

NONSTATIONARY ABSORPTION OF RADIATION WITHIN A VIBRATIONAL BAND WITH A RANDOM ROTATIONAL STRUCTURE

S.V. Ivanov and V.Ya. Panchenko

*Scientific-Research Center on Technological Lasers,
Academy of Sciences of the USSR, Troitsk
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Nonlinear nonstationary absorption of infrared laser radiation within vibrational bands of molecules with dense quasirandom rotational structure, which is typical of a number of atmospheric components, is considered. An analytic expression for the probability of incoherent photoexcitation of a vibrational transition is obtained. The conditions for nonstationary rotational population effects to be strong are determined; the role of laser pulse shape and duration is analyzed. These effects are estimated for O₃ molecules under laboratory and atmospheric conditions.

The effects of nonlinear absorption of infrared (IR) radiation in molecular gases are of significant interest for atmospheric optics.¹ In particular, it concerns the laser excitation of vibrational transitions with a dense and nearly-random rotational spectral structure, as is the case for many atmospheric constituents (O₃, SO₂, NO₂, etc.). The peculiarities of such an excitation were considered earlier in Refs. 2 and 3. In these papers the calculation of the probability of incoherent vibrational photoexcitation was carried out in the approximation of quasistationary rotational sublevel populations, which, naturally, restricts the applicability of the obtained results.

In the present paper an analytic solution is given of the problem of incoherent nonstationary (i.e., over time intervals comparable with the rotational relaxation time) excitation of a molecular vibrational transition with a random rotational structure by a laser IR pulse. The solution obtained coincides in the quasistationary limit with the result obtained in Ref. 3. The conditions for strong nonstationary absorption of radiation in vibrational transitions are found, and the role of pulse duration and shape is determined.

Let us consider the incoherent interaction of visible radiation with a nondegenerate vibrational transition possessing a rotational structure. The equations for the population differences Δn_i of the i th pair of vibrational-rotational (V-R) levels coupled by radiation, and for the vibrational populations N_0 and N_1 have the form³

$$\Delta \dot{n}_i = - \left(2W_{01}^i + \frac{1}{\tau_{RT}} \right) \Delta n_i + \frac{q_0^i N_0 - q_1^i N_1}{\tau_{RT}}, \quad (1)$$

$$\dot{N}_1 = -\dot{N}_0 = \sum_i W_{01}^i \Delta n_i, \quad (2)$$

where W_{01}^i is the probability per unit time of stimulated absorption of radiation in the i th line band; τ_{RT} is the characteristic rotational-translational relaxation time; q_0^i and q_1^i are the fractions of molecules in the upper and lower rotational sublevels (the rotational population factors). The summation in Eq. (2) is carried out over all the band lines. In writing down Eq. (1), the ratio between the statistical weights of the upper and lower V-R levels was proposed for simplicity to be close to unity, and vibrational energy exchange and other "slow" processes were neglected. Since the rotational energies of the V-R levels coupled by dipole-allowed transitions are roughly equal, it is possible to set $q_0^i \approx q_1^i = q_i$.

Assuming that at the moment the radiation is switched on $\Delta n_i(t=0) = q_i \Delta N_{in}$, where Δ is the initial vibrational level population difference, we obtain the solution of the inhomogeneous differential equation (1)

$$\Delta n_i = q_i \left[\Delta N_{in} \exp(-\int c_i d\tau) + \frac{S_i}{c_i} (1 - \exp(-\int c_i d\tau)) \right], \quad (3)$$

$$c_i(\tau) = 1 + 2W_{01}^i(\tau)\tau_{RT}, \quad S_i + \sum_{\kappa=0}^{\infty} \frac{(-1)^\kappa}{c_i^\kappa} \cdot \frac{d^\kappa \Delta N}{d\tau^\kappa}, \quad \tau = t/\tau_{RT}.$$

In the derivation of Eq. (3), the condition of radiation pulse adiabaticity $\left| \frac{dc_i}{d\tau} \right| \ll c_i^3 \exp(-\int c_i d\tau)$ was assumed. It breaks down only in the case of simultaneous fulfillment of the inequalities $\tau \ll 1$ and $W_{01}^i \tau_{RT} \ll 1$, i.e., if the pulse edge is very sharp,

when $2(W_{01}^i)_0 \cdot \tau_{RT} \left| \frac{df}{d\tau} \right| \geq 1$. Here $f(t)$ is the temporal pulse shape (the envelope of the intensity); $(W_{01}^i)_0$ is the peak value of W_{01}^i . It should be emphasized that the adiabaticity condition is most likely to break down if the radiation frequency coincides with the V–R transition center when the value of $(W_{01}^i)_0$ is large. Under nonresonant conditions $(W_{01}^i)_0$ is significantly smaller, and therefore that adiabaticity condition is fulfilled more easily.

Note that the quasistationary limit of the solution (3), which is equal to $q_1 S_1 / c_1$, coincides with the value obtained from Eq. (1) only when its right-hand side is set equal to zero in the zeroth order of the approximation for the series S_1 ($S_1 \approx \Delta N$). This has to do with the fact that in the given case the exact equality $\Delta \dot{n} = 0$ is in general unattainable because of the time dependence of $\Delta N(t)$. However, S_1 differs slightly from ΔN_{in} if the variation of ΔN_{in} is small within the time interval τ_{RT} . Such a situation is typical for the experiment analyzed earlier in Refs. 2 and 3. With this in mind we restrict ourselves to the approximation $S_1 \approx \Delta N \approx \Delta N_{in}$.

Assuming that the modified Goody model^{3,4} for the rotational structure of the vibrational band $|0\rangle - |1\rangle$ is valid in which the same Lorentzian lines are distributed randomly with equal probability within a certain frequency interval Δ (the bandwidth), we obtain from Eqs. (2) and (3):

$$\dot{N}_1 = W_{01}^i \Delta N;$$

$$W_{01} = W_{01}^{QS} \left[1 + \exp(-t/\tau_{RT}) \cdot \frac{a}{\pi} \sqrt{1+a} \times \int_0^1 \frac{\exp(-by) \sqrt{y}}{(1+ay) \sqrt{1-y}} dy \right]; \quad (4)$$

$$W_{01}^{QS} = qW \frac{\Delta \nu_1}{L \sqrt{1+a}}; \quad W(t) = \frac{\sigma I_0}{h\nu} f(t);$$

$$a(t) = \frac{4}{\pi} W(t) \tau_{RT}; \quad b(t) = \frac{4}{\pi} \int W(t) dt,$$

where ν , I_0 , and $f(t)$ are the carrier frequency, the peak intensity, and the radiation pulse shape, respectively; q , σ , $\Delta \nu_L$, and L are the rotational population factor, the resonance absorption cross section, the spectral width of V–R band lines, and the mean distance between them. In obtaining Eqs. (4), the relation natural for molecular bands was used: $\Delta \gg \Delta \nu_L$. The quantity W_{01} in Eqs. (4) has the meaning of a probability of excitation (per unit time) of a vibrational transition with the rotational structure taken into account. The quantity W_{01}^{QS} is the quasistationary limit of W_{01} obtained earlier in Ref. 3.

The definite integral in Eqs. (4) is to within a factor of $\pi/2$ the degenerate hypergeometrical series with two arguments (the Appel function).⁵

Equations (4) simplify if the saturation of the characteristic band lines is small, i.e., $a \ll 1$:

$$W_{01} = W_{01}^{QS} \left\{ 1 + \exp(-t/\tau_{RT} + b/2) \cdot \frac{a}{2} \times \left[I_0\left(\frac{b}{2}\right) - I_1\left(\frac{b}{2}\right) \right] \right\}, \quad (5)$$

where $I_0(x)$ and $I_1(x)$ are the modified Bessel functions of zeroth and first order, respectively.⁶ The relative difference between W_{01} and W_{01}^{QS} has the same order of magnitude as the quantity $a \cdot \times \exp(-t/\tau_{RT}) \ll 1$ when $b \ll 1$, and of $a \cdot b \cdot \times \exp(-t/\tau_{RT}) \ll 1$ when $b \gg 1$. The next important result follows immediately from Eqs. (4) and (5), namely that the equality $W_{01} \approx W_{01}^{QS}$ fulfilled not only for $t \gg \tau_{RT}$, but also at arbitrary t , if $b \gg 1$. This means that if $b \gg 1$ the rotational sublevel populations can be regarded as quasistationary in calculations of the vibrational transition photoexcitation probabilities, and there is no need to verify this assumption for every separate V–R transition. Simple estimates show that under the experimental conditions of Ref. 2, where (000)–(001) band of the O_3 molecule was excited (at a pressure of 3 Torr with a CO_2 -laser pulse duration of 75 ns), the inequality $b \gg 1$ is fulfilled for $I_0 \geq 1 \text{ kW/cm}^2$, i.e., over practically the entire range of the peak intensities used.

Note that the noticeable differences between W_{01} and W_{01}^{QS} can be realized only for $b < 1$. For $b \gg 1$ from Eqs. (4) after some transformations we obtain

$$W_{01} = W_{01}^{QS} \left(1 + \exp(-t/\tau_{RT}) \sqrt{a \frac{\sqrt{1+a}-1}{\sqrt{1+a}+1}} \right). \quad (6)$$

It is easy to see, that the additional term in Eq. (6) is always positive, increases as a increases and is equal to $\sqrt{a} \cdot \exp(-t/\tau_{RT})$ for $a \gg 1$. The square-root character of the dependence is caused by the Lorentzian shape of the absorption line wings. Therefore, it is necessary and sufficient for noticeable difference between W_{01} and W_{01}^{QS} to be formed that the following three conditions be satisfied:

$$t < \tau_{RT}, \quad a > 1, \quad b < 1. \quad (7)$$

Taking into account that $b(t)$ is an increasing function, and that $a(t)$ reproduces the radiation intensity envelope, the fulfillment of conditions (7) can be expected at the peak of a short intense pulse. More detailed conditions for this case look like this:

$$t_0 < \tau_{RT}, \quad \frac{1}{f(t) \tau_{RT}} \left(\frac{p}{p_0} \right)^2 < \frac{4}{\pi} \frac{\sigma_0 I_0}{h\nu} < \frac{4}{\pi} \frac{\sigma_0 I_0}{h\nu} < \frac{1}{\int_0^{t_0} f(t) dt} \left(\frac{p}{p_0} \right), \quad (8)$$

where p_0 and p are the two gas pressures; σ_0 and τ_{RT}^0 are the absorption cross section and the relaxation time τ_{RT} measured at the pressure p_0 ; and is the position of the peak of the pulse. From conditions (8) follows that the sharper the pulse front is (naturally, within the framework of the above-discussed adiabaticity condition), the better is this inequality fulfilled. Note also that at fixed p , t_0 , and $f(t)$ conditions (8) are valid only for a certain range of peak intensities I_0 .

Let us estimate the atmospheric ozone absorption at altitudes of 20–30 km ($p \approx 50$ Torr). The characteristic values of the parameters for Q-branch of the (000)–(001) O_3 band are: $p\sigma \approx 2 \cdot 10^{-17} \text{ cm}^2 \cdot \text{atm}$, $\Delta\nu_L p^{-1} \approx 0.16 \text{ cm}^{-1} \cdot \text{atm}^{-1}$ (Refs. 7 and 8), $p\tau_{RT} \approx 0.5 \text{ ns} \cdot \text{atm}$ (Ref. 9). Using these values, we find that condition (8) for the peak of a pulse with a front linear increasing during the time τ_f is fulfilled only for $\tau_f < 0.1 \text{ ns}$ and W/cm^2 . The difference between W_{01} and W_{01}^{QS} is negligible for other I_1 and I_0 values.

Thus, the probability W_{01} of nonstationary photoexcitation of a vibrational transition with rotational structure, determined by the modified Goody model, is described by Eq. (4). From this formula it follows that if the molecular spectra and radiation parameter values satisfy the relation $\frac{4}{\pi} \int W(t) dt \gg 1$,

then the equality $W_{01} \approx W_{01}^{QS}$ holds, i.e., in the calculation of W_{01} it is possible to regard the populations of all the rotational sublevels as quasistationary with no dependence on the actual validity of this approximation for each V–R transition in particular. The nonstationary absorption effects noticeably increase the value of W_{01} only when conditions (8) are simultaneously satisfied, which can be realized at the peak of a short intense pulse.

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