LASER EXCITATION OE MOLECULAR VIBRATIONAL TRANSITIONS WITH DENSE ROTATIONAL SPECTRAL STRUCTURE

S.V. Ivanov, and V.Ya. Panchenko

Research Center for Technological Lasers, USSR Academy of Sciences
Received September 27, 1988

Linear and nonlinear laser absorption in molecular vibrational transitions with the dense rotational spectrum typical of bent three-atom atmospheric molecules is examined. In the quas1st at ionary incoherent rate approximation to the equations for the energy level populations, we study the effect of various factors on the optical excitation probability for vibrational transitions, such as laser frequency stability, laser 1inewidth, spectral band rotational structure irregularities, and spectral line shape. Criteria for collective linear and nonlinear band absorption of laser radiation are formulated. Conditions for the square-root dependence of the excitation probability on laser intensity are determined.

INTRODUCTION

A conventional treatment of the optical excitation of IR-active molecular vibrational transitions makes use of the linear absorption and rotational saturation (the bottleneck effect) approximations[1]. The induced vibrational transition probability is a linear function of the optical intensity in the former case, but is a constant value determined by the R–T exchange time and the equilibrium rotational distribution in the latter. Our earlier work[2–4] examined of the ozone molecule to illustrate the feasibility of a new excitation regime resulting in the suppression of the bottleneck effect, due to a collective absorption process in which a number of quasiresonant vibration-rotation transitions are involved. Owing to the simplicity of the proposed model, with a fixed laser frequency interacting with a set of equally spaced but otherwise identical Lorentzian lines (Elsasser band[7]), this problem can be solved analytically. However, the O_3 spectrum, like that of many other atmospheric gases, is known to possess a complex, nearly random structure and the ozone line contour may not be Lorentzian. As for the laser radiation, it is usually not frequency-stable or exactly monochromatic, examples being the light derived from multimode laser output and nonlinear optical generators.

The present work studies the effect of a number of factors on the optical excitation probability for molecular vibrational transitions with a dense V–R spectrum: laser frequency stability and linewidth, absorption line shape , and rotational structure irregularities inherent in the molecular absorption band of interest.

STATEMENT OF THE PROBLEM

In the case of radiative excitation of the vibrational transition $|0\rangle - |1\rangle$ the incoherent rate equations for the rotational sublevel populations on the $i^{\text{-th}}$ V–R transition read[1]:

$$\frac{dn_1^i}{dt} = W_{01}^i n_0^i - W_{10}^i n_1^i + \frac{1}{\tau_{RT}}\left(N_1 q_1^i - n_1^i\right)$$

$$\frac{dn_0^i}{dt} = W_{10}^i n_1^i - W_{01}^i n_0^i + \frac{1}{\tau_{RT}}\left(N_0 q_0^i - n_0^i\right) \qquad (1)$$

Here n_0^i, n_1^i and q_0^i, q_1^i are the actual and dimensionless equilibrium rotational sublevel populations, respectively, N_0 and N_1 are the vibrational state populations, and τ_{RT} is the characteristic R–T relaxation time, assumed to be the same for all the sublevels.

The probabilities for the i-th induced upward and downward transitions have the form

$$W_{01}^i = \frac{g_1^i}{g_0^i} W_{10}^i, \quad W_{10}^i = \frac{\sigma_{10}^i I}{h\nu_i}, \quad \sigma_{10}^i = \frac{c^2 A_i}{8\pi\nu_i^2 \Delta\nu_L} F_i$$

$$F_i = \Delta\nu_i \int f_i(\nu-\nu_i)\, f_{las}(\nu-\nu_{las})\, d\nu \qquad (2)$$

where I is the total radiation intensity, f_{las} is the laser spectrum shape centered at frequency ν_{las}; f_i, ν_i, $\Delta\nu$ and A_i are the line shape, position and width and Einstein coefficient, respectively, for i-th absorption like: $g_1^i \simeq g_0^i$ are the statistical weights of the corresponding V–R levels; c is the velocity of light; h is Planck' s constant. The integration in Eq. (2) is over the laser spectrum. For monochromatic radiation F_i is a dimensionless form factor for the absorption line.

Assuming quasistationary rotational sublevel populations in Eq. (1) and summing over the con-

tribution from all lines of the $|0\rangle - |1\rangle$ band yields the optical excitation probability (per unit time) for the vibrational level[5] $|1\rangle$ as

$$W_{01} = \sum_i \frac{W_{01}^i q_0^i}{1 + 2 W_{01}^i \tau_{RT}} \qquad (3)$$

Complex absorption band spectra are conveniently represented as quasi random structures with statistically distributed parameters ν_i, A_i, q_0^i (the latter is here in after denoted as q_i). For collective absorption, W_{01} is to be statistically averaged over the above parameters. If the radiation is not frequency-stable, further averaging over the line center positions is required. Hence

$$\langle W_{01} \rangle_{\nu_{las}, q_1, A_1 \nu_1} = \int \sum_i \frac{W_{01}^i q_1}{1 + 2W_{01}^i \tau_{RT}} p(\nu_{las}) p(q_1(\nu_1)) \times$$

$$\times p(A_1(\nu_1)) p(\nu_1) d\nu_{las} dq_1 dA_1 d\nu_1 \qquad (4)$$

where $p(x)$ is the probability density distribution for the random quantity x. The integration is over the domains of ν_{las}, q_i, A_i, ν_i. Provided the spectral dependence of q_i and A_i can be neglected in the determination of $\langle W_{01} \rangle$ (see the relevant criterion later in this paper), Eq. (4) may be dramatically simplified. For example, averaging over q_i would then result in the mean value of q being a factor. It should be noted that unless an integration parameter is a random quantity, its distribution function reduces to a delta function.

NONSTABILIZED MONOCHROMATIC RADIATION

The effect of laser frequency stability and laser linewidth on $\langle W_{01} \rangle$ will be studied in terms of Elsasser's model (see Fig. 1). Consider the case where the radiation spectrum is represented by a single frequency (mode) lying randomly and equiprobably within a rectangular laser line contour of width Δ. Summing the infinite series in Eq. (4) and integrating only over ν_{las}, with the rest of the variables assumed regular, we obtain

$$\langle W_{01} \rangle_{\nu_{las}} = \frac{qW}{\beta} \frac{L}{\Delta} \left(\frac{\Delta\nu_L}{L} \right)^2 \left[\pi n + \operatorname{arctg}\left(a \operatorname{tg}\pi \frac{\delta + \frac{\Delta}{2}}{L} \right) - \right.$$

$$\left. - \operatorname{arctg}\left(a \operatorname{tg}\pi \frac{\delta - \frac{\Delta}{2}}{L} \right) \right] \qquad (5)$$

$$a = \operatorname{cth}\beta + \operatorname{csch}\beta, \quad \beta = \pi \frac{\Delta\nu_L}{L} \left(1 + \frac{4}{\pi} W\tau_{RT} \right)^{1/2},$$

$$W = \frac{\sigma I}{h\nu}, \quad \sigma = \frac{c^2 A}{8\pi \Delta\nu_L (\nu_{las}^0)^2}, \quad \delta = \nu_0 - \nu_{las}^0$$

Here ν_{las}^0 is the center of the laser frequensy range; A is the Einstein coefficient; $\Delta\nu_L$ is the linewidth; L is the line separation; δ is the offset of ν_{las}^0 from the nearest neighbouring absorption line; n is the number of singularities of the function $\tan(x)$ in the interval $\pi/L(\delta - \Delta/2) < x < \pi/L(\delta + \Delta/2)$. To within ± 1, n may be taken to be integer part of Δ/L.

It follows from Eq. (5) that as the frequency spread increases the excitation probability undergoes damped oscillations due to the involvement of more and more distant lines. Note that the β-parameter specifies the contribution of quasiresonant transitions to the excitation of vibrations, and is the product of alinear vibrational factor and an effective resonant transition saturation parameter. For $\beta \gg 1$, collective absorption occurs, being linear for $W\tau_{RT} \ll 1$ and nonlinear for $W\tau_{RT} \gg 1$.

Consider the following limiting cases for Eq. (5):

a) If $\Delta \ll \delta$, the radiation may be assumed stabilized, and Eq. (5) goes over into the formula derived earlier by Chugunov et al[3].

b) For $\Delta \gg L$, where the frequency range encompasses a number of absorption lines, the δ and Δ-dependence of the excitation probability vanishes:

$$\langle W_{01} \rangle_{\nu_{las}} = \pi \frac{qW}{\beta} \left(\frac{\Delta\nu_L}{L} \right) \qquad (6)$$

c) For $\beta \gg 1$ the excitation is affected by a number of quasiresonant lines. The excitation probability $\langle W_{01} \rangle$ becomes independent of δ and Δ just as in a), and we obtain the result of Eq. (6) accurate to a factor of order 2. The numerical value of the factor depends on whether the inequality $\Delta < L$ or $\Delta > L$ holds.

In the nonlinear collective absorption regime, the transitions in close proximity to the laser frequency are strongly saturated, and Eq. (6) becomes:

$$\langle W_{01} \rangle_{\nu_{las}} = \frac{q\Delta\nu_L}{2L} \left(\frac{\pi W}{\tau_{RT}} \right)^{1/2} \sim \left(\frac{I}{\tau_{RT}} \right)^{1/2} \qquad (7)$$

d) For $\beta \ll 1$, the $|1\rangle$-level excitation is determined solely by the V–R transition nearest the laser frequency. In that case (unless $\Delta \gg L$; (see (a)), $\langle W_{01} \rangle$ is a sensitive function of δ and Δ. If $|2\delta \pm \Delta| \ll L$ the radiation may be assumed to be absorbed by a single line immediately adjacent to ν_{las}^0.

Equation (5) can be used to explain experimental data on IR excitation of simple molecules in collisional interactions. Figure 1 plots the measured and calculated mean number of CO_2 laser photons absorbed by O_3 as a function of the radiation intensity. The calculated curves were obtained for a rectangular pulse area equal to that of the real pulse. The experimental points and Curve 1 are taken from Ref. 4. Curve 1 was calculated for fixed-frequency radiation, using spectral observations[6] of the (000)–(001) absorption

transition of O_3 and a Voigt absorption profile. Curve 2 was calculated using Eq. (5) for a typical TEA-CO_2-laser gain linewidth. Mean values of q, A and L were estimated based on the actual O_3 spectrum in the vicinity of the laser frequency. The value of δ was set to be equal to the real displacement of the 9P(30) CO_2 line center from the nearest V–R transition in O_3, 16_{88}–16_{89}. The considerable discrepancy between the calculations of Curve 1 and the measurements for low laser intensities was qualitatively accounted for by mode instabilities within the gain profile, resulting in detuning from perfect resonance with the nearest O_3 transition. Equation (5) provides for a quantitative understanding of this effect. For low intensities, curve 2 appears to describe the behavior of the experimental points much better than curve 1 does. For $I > 0.1$ MV/cm^2 ($\beta \gg 1$), the effect of laser frequency instability goes to zero and the two curves tend to merge. Collective absorption then becomes nonlinear, and the function $\bar{n}(I)$ has a square-root pattern in accordance with Eq. (7).

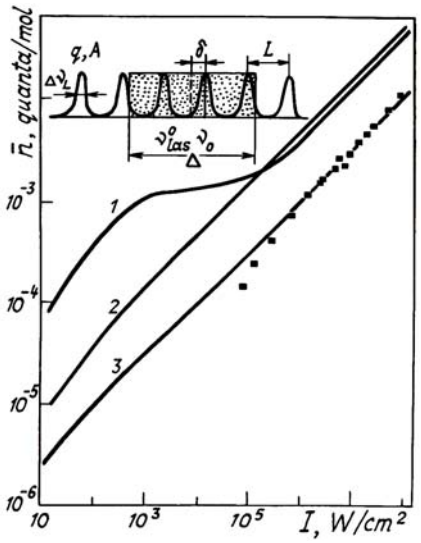

Fig. 1. Heart number of 9P(30) CO_2 *laser photons absorbed by* O_3 *molecules versus laser intensity at* 3 *torr and* 300 *K. Points for experimental results from Ref 4.*
Curve 1 *for fixed frequency calculated at* 1037.4341 cm^{-1} *(*9P(30) CO_2 *line center) using actual* (000)–(111) *band spectrum of* O_3. *Curve* 2 *for calculations using Eq. (5) for nonstabilized radiation,* $\nu^0_{las} = 1037.4341 cm^{-1}$, $\Delta = 0.03 cm^{-1}$, $\delta = 3\times10^{-4}$ cm^{-1}. *Curve* 3 *the same as curve 2 but with* $\tau_{RT} = 20\,\tau^0_{RT}$, *where* $\tau^0_{RT} = 0.127$ μs. *Torr, the value used for curves* 1 *and* 2. *Curves* 2 *and* 3 *were obtained for Elsasser model parameters:* $q = 2.63\times10^{-3}$, $A = 2.77 s^{-1}$, $L = 3.03\times10^{-2} cm^{-1}$, $\Delta\nu_L = 6.95\times10^{-4} cm^{-1}$, *averaged over* 100 *lines of the actual spectrum.*

The excitation probability varies with the rotational relaxation time. Due to a lack of reliable data on rotational exchange processes in O_3, no quantitative agreement of theory with experiment is to expected. At high intensities, the best agreement with observations is achieved by setting $\tau_{RT} \simeq 20\tau^0_{RT}$ (see curve 3 in Fig. 1), where τ_{RT} is the relaxation time[1] of O_2. The deviation of the experimental points from the calculations in curve 3 for $7 < 0.1$ MW/cm^2, where only one resonance transition contributes to $\langle W_{01} \rangle$, appears to be attributable to the difference between τ_{RT} and other relevant transition parameters and their average values.

QUASIMONOCHROMATIC CONTINUOUS SPECTRUM

Consider another limiting case of the interaction between an Elsasser band and a continuous spectrum with a finite spectral width A. For a rectangular laser line profile, we have:

$$F_i = \frac{\Delta\nu_L}{\pi\Delta}\left[\operatorname{arctg}\frac{\Delta - 2\delta_i}{\Delta\nu_L} + \operatorname{arctg}\frac{\Delta + 2\delta_i}{\Delta\nu_L}\right],$$

$$\delta_i = \nu_i - \nu^0_{las}$$

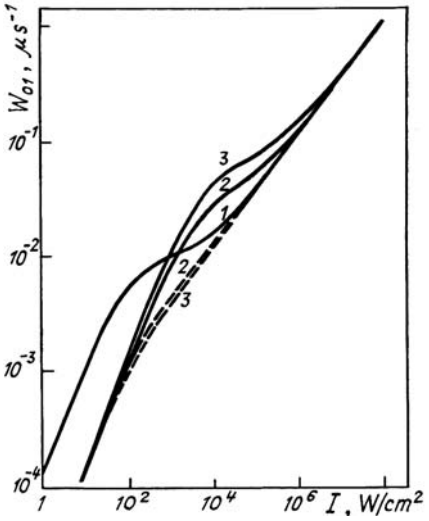

Fig. 2. Vibrational transition excitation probability versus continuous spectrum intensity with bandwidth Δ *(solid lines), and versus nonstabi1ized monochromatic radiation intensity within the same interval* Δ *(dashed lines). Curves* 1, 2 and 3 *correspond to* $\Delta = 0, 0.1$ *and* 0.2 cm^{-1}. *Elsasser's model with* $\delta = 0$, $\Delta\nu_L = 2.24 \times 10^{-3}$ cm^{-1}, $\tau_{RT} = \tau^0_{RT}$ *is assumed for vibrational transitions. The rest of the parameters are the same as in Fig. 1.*

Figure 2 illustrates variations of W_{01} for the $|0\rangle - |1\rangle$ transition versus laser intensity. The plots depict the cases of monochromatic exciting radiation with nonstabi1ized frequency in the interval Δ, and a continuous spectrum with spectral width Δ. The curves are seen to differ greatly in the moderate intensity

range where the saturation of the V–R transitions in Δ is not very strong. As the continuous spectrum widens, there is also an expansion of the intensity range where the absorption is nearly linear. The major contribution to W_{01} then comes from lines in the interval Δ. For $\Delta \gg \Delta\nu_L$, $F \le \Delta\nu_L/L$, and the excitation probability can be approximated by the Δ- and δ- independent quantity

$$W_{01}^{\infty} \approx qW \frac{\Delta\nu_L}{L} \tag{8}$$

Interestingly, this result is the same as Eq. (6) for $W\tau_{RT} \ll 1$. Hence, it follows that in the linear absorption regime for $\Delta \gg \Delta\nu_L$, L the excitation probability W_{01} is independent of the laser spectral width and stability and is given approximately by Eq. (8). In the case of the nonlinear collective absorption, the laser spectrum structure is also immaterial. The above considerations are confirmed by the behaviour of $W_{01}(\Delta)$ shown in Fig. 3 for two total intensities. Equation (8) is readily seen to provide an adequate accuracy.

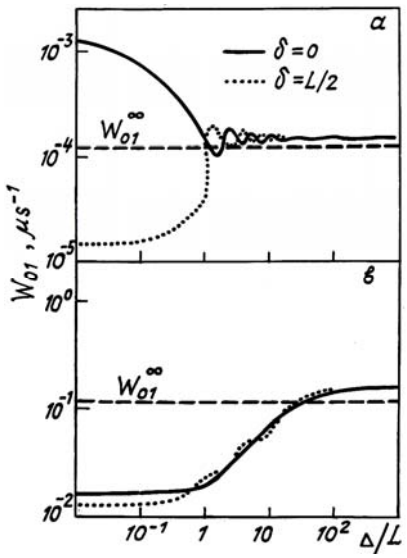

Fig 3. Vibrational transition excitation probability approximated by Elsasser band versus continuous radiation width for fixed total intensity: a) – for I = 10 W/cm^2, b) – for I = 10 kW/cm^2. Band parameters are the same as in Fig. 2.

ABSORPTION SPECTRUM WITH CHAOTIC ROTATIONAL STRUCTURE

The correlation between the excitation of the $|0\rangle - |1\rangle$ transition and the random quality of the absorption line parameters will now be addressed . For the sake of simplicity, it is assumed that the radiation is monochromatic at frequency ν, and the absorption lines have a Lorentzian profile. The band spectrum is approximated by Goody's model[7], i.e., the number-N of identical lines is randomly and equiprobably $(1/NL)$ distributed over the interval $[\nu - NL/2, \nu + NL/2]$, with L then giving the mean line separation. Averaging over q_1 and ν_1 in Eq. (4) yields

$$\langle W_{01} \rangle_{q_1,\nu_1} = 2\frac{qW}{\beta}\left(\frac{\Delta\nu_L}{L}\right)^2 \operatorname{arctg} \pi\xi\,, \quad \xi = \frac{N}{\beta} \tag{9}$$

where ξ allows for the effect of finite bandwidth on $\langle W_{01} \rangle$. For $\xi \gg 1$ it can be assumed that the bandwidth is infinite and the excitation probability is independent of N. In that event, the expression for $\langle W_{01} \rangle$ coincides with Eq. (6):

$$\langle W_{01} \rangle_{q_1,\nu_1} = \pi\frac{qW}{\beta}\left(\frac{\Delta\nu_L}{L}\right)^2 \tag{10}$$

For $\xi < 1$, the finiteness of the number of lines within the band sets a limit on the excitation of the vibrational transition. For $W\tau_{RT} \gg 1$, the vibrational transition becomes saturated, causing the bottleneck effect to occur. In the case of the linear absorption, Eq. (9) implies Eq. (8). The latter differs only by a numerical factor from the relation derived in Ref. 4 for the Elsasser model; the factor results from averaging over frequency offsets.

In the generalized random-band model, all three parameters q_1, ν_1, A_1 are statistically distributed. In calculating $\langle W_{01} \rangle$, the probability distribution for these quantities can be approximated as being uniform over the entire spectrum provided the characteristic scales of their variations with frequency satisfy the condition implied by Eq.(4):

$$\Omega_x \gg \Delta\nu_L\left(1 + \frac{4}{\pi} W\tau_{RT}\right)^{1/2} = \beta\frac{L}{\pi}\,,$$

$$x = q_1,\ \nu_1,\ A_1 \tag{11}$$

We emphasize that this condition is sufficient but not necessary.

The expression for the $|0\rangle - |1\rangle$ transition probability in the generalized infinite-band model can be obtained by averaging Eq. (10) over A_1 for $A_1 < A_2$. Consider the limiting cases of narrow and broad distributions $p(A_1)$ against the background of dependence (10) on A. The narrow distribution yields Eq. (10) for $\langle W_{01} \rangle$ with $A = A_0$, where A_0 is the location of the maximum for $p(A_1)$. Assuming $p(A_1) \simeq p(A_0)$ and a broad distribution, $\langle W_{01} \rangle$ reads

$$\langle W_{01} \rangle_{q_1,\nu_1,A_1} = q\frac{\Delta\nu_L}{L}\frac{\pi}{6b\tau_{RT}}\,p(A_0)\,(1+bA_1)^{1/2}\,(bA_1 - 2)\Big|_{A_1}^{A_2}$$

$$b = \frac{c^2 I \tau_{RT}}{2\pi^2 \Delta\nu_L h\nu^3} \tag{12}$$

For $W\tau_{RT} \ll T$, Eqs. (10) and (12) are independent of and vary linearly with I, whereas in the nonlinear collective absorption regime the result (7) is obtained, up to a numerical factor. Our earlier analytic expressions for $\langle W_{01} \rangle$ employing particular distribution functions $p(A_1)$ appear to exhibit similar behavior.[5] The frequency-independent probability distribution for random absorption line parameters adequately describes the actual vibration-rotation bands as a whole or at least a reasonable large segment.[7] However, there may be certain spectrally inhomogeneous intervals. Calculations based on the model functions $A_i \sim |\nu - \nu_i|^\alpha$ and $p(\nu_i) \sim |\nu - \nu_i|^\alpha$ (where $0 \ll \alpha \ll 1$) have indicated that the frequency dependence of A_i and the nonuniform line density within the band may appreciably affect $\langle W_{01} \rangle$ as a function I and τ_{RT}. For example, for identical Lorentzian lines within the infinite band with $p(\nu_i) \sim |\nu - \nu_i|^\alpha$ in the nonlinear collective absorption regime we have

$$\langle W_{01} \rangle_{q_i, \nu_i} \sim (I/\tau_{RT})^{1/2} (I\tau_{RT})^{\alpha/2} \qquad (13)$$

Evidently, Eq. (7) results from Eq. (13) only for $\alpha = 0$.

EFFECT OF ABSORPTION LINE SHAPE

If the absorption is linear the lineshape influences only the magnitude of the excitation probability but not its dependence on intensity. For nonlinear absorption, on the other hand, W_{01} is determined by the wings of the quasiresonant lines that can be assumed Lorentzian[8] for collisional broadening and a frequency offset of < 10 cm^{-1}. Thus the deviation of the experimental function $W_{01}(I)$ from a square-root dependence would suggest a pronounced effect of frequency on the spectral line parameters. It follows from simple estimates that in the case of nonlinear absorption and experimentally attainable laser intensities, the far wings (frequency offsets of the order of tens and hundreds of cm ') make no contribution to the excitation probability. For exponentially decreasing wings (Doppler profile), the effect of collective absorption is negligible and the vibrational excitation probability is well approximated by the vibrational bottleneck assumption, taking into account a few V–R transitions close to the laser frequency.

In conclusion, the specific features inherent in the laser excitation of vibrational transitions with a dense spectrum can be summarized as follows:

1. The collective absorption regime is found to occur when $\beta = \pi\Delta\nu_L/L(1 + 4/\pi W\tau_{RT})^{1/2} \gg 1$. Note that the absorption is linear for $W\tau_{RT} \ll 1$ and nonlinear for $W\tau_{RT} \gg 1$. It should be emphasized that the bottleneck effect occurs in strong laser fields for $\beta \ll 1$.

In the case of collective absorption, the vibrational transition excitation probability is insensitive to frequency offset from the nearest V–R transition, laser linewidth, and stability (see Figs. 1 and 2 for $I \geq 0.1$ MW/cm^2). With increased width A of the continuous spectrum, saturation of the transitions involved is found to decrease, and with linear absorption, the vibrational excitation probability for $\Delta \gg \Delta\nu_L$ appears to be independent of Δ and is approximated by Eq. (8).

2. In the nonlinear collective absorption regime, the intensity dependence of W_{01} is determined by the shape of the absorption line wings, the variations of $A(\nu_i)$ and $q(\nu_i)$, and the spectral line density with frequency. The effect of nonuniform line density within the band on the intensity dependence of W_{01} is illustrated by Eq. (13). For spectral line contours with Lorentzian wings and subject to Eq. (12) we have $W_{01} \sim (I/\tau_{RT})^{1/2}$.

ACKNOWLEDGEMENT

The authors are grateful to Dr. A.P. Sukhorukov for his interest in this work and helpful discussions.

REFERENCES

1. V.F. Gordietz, A.F. Osipov and L.A. Shelepin *Kinetic Processes in Gases and Molecular Lasers*. (Nauka, Moscow, **512**, 1980)
2. S.V. Ivanov, V.Ya. Panchenko and A.P. Sukhorukov Vestnik MSU, ser. Fizika, Astronomia, **25**, 64 (1984)
3. A.V. Chugunov, M.S. Djidjoev, S.V. Ivanov and V.Ya. Panchenko Opt.Lett., **10**, 615 (1985)
4. M.S. Djidjoev, S.V. Ivanov, V.Ya. Panchenko and A.V. Chugunov Kvantovaja Elektron., **13**, 740 (1986)
5. S.V. Ivanov and V.Ya. Panchenko Preprint NITTSLAN, No. 28 (1987)
6. A. Barbe, C. Secroun, P. Jouve et al. J. Molec. Spectrosc., **64**, 343 (1977)
7. R.M. Goody *Atmospheric Radiation, Part I, Theoretical Bases*. (Oxford at the Clarendon Press., 1964)
8. V.V. Fomin in: *Spectral Manifestation of Molecular Interactions in Gases* Ed. by Yu.S. Makushkin, (Nauka, Novosibirsk 1982)