

ABSORPTION AND RELAXATION OF MOLECULES IN STRONG NONRESONANCE OPTICAL FIELD

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A sequential analysis of an influence of intense laser radiation on the potential of intermolecular interaction has been conducted. The expressions for radiation intensity dependence of the potential have been obtained which explain the available experimental results on nonlinear dependence of the CO₂-laser radiation absorption in the H₂O line wing and on the time of the H₂O vibrational-translational relaxation under nonresonance excitation.

INTRODUCTION

Saturation of resonance absorption¹⁻³ and reduction of relaxation time of selectively excited vibrational state (to several times) are observed under resonance interaction of intense optical radiation with vibrational-rotational transitions of molecules at 10⁵–10⁸ W/cm² radiation intensity. The reason of the phenomenon is an increase of the gas temperature and an inclusion of additional relaxation channels due to intra- and inter-mode vibrational exchange.⁴

At large tuning away of the radiation frequency from the frequency of radiation transition, the thresholds of the resonance nonlinear phenomena significantly increase, and nonresonance nonlinear effects appear along with the resonance ones. It was experimentally shown in Ref. 5 that there exists a nonlinear spectroscopic effect – a decrease of absorption in far wing of the H₂O spectral band at increase of the radiation intensity of CO₂-laser, the frequency of which is tens of halfwidths tuned away from the line center frequency. This situation is to some extent nontraditional for the nonlinear laser spectroscopy, where effects are usually obtained by creation of such conditions for resonance interaction of radiation with an isolated line, under which the small-level approximation holds. Nevertheless, sufficiently general prerequisites for explanation of the effect exist also for the case of the absorption line wing “clearing up”.

The first of them is in the decisive role of the classic intermolecular interaction potential V in formation of the periphery of the spectral line contour. The detailed argumentation to that was firstly given in Ref. 6, and now this opinion is universally accepted.^{7,8} The potential V appears in the description of classic centers of mass of colliding molecules, with which its name is, in fact, associated.

Another prerequisite is in the definition of V itself as a corresponding quantum mean over intramolecular degrees of freedom z of the Coulomb energy $U(z; q)$ of intermolecular interaction; q are the coordinates of centers of mass. The particular variants of the V definition are represented by the quantum chemistry equations,⁹ the method of semiclassical representation,¹⁰ the methods of the statistical physics of molecules,¹¹ and so on.

To take into account the influence of strong enough electromagnetic field on the spectral line contour, the term describing the interaction of the field with an absorbing molecule should be added to the Hamiltonian of a free molecule. This term influences the classic potential and the absorptance in the line wing.¹² The summarized contribution of many far wings of the spectral lines determining the absorption beyond the band edge turns to be “an amplifier” of weak nonresonance interaction between optical radiation and a single molecular transition.

The presented qualitative pattern is far from the common interpretation of the saturation effect of the resonance absorption, although the dependence of the absorptance in a line wing on the radiation intensity $\kappa_w(I)$ presented further reminds in appearance the behavior of $\kappa(I)$ in the saturation effect. It should be noted that the saturation effect disappears very quickly if the radiation frequency ω is tuned away from the molecular transition frequency ω_0 by greater than several halfwidths of the absorption line γ (Fig. 1). The effect of “clearing up” in the absorption line wing is observable at the tuning $|\omega - \omega_0| \approx 50 \gamma$ and, as it will be shown further based on the analysis of the experimental data from Refs. 5 and 12, it is determined by the “new” field-depended potential of intermolecular interaction, which should be substituted into the standard expression for the absorptance $\kappa(\omega)$.

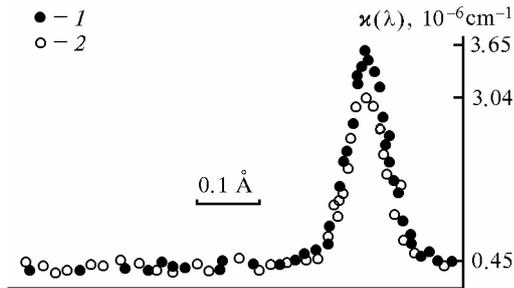


FIG. 1. Saturation of absorption in the 694.38 nm line of H₂O in air ($P = 1.01 \cdot 10^5$ Pa). $I = 10^{-2}$ MW/cm² (1) and 10 MW/cm² (2).

The aim of the given paper is a sequential analysis of an influence of the intense laser radiation field on the potential of intermolecular interaction in order to explain the experimental results on the dependence of the absorption in the H₂O line wing and the time of the H₂O vibrational relaxation on the laser radiation intensity under nonresonance interaction from unified point of view.

EXPERIMENTAL DATA ON THE FUNCTION $\kappa(I)$ IN FAR WING OF SPECTRAL LINE

A detailed description of the experiments determining the $\kappa(I)$ function at $|\omega - \omega_0| \gg \gamma$ can be found in Refs. 3, 5, and 12. The dependence of the H₂O and D₂O vapor absorption on the pulsed CO₂-laser radiation intensity at 10.6 μm wavelength was measured by optoacoustic method. The optoacoustic spectrometer comprised of the pulsed CO₂-laser, the system for recording of the laser pulse characteristics (pulsewidth and a shape of time sweep, energy in a pulse, wavelength), the optoacoustic detector (OAD) with the wideband amplifier for measuring the energy of optical radiation absorbed by gas, and the vacuum system for preparing gas mixtures.

The shape of the CO₂-laser radiation pulse is typical, i.e. it has a peak of 300 ns width at halfheight embodying 50% general energy of the pulse and a slow decay of 1 μs duration. The optoacoustic receiver with the wideband amplifier and cylindrical gas cell of 30 mm diameter and 150 mm length was used to determine the energy absorbed by gas at various values of the radiation intensity at the OAD gas cell input.

The measured parameter is given by the relation

$$A(I) = \frac{U(I)}{W} = \tilde{\alpha} \frac{E_{\text{abs}}}{W} = \tilde{\alpha} \int_0^\tau \kappa(I(t)) I(t) dt / \int_0^\tau I(t) dt,$$

where U is the amplitude of an electric pulse at the OAD amplifier output; W is the energy of the laser pulse; τ is the pulsewidth; $I(t)$ is the time-dependent intensity; $\tilde{\alpha}$ is the experimentally determined calibration constant characterizing the magnitude of the

energy absorbed in the cell at given values of W or I . In the presented below Figs. 2 and 3, the behavior of the ratio $\tilde{A} = A(\omega, W) / A(\omega, W \rightarrow 0)$ is shown, i.e. the ratio of the energy absorbed by gas at large values of W to the corresponding energy at $W \rightarrow 0$. The effective pulsewidth can be given as $\tau = \int t I(t) dt / W$, so, the mean intensity is $I = W / \tau$.

The experimental data for characteristic W -dependence of \tilde{A} for pure H₂O and D₂O vapor as well as for binary mixtures of H₂O and N₂ are presented in Figs. 2 and 3. The error of \tilde{A} measurement does not exceed 10–12%. The observed decrease of \tilde{A} at W growth is much greater than the measurement error.

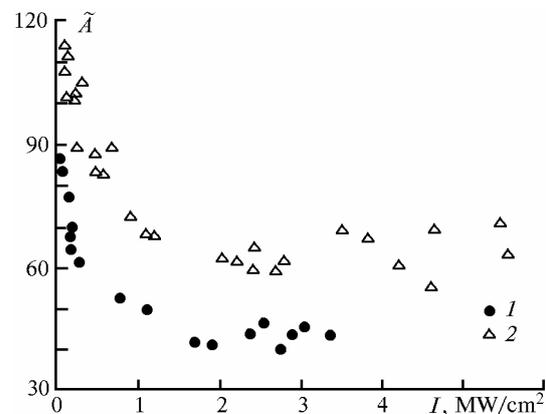


FIG. 2. Dependence of H₂O (1) and D₂O (2) vapor absorptivity ($P = 1330$ Pa) on the intensity of the pulsed CO₂-laser radiation of 10.6 μm wavelength.

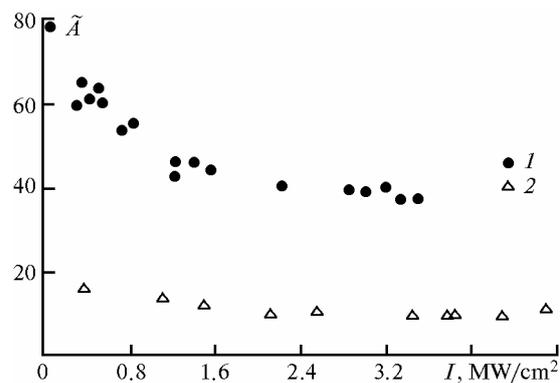


FIG. 3. Absorptivity dependence of the mixture of H₂O vapor with nitrogen (1) at $P = 10^5$ Pa and in pure N₂ (2) ($P_{\text{N}_2} = 1.3 \cdot 10^3$ Pa) on the intensity of the pulsed CO₂-laser radiation of 10.6 μm wavelength.

THEORY OF THE “CLEARING UP” EFFECT IN SPECTRAL LINE FAR WING

We will use the following notations in our presentation: $\hat{H}_1(x)$ is the Hamiltonian of the active

(interacting with the field) molecule, where x is the set of intermolecular coordinates; $\hat{\rho}^{(1)}$ is the Gibbs density function; \hat{H}_{1R} is the Hamiltonian of the absorbing molecule interaction with electromagnetic field of optical radiation; symbols $a, b; |\alpha\rangle, |\beta\rangle; W_a^{(1)}, W_b^{(1)}$ are for quantum indices, wave functions, and eigenvalues of $\hat{H}_1(x)$; the analogous notations are used for description of the buffer gas molecule: $\hat{H}_2(y), y, \hat{\rho}^{(2)}, \alpha, \beta; |\alpha\rangle, |\beta\rangle; W_\alpha^{(2)}, W_\beta^{(2)}$. $U(x, y, \mathbf{r}(t); \mathbf{r}, \mathbf{v})$ is the Coulomb potential of interaction between the first and the second molecules, where $\mathbf{r}(t; \mathbf{r}, \mathbf{v})$ is the vector describing the classical trajectory of relative motion of the center of mass under initial condition $\mathbf{r}(0; \mathbf{r}, \mathbf{v}) = \mathbf{r}$ and initial velocity \mathbf{v} . (The quantified centers of mass are denoted further as \mathbf{s}).

Notations \hat{C} and \hat{S} denote the evolution operators in the Schrödinger equation

$$i\hbar \frac{\partial \hat{C}}{\partial t} = (\hat{H}_1 + \hat{H}_2 + U(t)) \hat{C} \equiv \hat{H}(t) \hat{C}(t), \quad (1)$$

$$i\hbar \frac{\partial \hat{S}}{\partial t} = (H(t) + H_{1R}(x, t)) \hat{S}. \quad (2)$$

The initial relation for the classic potential is given as

$$V = \text{Sp}_{xy} \hat{\rho}^{(1)} \hat{\rho}^{(2)} \hat{S}^{-1}(t) U(0) \hat{S}(t), \quad (3)$$

where Sp_{xy} is the "spur" operation over x and y . The relation (3) well corresponds to quantum definition "an operator of one of subsystems." But, strictly speaking, the "start" expression for interaction potential should be

$$\tilde{V} = \text{Sp}_{xy} \tilde{S}^{-1} \hat{\rho}_0 \tilde{S}^{-1} U(x, y, \mathbf{r}) \quad (4)$$

with $\hat{\rho}_0$ – the Gibbs density matrix for the molecular system (its Hamiltonian is $\hat{H} = H_1 + H_2 + U(x, y, \mathbf{s}) + \hat{K}$, where \hat{K} is the operator of the kinetic energy of centers of mass) and the operator \tilde{S} is the solution of equation of the type (2) with \hat{H} instead of $\hat{H}(t)$. However, \tilde{V} is an operator relative to \mathbf{s} , what presents absolutely unnecessary complexity in the description of the classic centers of mass behavior. The method of semiclassical representation¹⁰ solves this problem by using Eq. (3). Naturally, Eq. (3) should be statistically averaged since Eqs. (1)–(3) describe a binary collision. Detailed description of this operation, as well as some notes concerning Eq. (3) is presented below.

Technically, this procedure is absolutely standard: for Eq. (2) we introduce the representation of interaction $\hat{S} = \hat{C} \hat{B}$ with ordinary Neimann series in powers of \hat{H}_{1R} relative to \hat{B} . Its substitution into Eq. (3) gives an expansion in strength powers of the optical wave electromagnetic field. Let us write the first terms of the expansion

$$V = \text{Sp}_{xy} \hat{C}(t) \hat{\rho}^{(1)} \hat{\rho}^{(2)} \hat{C}^{-1}(t) \times \left\{ U(0) + \int_0^\infty dt_1 [U(0), \hat{C}(t_1) \hat{H}_{1R}(t-t_1) \hat{C}^{-1}(t_1)] + \int_0^\infty dt_1 \int_0^\infty dt_2 [[U(0), \hat{C}(t_1) \hat{H}_{1R}(t-t_1) \hat{C}^{-1}(t_1)], \hat{C}(t_2) \hat{H}_{1R}(t-t_2) \hat{C}^{-1}(t_2)] + \dots \right\}. \quad (5)$$

The first term presents the "fieldless" situation, and, following Ref. 13, the thermodynamical limit is sufficient here

$$\begin{aligned} \text{Sp}_{xy} \hat{C} \hat{\rho}^{(1)} \hat{\rho}^{(2)} \hat{C}^{-1} U(0) &\equiv \text{Sp}_{xy} \hat{g}(t) U(0) = \\ &= \text{Sp}_{yz} \frac{1}{Z} \exp\left(-\frac{H_1 + H_2 + U(x, y, \mathbf{r})}{k\Theta}\right) U(x, y, \mathbf{r}), \end{aligned} \quad (6)$$

where k is the Boltzmann constant; Θ is the temperature, Z is the normalizing multiplier ($\text{Sp}_{xy} \hat{g} = 1$).

The Hamiltonian \hat{H}_{1R} for the case of monochromatic radiation is

$$\hat{H}_{1R} = \hat{\Omega} (A e^{-i\omega t} + A^* e^{i\omega t}) \quad (7)$$

with matrix elements $\Omega_{ba} = \langle b | \hat{\Omega} | a \rangle = -\frac{i}{c} \mu_{ba} \omega_{ba}$,

where μ_{ba} is a matrix element of the active molecule dipole moment projection on the direction of the field polarization; c is the speed of light; and $\omega_{ba} = (W_b^{(1)} - W_a^{(1)})/\hbar$. The vector potential amplitude A

is related to the field intensity as $I = \left(\frac{\omega^2}{2\pi c}\right) |A|^2$. In

the case of pulse radiation with pulsewidth τ , $|A|^2$ should be substituted by $\frac{1}{\tau} \int_0^\tau |A|^2 dt$. A substitution of

Eq. (7) into the second term of Eq. (5) will imply an appearance of rapidly oscillating multipliers $\exp(\pm i\omega t)$, which are absolutely unessential in description of statistical and dynamical properties of classical centers of mass.¹⁴ So, the second term in Eq. (5) can be omitted, what immediately extends to all members of the series (5) with odd powers of the field.

The first nonvanishing order of the perturbation theory, i.e. the third term of Eq. (5), is to be calculated according to the scenario “periphery of the contour.”⁶ An efficient approximation for Eq. (1) is

$$\langle a\alpha | \hat{C} | b\beta \rangle \cong \delta_{ab} \delta_{\alpha\beta} \exp\left(\frac{1}{i\hbar} \int_{t_0}^t W_{\alpha\alpha}(t') dt'\right)$$

with $W_{\alpha\alpha}(t) = W_a^{(1)} + W_\alpha^{(2)} + \tilde{W}_{\alpha\alpha}(t)$ being eigenvalues of $\hat{H}(t)$ and t treated as a parameter; the sense of $\tilde{W}_{\alpha\alpha}$ is quite evident. It is clear that t_0 is the start of collision and $t_0 \in \tau$. An averaging over such uncertain parameter is usual for the binary variant, so the corresponding operation $(1/\tau) \int_0^\tau dt_0(\dots)$ is certain.

The appearing then integrals (structurally simple) with t_1 and t_2 are estimated asymptotically from the parameter proportional to the greater biased frequency $|\omega - \omega_j|$ (“line index” j is the set of the transition quantum numbers). Therewith the method of stationary phase is applicable, what is exactly proved. The essence of simplifications is in elimination of oscillating terms.

A noticeable role here is played by $\int dt_0$ and, mainly, by the choice of identical stationary points for t_1 and t_2 . The same requirement confines the summation indices. The only heuristic element here is a “break in summation” in the combination

$$\sum_{a\alpha} \langle n\alpha | \hat{g} U(0) | a\alpha \rangle (\dots)_{a\alpha} \rightarrow \sum_{a\alpha} \langle a\alpha | \hat{g} U(0) | a\alpha \rangle \sum_{a\alpha} \rho_a^{(1)} \rho_\alpha^{(2)} (\dots)_{a\alpha}$$

in order to use Eq. (6). ($\rho_a^{(1)}$ and $\rho_\alpha^{(2)}$ are the eigenvalues of $\hat{\rho}^{(1)}$ and $\hat{\rho}^{(2)}$). Generally speaking, such procedure is rather popular: first we address ourselves to the laws of the mean and then replace the mathematical mean by the statistical one with the density function $\hat{\rho}^{(1)} \hat{\rho}^{(2)}$ corresponding to the operation Sp_{xy} .

The result of simplification of Eq. (5) looks like

$$V = V_0 \left(1 - \frac{|A|^2}{\hbar^2} \sum_j \sum_\alpha \rho_a^{(1)} \rho_\alpha^{(2)} |\Omega_{ba}|^2 2\text{Re} \Pi(t_{ba\alpha}) + \dots \right) \quad (8)$$

where \sum_j is a sum over spectral lines centered at $\omega_{ba} > 0$ (quantum transition $a \rightarrow b$). Π denotes the asymptotic value of the integral

$$\Xi^{(2)} = \int_0^\infty dt_1 \int_{t_1}^\infty dt_2 e^{i(f(t_1) - f(t_2))},$$

$$f(t) = (\omega - \omega_{ba})t - \frac{1}{\hbar} \int_{t_0}^t (W_{ba\alpha} - W_{a\alpha}) dt' \quad (9)$$

and $t_{ba\alpha}$ is the root of equation

$$W_{ba\alpha}(t) = \omega - \omega_{ba},$$

$$W_{ba\alpha}(t) = \frac{\tilde{W}_{ba\alpha}(t) - \tilde{W}_{a\alpha}(t)}{\hbar}, \quad (10)$$

being equivalent to $f'(t) = 0$, i.e. a definition of a stationary point. It is seen from the structure of $\hat{H}(t)$ in Eq. (1) that Eq. (10) depends only on intermolecular space; so, $t_{ba\alpha}$ is in fact the root of Eq. (10); $t_{ba\alpha}$ results then $|\mathbf{r}(t; \mathbf{r}, \mathbf{v})| = r'_{ba\alpha}$.

The final solution of Eq. (9) is preceded by classifying the classic trajectories of centers of mass illustrated by Fig. 4; the corresponding analysis combines exact relationships of the classic mechanics and the asymptotic estimate (9). As it becomes clear, at $r \geq r'$ the main contributors are the trajectories like (I), $f'(t_{ba\alpha}) = 0$, and

$$2\text{Re} \Pi(t_{ba\alpha}) = \frac{(3!)^{2/3}}{3} \Gamma^2\left(\frac{1}{3}\right) \frac{1}{|(\partial^3 f / \partial t^3) t_{ba\alpha}|^{2/3}}$$

with Γ -function. If $r < r'$, then the trajectories of type (II) should operate, for which $f'(t_{ba\alpha}) \neq 0$ and

$$2\text{Re} \Pi(t_{ba\alpha}) = \frac{2\pi}{|(\partial^2 f / \partial t^2) t_{ba\alpha}|}.$$

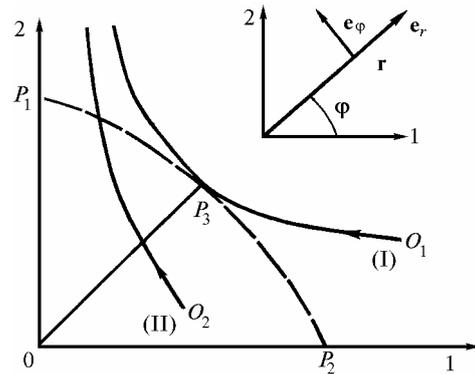


FIG. 4. Trajectories of the colliding molecules: the plane $\mathbf{r}(t; \mathbf{r}, \mathbf{v})$ (1 and 2); $P_1 P_2$ is a portion of circumference of $r'_{ba\alpha}$ radius (indices are omitted); O_1 and O_2 are the initial points of the trajectory with $r \geq r'$ (I) and $r < r'$ (II); $0P_3$ is a minimum distance from the center (in the classic problem about binary collision) for the trajectory I. The initial velocity is $\mathbf{v} = v_r \mathbf{e}_r + v_\phi \mathbf{e}_\phi$ with unit vectors \mathbf{e}_r and \mathbf{e}_ϕ of the curvilinear coordinate system in the point \mathbf{r} .

Then the concept of “determining multifield,” well justified in Ref. 9, is worthy to be used: the approximation $W_{ba\alpha} = \gamma_{ba\alpha}/s^\nu$ is sufficient for Eq. (10); ν is the minimal order of this multifield (in fact, in the Coloumb potential $U(x, y; \mathbf{r})$ of quantum Hamiltonian from Eqs. (1) and (2)), for which the corresponding constant $\gamma_{ba\alpha}$ and $(\omega - \omega_{ba})$ are of the same sign (then $r'_{ba\alpha} = (\gamma_{ba\alpha}/(\omega - \omega_{ba\alpha}))^{1/\nu}$). Now in $(\partial^2 f/\partial t^2)$ and $(\partial^3 f/\partial t^3)$ from Eqs. (9) and (10) with their properties enumerated, the derivatives with respect to s can be calculated immediately and the derivatives of $r(t; \mathbf{r}, \mathbf{v})$ with respect to t corresponding to r' can be expressed through $r = |\mathbf{r}|$ and the components of \mathbf{v} by means of exact formulas of the classic problem on binary collision. The obvious simplifications are based on the statement being realistic for nonresonant variant (see, for example, Ref. 15), that r' is in the vicinity of the classic potential minimum. Then

$$\frac{1}{|\partial^3 f/\partial t^3|^{2/3}} \cong \frac{1}{(v|\omega - \omega_0|)^{2/3}} \frac{r'^{8/3}}{r^{4/3} v_\phi^{4/3}},$$

$$\frac{1}{|\partial^2 f/\partial t^2|} = \frac{r'}{v|\omega - \omega_0|} \frac{1}{\sqrt{v_r^2 + v_\phi^2}},$$

where ω_0 plays the role of the line center. The last step is rather important. It approximates Eq. (3) to exact Eq. (4) by taking into account quantum fluctuations in the dynamics of the centers of mass. By analogy with the method of semiclassical representation, this procedure can be expanded to the statistical part of the problem by averaging over v_r and v_ϕ with the distribution function $G(t, v_r, v_\phi)$, the necessary equation for which can be found in Ref. 10. It follows from the very essence of the problem under treating that the probability of the shift from r to r' for time t for the classical trajectory with initial r and \mathbf{v} should be known; the former asymptotic ways give the following estimates for the trajectories of types (I) and (II) (see Fig. 4)

$$\tau \cong \frac{r'}{r} \sqrt{2r'} \frac{1}{v_\phi} \sqrt{r - r'}, \quad \tau \cong \sqrt{2r} \sqrt{r' - r} \frac{1}{v_\phi}.$$

Of course, the general rules of the probability theory allow finding of the desired probability through $G(t, v_r, v_\phi)$.

But a serious handicap to such program is in the complexity of the problem of G . So, we have to use the “model” solution based on the fact that G complies with an equation of the Fokker-Planck type. We choose the simplest “diffusive” variant for the conditional probability of the shift

$$\Phi = \frac{1}{(\pi D \tau)^{1/2}} e^{-(r - r')^2/4D\tau},$$

declaring D as “the coefficient of quantum diffusion.” Obviously, Φ should be then multiplied by the molecule velocity distribution. It is reasonable to take the Maxwell distribution, and then the appearing $\int dv_r dv_\phi$ can even be expressed through the special functions. But it is hardly worth to be done if the “model” description of Φ is remembered; so, for the sake of estimates, we replace v_r and v_ϕ with the corresponding statistical mean values.

Summarizing all the mentioned details of the problem, we will have got in Eq. (8)

$$2\text{Re } \Pi(t_{ba\alpha}) =$$

$$= \frac{(3!)^{2/3}}{3} \Gamma^2\left(\frac{1}{3}\right) \frac{1}{(\sqrt{2\pi}D)^{1/2}} \frac{1}{(v|\omega - \omega_{ba}|)^{2/3}} \times$$

$$\times \frac{1}{v_\phi^{5/6}} \frac{r'^{23/12}}{r^{5/6}} \frac{1}{(r - r'_{ba\alpha})^{1/4}} \times$$

$$\times \exp\left(-\frac{r}{r'_{ba\alpha}} \frac{v_\phi}{4D\sqrt{2}} \frac{1}{r'_{ba\alpha}} (r - r'_{ba\alpha})^{3/2}\right) \quad (11a)$$

at $r > r'_{ba\alpha}$,

$$= 2 \left(\frac{\pi}{\sqrt{2}D}\right)^{1/2} \frac{1}{v|\omega - \omega_{ba}|} \frac{1}{(r'_{ba\alpha} - r)^{1/4}} \frac{r'_{ba\alpha}}{r^{1/4}} \times$$

$$\times \sqrt{\frac{v_\phi}{v_r^2 + v_\phi^2}} \exp\left(-\frac{r}{r'_{ba\alpha}} \frac{v_\phi}{4D\sqrt{2}} \frac{1}{r'_{ba\alpha}} (r - r'_{ba\alpha})^{3/2}\right) \quad (11b)$$

at $r < r'_{ba\alpha}$,

$$= \frac{(3!)^{2/3}}{3} \Gamma^2\left(\frac{1}{3}\right) \frac{1}{(v|\omega - \omega_{ba}|)^{2/3}} \frac{r'^{4/3}}{v_\phi^{4/3}} \quad (11c)$$

at $r = r'_{ba\alpha}$.

COMPARISON OF THE THEORY AND THE EXPERIMENT

For rigorous quantitative comparison of the above-described theoretical results and the experimental data from Section 2, the values of $\gamma_{ba\alpha}$ and ν are required. These quantities can be obtained from solution of rather cumbersome inverse problem. They occur to be “step” functions of the biased frequency (frequency tuning).⁶ In addition, Eq. (11) includes the constant D being declared now as empirical. Nevertheless, the above-presented solution makes the preliminary analysis from Refs. 5 and 12 much more accurate in many respects.

Note, first of all, that the absorption coefficient κ_j of the j th line centered at $\omega_j = \omega_{ba}$ in the linear, over the field, approximation is expressed as

$$\chi_j(\omega) \sim F = \frac{1}{r'_{ba\alpha}} \int_0^{r'_{ba\alpha}} \frac{\exp(-V(s)/k\Theta) ds}{\sqrt{r'_{ba\alpha}{}^2 - s^2}} \quad (12)$$

and F owes its origin to the Gibbs probability of intermolecular space r (Ref. 6). The Lenard-Jones potential $V = \epsilon((\sigma/s)^{12} - (\sigma/s)^6)$ is plotted in Fig. 5; ϵ and σ are standard parameters of the potential. It was determined in Ref. 16 that $r'_{ba\alpha}$ values filled the interval $\cong 3 - 4 \text{ \AA}$ (for H_2O and D_2O molecular lines) under self-broadening and $r'_{ba\alpha} \in \cong 3 - 3.6 \text{ \AA}$ under broadening by N_2 ; $\delta = 3.12 \text{ \AA}$ for $\text{H}_2\text{O}-\text{H}_2\text{O}$ pair and $\delta = 3.19$ for $\text{H}_2\text{O}-\text{N}_2$ (ϵ/k is equal to 506 K and 217 K, respectively). Therefore, we occur in a region where a decrease of the potential causes a decrease of the absorption (Eqs. (8) and (11) testify to such I -dependence of V).

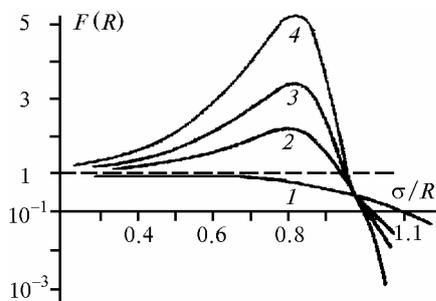


FIG. 5. Behavior of function $F(R)$ for Lenard-Jones potential. $\epsilon/k = 75 \text{ K}$ (1), 450 K (2), 600 K (3), 750 K (4); $\Theta = 300 \text{ K}$.

In order to refine the nonlinearity character we extend the series (5) and then (8). The former asymptotical techniques give the following expression for the summand proportional to the fourth power of the field:

$$+ \frac{1}{\hbar^4} |A|^4 V_0(r) 2\text{Re} \sum_j \sum_\alpha \rho_a^{(1)} \rho_\alpha^{(2)} |\Omega_{ba}|^4 \Xi^{(4)}(t_{ba\alpha}),$$

$$\Xi^{(4)} = \int_0^\infty dt_1 \int_{t_1}^\infty dt_2 \int_{t_2}^\infty dt_3 \int_{t_3}^\infty dt_4 e^{i(f(t_1) - f(t_2) + f(t_3) - f(t_4))},$$

which shows the computational procedure to hold for the consequent members of the expansion (5) as well. The appearing series of the perturbation theory becomes summable, so

$$V = V_0(r) 2\text{Re} \sum_j \sum_\alpha \rho_a^{(1)} \rho_\alpha^{(2)} (Q_{j\alpha}(J))_{av}, \quad (13)$$

$$Q(J) = \frac{1 - 2\xi}{1 + \xi},$$

$$\xi = \frac{1}{3^2} \Gamma^2\left(\frac{1}{3}\right) \frac{2\pi cJ}{\omega^2 \hbar^2} \frac{(3!)^{2/3}}{|\partial^3 f / \partial t^3|^2/3}, \text{ for (11.a) and (11.c),}$$

$$Q(J) = \frac{1 - 3\xi}{1 + \xi}, \quad \xi = \frac{\pi^2 cJ}{\omega^2 \hbar^2} \frac{1}{|\partial^2 f / \partial t^2|} \quad \text{for (11b).}$$

The indices $j\alpha$ are connected with substitution of $t_{ba\alpha}$ and execution of the operation $(\dots)_{av}$ i.e. averaging over quantum fluctuations. Plot of $Q(J)$ fully corresponds to Figs. 2 and 3, and numerical estimates give the proper order of “saturation straight line.”

When treating the isotopic (μ is the mass of a molecule) variations of the effect, we, first of all, have to settle the question of D . Physical sense of Φ almost forces us to assume $D \sim 1/\mu$. An appearance of the velocity v is stipulated by the common statistical sense of the diffusion coefficient; and the de Broglie wavelength λ corresponds to quantum origin of Φ : at $\lambda \rightarrow 0$ “the quantum influence” should disappear. Since $\lambda \sim 1/\text{pulse}$, then $D \sim 1/\mu$. A similar estimate will arise when the coefficient of “microscopic” diffusion (in terms of Ref. 17) is expressed through the similar viscosity with the same dependence of the latter on μ as in statistical physics.¹⁸

Assuming all velocities in Eq. (11) to be $\sim 1/\sqrt{\mu}$, we obtain, that Eqs. (11.a) and (11.b) are proportional to

$$\mu^n e^{-u} \sqrt{\mu}; \quad n, u > 0.$$

Conceptually empirical u should be declared such that m will fall on the decreasing portion of the latter function (the variant (11.c) falls out of this scheme, but it is only one line from \sum_j , and, moreover, a coincidence of r and r' might be sooner random). A simple calculation convinces that then after writing $D = \eta/\mu$ we will have an estimate of the constant $\eta \cong 0$ ($10^{-27} \text{ g}\cdot\text{cm}^2/\text{s}$), i.e. $\eta = 0(\hbar)$, which perfectly agrees both with quantum sense of D , discussed earlier, and the preliminary quantitative arguments.

A dependence of intermolecular interaction potential on the intensity of nonresonance optical radiation, stipulating the “clearing up” effect in the line wing due to decrease of V at I increase, should also result in a specific change of time of the vibrational-translational relaxation (τ_{VT}). Just as the absorptance in a line wing, the probability VT of the relaxation w_{VT} is determined through $V(R)$. According to Ref. 19, the semiclassical representation in the first order of the perturbation theory for the simplest situation of diatomic molecule interaction with a neutral atom gives

$$w_{VT} = |x_{v'v}|^2 \int_{-\infty}^{+\infty} \frac{V'(R)}{\hbar} \exp\left[\frac{i}{\hbar}(E_v - E_{v'})t\right] dt \quad (14)$$

where $x_{v'v}$ is a matrix element of $x = r - r_e$ (r_e is an average size of nonvibrating molecule); E_v , $E_{v'}$ are molecule energies in vibrational states v and v' ,

correspondingly; $V'(R) \sim \tilde{\beta} V(R)$, where $V(R)$ is classic potential of intermolecular interaction; $1/\tilde{\beta}$ is a characteristic width of the potential well. The foregoing theoretical analysis shows, that the decrease of V at I increase should imply the corresponding decrease of w_{VT} and, consequently, a growth of τ_{VT} under nonresonance excitation of molecule.

This situation is exactly the opposite to what eventuates under resonance excitation of molecules by intense laser radiation causing a saturation of absorption in the vibrational transition. The absorption coefficient in this case lowers at a growth of radiation intensity, but magnitude of τ_{VT} decreases. There are experimental data on SF₆, CH₃F, and diacetile resonance excitation^{4,23} testifying to noticeable (several times) increase of VT relaxation rate; as well the measurements are presented in Ref. 24 pointing to the vibrational-vibrational exchange rate in mixtures CH₄:SF₆ and CD₄:CH₄ exposed to the CO₂-laser high-power radiation of 10.6 μm wavelength. The decrease of the vibrational relaxation time in strong resonance field is stipulated by intra- and intermode vibrational exchange, anharmonicity of vibrations, and heating of gas.⁴

The difference in the behaviors of VT relaxation time in the cases of resonance and nonresonance excitation of small molecules (CO₂ and H₂O) by intense radiation of the pulsed CO₂-laser was first described in Ref. 24. The experimental results can be interpreted as a consequence of the above-discussed mechanism of the strong field action on interaction of molecules. We will cite them briefly.

EXPERIMENT ON DETECTION OF τ_{VT} DEPENDENCE ON THE RADIATION INTENSITY

The dependence of τ_{VT} on the pulsed CO₂-laser radiation intensity (10.6 μm wavelength) in CO₂ and H₂O vapor was measured using the optoacoustic method as well as the earlier measurements of the effect of absorption saturation in CO₂ (Ref. 20) and the "clearing up" in the H₂O line far wing (Ref. 5). The method of τ_{VT} determination is as follows: when the gas, filling the OA detector cell, absorbs the pulse laser radiation, a pressure pulse is produced, which then is recorded with microphone. The amplitude of the electric signal, taken off the microphone, is written as

$$U = C \cdot \Delta P \cdot \varepsilon(p), \tag{15}$$

where ΔP is the pressure gain in the OA cell due to gas heating; p is the total gas pressure in the cell; $\varepsilon(p)$ is a coefficient describing a change of elasticity properties of the microphone membrane under variation of p ; C is the calibrating constant of the given OA cell independent of p .

At low gas pressure in the cell, ΔP is determined by competition of the processes of VT relaxation and deactivation of the vibrationally excited molecules on the cell walls

$$\Delta P = (\gamma - 1) \frac{\kappa l E}{Q} \cdot F(w_{VT}, w_T, w_d, \tau), \tag{16}$$

where γ is isentropic exponent; κ is the absorption coefficient of the gas under study; l and Q are the length and the volume of the OA cell; w_{VT} and w_T are the rates of VT and thermal relaxation; w_d is the rate of molecules deactivation in their collisions with wall.

In the case of the gas excitation by short pulses at $\tau \ll \tau_{VT}(p), \tau_d(p), \tau_T(p)$, the function F is²²

$$F(w_{VT}, w_d, w_T) = \frac{w_{VT}}{w_{VT} + w_d} \left(\frac{w_{VT} + w_d}{w_T} \right)^{-w_T/(w_{VT} + w_d - w_T)}, \tag{17}$$

where $w_{VT} = w_{VT}^0 p$; $w_{T,d} = w_{T,d}^0 / p$, (index 0 corresponds to pressure $p_0 = 1$ mm Hg). The values of w_T, w_d can be calculated from the known radius of the OA cell and the coefficients of molecular diffusion in the ground and excited vibrational states.²² Function $\varepsilon(p)$ for the given microphone is found by the electric activation method²³; τ_{VT} at various I can be found from the measured values of $\Delta P, \kappa, E$, and calculated w_T, w_d using Eqs. (16) and (17). A particular example of this procedure use is described in Ref. 21; and the function $\tau_{VT}(I)/\tau_{VT}(0)$ for CO₂ and H₂O, obtained experimentally, are presented in Fig. 6, which shows a qualitative difference between $\tau_{VT}(I)$ functions in the cases of resonance (CO₂) and nonresonance (H₂O) absorption in vibrational transition.

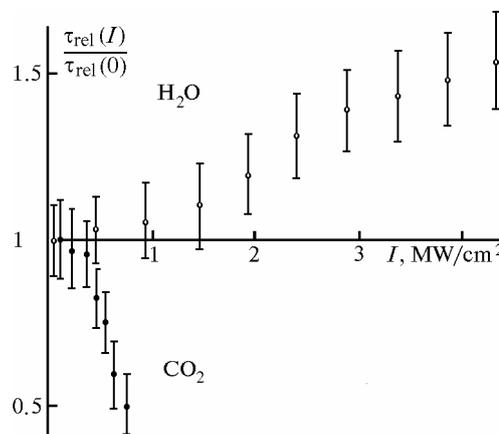


FIG. 6. Dependence of the vibrational relaxation time of H₂O (nonresonance excitation) and CO₂ (resonance excitation) on the intensity of the CO₂-laser radiation.

In the case of resonance excitation of vibrational transition in CO₂, the increase of I is accompanied by decreasing VT relaxation time, because at $I \sim I_{sat} \cong 0.3$ MW/cm² the ratio $\tau_{VT}(I)/\tau_{VT}(0) \cong 0.6$. This result well agrees with the data of Ref. 4 and references therein, where the shortening of VT relaxation time under resonance excitation of complex molecules by intense laser radiation was observed.

Under excitation of H₂O molecules by nonresonance radiation in far wing of a spectral line, the time of the VT relaxation increases at a growth of I . The growth begins at $I \gtrsim I_w$, where I_w is the threshold intensity of the "clearing up" effect in the H₂O spectral line wing (~ 2 – 2.5 MW/cm²). The physical cause of such increase of τ_{VT} is a dependence of the intermolecular interaction potential on I , i.e. just the mechanism considered above, which describes the absorption of intense optical radiation by spectral line wings.

CONCLUSION

The considered theoretical model of the influence of the optical strong field on interaction of molecules in a gas allows a uniform interpretation of nonresonance nonlinear effects in light absorption and vibrational kinetics. A characteristic property of these effects is that in the case of nonresonance interaction of the intense optical radiation with vibrational transition in a molecule, the absorption suffers saturation (just as in the case of resonance interaction), whereas the dependence of the vibrational relaxation time on the radiation intensity is opposite to that in the case of resonance excitation. A combination of these effects can result in complex dynamics of optical characteristics of gaseous media in a volume occupied by the laser beam and in new peculiarities of self-action of the intense optical radiation in molecular media.

From our point of view, the experimental data on light absorption in a line wing and VT relaxation time, available now, as well as measurements of the dependence of absorption in the wing and VT relaxation on the radiation intensity can be used for reliable reconstruction of the repulsing portion of intermolecular interaction potential in monomolecular gases and especially in binary mixtures. These experimental data can be obtained with a single experimental setup allowing measurements of a magnitude of the laser radiation energy absorbed by gas and the time of radiationless relaxation of selectively excited vibrational state.

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