importance among renormalization effects is of the order $v^2 \ll 1$, but it is larger than the friction forces owing to binary collisions for $|E_1|^2/4\pi nT > c^4\hbar\omega_1/v_T^4 T$. In the ultrarelativistic limit its contribution to the renormalization effects is sizable or even predominant [larger by a factor $\ln(\varepsilon/m)$ than the terms that describe the dispersion in energy]. The presence of the friction force makes possible the existence of equilibrium distributions of the particles. In the region of nonrelativistic velocities such distributions are Maxwellian with the relativistic temperature $T_{\text{eff}} \approx 3mc^2/4\alpha\varkappa$; i.e., they do not completely forbid escape (for example for ionic-acoustic oscillations[9]) at nonrelativistic energies. For $v \to 1$, i.e., in the ultrarelativistic limit, the equilibrium distribution will be a power law, $1/\varepsilon^\gamma$, both for ions and for electrons.

To answer the question as to whether one can explain in this way the observed power-law spectrum of cosmic rays, it is necessary to obtain a quantum-theoretical expression for $\varkappa = \varkappa(\gamma)$. It is important that this is almost the only mechanism which, when one uses resonance acceleration,[2] can give a power-law spectrum for ions (for electrons there also exists the model of the so-called turbulent plasma reactor[10,11]). The mass renormalization effect can also affect the propagation of transverse electromagnetic waves of high frequency, since an electromagnetic wave can vibrate particles at a frequency corresponding to those that contribute to the mass renormalization. For isotropic particles

there is an additional anomalous absorption, which was calculated earlier in Ref. 12.

[1] Here the resonance field is given a subscript 1 throughout.
[2] The physical meaning of these parts of the work done by the forces, which parts are due respectively to the transverse (superscript t) and longitudinal (superscript l) mass renormalizations, will be explained in Sec. 3.

[1] E. Fermi, Phys. Rev. 57, 485 (1949).
[2] V. N. Tsytovich, Izv. Vyssh. Uchebn, Zaved. Radiofiz. 6, 1641 (1963).
[3] V. N. Tsytovich, Usp. Fiz. Nauk 89, 89 (1965) [Sov. Phys. Uspekhi 9, 370 (1966)].
[4] L. I. Rudakov and V. N. Tsytovich, Phys. Rep. C40, 1 (1978).
[5] V. N. Tsytovich, Astron. Zh. 42, 33 (1965) [Sov. Astron. 9, 24 (1965)].
[6] V. N. Tsytovich, Teoriya turvulentnoĭ plasmy (Theory of Turbulent Plasma), Atomizdat, 1971.
[7] V. L. Ginzburg and V. N. Tsytovich, Phys. Rep. C49, 1 (1979).
[8] A. G. Sitenko, Fluctuatsiĭ i nelineĭnye vzamimodeĭstviya voln v plasme (Fluctuations and Nonlinear Interactions in a Plasma), Kiev, Naukova Dumka, 1977.
[9] L. I. Rudakov and L. V. Korablev, Zh. Eksp. Teor. Fiz. 50, 220 (1966) [Sov. Phys. JETP 23, 145 (1966)].
[10] V. N. Tsytovich and A. S. Chikhachev, Astron. Zh. 46, 486 (1969) [Sov. Astron. 13, 385 (1969)].
[11] C. Norman and D. ter Haar, Phys. Rep. C17, 307 (1975).
[12] V. N. Tsytovich, Preprint FIAN (Phys. Inst. Acad. Sci.), No. 159 (1971).

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Vibrational bistability in an optically excited nonequilibrium molecular gas

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It is shown that a molecular gas subjected to sufficiently strong optical excitation of the electron transition can exist in two stationary states with different degree of excitation of the vibrational degrees of freedom. The transition from one state to the other is discontinuous when the parameters of the external action reach their critical values, and is an analog of first-order phase transitions. The case of a collision gas of molecules with few atoms and of a rarefied gas of complex polyatomic molecules are considered separately. The vibrational bistability of a molecular gas manifests itself, in particular, in ambiguity and jumplike changes of the optical characteristics of the gas. The effect is subject to hysteresis.

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§1. INTRODUCTION

The optics of electron-vibrational molecular systems in weak electromagnetic fields has been well investigated both experimentally and theoretically. If the probability of optical excitation is much smaller than the reciprocal times of the different relaxation processes, then the absorbing electron-vibrational system is in a state of thermodynamic equilibrium, as is usually assumed in the study of the optics of these objects. In modern spectroscopy, however, a situation arises

wherein, owing to the large power of the absorbed radiation, the molecular gas is in an essentially nonequilibrium state. The disequilibrium of the absorbing system should in turn exert an influence on the absorption process itself. This change in the properties of the medium under the influence of the radiation can manifest itself in a large number of specific nonlinear effects, to which the present paper is devoted.

Consider a gas of molecules having two electronic states, 1 and 2, and N vibrational degrees of freedom

interacting with each other and with the electron subsystem. Let the molecule be excited by optical radiation into state 2 from state 1. The reverse transition (2 → 1) can be realized nonradiatively, followed by excitation of oscillations that relax subsequently into a thermostat. The thermostat can comprise the remaining degrees of freedom of the molecule and its surrounding. The 2 → 1 transition can be also the result of spontaneous radiation. If the frequency $\bar{\Omega}$ of this radiation, averaged over the ensemble, is less than the frequency Ω of the exciting light, then the vibrational subsystem also becomes excited on the average as a result. If the electron subsystem again goes over from 1 into 2 within a time shorter than the relaxation time of the vibrational energy into the thermostat, then the degree of excitation of the oscillations can subsequently accumulate. The ability of the molecule to absorb light depends substantially on the degree of excitation of its vibrational subsystem. Since the disequilibrium of the oscillations is itself determined in turn by the absorbed radiation, a new class of nonlinear optical phenomena should be observed in this situation. We note that such systems are reminescent, in a certain sense, of a self-excited amplifier with positive feedback.

We assume that the redistribution energy among the vibrational degrees of freedom is much faster than the electronic transitions and the relaxation into the thermostat. If at the same time the vibrational energy acquired as a result of optical absorption becomes redistributed among many oscillations, then it can be assumed that an effective temperature T is established within a short time in the vibrational subsystem and differs from the thermostat temperature T_0. This situation is perfectly feasible in a large number of molecular gases, in which the mean free path time τ_{V-V}, relative to exchange of vibrational energy, is much shorter than the time τ_{V-T} or τ_{V-R} of the transfer of this energy to the translational or rotational degrees of freedom.[1–4] In particular, the last of these references reports experimentally observed establishment a vibrational temperature deviating from the temperature of the translation degrees of freedom in SF_6 gas excited by an IR laser.

Additional possibilities appear in a gas of polyatomic molecules, which have a large number of vibrational degrees of freedom and interact with the electron subsystem and with one another. The last of these interactions ensures redistribution of the vibrational energy and can lead to establishment of an effective vibrational temperature in each of the molecules independently (see, e.g., Ref. 5). In both cases the temperature T is determined by the total energy E_V stored in the vibrational subsystem

$$E_v = \sum_{\varkappa=1}^{N} \hbar\omega_\varkappa \left(\bar{n}_\varkappa + \frac{1}{2}\right) \tag{1}$$

$\bar{n}_\varkappa(T)$ is the average occupation number of the vibrations of frequency $\omega_\varkappa$.

2. OPTICAL EXCITATION OF OSCILLATIONS IN A COLLISION GAS OF MOLECULES WITH FEW ATOMS

We consider the first of the cases indicated above, when the collisions establish rapidly in the gas a single vibrational temperature T that differs from the temperature T_0 of the remaining degrees of freedom. The slow processes of interaction with the thermostat and with the external light, nonradiative transitions, and spontaneous emission all lead to a change of the vibrational energy E_V and of the populations n_1 and n_2 of the electronic states 1 and 2 in accordance with the equations

$$\dot{n}_1 = -(W_{12}{}^{rl}+W_{12}{}')n_1 + (W_{21}{}^{rl}+W_{21}{}'+\bar{W}_{21}{}^{sp})n_2, \tag{2}$$

$$\dot{n}_2 = -\dot{n}_1 \quad (n_1+n_2=1), \tag{3}$$

$$\dot{E}_v = -\sum_{\varkappa=1}^{N} \gamma_\varkappa(\bar{n}_\varkappa-\bar{n}_\varkappa^{(0)})\hbar\omega_\varkappa - n_1(\Delta W_{12}{}^{rl}-\Delta_f W_{12}{}')$$
$$+ n_2[\Delta W_{21}{}^{rl}-\Delta_f W_{21}{}'+(\Delta-\hbar\bar{\Omega}(T))\bar{W}_{21}{}^{sp}]. \tag{4}$$

Here $W_{12,21}^{rl}$, $W_{12,21}^{f}$ are the probabilities, averaged over the state of the vibrational subsystem, of the nonradiative and externally induced transitions, respectively. The quantities $\bar{W}_{21}^{s}(T)$ and $\bar{\Omega}(T)$ are determined by the formulas

$$\bar{W}_{21}{}^{sp}(T) = \int d\Omega' W_{21}{}^{sp}(\Omega',T), \tag{5}$$

$$\bar{\Omega}(T) = \frac{1}{\bar{W}_{21}{}^{sp}(T)} \int d\Omega' \cdot \Omega' W_{21}{}^{sp}(\Omega',T), \tag{6}$$

where $W_{21}^{sp}(\Omega',T)$ is the probability, averaged over the state of the vibrational subsystem, of the spontaneous emission at the frequency Ω', and $\bar{\Omega}(T)$ is the average frequency of the spontaneous emission. γ is the damping constant of the $\varkappa$-th vibration, $\bar{n}_\varkappa^{(0)}$ are the equilibrium occupation numbers of the $\varkappa$-th vibration at the thermostat temperature T_0, Δ is the electron excitation energy, and $\Delta_f = \hbar\Omega - \Delta$. Equation (4) for the vibrational energy takes into account the fact that an energy Δ is released (absorbed) in each act of nonradiative transition in the vibrational subsystem, an energy Δ_f is released in transition induced by external light, and the average energy released in spontaneous transitions is $\Delta - \hbar\bar{\Omega}(T)$. The balance Eqs. (2)–(4), which have a lucid physical meaning, can be easily obtained by the density-matrix method in the rate-equation approximation. Equations of similar type were derived in Refs. 6 and 7 (see also Ref. 8).

Under nonequilibrium stationary conditions, the effective vibrational temperature is determined by the balance equation of the energy fluxes in the vibrational
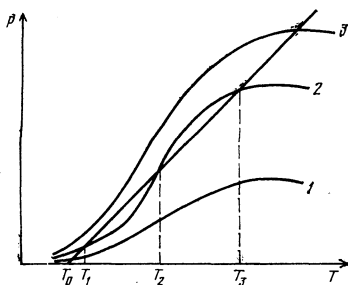

FIG. 1. Dependence of the power dissipated into the thermostat (straight line) and the power absorbed in the optical transition (curves 1, 2, 3) on the effective vibrational temperature T. T_1, T_2, and T_3 are the stationary values of the effective temperature.

subsystem:

$$\sum_{\varkappa=1}^{N} \gamma_\varkappa (\bar{n}_\varkappa - \bar{n}_\varkappa^{(0)}) \hbar\omega_\varkappa \qquad (7)$$

$$= \frac{\hbar\Omega(W_{12}{}'W_{21}{}^{rl} - W_{21}{}'W_{12}{}^{rl} + W_{12}{}'\overline{W}_{21}{}^{sp}) - \hbar\overline{\Omega}(T)\overline{W}_{21}{}^{sp}(W_{12}{}^{rl} + W_{12}{}')}{W_{12}{}' + W_{12}{}^{rl} + W_{21}{}' + W_{21}{}^{rl} + \overline{W}_{21}{}^{sp}}.$$

We consider a number of particular cases.

1. Let the probability of the nonradiative de-excitation W_{21}^{rl} of the electron subsystem be much higher than the probabilities $W_{12}^f, W_{21}^f, \overline{W}_{21}^{sp}$ of the optical transitions. In addition, we assume that $\Delta/T \gg 1$, so that $W_{12}^{rl}/W_{21}^{rl} = e^{-\Delta/T} \ll 1$. Under these assumptions, Eq. (1) takes the form

$$\sum_{\varkappa=1}^{N} \gamma_\varkappa (\bar{n}_\varkappa - \bar{n}_\varkappa^{(0)}) \hbar\omega_\varkappa = \hbar\Omega W_{12}{}'(T). \qquad (8)$$

2. Let $\overline{W}_{21}^{sp} \gg W_{21,12}^{rl}, W_{21,12}^f$. In this case Eq. (7) takes on a form similar to (8):

$$\sum_{\varkappa=1}^{N} \gamma_\varkappa (\bar{n}_\varkappa - \bar{n}_\varkappa^{(0)}) \hbar\omega_\varkappa = \hbar[\Omega - \overline{\Omega}(T)] W_{12}{}'(T). \qquad (9)$$

3. The probabilities of excitation and de-excitation of the electron subsystem are comparable, and it is necessary to take into account the saturation of the electron transition.

Equations (8) and (9) have a simple physical meaning. Their left-hand sides represent the power dissipated into the thermostat, and the right-hand sides the power released into the vibrational subsystem by the external radiation (with the spontaneous-emission energy subtracted in case 2). The latter is determined only by the probability $W_{21}^f(T)$ of the optical excitation, inasmuch as within the framework of the assumptions made the molecules are with overwhelming probability in the electronic ground state, and the electron de-excitation $2 \to 1$, which follows the optical absorption, takes place almost instantaneously.

We continue the analysis by considering first the case of strong electron-vibrational coupling, when a large number of vibrational quanta participate in the optical absorption (molecules with wide absorption bands). In this case the expression for the probability of the optical absorption is well known.[9,10] For example, for close frequencies ($\omega_\varkappa = \omega$) of oscillations that interact actively with the electrons, it takes the form

$$W_{12}{}'(T) = \frac{1}{3} \frac{|d_{12}|^2 F^2}{2\hbar^2} \frac{\tau_2}{\delta^2 \tau_2{}^2 + 1} e^{-(2\bar{n}+1)a/2} \left(\frac{\bar{n}}{\bar{n}+1}\right)^{-p/2} I_p(a(\bar{n}(\bar{n}+1))^{1/2}), \qquad (10)$$

where d_{12} is the dipole matrix element of the electronic transition, F is the optical pumping field intensity, τ_2 is the time of transverse relaxation in the electronic subsystem, $p = [\Delta_f/\hbar\omega]$ is the number of vibrational quanta released in the optical electronic transition ([x] is the integer part of x), $\delta = \Delta_f - p\hbar\omega$ is the resonance detuning between the electron-vibrational levels, $I_p(x)$ is a modified Bessel function, and is the so-called heat-release constant. The factor $\frac{1}{3}$ in Eq. (10) is the result of averaging over all the possible orientations of the molecule. To simplify the analysis of Eqs. (8) and (9), we consider the case of relatively high tem-

peratures $T, T_0 > \hbar\omega$. In this case $W_{12}'(T)$ takes the form

$$W_{12}{}'(T) = \frac{|d_{12}|^2 F^2}{6\hbar^2} \frac{\tau_2}{\delta^2 \tau_2{}^2 + 1} \left(\frac{\hbar\omega}{2\pi aT}\right)^{1/2} \exp\left\{-\frac{(\Delta - \hbar\Omega - \frac{1}{2}a\hbar\omega)^2}{2a\hbar\omega T}\right\}. \qquad (11)$$

We note that in the case of strong electron-vibrational coupling the maximum Ω_{max}^l of the luminescence band is shifted towards lower frequencies relative to the maximum of the absorption band. Therefore the condition $\Omega > \overline{\Omega}(T)$, which is necessary in case 2 for vibrational excitation, is satisfied in the case of excitation in the region of the absorption maximum. We note also that within the framework of the high-temperature approximation used above, the luminescence band also assumes a Gaussian form and $\overline{\Omega}(T) = \Omega_{max}^l$.

We define the parameter α by the relation

$$\alpha = \frac{\varepsilon\tau_2}{\delta^2\tau_2{}^2 + 1} \frac{|d_{12}|^2 F^2}{6\hbar^2 N\gamma T_0} \left(\frac{\hbar\omega}{2\pi aT_0}\right)^{1/2}, \quad \gamma = \frac{1}{N}\sum_{\varkappa=1}^{N}\gamma_\varkappa \qquad (12)$$

[$\varepsilon = \hbar\Omega$ in case 1 and $\varepsilon = \hbar(\Omega - \Omega_{max})$ in case 2]. If α is much less than unity, then it follows from (8) and (9) that $(T - T_0)/T_0 \ll 1$. The parameter α is the ratio of the power of the optical radiation absorbed at the maximum of the band at $T = T_0$ (with the power lost to spontaneous radiation subtracted in case 2), to the characteristic power $\sim \gamma N T_0$ dissipated into the thermostat at $T - T_0 \sim T_0$. We introduce the dimensionless variable $x = T/T_0$ and rewrite Eqs. (8) and (9) in the form

$$x - 1 = \frac{\alpha}{x^{1/2}} \exp\left(-\frac{\xi^2}{x}\right), \qquad (13)$$

$$\xi = \frac{\Delta - \frac{1}{2}a\hbar\omega - \hbar\Omega}{(2a\hbar\omega T_0)^{1/2}}. \qquad (14)$$

The parameter ξ characterizes the frequency shift of the external light relative to the maximum of the absorption bands in units of its half-width at $T = T_0$. Figure 1 shows a graphic solution of Eq. (13) at a fixed value of ξ and three values of the parameter $\alpha (\alpha_1 < \alpha_2 < \alpha_3)$. At $\alpha \ll 1$ (curve 1) the equation has a single root ($x \gg 1, T \gg T_0$). At sufficiently large α (curve 3), Eq. (13) also has one root corresponding to a strong disequilibrium of the system ($x \gg 1, T \gg T_0$).

In some interval of α, however, the temperature T has three stationary values (curve 2). It is easy to verify that the central state T_2 is unstable, and the outermost T_1 and T_3 are stable with respect to small deviations. For such a situation to arise the absorption curve for fixed ξ and continuous variation of α from α_1 to α_3 must be tangent twice to the loss line (straight line in Fig. 1), i.e., at fixed ξ there should exist values $\alpha_\pm$ of the parameter α such that the system (13) is compatible and

$$1 = \frac{d}{dx}\left(\frac{\alpha}{x^{1/2}} e^{-\xi^2/x}\right). \qquad (15)$$

From this we easily find that Eq. (13) has three roots only at

$$\xi^2 \geq \xi_{cr}^2 = \frac{5 + \sqrt{24}}{2} \approx 4.95. \qquad (16)$$

The parameter α should be located in this case in the interval

$$\alpha_- \leq \alpha \leq \alpha_+, \quad \alpha_\pm = x_\pm^{1/2} \exp(\xi^2/x_\pm), \qquad (17)$$
$$x_\pm = \frac{1}{3}[\xi^2 + \frac{1}{2} \pm (\xi^4 - 5\xi^2 + \frac{1}{4})^{1/2}].$$

In this interval of α, a bistable regime is realized in the system, i.e., at the same values of the optical-radiation parameter and of the temperature of the thermostat, the system can be in one of two stable states with different vibrational temperatures.

Figure 2 shows the power absorbed by a molecular gas (per molecule) in units of $\gamma N T_0$ [it is numerically equal to $(T - T_0)/T_0$ in a stationary case] as a function of the parameter α at $\xi^2 = 6$. When α increases from zero to a value $\alpha = \alpha_+$ because of the change in the field intensity, of the radiation frequency, or of the thermostat temperature, the absorption in the gas (and its vibrational temperature) follows the lower branch of the plot of Fig. 2. With further increase of α, only one stable state becomes possible in the system, corresponding to the upper branch of this plot, and the transition to this state takes place jumpwise. With further decrease of α, the gas remains in the upper stable state up to a value $\alpha = \alpha_-$, beyond which it returns to the initial low-temperature state, likewise jumpwise. Thus, the dependence of the power absorbed by the molecular gas on the parameters contained in α exhibits a clearly pronounced hysteresis. The absorption in regimes corresponding to the different vibrational temperatures can differ by one or several orders of magnitude (in the case shown in Fig. 2, the absorbed powers differ approximately by a factor of 25). Since the behavior of this system is determined by its prior history, the system has optical memory and constitutes an "optical flip-flop."

We now estimate the exciting-field frequency at which the condition $\alpha \gtrsim 1$, which is needed for the observation of the effects indicated above, is ensured. At normal gas density and typical parameters $\alpha \sim 10, T_0/\hbar\omega \sim 1, \Delta/\hbar\omega \sim 10^2, d_{12} \sim 1\,D, \gamma \sim 10^6 - 10^7\,\mathrm{sec}^{-1}, \tau_2^{-1} \sim 10^{10} - 10^{11}\,\mathrm{sec}^{-1}$, and F is of the order of $1 - 10^2\,\mathrm{W/cm^2}$. In the forgoing analysis we did not take into account the possibility of direct transfer of part of the electronic excitation energy to the translational degrees of freedom in the collisions. In gases where these processes are substantial, they lead, as shown by an estimate, to a certain increase (within the limits of one order of magnitude) in the threshold of the effect in terms of the field intensity F, without changing qualitatively the picture of the phenomenon.
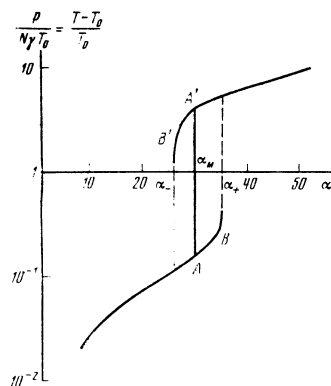
Obviously, the triple crossing of the loss line by the absorption curve, which is needed for the onset of bistability (see Fig. 1), is possible only when the loss curve has an inflection point. In the situation considered above, this inflection is the result of the complicated nonlinear temperature dependence of the probability of the optical transition with participation of many vibrational quanta in the case of a sufficiently strong electron-vibrational coupling. It is easily seen, however, that a similar inflection can occur also for optical excitation with participation of only several vibrational quanta at a relatively weak electron-vibrational coupling, as a result of saturation of the electronic transition in sufficiently strong fields. Consider, for example, case 3 for a weak electron-vibrational coupling, when the maximum of the luminescence band occurs in a purely electronic transition ($\Omega^l_{\max} = \Delta/\hbar$) and $\overline{W}^{sp}_{21}(T) = \gamma_{sp}$, where γ_{sp} is the spontaneous width of the electronic level. Let the gas be excited by light of frequency $\Omega = \Delta/\hbar + k\omega$ (k is a positive integer). In this case the transition probability takes the form

$$W_{12}' = AF^2(\bar{n}+1)^k, \tag{18}$$

where A is the constant. Neglecting the probability of the nonradiative transitions in (7), we get

$$\gamma(\bar{n}-\bar{n}^{(0)}) = k\frac{\gamma_{sp}AF^2(\bar{n}+1)^k}{\gamma_{sp}+AF^2(\bar{n}+1)^k}. \tag{19}$$

If $k \geq 2$, then the second derivative of the right-hand side of (19) is positive at small n, and negative at large n (because of the saturation of the electronic transition). Thus, the absorption curve has an inflection and at certain values of the parameters Eq. (9) can have three roots, which in this case leads to bistability of the system.

Hysteresis in the optical properties of a molecular gas manifests itself not only in the dependence of the absorbed power on the intensity of the optical radiation, but also in the frequency dependence of the absorption coefficient. For case 1 considered above, Fig. 3 shows the contour of an individual line of the structure absorption band corresponding to a transition with a fixed number of vibrational quanta. In the limiting case of weak fields, this line has a Lorentz shape [see (10)]. The parameters of the numerical example shown in Fig. 3 are chosen such that the condition $\alpha > \alpha_+$ is satisfied

FIG. 2. Hysteresis of the absorbed power as a function of the parameter $\alpha(\xi^2 = 6)$. AA' is the phase-coexistence line.
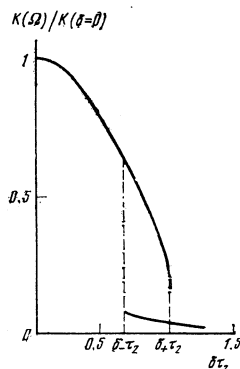

FIG. 3. Shape of individual line of the frequency dependence of the absorption coefficient $K(\Omega)$ in the bistable regime at $\xi^2 = 6$, $\alpha(\delta = 0) = 50$, $\delta = \Delta_f - p\hbar\omega$.

at the maximum of the line. On going from the maximum of the line to its wings, the parameter α decreases, the line contour follows the upper branch of Fig. 3 and then, at a certain detuning, α_+ a jumplike transition takes place to the lower branch. At the reverse frequency variation (from the wing towards the center) the line contour follows the lower branch of Fig. 3 and goes over into the upper branch at $\delta_- < \delta_+$. At the points $\delta_\pm$ the frequency dependence has a singularity in the derivative and a break. The hysteresis character of the frequency dependence of the absorption coefficient leads to a strong asymmetry of the line shape when the frequency is scanned from one wing to the other. It is interesting to note that the line shapes obtained by scanning from the "blue" wing to the "red" wing and back do not coincide, but have mirror symmetry with respect to the center of the line.

The nonlinear dependence of the absorption coefficient on the radiation intensity should manifest itself also in the law governing the damping of the stationary light flux into the interior of the absorbing gas. Thus, in particular, if the intensity of the radiation at the boundary ensures the condition $\alpha > \alpha_+$, then a break, due to the change in the absorption regime, should appear in its spatial distribution.

When the parameter ξ decreases to a value $\xi = \xi_{cr}$, the hysteresis region (see Fig. 2) becomes narrower and subsequently vanishes. However, interesting nonlinear effects can be observed also at $\xi < \xi_{cr}$. Thus, the individual absorption line shape considered above continues to differ substantially from a Lorentz shape because of the nonuniform buildup of the oscillations when the frequency is scanned along the line contour. The frequency dependence of the absorption coefficient, shown in Fig. 4, is then strongly drawn out at the center of the line, where the buildup is maximal and tends to the weak-light absorption line (dashed) on the wings. A considerable distortion of the Lorentz shape of the

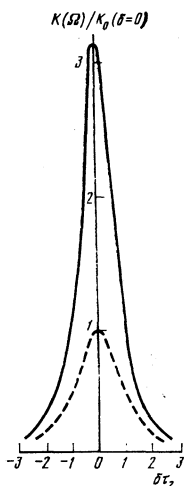$K(\Omega)/K_0(\delta=0)$

$\delta\tau_2$

FIG. 4. Shape of individual line of the frequency dependence of the absorption coefficient $K(\Omega)$ at $\xi^2 = 2.5$, $\alpha(\delta = 0) = 10$ in units of the absorption coefficient of weak light $K_0(\delta = 0)$ at the center of the line. For comparison, the dashed curve is the normalized weak-light absorption line ($\alpha \ll 1$).

line, which is due to the frequency dependence of the stationary value of the vibrational temperature, should be observed also in the example given above with saturation of the electronic transition.

The existence of two stable states of the vibrational subsystem of the molecular gas is analogous in a certain sense to the presence of two phases in a thermodynamic first-order phase transition.[11] Just as in the case of an ordinary phase transition, the existence of two phases is possible only when the system parameters reach critical values (e.g., at $\xi^2 \geq 4.95$ in one of the cases discussed above). Such a bistability is one of the examples of the so-called dissipative structures which appear in a large number of open systems far from the state of thermodynamic equilibrium.[12-17] The most important specific property of these structures is their ability of appear and disappear jumpwise at definite critical values of the external action, undergoing thereby a "kinetic phase transition."

The foregoing analysis pertained to the case of a spatially uniform distribution of the radiation, when one phase or the other occupies the entire volume of the absorbing gas. Nonetheless, a case is possible when some spatially inhomogeneous action (e.g., heating, inhomogeneity of the exciting light itself, or an additional spatially bounded radiation pulse) "switches over" the gas from one stable state to another in a spatially bounded region. In this case the question arises of the spatial separation and coexistence of the phases. An important role is played here by the diffusion of the gas molecules, which leads to heat exahange between the vibrationally "hot" and "cold" regions. The gas density remains uniform in this case, if the heat transfer is mainly between the vibrational degrees of freedom.

For simplicity we consider the cases 1 and 2 analyzed above, when the populations of the electron levels are practically independent of either the vibrational temperature or the time ($n_1 = 1, n_2 = 0$). Confining ourselves to the high-temperature approximation, we easily obtain an equation in closed form for the vibrational temperature:

$$\frac{\partial T}{\partial t} = D\Delta T + Q(T),$$
$$Q(T) = \frac{1}{N} \varepsilon W_{12}{}^{J}(T) - \gamma(T - T_0). \tag{20}$$

Here D is the coefficient of the vibrational thermal diffusivity of the gas, which coincides in this case with the diffusion coefficient. The quantity Q is the power that is effectively "pumped in" into each vibrational degree of freedom. The coefficient D depends only on the temperature of the translation degrees of freedom and is constant. The spatial coexistence of phases in a bistable system, with allowance for diffusion, was investigated in connection with bistable chemical reactions, in which different phases correspond to two stationary concentrations of the reagents.[12,13,17] Following Ref. 12, it is easy to show that the narrow transition region between the two phases is a moving temperature front whose velocity from the "hot" region to the "cold" region satisfies the equation

$$\dot{R}=u-\frac{\nu-1}{R}D, \tag{21}$$

where R is the coordinate of the front, and $\nu=1$, 2, and 3 respectively for planar and cylindrically and spherically symmetrical fronts. The velocity u is determined by the stationary values of the temperature T_1 and T_3:

$$u=\int_{T_1}^{T_3} Q(T)dT \Big/ \int \left(\frac{\partial T}{\partial r}\right)^2 dr. \tag{22}$$

The integration in the denominator of (22) is over a transition layer in the region of the front, with a width $\sim(D\,|Q'|)^{1/2}$ (Q' is the characteristic value of the derivative in the temperature interval $T_1 < T < T_3$). In the case of a planar front, u is its velocity. Both phases coexist stationarily (the front is immobile) only if a condition similar to the Maxwell rule in the theory of a van der Waals gas is satisfied:

$$\int_{T_1}^{T_3} Q(T)dT=0. \tag{23}$$

If the condition (23) is not satisfied, then the front moves, and after a certain time one of the phases (depending on the sign of the integral in (23) fills the entire volume. Just as in the case of a bistable chemical reaction, it follows from (21) that for cylindrical and spherical vibrational-temperature fronts there exist stationary but instable phase separation boundaries with radius $R_{cr}=u/D(\nu-1)$. If e.g., $u>0$, but the initial radius R_i of the hot phase is less than the critical value R_{cr}, then subsequently the region of the hot phase "collapses." On the other hand if $R_i > R_{cr}$, then, just as in the planar case, the hot phase expands and fills the entire volume. We note that, in contrast to the bistable chemical reaction, in our case the formation of the initial phase separation boundary with specified geometry can be easily effected, e.g., by specifying the geometry of the additional light beam that "switches over" the gas from one phase to the other.

3. VIBRATIONAL BISTABILITY IN A RAREFIED GAS OF POLYATOMIC MOLECULES

In the case of a collision molecular gas considered above, the energy $\hbar\Omega$ acquired as a result of optical absorption is rapidly redistributed among a large number of molecules, so that the gas can be characterized by a single vibrational temperature. If the molecule has a sufficiently large number of interacting vibrational degrees of freedom, the energy acquired by a single vibration becomes redistributed among all the remaining vibrations after a short time ($\sim10^{-11}-10^{-12}$ sec)[18,19] and then, as already noted in the Introduction, the molecule can also be characterized by a vibrational temperature even in the absence of collisions. In this case, however, owing to the absence of exchange of vibrational energy between the different molecules, after the lapse of a definite time interval the different gas molecules will have different vibrational energies, and consequently different temperatures. The resultant spread of individual vibrational temperatures in the ensemble of absorbing molecules has a quantum character. It is due to the discrete character of the acquisition of vibrational energy as a result of absorption of

the quantum $\hbar\Omega$, and also to the probabilistic quantum-mechanical character of the absorption process itself. It is thus necessary to consider the distribution of the gas molecules in vibrational energy, which generally speaking is different in different electronic states. For simplicity we confine ourselves to molecules with small quantum luminescence yield ($\overline{W}_{21}^{sp} \ll W_{21}^{r}$) and to case 1 of the preceding section, when the excited state 2 is rapidly depleted as a result of nonradiative transition. It can then be assumed that all the molecules are mainly in the lower electronic state and are distributed with respect to an individual vibrational energy with a distribution function $f(E_V)$. In accordance with the assumptions made, this function satisfies the equation

$$\frac{\partial f(E_V)}{\partial t} = \gamma\frac{\partial}{\partial E_V}[(E_V-E_0)f(E_V)]-W_{12}'[T(E_V)]f(E_V)$$
$$+ W_{12}'[T(E_V-\hbar\Omega)]f(E_V-\hbar\Omega). \tag{24}$$

Here E_0 is the equilibrium vibrational energy at a thermostat temperature T_0 (we have assumed for simplicity $\gamma_x \equiv \gamma$). The dependence of the vibrational temperature on the total vibrational energy is determined, as before, by (1).

The first term in the right-hand side of (24) corresponds to the process of energy dissipation into the thermostat, the second and third terms describe the molecules that go out of the energy interval (E_V, E_V+dE_V) and enter it, respectively, as a result of the interaction with the exciting light. For a qualitative investigation of the solutions of the differential-difference Eq. (24) and for a comparison with the results of the preceding section, we consider the case when the quantum $\hbar\Omega$ is much less than the total vibrational energy stored in the molecule. At sufficiently high temperatures ($T > \hbar\omega, E_V = NT$) this condition takes the form $\hbar\Omega/NT \ll 1$. Expanding the last term of (24) in terms of this parameter up to second order, we obtain an equation of the Fokker-Planck type:

$$\frac{\partial f(T)}{\partial t} = \frac{\partial}{\partial T}\Big[\gamma(T-T_0)f(T)-\frac{\hbar\Omega}{N}W_{12}'(T)f(T)\Big]$$
$$+\frac{1}{2}\Big(\frac{\hbar\Omega}{N}\Big)^2 \frac{\partial^2}{\partial T^2}[W_{12}'(T)f(T)]. \tag{25}$$

If we leave out of (25) the last term, which is responsible for the spreading of the distribution function on account of the quantum fluctuations in absorption, then the characteristics of the remaining linear equation are determined by a formula of the type (8). The stationary solution of (25) takes the form

$$f(T) = \frac{C}{W_{12}'(T)}\exp\Big\{-\frac{1}{\frac{1}{2}(\hbar\Omega/N)^2}\int_{T_0}^{T} dT'\Big[\frac{\gamma(T'-T_0)}{W_{12}'(T')}-\frac{\hbar\Omega}{N}\Big]\Big\}, \tag{26}$$

where C is the normalization constant. It is easily seen that the condition used above, that the energy fluxes in the vibrational subsystem (8) be in equilibrium, determines the extrema of the function (26). At $\xi > \xi_{cr}$ the distribution function has maxima at the points T_1 and T_3 and a minimum at $T=T_2$. At $\hbar\Omega/NT \ll 1$ and at ξ not too close to the critical value ξ_{cr}, these maxima are well separated and have Gaussian profiles, so that one can speak of simultaneous coexistence of two phases in the ensemble of molecules excited by the light. By transferring the gas molecules from one state to anoth-

er, the quantum fluctuations lead to a stationary relation between the phases. The fraction of the molecules in one phase or another is determined by the area under each of the maxima. These numbers are comparable in order of magnitude only when the parameter α lies in a narrow interval near the value α_M satisfying the condition

$$\int_{T_1}^{T_2} dT' \left[\frac{\gamma(T'-T_0)}{W_{12}'(T')} - \frac{\hbar\Omega}{N} \right] = 0, \tag{27}$$

which is also an analog of the Maxwell rule. In the entire interval $\alpha_- < \alpha < \alpha_+$, with the exception of the indicated vicinity of the value α_M, one of the phases prevails exponentially over the other. Thus, at $\alpha = \alpha_M$ the molecular gas changes its state abruptly and undergoes a nonequilibrium first-order phase transition.[11] The optical manifestations of this phase transition are similar to those considered in the preceding section. Thus, in particular, the dependence of the absorbed power on the parameter α takes a form similar to Fig. 2. The segments AB and $A'B'$ (Fig. 2) are, however, metastable. These states are analogous to a superheated liquid (supercooled vapor). They can be attained by a rapid transition of F, Ω, or T_0 from the stable region and are observed during their lifetime, which is determined by the fluctuations. The effects considered in the present section can apparently be observed in vapors of complex molecules, in which the deviation of an individual vibrational temperature from the equilibrium value after optical excitation has been experimentally established, e.g., in the vapors of perylene, anthracene, and 3,6-tetramethyl diaminophthalamide.[5] See also the work on POPOP vapor.[20]

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Note added in proof (26 May 1980). In the recently published collection "Lazernye sistemy" (Laser Systems, Novosibirsk, Nauka, 1980, p. 192), Yu. N. Samsonov and A. K. Petrov call attention to the fact that a number of threshold phenomena observed in IR excitation of molecular gases can be interpreted as the result of a jumplike change of the gas temperature when the laser-radiation power is continuously increased. The mechanism of the onset of temperature jumps, which

they have considered, is based essentially on the temperature dependence of the IR absorption coefficient, a dependence similar to that shown in Fig. 1 of the present paper, and is essentially analogous to the mechanism proposed by us earlier.[11]

[1] Ya. B. Zel'dovich and Yu. P. Raĭzer, Fizika udarnykh voln i vysoko-temperaturnykh gidrodinamicheskikh yavleniĭ (Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena), Nauka, 1966, p. 298 [Academic, 1967].

[2] E. E. Nikitin, Teoriya élementarnykh atomno-molekulyarnykh protsessov v gazakh (Theory of Elementary Atomic-Molecular Processes in Gases), Khimiya, 1970, p. 48.

[3] B. F. Gordiets, A. I. Osipov, V. E. Stupochenko, and L. A. Shelepin, Usp. Fiz. Nauk 108, 655 (1972) [Sov. Phys. Usp. 15, 759 (1973)].

[4] V. N. Bagratashvili, V. S. Dolzhikov, and V. S. Letokhov, Zh. Eksp. Teor. Fiz. 76, 18 (1979) [Sov. Phys. JETP 49, 8 (1979)]. (1979)].

[5] N. A. Borisevich, Vozbuzhdennye sostovaniya slozhnykh molekul v gazovoĭ faze (Excited States of Complex Molecules in the Gas Phase), Nauka i tekhnika, Minsk, 1967.

[6] V. A. Kovarskiĭ, E. A. Popov, I. A. Chaĭkovskiĭ, and N. F. Perel'man, Fiz. Tverd. Tela (Leningrad) 16, 943 (1974) [Sov. Phys. Solid State 16, 607 (1964)].

[7] V. M. Fain, J. Chem. Phys. 65, 1854 (1976).

[8] V. A. Kovarsky, E. Popov, I. A. Chaĭkovskii, Phys. Stat. Sol. (b) 67, 427 (1975).

[9] Yu. E. Perlin, Usp. Fiz. Nauk 80, 553 (1963) [Sov. Phys. Usp. 6, 542 (1964).

[10] M. D. Frank-Kamenetskiĭ and A. V. Lukashin, ibid. 116, 193 (1975) [18, 391 (1975)].

[11] I. Sh. Averbukh, V. A. Kovarsky, and N. F. Perel'man, Phys. Lett. 74A, 36 (1979).

[12] W. Ebeling, Structure Formation in Nonequilibrium Processes [Russ. transl.], Mir, 1979.

[13] G. Nicolis and I. Prigogine, Self-Organization in Non-Equilibrium Systems, Wiley, 1977.

[14] H. Haken, Synergetics, an Introduction, Springer, 1978.

[15] R. Bonifacio and L. A. Lugiat, Opt. Commun. 19, 172 (1976).

[16] R. Bonifacio, M. Gronchi, and L. A. Lugiato, Phys. Rev. 18A, 2266 (1978).

[17] F. Schlögl, Z. Physik 253, 147 (1972).

[18] J. P. Maier, A. Seilmeier, A. Alubereau, and W. Kaiser, Chem. Phys. Lett. 46, 527 (1977).

[19] G. Walter, transl. in: Lazernaya spektroskopiya atomov i molekul (Laser Spectroscopy of Atoms and Molecules), V. S. Letokhov, ed., Mir, 1979.

[20] V. A. Tugbaev, Dokl. Akad. Nauk BSSR 23, 882 (1979).

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