ABSORPTION OF LASER RADIATION BY AEROSOL PARTICLES I N AN ATMOSPHERE CONSISTING OF A RESONANTLY ABSORBING GAS

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The problem on energy transfer from vibrationally excited molecules to the atmospheric-aerosol particles is studied.

The ratio of the energy transferred from the molecules to the energy absorbed by the aerosol particles itself is estimated. The results of the estimates and preliminary experiments, which indicate that such exchange can exist under the real atmospheric conditions, are discussed.

As laser radiation propagates through an aerosol-gas atmosphere the energy dissipated by an individual aerosol particle can depend on the character of the absorption of the radiation by the gaseous medium.

If the radiation is in resonance with a vibrational-rotational transition in the molecules of the gas, then for radiation intensity I approximately equal to I_s, the saturation intensity, a large number of exited molecules appear in the gas. In the case when the relaxation of the vibrational energy due to collisions of molecules with one smother is slow, a significant fraction of the vibrational excitation energy cam be transferred to the aerosol component owing to heterogeneous relaxation of the exited molecules on the surface of the aerosol particles.

Taking this transfer into account the total energy absorbed by an aerosol particle can be written in the form

$$\Delta E = \Delta E_a + \Delta E_{m.a} \tag{1}$$

where ΔE_a is the energy of the radiation absorbed in the material of the aerosol particle and $\Delta E_{m.a}$ is the energy acquired by an aerosol particle owing to transfer to the particle of a vibrational quantum from the molecules colliding with the particle.

The effect of the second term will be greatest in the initial time intervals $\Delta t \le \tau_{VT}$, where τ_{VT} is a vibrational-translational relaxation time in the gas. We shall study both terms in Eq. (1) in greater detail.

According to Ref. 1 the first term can be estimated by the expression

$$\Delta E_a \simeq I \cdot \Delta t \cdot \alpha \cdot V_a \tag{2}$$

where I is the intensity of the laser radiation, Δt is the photoexcitation time, α is the volume absorption coefficient of the material of the aerosol particle, and $V_a = \frac{3}{4} \cdot \pi a^3$ is the volume of an aerosol particle of radius a. The expression (2) describes adequately the absorption by small homogeneous aerosol particles.

The quantity $\Delta E_{m.a}$ can be estimated from the formula

$$\Delta E_{m.a} = \xi h\nu_{vib} \cdot \nu_{col} \cdot \Delta t, \tag{3}$$

where

$$\nu_{col} = n_m^* \cdot v_m \cdot \sigma_a = n_m^* \cdot v_m \cdot \pi a^2$$

is the frequency of collisions between the aerosol particle and the vibrationally exited molecules, whose density is n_m^* and v_m is the velocity; hv_{vib} is the energy of the vibrational quantum and ξ is the accommodation coefficient, defined as the probability of deactivation of a vibrational quantumin a collision between an excited molecule and an aerosol particle with the transverse cross section $\sigma_a = \pi a^2$.

For the ratio of Eq. (3) to Eq. (2) we obtain the expression

$$\Delta E_{m.a}/\Delta E_a = \frac{3}{4} \cdot \xi \frac{h\nu_{vib} \cdot n_m^* \cdot v_m}{I \cdot \alpha} \frac{1}{a} \tag{4}$$

The quantity $\Delta E_{m.a}/\Delta E_a$ has a sharp resonance character, since $n_m^* \simeq n_m^0 \cdot \sigma(\nu) \cdot I \cdot \tau_p = \kappa(\nu) \cdot W_p$ (n_m^0 is the density of the particles of the absorbing gas when there is no laser radiation; $\sigma(\nu)$ is the resonance absorption cross section and $\kappa(\nu)$ is the resonance absorption coefficient; and, $\tau_з$ and $V_з$ are the width and the energy density of the pulse). It should also be noted that the ratio $\Delta E_{m.a}/\Delta E_a$ increases as size of the aerosol particles decreases and the energy of the vibrational quantum increases, including when the aerosol particles in a gas of light molecules.

We shall study the case of the propagation of a pulsed CO_2 laser radiation through a layer of the atmosphere near the ground. For pulsed radiation with wavelength $\lambda = 10.6$ μ and the pulse with $\tau_p \sim 10^{-6}$ s ($\tau_p < \tau_{VT} \sim 10^{-5}$ sec · atm (Ref. 2)) the absorption co-

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efficient of the carbon dioxide gas in the P20 line of the 10°0–00°1 line is equal to $0.75 \cdot 10^{-6}$ cm^{-1}.[3] For a pulse with energy density ~ 1 J/cm^2, $\xi \sim 1$, $a \sim 1$ μ the aerosol particle acquires from a gas molecule energy $\Delta E_{m.a} \sim 9 \cdot 10^{-15}$ J in the time interval $\Delta t \sim \tau_{VT} \sim 10^{-5}$ sec. The energy absorbed by a particle having an absorption coefficient $10^{-2} \ldots 10^{-3}$ cm^{-1} will be equal to $\sim 4 \cdot (10^{-14} \ldots 10^{-15})$ J. Correspondingly $\Delta E_{m.a}/\Delta E_a \sim (0.2 \ldots 2.0)$ and it increases rapidly as a decreases.

The analogous situation is observed in the case of absorption of the second-harmonic radiation of the CO_2 laser in the vibrational-rotational band of atmospheric water vapor.

For the same energy density per pulse 1 J/cm^2 and the pulsewidth ~ 10^{-7} sec (less than the VT relaxation time of the ν_2 vibration of H_2O molecule in air) the ratio $\Delta E_{m.a}/\Delta E_a$ for comparatively transparent aerosol particles ($\alpha \sim 10^{-3}$ cm^{-1}, $a \sim 1$ μm) and concentration of exited molecules about $5 \cdot 10^{13}$ cm^{-3} (which corresponds to absorption in the weak line $\kappa \sim 10^{-6}$ cm^{-1}) will be equal to ~ 0.1.

Since this energy is released in the surface layer of the aerosol particle within short time intervals ~ $10^{-S} \ldots 10^{-7}$ sec, the question of the conservation of the optical characteristics of aerosol particles (for example, the scattering cross section) becomes problematical.

When the wavelength of the radiation in differential absorption and scattering lidars, where one of the wavelengths is equal to the absorption line of the gas under study and the other is far off resonance, and the aerosol is used as a tracer, is varied a systematic error associated with the above-discussed additional energy transfer from the molecules of the gas excited by the radiation to the aerosol particles can arise.

For these reasons, in the case of intensive laser radiation in resonance with the molecular transition propagates in the atmosphere the traditional expression for the transmission of the atmospheric channel[4] containing aerosol $T = T_m \cdot T_a$ (T_m is the transmission of the molecular component and T_a is the aerosol component) is hardly appl1cable.

In any case, in both direct and inverse problems of the optics of the atmosphere energy transfer between the molecules and the aerosol particles must be evaluated.

The effect of the presence of aerosol particles on the absorption of intense resonance radiation by the molecular gas, especially with slow VT relaxation, can be appreciable when the saturation of absorption effect is recorded.

For a certain concentration of aerosol particles (> 10^3 cm^{-3}) and particle size > 2–5 μm heterogeneous relaxation of vibrationally exited molecules on the surface of the aerosol can become the faster process in the case of VT relation in collisions of molecules with one another. This increase in the relaxation rate results in a decrease of the saturation, since the saturation parameter of the vibrational-rotational transition $I_s \sim \frac{1}{2\sigma T_1}$, where σ is the absorption cross section, and T_1 is the relaxation time of the population.

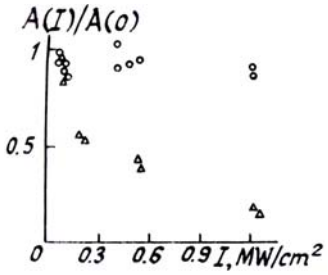

FIG. 1. The amplitude of the signal of the optoacoustic detector versus the intensity of the CO_2 laser radiation (the amplitude is normalized to the amplitude of the signal in a weak field $I \to 0$): the triangles are for air with an addition of CO_2 with a total pressure of 760 mm Hg, *the circles are the same with an addition of a solid aerosol (haze, $N_a \geq 10^3$ cm^{-3})*

Figure 1 shows the results of observations of the saturation effect in CO_2-enriched air and vanishing of this effect when solid aerosol with concentration ≥ 10^3 cm^{-3} (haze) is added to the air.[5] The measurements were performed by the photoacoustic method with a pulsed CO_2 laser; the details of the photoacoustic detection of saturated absorption in gases are described, for example, in Ref. 2.

These preliminary results can be regarded as an indirect confirmation of the importance of energy transfer between the excited molecules and aerosol particles. To make quantitative estimates it is necessary to perform direct experiments on observation of the change in the optical characteristics of a finely dispersed aerosol in the atmosphere of a gas absorbing and not absorbing radiation.

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