

9. Zvereva N.A., Nabiev Sh.Sh., Ponomarev Yu.N. Structure and properties of molecular complexes of water with low gas components of atmosphere. – Tomsk: RAS SD, 2003. – 139 p.
10. Gordiets B.F., Osipov A.I., Shelepin L.A. Kinetic processes in gases and molecular lasers. – Moscow: Nauka, 1980. – P. 416–436.
11. Ogilvie F., Rodwell W.R., Tipping R.H. Dipole moment function of the hydrogen halides // *J. Chem. Phys.* – 1980. – V. 73. – P. 5231–5229.
12. Spirko V., Piecuch P., Condo A.E., Paldus J. Molecular quadrupole moment function of HF and N<sub>2</sub>. II. Rovibration effects // *J. Chem. Phys.* – 1996. – V. 104. – P. 4716–4727.
13. Buldakov M.A., Cherepanov V.N., Nagornova N.S. Polarizability functions of HF and HCl molecules // *Proc. SPIE.* – 2005. – V. 6160. – P. 51–56.
14. Cherkasov M.R. Formalism of quantum-mechanical operator of Liuvill in calculations of relaxation parameters. – Tomsk: IOA of USSR AS SD, 1975. – 47 p. (Preprint № 26).
15. Varshalovich D.A., Moskalev A.N., Khersonskii V.K. Quantum theory of angular moment. – Leningrad: Nauka, 1975. – 436 p.
16. Huiszoon C. Ab initio calculations of multipole moments, polarizabilities and isotropic long range interaction coefficients for dimethylether, methanol, methane, and water // *Molecular Physics.* – 1986. – V. 88. – P. 865–885.
17. Bykov A.D., Stroinoва V.N. Shift of centers of H<sub>2</sub>O absorption lines in the range of 13550–13950 cm<sup>-1</sup> // *Optics of atmosphere and ocean.* – 2006. – V. 19. – № 1. – P. 31–38.
18. Huber K.P., Herzberg G. Molecular spectra and molecular structure. IV. Constants of diatomic molecules. – N.Y.: Van Nostrand Reinhold Company, 1979. – 408 p.
19. Stroinoва V.N. Calculations of broadening coefficients of H<sub>2</sub>O absorption lines in the range of 13550–13950 cm<sup>-1</sup> // *Optics of atmosphere and ocean.* – 2005. – V. 18. – № 9. – P. 820–824.

*Received on 20.11.2006*

UDC 539.194,535.621

## HALF-WIDTH AND LINE CENTER SHIFTS FORMED BY TRANSITIONS INTO HIGHLY EXCITED VIBRATION STATES OF CO MOLECULE

V.N. Stroinoва

Tomsk Polytechnic University

E-mail: vns@tpu.ru

*Within the proposed model the half-width and shift of centers of spectral lines formed by transitions on high vibration conditions of CO molecule to dissociation bound have been calculated. The given results allow investigating kinetic processes and characteristics of CO-laser cold plasma.*

### Introduction

At present much attention is paid to the development of CO-lasers capable of serving as frequency standards. In modern CO-lasers with cascade mechanism of generation the transitions to highly excited vibrational states up to  $v=41$  [1],  $v=36, 38$  [2, 3] are used. In order to construct laser kinetic models generating at high vibrational-rotational (VR) transitions it is necessary to know relaxation parameters of contour of lines of vibrationally excited working substance. The investigation of vibrational dependence of half-width and shift of centers of CO molecule lines in lasers with optical pumping and cascade generation mechanism gains a special importance [4, 5]. In [4] the properties of plasma of CO-laser with optical pumping were studied and it was ascertained that population of high vibrational states calculated within the bounds of kinetic model does not conform to the measured value (a divergence is almost twice as much). Evidently, the substantial difference of calculation from the experiment is conditioned by ill-posed values of relaxation parameters of high vibrational states of CO molecule.

In [6] the influence of intramolecular dynamics of highly excited vibrational states of diatomic molecules on relaxation parameters of line contour was studied. It was shown that peculiarities of behavior of dipole, qua-

drupole moments, polarizability, rotational constant at strong vibrational excitation may change considerably relaxation parameters of lines of CO molecule belonging to high vibrational states up to  $v=50$ . In [7] half-width and line center shift of CO molecule formed by cold transitions to low vibrational states to  $v=3$  were measured. Measurements of half-widths, line center shifts for transitions with higher value of vibrational quantum number of upper state are absent at present.

The aim of this paper is to develop the model which allows calculating relaxation parameters of lines of CO molecule at strong vibrational excitation up to dissociation bound. The suggested model is based on one of the variants of semiclassical impact theory; on functions of multipole moments and polarizability calculated by *ab initio*; on the model of Morse oscillator. Rotational and vibrational dependence of half-width and line center shift of CO-CO cold and hot bands at change of vibrational quantum number up to  $v=65$  were studied as a validity test of the new model. The investigation of cold plasma properties occurring at generation of radiation of CO-laser with optical pumping at high vibrational transitions of working substance; use of relaxation parameters of high vibrational states for constructing kinetic models may be practical application of the results.

### Theoretical analysis

Traditional approach of determining VR energy levels and wave functions is connected with application of perturbation theory (in general case in the form of the method of effective rotational Hamiltonian). The main supposition of perturbation method is the smallness of intramolecular interaction in comparison with energy of zero-order approximation. Harmonic oscillator is selected as the latter and all the magnitudes, for example, dipole moment, potential energy function or the second moments are given in the form of expansion in a Taylor series close to equilibrium molecule configuration.

For moderately excited vibrational states the VR wave functions are located in a small neighborhood close to equilibrium molecule configuration. As a result, average values of dipole and quadrupole moments, polarizability determining intermolecular potential are insignificantly changed at excitation of one or several vibrational quanta. Change of average values of multipole moments as well as the change of rotational and centrifugal constants, rotational energy spectrum may be easily taken into account within the bounds of perturbation theory.

A totally different picture should be expected at strong vibrational excitation. Potential curve, function of dipole [8], quadrupole [9] moments and polarizability [10] calculated in this work are given in Fig. 1 and in the Table.

Morse oscillator model was used in the work for determining wave functions; parameters of Morse potential for CO were determined by fitting to potential function calculated by *ab initio*. CO molecule has the dissociation limit  $89500 \text{ cm}^{-1}$ , potential function maintains 83 vibrational states. As a result of significant increase (in 14 times) of the distance between swivel points of wave function close to dissociation limit the most part of functions of dipole and quadrupole moments, polarizability is overlapped. Calculating relaxation parameters of CO line formed by transitions to high vibrational states the asymptotic behavior of functions of multipole moments and polarizability at  $r \rightarrow \infty$ ,  $r \rightarrow 0$  should be preliminarily analyzed. You can see (Fig. 1) that wave function of the ground state is located in a small region close to equilibrium position but wave functions of highly excited states ( $\nu=10, 30, 50$ ) take a broad region overlapping almost the whole region of variation of dipole moment. It is obvious that at such high amplitude of atom oscillation the behavior of functions of dipole, quadrupole moments and polarizability of CO at  $r \rightarrow 0$ ,  $r \rightarrow \infty$  should be taken into account. At  $r \rightarrow 0$  the value of average dipole moment tends to the value of dipole moment of united atom (to zero); at  $r \rightarrow \infty$  (molecule dissociation) dipole moment of CO molecule also tends to 0. The similar behavior is observed for quadrupole moment and for average dipole polarizability. The values of diagonal matrix elements of dipole, quadrupole moments, polarizability, rotational constant calculated in the work by numerical integration are given in the Table. It is seen from the Table that strong vibrational exci-

tation results in significant changes of intramolecular parameters of CO molecule and one of them increase and the others decrease. For example, the calculated average dipole moment of the ground state equals  $0,12 \text{ D}$  (the calculated value conforms well to experimentally determined one) and its value in vibrational state  $\nu=50$  equals  $1,04 \text{ D}$  that is 8,7 times higher and has an opposite sign. An average quadrupole moment of CO molecule decreases from the value  $-2,0$  at  $\nu=0$  to  $0,842$  at  $\nu=50$  that is 2,4 times by absolute value. The preliminary analysis [6] showed that intramolecular interactions could not be considered as small ones any more and average values of intramolecular parameters should be calculated with proper wave functions.

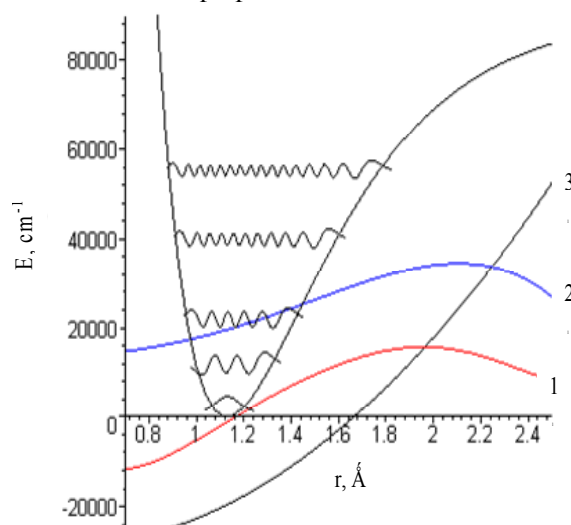


Fig. 1. Potential function ( $\text{cm}^{-1}$ ), wave functions ( $10^3$ ) of vibrational states  $\nu=0, 5, 10, 20, 30$  of CO molecule. Functions of: 1) dipole moment ( $10^4 \text{ D}$ ), 2) polarizability ( $10^4 \text{ \AA}^3$ ), 3) quadrupole moment ( $10^4 \text{ D\AA}$ )

Thus, broadening and shift of line centers of CO molecule in highly excited states are determined by a change of diagonal matrix elements of multipole moments and polarizability as well as by the dependence of rotational and centrifugal constants on vibrational quantum number  $\nu$ . Table data show that significant changes of half-width and shift of line centers formed by transitions into highly excited vibrational states of CO in comparison with their values for low vibrational states should be expected.

Table. Average values of CO intramolecular parameters in excited vibrational states

$\nu$	$\Delta r, \text{ \AA}$	$B, \text{ cm}^{-1}$	$\mu, \text{ D}$	$q, \text{ D\AA}$	$\alpha, \text{ \AA}^3$
0	0,12	1,923	-0,112	-1,951	1,962
3	0,28	1,889	-0,060	-1,846	2,021
10	0,45	1,771	0,120	-1,699	2,102
20	0,72	1,595	0,386	-1,339	2,289
30	0,92	1,411	0,658	-0,855	2,510
40	1,03	1,220	0,906	-0,176	2,756
50	1,12	1,018	1,042	0,842	2,968
60	1,33	0,797	0,922	2,542	2,861
65	1,68	0,676	0,772	3,921	2,321

## Results and discussion

Within the bounds of one of the variants of broadening theory in collision approximation [11, 12] half-width and line center shifts are determined by expansion in a series of perturbation theory of scattering matrix  $S(b) = \text{Re}S(b) + i\text{Im}S(b)$ :

$$\begin{aligned} \text{Re}S(b) &= \\ &= 1 - \exp\{-\text{Re}S_2^{\text{outer}}(b)\} \cos\{\text{Im}S_2^{\text{outer}}(b) + S_1(b)\}, \\ \text{Im}S(b) &= \\ &= \exp\{-\text{Re}S_2^{\text{outer}}(b)\} \sin\{\text{Im}S_2^{\text{outer}}(b) + S_1(b)\}. \quad (1) \end{aligned}$$

Restricting by the second order of expansion and considering contributions from electrostatic and polarization part of intermolecular potential the expression for a half-width

$$\begin{aligned} \gamma(i, f) &= \\ &= \frac{m\nu}{c} \sum_j \rho(j) \int_0^\infty \left[ 1 - \exp\{-\text{Re}S_2^{\text{outer}}(b)\} \times \right. \\ &\quad \left. \times \cos\{S_1(b) + \text{Im}S_2^{\text{outer}}(b)\} \right] b db, \quad (2) \end{aligned}$$

and line center shifts written down

$$\begin{aligned} \delta(i, f) &= \frac{m\nu}{c} \sum_j \rho(j) \int_0^\infty \sin\{S_1(b) + \text{Im}S_2^{\text{outer}}(b)\} \times \\ &\quad \times \exp\{-\text{Re}S_2^{\text{outer}}(b)\} b db. \quad (3) \end{aligned}$$

In (2), (3) approximation of linear paths and average velocity of collisions was used. Here  $i, f$  are the vibrational quantum numbers of initial and finite state of VR transition;  $b$  is the impact parameter;  $\nu$  is the average relative velocity of colliding particles;  $\rho(j)$  is the density matrix.

In the first order of perturbation theory the contribution into line relaxation parameters is determined by isotropic part of intermolecular potential (induction and dispersion interaction). Contribution of dispersion interaction was calculated in Unzold approximation [13].

$$\begin{aligned} S_1(i, f, b, \nu) &= \frac{3\pi}{8\hbar\nu b^5} \times \\ &\times \left\{ \alpha_2 \left\{ \langle V_i | \mu_1^2 | V_i \rangle - \langle V_f | \mu_1^2 | V_f \rangle \right\} + \right. \\ &\quad \left. + \left[ \mu_2^2 + \frac{3}{2} \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \alpha_2 \right] \left\{ \langle V_i | \alpha_1 | V_i \rangle - \langle V_f | \alpha_1 | V_f \rangle \right\} \right\}. \quad (4) \end{aligned}$$

Here  $\mu_1, \mu_2, \alpha_1, \alpha_2$  is the function of dipole moment and polarizability of absorbing and disturbing molecule;  $\varepsilon_1, \varepsilon_2$  are the ionization potentials;  $|V_i\rangle, |V_f\rangle$  are the wave functions of initial and finite vibrational states of absorbing molecule. In the case of self-broadening  $\mu_1 = \mu_2, \alpha_1 = \alpha_2, \varepsilon_1 = \varepsilon_2$ .

In the second order of perturbation theory the contribution into line relaxation parameters is determined by dipole-dipole, dipole-quadrupole and quadrupole-quadrupole moments. For brevity formulas only for the case of real part of scattering matrix and dipole-dipole interaction are given here:

$$\begin{aligned} \text{Re}S_2^{\text{outer}}(i, f, b, \nu) &= \frac{4}{9} \frac{1}{(\hbar\nu b^2)^2} \times \\ &\times \sum_{j'} D(jj'|1) \left\{ \sum_{i'} D(ii'|1) \text{Re}\varphi_{11}(k_{i'i'j'}) + \right. \\ &\quad \left. + \sum_{f'} D(ff'|1) \text{Re}\varphi_{11}(k_{f'f'j'}) \right\}. \quad (5) \end{aligned}$$

Here  $\varphi_{11} = \text{Re}\varphi_{11} + i\text{Im}\varphi_{11}$  is the complex resonant function for dipole-dipole interaction. The generalized force of line  $D$  is determined as a square of reduced matrix element of dipole moment operator  $\mu_i$  of absorbing molecule in vibrational state  $i$  or  $f$ . For cold transitions  $0 \rightarrow \nu_i$  a diagonal matrix element of dipole moment was calculated:

$$D(ii'|1) = \left| \langle V_i | \mu | V_i \rangle \right|^2 (J_i 100 | J_i' 0)^2. \quad (6)$$

Here  $(J_i 100 | J_i' 0)$  are the coefficients of Klebsch-Gordon [14] for diatomic molecules. Resonant parameter  $k$  in (5) is determined by the balance of rotational level energies in upper or lower vibrational states:

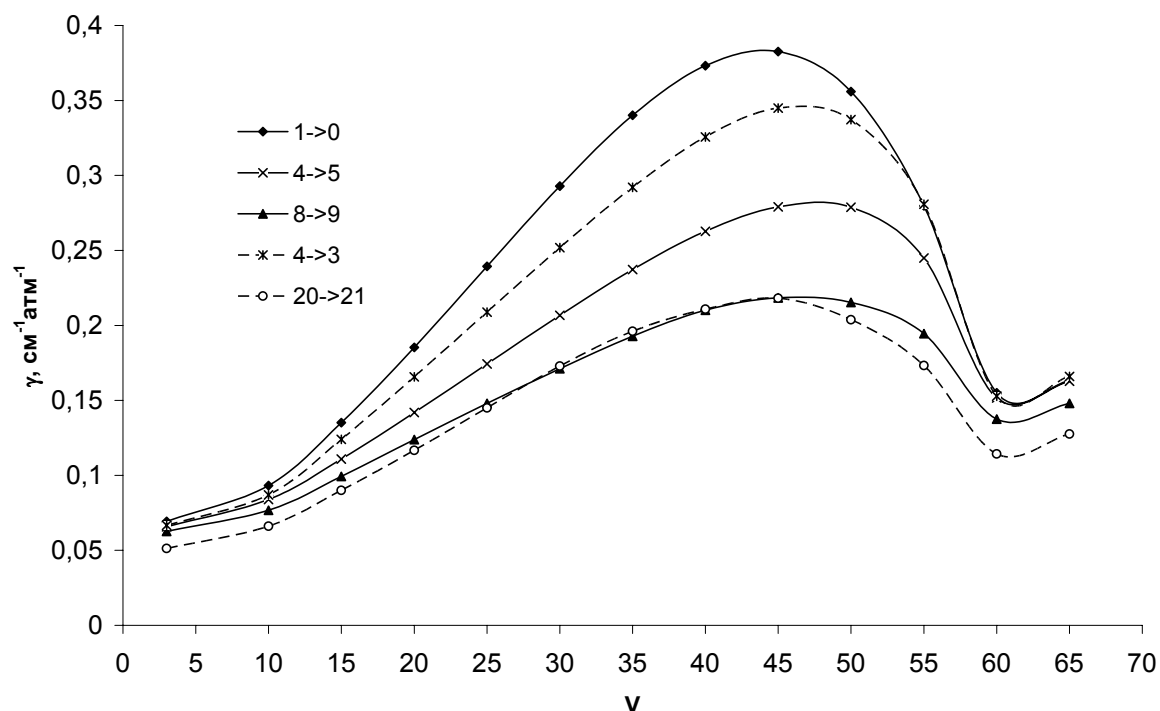
$$\begin{aligned} k_{i'i'j'} &= \frac{2\pi cb}{\nu} (E_i - E_{i'} + E_j - E_{j'}) = \\ &= \frac{2\pi cb}{\nu} (\omega_{i'} + \omega_{j'}). \quad (7) \end{aligned}$$

Substituting indices  $i, i'$  by  $f, f'$  resonant parameter  $k_{f'f'j'}$  may be obtained in upper vibrational state of transition.

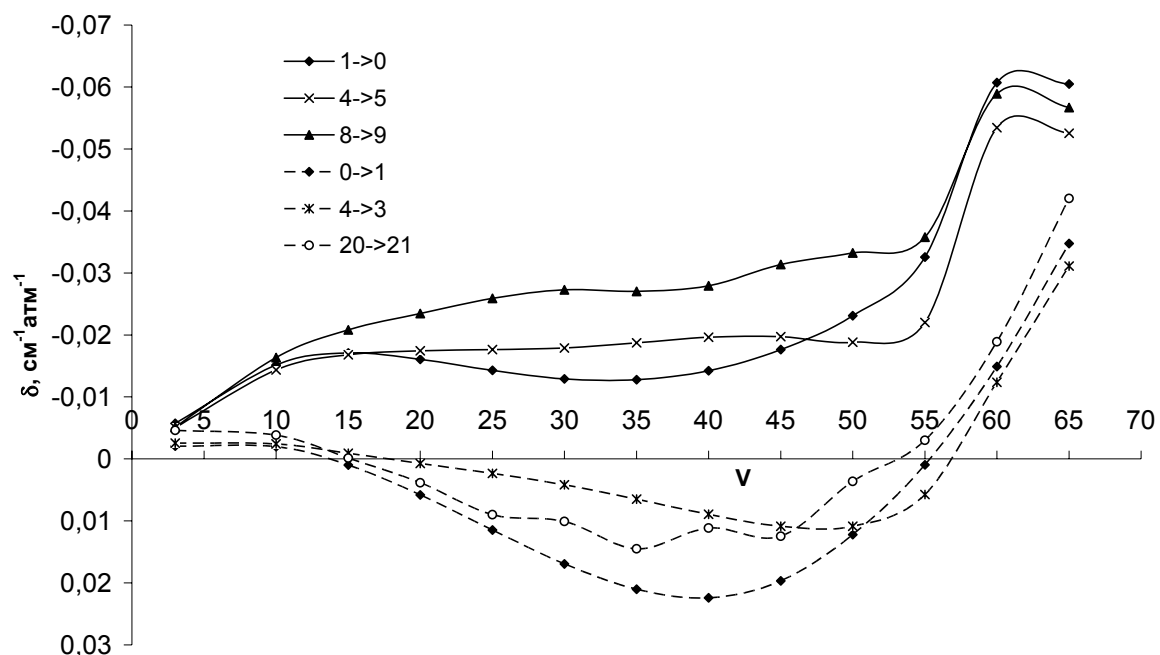
Functions of dipole [8], quadrupole [9] moments, polarizability [10] calculated by *ab initio* or semi-empirically were applied for analyzing vibrational and rotational dependence of line relaxation parameters. Rotational constant for  $\nu=0$  and some constants of CO molecule are taken from [15]. Matrix elements of dipole moment (4), (6), (7), quadrupole moment, polarizability (4) and rotational constant required for calculation of relaxation parameters were determined by numerical integration. It is shown in the Table that polarizability increases 1,5 times, rotational constant decreases twice; that is partial compensation of intramolecular dynamics effects is possible. For example, rotational constant decrease results in increase of half-widths of CO-CO lines (22 % in state  $\nu=23$  in comparison with  $\nu=1$ ), increase of average dipole moment results in decrease of line half-widths. To study total effect of vibrational excitation influence on relaxation parameters of CO-CO lines the calculations by the formulas (1)–(8) were carried out. Half-widths and shifts of CO-CO lines centers of 0-3 bands calculated in this paper conform satisfactorily to those measured in [7].

Vibrational dependence of half-widths of CO-CO lines is complex (Fig. 2): half-widths of five lines increase at growth of vibrational quantum number up to  $\nu=45$ , then they decrease again up to  $\nu=65$ . Half-width of line 0–1 in vibrational state  $\nu=45$  exceeds the half-width of the same line in state  $\nu=3$  by 2,7 times. Vibrational dependence of half-width is caused by the influence of behavior of the function of dipole, quadrupole moments and to less degree of polarizability and rotational constant. The results of calculations of line center shifts of CO cold and hot bands in self-broadening conditions are given in Fig. 3. You can see from Fig. 3 that for four lines the dependence of center shift from vibrational quantum number is monotone increasing to  $\nu=60$  then it slightly decreases to  $\nu=65$ .

Shift of 0-1 line center in vibrational state  $\nu=60$  increases 12 times in comparison with the shift of the same line in the state  $\nu=3$ . It should be noted that vibrational dependence of the shift of CO-CO line centers (Fig. 3)



**Fig. 2.** Dependence of half-widths of CO-CO lines on vibrational quantum number  $v$  of upper state for cold (full curve) and hot (dashed curve) bands



**Fig. 3.** Dependence of shift of centers of CO-CO lines on vibrational quantum number  $v$  of upper state for cold (full curve) and hot (dashed curve) bands

is determined in general by polarizability function behavior while vibrational dependence of rotational constant, dipole and quadrupole moments result as well in a slight shift increase.

Rotational dependence of half-widths of CO-CO lines are given in Fig. 4. One can see that line half-widths slightly increase to  $J=4$  (Fig. 4, a);  $J=2$  (Fig. 4, b); then decrease at growth of rotational quantum number  $J$ . It is connected with increase of frequencies  $\omega_{JJ'}$  of rotational

transitions into upper vibrational state (7). A similar rotational dependence is observed for half-widths of  $H_2O$  lines at air broadening [16].

Rotational dependence of the shift of CO-CO lines center of cold bands given in Fig. 5, a, is nonmonotonic that is explained by competition of frequencies of rotational transitions  $\omega_{JJ'}$  in upper vibrational state and  $\omega_{ijj'}$  – in lower one. It should be noted that the shift of centers of lines  $H_2O$ -air increases steadily depending on ro-

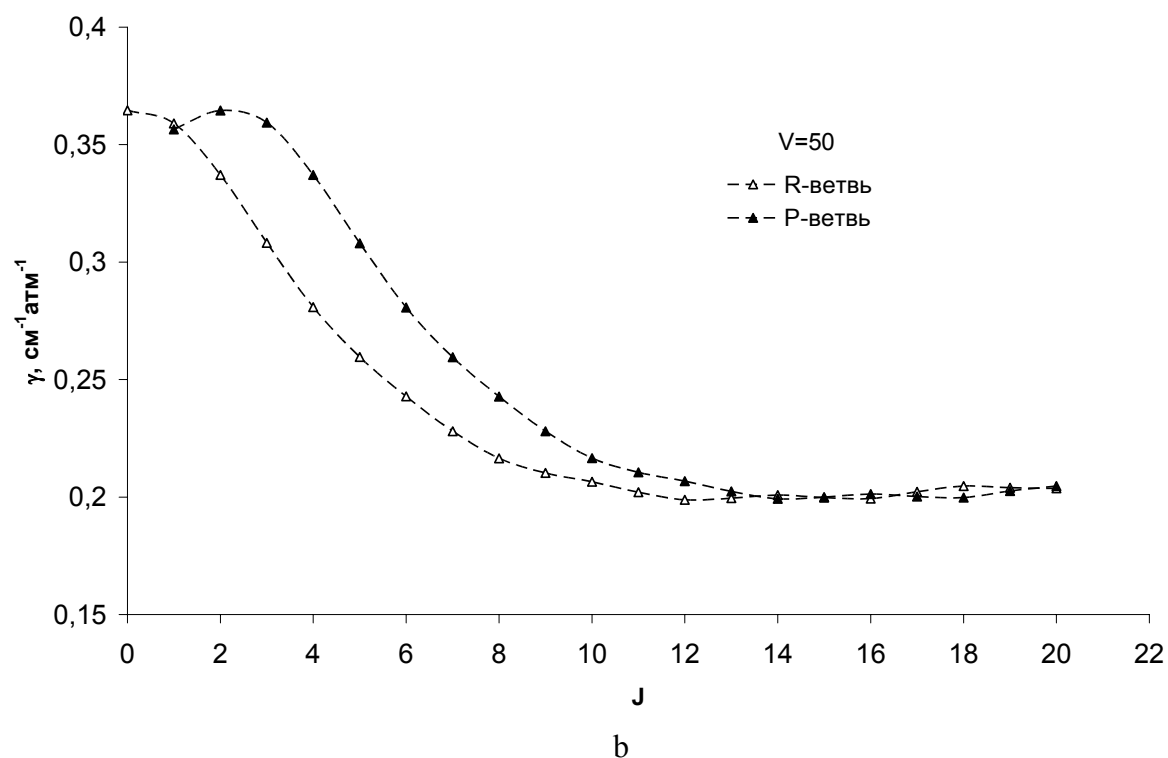
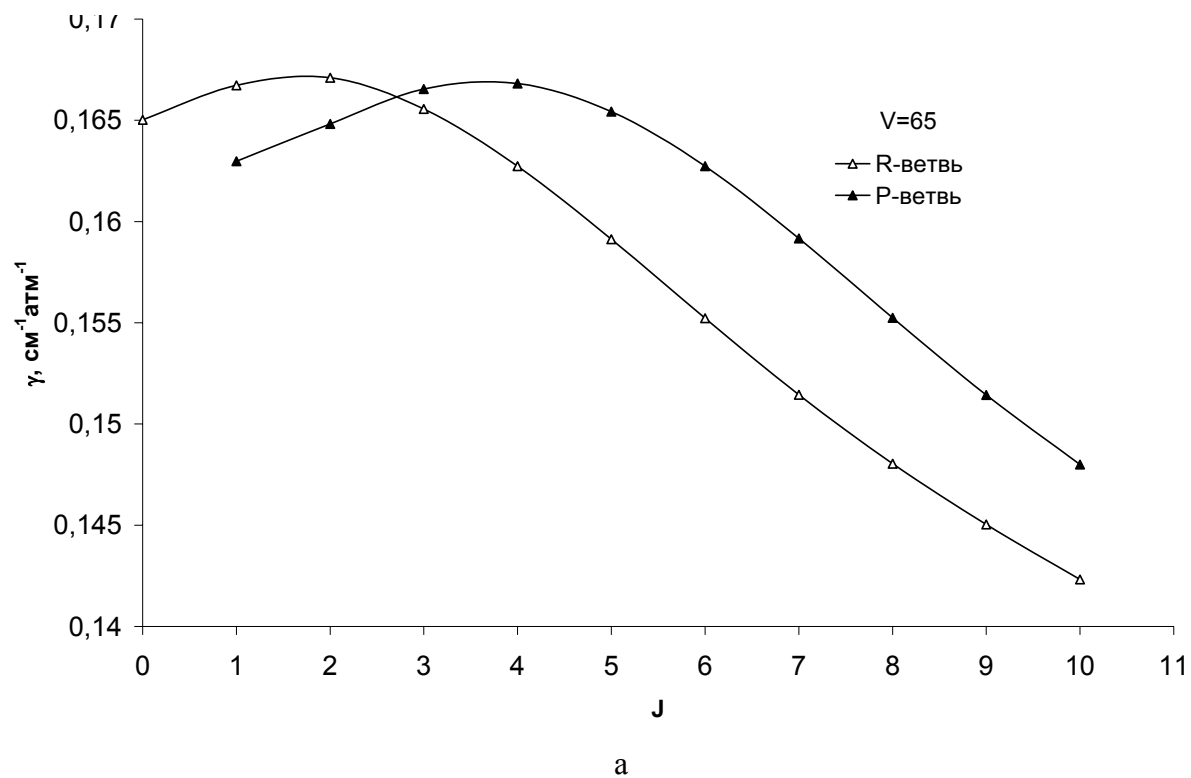
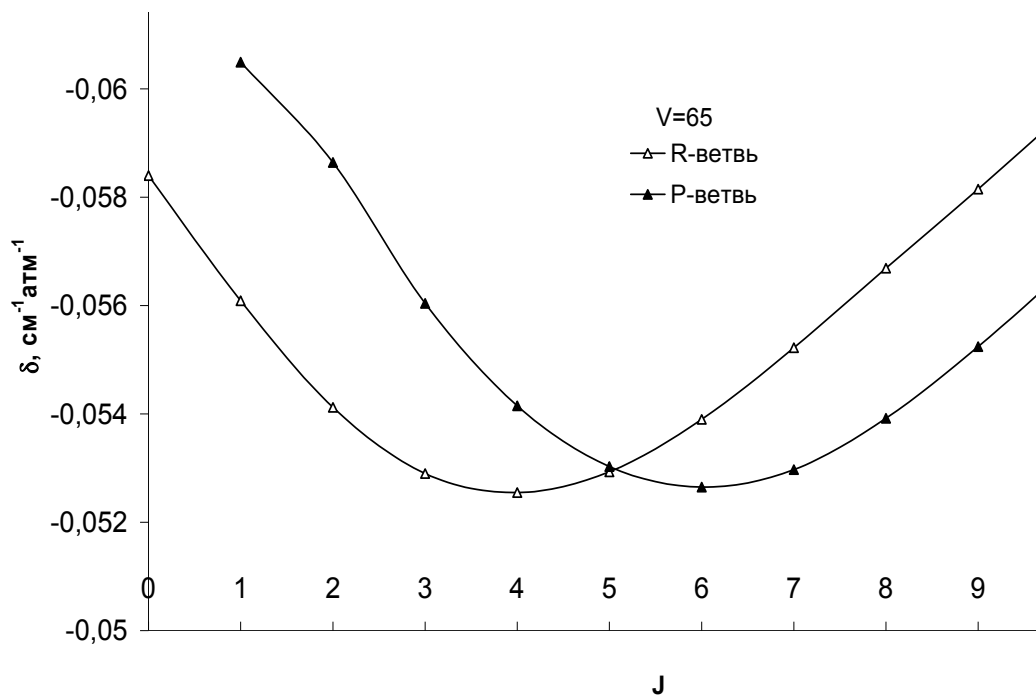
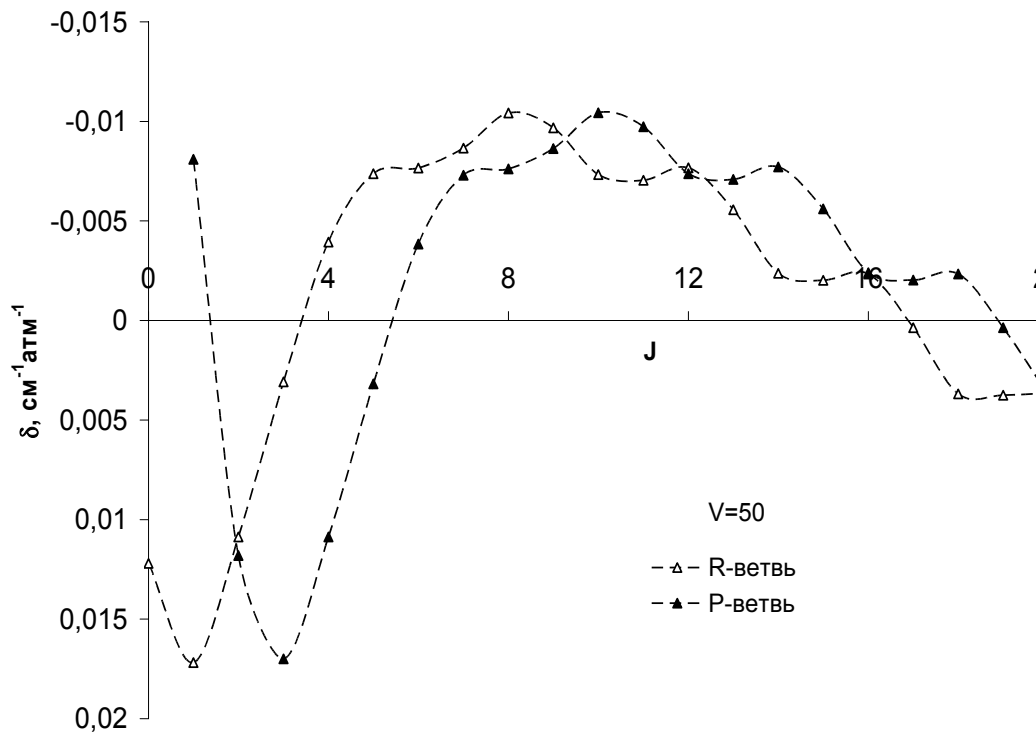


Fig. 4. Dependence of half-widths of CO-CO lines on rotational quantum number of lower state for: a) cold bands b) hot bands



a



b

Fig. 5. Dependence of shift of centers of CO-CO lines on rotational quantum number of lower state for: a) cold bands b) hot bands

tational quantum number [17]. For lines of hot bands (Fig. 5, *b*) a change of sign of center shift of some CO-CO lines, so-called oscillating shifts, observed experimentally in [18] for lines  $\text{H}_2\text{O}-\text{H}_2\text{O}$  takes place.

It should be noted that adiabatic contribution (4) into half-widths of CO-CO lines determining dependence of half-width on vibrational quantum number was studied as well (Fig. 2). It was revealed that for lines of a band 0-65 it averages 20 % and conditions strong vibrational dependence of half-width.

### Conclusion

Vibrational and rotational dependences of line relaxation parameters caused by transitions to highly excited vibrational states of CO molecule were firstly studied. The proposed model allows advancing to the field of

high VR states up to dissociation limit of CO molecule. It should be noted that use of functions of dipole, quadrupole moments, polarizability calculated by *ab initio* for computing the required matrix elements increase considerably the value and validity of calculated values of half-width and shift of line center. Specific effects of vibrational excitation: influence of rotational constant change and influence of adiabatic effect on line half-width were studied as well. The influence of strong vibrational excitation on line relaxation parameters was studied before only for  $\text{H}_2\text{O}$  molecule [17, 19, 20]. The results of this work may be used at construction of kinetic models of vibrationally excited working substance of CO-laser, for studying cold laser plasma properties.

*The author is grateful to professor doctor of physical-mathematical science A.D. Bykov for discussion of work results.*

### REFERENCES

- Coxon J.A., Hajigeorgiou Ph.G. Direct potential fit analysis of the  $X^1\Sigma^+$  ground state of CO // *J. Chem. Phys.* – V. 121. – № 7. – P. 2992–3008.
- Ionin A., Kotkov A., Klimachev Yu., Seleznev L., Sinitsyn D. Small-signal gain and kinetic processes on highly excited vibrational levels in active medium of pulsed first-overtone CO laser // *Proc. SPIE.* – 2002. – V. 4760. – P. 1047–1054.
- Ionin A., Napartovich A. Physics of overtone CO laser operating on highly excited vibrational transitions // *Abstracts IQEC/LAT* – 2002. – Moscow, 2002. – P. 122.
- Lee W., Adamovich I. V., Walter R. L. Optical pumping studies of vibrational energy transfer in high-pressure diatomic gases // *J. Chem. Phys.* – 2001. – V. 114. – № 3. – P.1178–1186.
- Gordiets B.F., Osipov A.I., Shelepin L.A. Kinetic process in gases and molecular lasers. – Moscow: Nauka, 1980. – 542 p.
- Bykov A.D., Stroinoва V.N. Half-width and line center shifts of diatomic molecules at strong vibration excitation // *Optics of atmosphere and ocean.* – 2006. – V. 19. – № 8. – P. 719–726.
- Chackerian C., Freedman R.S., Giver L.P., Brown L.R. Absolute rovibrational intensities and self-broadening and self-shift coefficients for the  $X^1\Sigma^+ V=3\leftarrow V=0$  band of CO // *J. Mol. Spectrosc.* – 2001. – V. 210. – P. 119–126.
- Buldaikov M.A., Cherepanov V.N. Semi-empirical functions of dipole moment of CO and NO molecule // *Optics of atmosphere and ocean.* – 2004. – V. 17. – № 1. – P. 42–46.
- Maroulis G. Accurate higher electric multipole moments for carbon monoxide // *J. Chem. Phys. Lett.* – 2001. – V. 334. – P. 214–219.
- Maroulis G. Electric polarizability and hyperpolarizability of carbon monoxide // *J. Phys. Chem.* – 1996. – V. 100. – P. 13466–13473.
- Leawitt R.P. Pressure broadening and shifting in microwave and infrared spectra of molecules of arbitrary symmetry: An irreducible tensor approach // *J. Chem. Phys.* – 1980. – V. 73. – P. 5432–5450.
- Cherkasov M.R. Formalism of quantum-mechanical operator of Liouville in calculations of relaxation parameters. – Tomsk: IOA of USSR AS SD, 1975. – 47 p. Preprint № 26.
- Huiszoon C. Ab initio calculations of multipole moments, polarizabilities and isotropic long range interaction coefficients for dimethylether, methanol, methane, and water // *Molecular Physics.* – 1986. – V. 88. – P. 865–885.
- Varshalovich D.A., Moskalev A.N., Khersonskii V.K. Quantum theory of angular moment. – Leningrad: Nauka, 1975. – 436 p.
- Huber K.P., Herzberg G. Molecular spectra and molecular structure. IV. Constants of diatomic molecules. – N.Y.: Van Nostrand Reinhold Company, 1979. – 408 p.
- Stroinoва V.N. Calculations of broadening coefficients of  $\text{H}_2\text{O}$  absorption lines in the range 13550–13950  $\text{cm}^{-1}$  // *Optics of atmosphere and ocean.* – 2005. – V. 18. – № 9. – P. 820–824.
- Bykov A.D., Stroinoва V.N. Shift of centers of  $\text{H}_2\text{O}$  absorption lines in the range 13550–13950  $\text{cm}^{-1}$  // *Optics of atmosphere and ocean.* – 2006. – V. 19. – № 1. – P. 31–38.
- Grossmann B.E., Browell E.V. Spectroscopy of water vapor in the 720-nm wavelength region: line strengths, self-induced pressure broadenings and shifts, and temperature dependence of linewidths and shifts // *J. Mol. Spectrosc.* – 1989. – V. 136. – P. 264–294.
- Bykov A.D., Makushin Yu.S., Stroinoва V.N. The analysis of vibration excitation influence on half-widths of  $\text{H}_2\text{O}$  lines of  $n\nu_2$  bands // *Optics and spectroscopy.* – 1988. – V. 64. – P. 517–521.
- Lynch R., Gamache R.R., Neshiba S.P.  $\text{N}_2$  and  $\text{O}_2$  induced halfwidths and line shifts of water vapour transitions in the 301-000 and 221-000 bands // *J. Quant. Spectrosc. Radiat. Transfer.* – 1998. – V. 59. – № 4. – P. 595–413.

*Received on 20.11.2006*