generator operating in the capacitor partial discharge mode. These sources are shown schematically in Fig. 1. They were chosen by the following reasons.

As is well-known, the density of excited particles in a nonequilibrium plasma is an individual property of an excited state. It is described by the balance equation

$$g_i \frac{dN_i}{dt} = g_0 N_0 < \sigma v > - g_i N_i A_i,$$

where N_0 and N_i are the densities of particles in the ground and excited states, respectively; $N_0 < \sigma_i v >$ is the averaged (over the electron distribution) rate of particle excitation from the ground state to the state i; σ_i is the cross section of particle excitation from the

ground state to the state i, v is the speed of electrons. The value of

$$< \sigma v > = \int\limits_{E_i}^{\infty} \sigma v \times f(v) \, dv$$

is the rate of excitation per one particle, where $f(v)$ is the function of energy distribution of electrons. The parameter $f(v)$ is an individual characteristic of the source of low-temperature plasma.
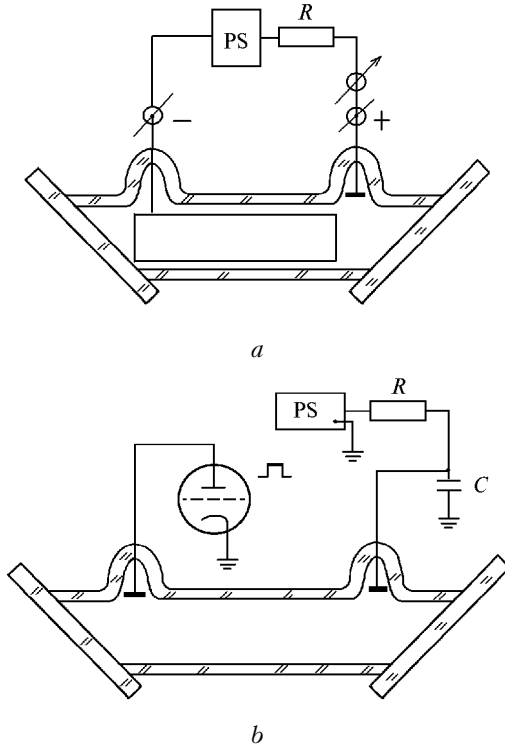
a

b

Fig. 1. Gas discharge tube with a hollow cathode (*a*) and with longitudinal pulsed discharge (*b*).
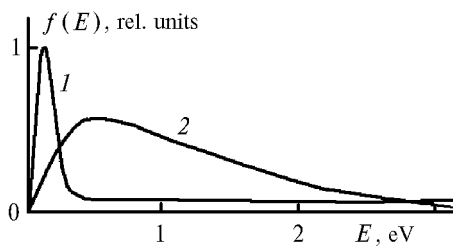
Fig. 2. Energy distribution of electrons for discharge in the hollow cathode (*1*) and in longitudinal pulsed discharge (*2*).

Figure 2 shows the typical energy distributions of electrons for the discharge in the hollow cathode and in the longitudinal pulsed discharge. Since these distributions differ, the used sources of plasma are significantly different in their absorptive and emissive properties.

The processes of emission and absorption in plasma sources are divided into line and continual ones. The line processes proceed between bound states of particles, whereas the continual processes take place between the

bound states and the continuous spectrum of electron energies (the ionization and recombination processes).

The radiation power of a source at an optical transition corresponding to the energy $h\nu_i$ can be expressed (in J/s) as:
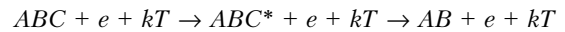
$$W_i = h\nu_i N_i \times A_i V$$

where N_i is the density of the state i; A_i is the probability of the optical transition, in s^{-1}; V is the plasma volume, in cm^3.

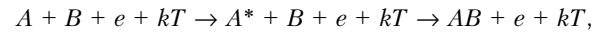Absorption in the plasma layer of length L at the transition i can be found as

$$K_i = g_i \, \Delta N_i \, \sigma_i \, L,$$

where σ_i is the absorption cross section, in cm^2; ΔN_i is the difference in the densities of the upper and lower states of the transition i per unit statistical weight g. Since the densities of excited states in the plasma sources are individual, ΔN_i can take negative, positive, and zero values. Consequently, plasma sources are convenient tools for studying processes in intracavity spectroscopy.

Radicals are necessary components of the low-temperature plasma. They are formed in physical-chemical processes with participation of electrons, such as dissociation
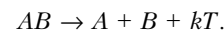
$$ABC + e + kT \rightarrow ABC^* + e + kT \rightarrow AB + e + kT$$

and association

$$A + B + e + kT \rightarrow A^* + B + e + kT \rightarrow AB + e + kT,$$

where ABC^* is a molecule in a certain state; A^* is an excited particle; AB is a radical; e is an electron.

Radicals are destructed, as a rule, without participation of electrons

$$AB \rightarrow A + B + kT.$$

We have developed a two-channel setup, which records the high-resolution absorption spectrum by the intracavity method in the first channel, and the time pattern of emission at a selected wavelength corresponding to the emission band of the radical under study − in the second channel.

The experimental setup is shown in Fig. 3. The gas-discharge cell *2* filled with the gas mixture is placed in the cavity. The synchronization system generates two pulses with a regulated delay between them. Thus, the lasing can be obtained at almost any moment after beginning of the discharge pulse. The laser radiation is directed to the entrance slit of a high-resolution spectrograph with a diffraction grating of 300 grooves/mm. The absorption spectrum in the laser frequency region is recorded on a linear CCD array.

The absorption spectrum of the plasma was recorded with the inverse linear dispersion up to 0.5 cm^{-1}/mm and the spectral resolution of 0.02 cm^{-1}. The noise of the recording system was far lower than the laser noise restricting the method sensitivity.
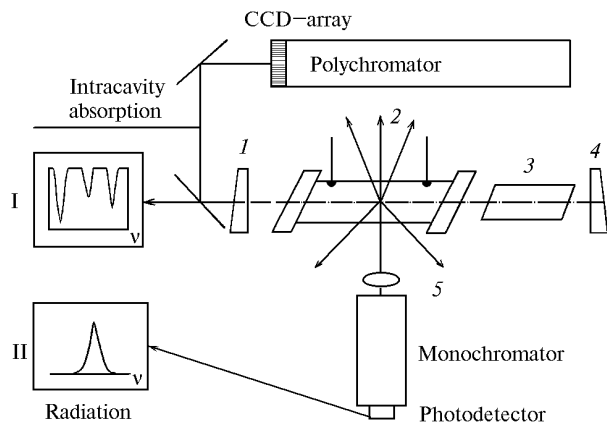
Fig. 3. Intracavity neodymium glass laser spectrometer: cavity mirrors *1* and *4*, gas-discharge cell *2*, active element *3*, and focusing length *5*.

There exists a problem of wavelength calibration for intracavity spectrometers. Usually, an intracavity spectrum is calibrated against reference absorption or emission spectra of some gases. As reference lines, we took spectral lines of water vapor, which were recorded earlier with a Fourier-transform spectrometer.[4,5] To determine the frequencies of lines situated between two lines with the known wavelength, the Fabry–Perot etalon was used. For this purpose, a thin plane-parallel plate was placed in the laser cavity, and the calibration was performed against the peaks of the interference pattern. The application of etalons significantly increased the accuracy of frequency calibration.

As a second recording channel, we used an MDR–12 monochromator with a FEU–20 photodetector. The plasma radiation coming from the gas-discharge tube in the cross direction was focused onto the slit of the monochromator with the lens *5*. The spectral resolution of the monochromator was 1 nm; the frequency tuning range was from 300 to 800 nm. A 8-bit ADC provided the time resolution of 25 ns in the emission spectrum.

The developed system is capable of recording very weak absorption spectra in plasma with high threshold sensitivity to the absorption coefficient (10^{-7}–10^{-8} cm^{-1}) with prior monitoring of the molecular composition of the gas mixture based on the data on visible and UV emission spectra.

Experimental results

The spectra of radicals were studied in two stages. At the first stage, the monochromator, recording emission spectra, was tuned to the spectral region where the emission bands of the studied radical lie. Changing the parameters of the electric discharge and recording the time pattern of plasma emission, we determined the time interval under optimal recording conditions, i.e., at exciting the necessary electronic level. At the second stage, the radical absorption spectra were recorded with high spectral resolution (0.02 cm^{-1}). Figure 4 shows the time scans of emission

of the plasma of the longitudinal pulsed discharge at different wavelengths. On the time scan, three peaks can be distinguished that correspond to excitation of three different vibrational-electronic states of the radical in plasma. The first peak at the wavelength of 580 nm arose at the beginning of the pulse and vanished for ~ 100 µs. The second peak with the maximum at ~ 200 µs was present at all wavelengths from 560 to 600 nm. And, finally, the third peak, most pronounced at the wavelength of 560 nm, existed at the times from 400 to 500 µs.
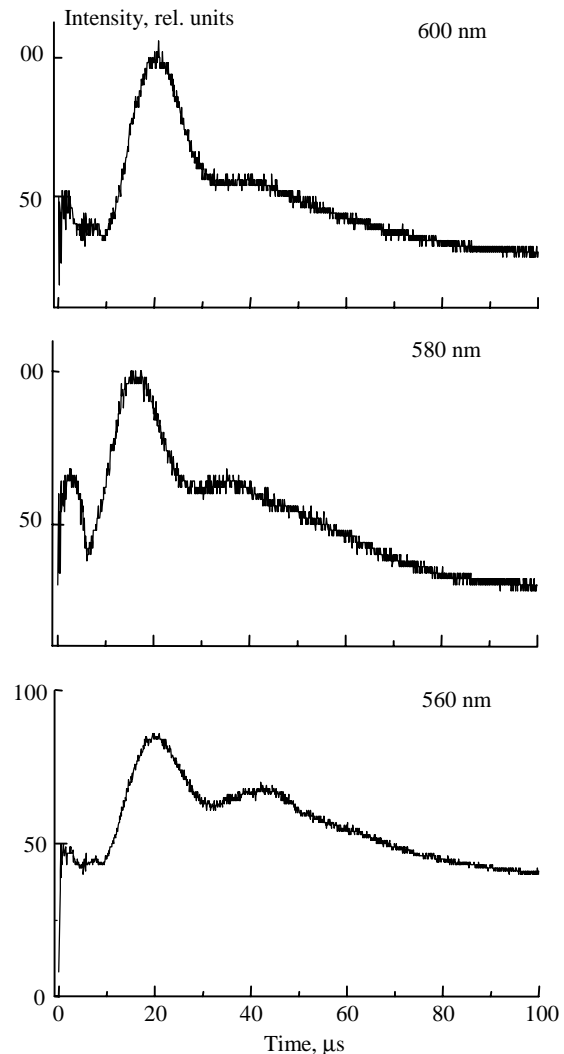

Fig. 4. Time scans of emission of the plasma of longitudinal pulsed discharge.

Thus, if of concern to us is the absorption from the excited electronic state, which is the upper state for the emission at 580 nm, then the delay between the beginning of lasing and the beginning of the discharge pulse should be 0–100 µs. Conversely, if our prime interest is in the electronic state, which is the upper state for the emission at 560 nm, then the intracavity spectrum should be recorded 400–500 µs after the beginning of the electric discharge pulse.
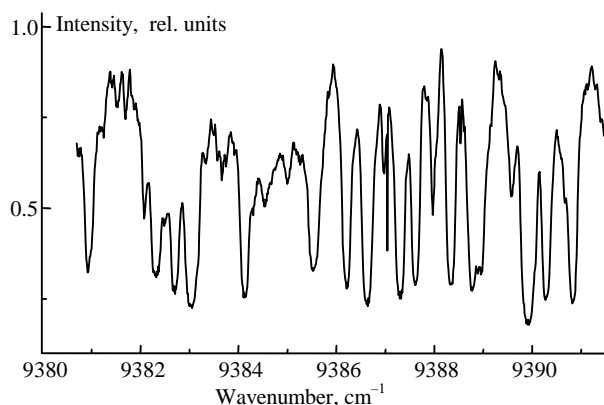
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Fig. 5. Intracavity absorption spectrum of N_2 in the region from 9380 to 9392 cm^{-1}.

Figure 5 shows the intracavity absorption spectrum of molecular nitrogen in the plasma of electric discharge in the spectral region from 9380 to 9392 cm^{-1}. Due to high sensitivity of the intracavity spectrometer, a great number of the N_2 lines, earlier unknown, have been recorded.

Conclusion

The conducted investigations show the two-channel recording system, developed for studying the energetic structure of radicals, to be highly efficient. The system includes the high-sensitive channel for recording absorption spectra by the intracavity spectrometer, as well as the emission channel, which allows one to synchronize the recording with the time of excitation in the discharge of the needed electronic state of a radical.

Acknowledgments

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