DATABASE ON THE PARAMETERS OF SPECTRAL LINES OF NITROGEN AND CARBON OXIDES IN THE TEMPERATURE RANGE 300–3000 K

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Received June 25, 1992

A structure of the database on the parameters of spectral lines (PSL) of rovibrational spectra of nitrogen and carbon oxides is proposed based on generated program modules of PSL calculation. The program complexes for the CO *molecule have been organized based on the semiempirical approach to the dipole moment matrix elements and F–factor of rovibrational interaction calculations, which were presented in the polynomial form over the vibrational and rotational quantum numbers.*

For the nitrogen oxide new expressions for the line intensities have been obtained owing to more rigorous determination of the molecular wave function using the effective Hamiltonian with parameters determined from the processing of spectra corresponding to transitions with high values of quantum numbers ($v \le 22$) and, correspondingly, at high temperature $T \sim$ 3000 K. *The calculations of* CO *and* NO *absorption coefficients for different temperatures have been made in the approach of optically thin layer and the results adequate to the experimental spectra of the considered gases were obtained.*

The development of remote methods for the control of the high temperature furnace and combustion chambers, as well as for monitoring the industrial atmospheric emissions stimulates the high temperature gas spectra investigations and, first of all, of the main combustion products like nitrogen and carbon oxides (NO, CO). Moreover, there is a need for accurate analysis of the absorption of heated gas emission by the atmospheric layer with the account for temperature gradient along the path.

Actually, these problems are being extensively studied (see, e.g., Refs. 1–4). As a rule the analysis was carried out on the basis of the gas spectra measured at normal temperatures ($T \sim 300$ K) which correspond to the optical transitions with small values of vibrational quantum number ($\nu \sim 1$).

This paper continues the work done in Refs. 5–7 devoted to the databases (DB) formation based on the parameters of spectral lines (PSL) of heated gases which serve as the initial information in direct calculations of the radiation and absorption spectral characteristics.

The basic stages of this work are the following:

1. Development of the methods for the PSL calculations, applicable at temperatures 300–3000 K.
2. Development of the DB conceptual project and its realization on IBM PC with a corresponding control system.
3. Analysis of the physical authenticity of the DB.

These stages are being discussed below.

METHODS OF CALCULATION OF THE ROVIBRATIONAL LINE PARAMETERS OF THE HEATED NITROGEN AND CARBON OXIDES

The carbon oxide line centers and intensities are calculated based on a semiempirical approach which gives most adequate to the experiment a theoretical description of the CO spectra. The Dunham's parameters and the matrix elements of the dipole moment involved in the algorithm being described were approximated by polynomials over vibrational and rotational quantum numbers in accordance with Refs. 8 and 9.

In Ref. 8 the polynomial coefficients have been determined by the method of least squares by processing the spectra measured at $T = 100$–3500 K.

The rovibrational energies were calculated by formula

$$E_{\mathrm{RV}} = \sum Y_{k\,l}\, \nu^k (\nu + 1/2)^k j^l (j+1)^l , \tag{1}$$

where

$$Y_{k\,l} = \mu^{-(k/2+l)} \left[1 + m_{\mathrm{e}} \left(\frac{\Delta^{\mathrm{C}}_{k\,l}}{M_{\mathrm{C}}} + \frac{\Delta^{\mathrm{O}}_{k\,l}}{M_{\mathrm{O}}} \right) \right] U_{k\,l} \tag{2}$$

involves the isotopic dependence.

In Eqs. (1) and (2) M_{C} and M_{O} are the mass of carbon and oxygen atoms, respectively; m_{e} is the electron mass (in u); $\Delta^{\mathrm{C}}_{k\,l}$ and $\Delta^{\mathrm{O}}_{k\,l}$ are parameters; and, $\mu = (M_{\mathrm{C}}^{-1} + M_{\mathrm{O}}^{-1})^{-1}$.

The values of $U_{k\,l}$, $\Delta^{\mathrm{C}}_{k\,l}$, $\Delta^{\mathrm{O}}_{k\,l}$ were taken from Ref. 8, because in this paper the values of $U_{k\,l}$ were obtained up to $k = 9$ and $l = 4$. This allows one to determine the values of $Y_{k\,l}$ corresponding to the levels with high vibrational quantum numbers and, as a result, to transitions essentially contributing to spectra at temperatures 100–3000 K.

In accordance with Ref. 9, the dipole moment matrix element for rovibrational transitions of a CO molecule can be represented as a product of polynomials over vibrational and rotational quantum numbers

$$< \nu j \,|M|\, \nu + n, j' > = \frac{M(n)^2 (\nu + n)!}{\nu!\, n!} H_n(\nu)\, F_n(\nu, m) , \tag{3}$$

where

$$H_n = \sum_{i=0}^{9} n_i^{(n)} \nu_i = \frac{\nu!\, n! < \nu 0 \,|M|\, \nu + n0 >}{(\nu + n)! < 00 \,|M|\, n0 >} ; \tag{4}$$

0235-6880/92/09 626-04 $02.00

$$F_n(\nu, m) = \sum_{i=0}^{6} \sum_{j=0}^{3} g_{ij}^{(n)}\, m^i\, j^j \,, \tag{5}$$

where

$$m = \frac{j'(j'+1) - j(j+1)}{2} = \begin{array}{l} j + 1\ R\text{–branch } (j' = j + 1)\,, \\ -\,j\ P\text{–branch } (j' = j - 1)\,. \end{array}$$

The function $H_n(\nu)$ models the vibrational anharmonicity and its polynomial constants were determined in Ref. 9 by the fitting method in the range of vibrational quantum numbers from $\nu = 0$ to $\nu = 27$. The function $F_n(\nu, m)$ corresponds to a factor accounting for the rovibrational interaction in calculations of the dipole moment matrix element.

For five, most widely spread CO isotopes ($C^{12}O^{16}$, $C^{12}O^{17}$, $C^{12}O^{18}$, $C^{13}O^{16}$, and $C^{13}O^{18}$) the polynomial constants were determined using a vast experimental material. The processing of spectra carried out in Refs. 8 and 9 allows one to use their data for calculating the line intensities in the bands with high values of vibrational quantum number and large differences $\nu' - \nu = \Delta\nu \le 4$, with the highest, at present, accuracy in the temperature range 300–3000 K.

The nitric oxide spectrum at the normal temperatures (~ 300 K) was studied very intensively. In this case the effects of spin–rotational and spin–orbital interactions are of particular interest. However at temperatures 2000–3000 K the existing methods need for certain corrections because they, as a rule, have been developed based on the experimental data obtained at T ~ 300 K.

The Hamiltonian commonly used for an NO molecule having a half–integral total electronic spin,[4] has a block–diagonal structure when it is defined in a subspace constructed of the "a" type functions: $|\ \nu\Lambda S\Sigma\Omega jM >$, where the quantum numbers j, M, and v are fixed within a given block, and Λ and Σ take values ±1 and ±1/2, respectively,

$$\begin{array}{c|cc} & {}^2P_{1/2} & {}^2P_{3/2} \\ \hline {}^2P_{1/2} & a_{11} & a_{12} \\ {}^2P_{3/2} & a_{21} & a_{22} \end{array}\,,$$

where a_{11}, a_{12}, and a_{22} are functions of the effective spectroscopic constants. When forming the base of the NO line parameters in the band sequence with $\Delta\nu = 2$ (near 2.7 μm) we used the data from Ref. 11 in which the rovibrational spectrum was recorded in the spectral region 2900–3810 cm^{-1} by a Fourier–spectrometer and fourteen bands with $\Delta\nu = 2$ were analyzed. The quantities a_{11}, a_{12}, and a_{22} are given in the form

$$\begin{aligned} a_{11} &= T - \frac{A}{2} - (B - A_1)(X + 1) - D[X + (X + 1)^2]\,; \\ a_{12} &= BX^{1/2} + 2DXX^{1/2} = a_{21}\,; \qquad (6) \\ a_{22} &= T + \frac{A}{2} + (B + A_j)(X - 1) - D[X + (X - 1)^2]\,; \\ X &= (j + 1/2)^2 - 1\,, \end{aligned}$$

and the values of effective molecular constants $A_{\text{eff}} = A$, B, D, and A_j and vibrational level energies have been determined by a minimization method from the spectra recorded for electronic ground state and vibrational states ranged from $v = 0$ to $v = 15$.

In Ref. 12, which continues the work done in Ref. 11, the higher vibrational states (up to $\nu = 22$) were considered. In this case the Hamiltonian matrix elements for the electronic state $^2\Pi$ become more complicated:

$$\begin{aligned} a_{11} &= T - \frac{A}{2} - A_{\text{D}}\left(\frac{X+2}{2}\right) + B(X + 2) - \\ &\quad - D(X + 1)(X + 4) + H(X + 1)(X^2 + 8X + 8)\,; \\ a_{12} &= -\,BX^{1/2} + 2D(X + 1)X^{1/2} - HX^{1/2}(X + 1)(3X + 4)\,; \qquad (7) \\ a_{22} &= T + \frac{A}{2} + A_D\left(\frac{X}{2}\right) + BX - DX(X + 1) + HX(X + 1)(X + 2). \end{aligned}$$

In addition, the number of fitting parameters is increased (up to 6 in comparison with 5 in Ref. 11) owing to the growth of bulk of information to be processed and in connection with the necessity for an accurate restoration of spectral characteristics involved in the processing. The values of the effective molecular constants T, A, A_D, B, D, and H for $\nu = 0$–22 determined by the minimization method are given in Ref. 12. The energy levels and, correspondingly, the line centres are trivially obtained from the Hamiltonian matrices because the eigenvalues and the eigenvectors of 2 × 2 matrix are determined analytically

$$E_1 = 1/2\,(a_{11} + a_{22} + D)\,,$$

$$E_2 = 1/2\,(a_{11} + a_{22} - D)\,,$$

$$D = \sqrt{4a_{12}^2 + (a_{11} - a_{22})^2}\,; \tag{8}$$

$$\psi_1^{(1)} = \pm\frac{1}{\sqrt{2}}\sqrt{1 + (a_{11} - a_{22})D}\,, \quad \psi_1^{(2)} = -\,\psi_2^{(1)}\,;$$

$$\psi_2^{(1)} = \pm\frac{\text{sign}(a_{12})}{\sqrt{2}}\sqrt{1 - (a_{11} - a_{22})D}\,, \qquad \psi_2^{(2)} = \psi_1^{(1)}\,. \tag{9}$$

When the line centers are found, it is necessary to calculate the dipole moment matrix elements in order to calculate intensities of the rovibrational lines. An ambiguity in determination of coefficients of a series expansion of the NO dipole moment matrix elements makes a difficulty in their calculation.

Integral intensities of the NO fundamental band measured by different anthors are summarized in Ref. 13, where a significant spread of data is pointed out. But it can be shown that the average integral intensity of the band is $S_{0¢1}(\text{NO}) = (125 \pm 14)\cdot\text{cm}^{-2}\cdot\text{atm}^{-1}$ at STP with the error of 12 %. This shows that the value of the first derivative of the NO dipole moment given in Ref. 10 is sufficiently correct because it gives the value of $S_{0¢1}$ falling into the above–indicated error interval. Thus, all the necessary initial data for the program modules of the NO and CO PSL calculations to function are determined.

Formally the scheme of calculations of the line half–widths and shifts is traditional

$$\gamma_{f\,i} + i\delta_{f\,i} = \frac{\eta_{\text{b}}}{2\pi c}\int \text{d}\nu\, P(\nu) \sum_{\text{b}l} \rho_{\text{b}l}^{l}\, \sigma_{f\,i}(\beta\, l\,|\,\nu)\,, \tag{10}$$

where γ_{fi} and δ_{fi} are the half–width and the line center shift of the transition $f \leftarrow i$, respectively, η_{b} is the broadening gas density, $\int d_{\mathrm{v}} P(\mathrm{v})$ is the operator of averaging over classical collisional parameters, $\rho^{\mathrm{b}}_{\beta l}$ is the population of the broadening molecule $\beta\, l$–state (l is the quantum number of the total angular momentum, and β denotes the set of other quantum numbers), $\sigma_{fi}(\beta\, l/\mathrm{v})$ is the differential cross section of collisions determined by formula[13]

$$\gamma_{fi}(\beta\, l | \mathrm{v}) = 1 - [1 - S^{l}_{2\mathrm{middle}}(f i | \beta\, l;\, \mathrm{v})][\, - iS_1(f i | \beta\, l;\, \mathrm{v}) -$$

$$- S_{2\mathrm{outer}}(f i | \beta\, l;\, \mathrm{v}) - S_{2\mathrm{middle}}(f i | \beta\, l;\, \mathrm{v})\,. \qquad (11)$$

Here $S_1(f i | \beta\, l;\, \mathrm{v})$ and $S_{2\mathrm{outer}}(f i | \beta\, l;\, \mathrm{v})$ are the quantities similar to $S_1(b)$ and $S_{2\mathrm{outer}}$ from Anderson's theory[14,15] and $S^{(l)}_2(f i | \beta\, l;\, \mathrm{v})$ and $S^{(l)}_{2\mathrm{middle}}(f i | \beta\, l;\, \mathrm{v})$ are expressed through the diagonal and off–diagonal, with respect to the states of broadening molecule, parts of the term $S^{(l)}_{2\mathrm{middle}}$ from this theory.

Specific features of the half–width and line shift calculations at high temperatures are the following. First, it should be noted that the temperature growth causes a growth of highly excited state populations, which makes it necessary to involve averaging over the broadening molecule quantum states, large number of their energy levels, and, in some cases, perhaps, few low–energy vibrational states. On the one hand, this significantly increases computation time, and, on the other hand, it requires accurate an account of the effects of the broadening molecule nonrigidity. Second, when the temperature is very high (near 3000 K and above) it is necessary to take into account the variation of the gas mixture composition due to the collisional dissociation processes. The ratio of a number of molecules dissociated in a unit volume to the total number of molecules is called the degree (coefficient) of dissociation and depends on the type of molecules, temperature, and pressure. The values of the degree of dissociation can be found in Refs. 16 and 17. Let us consider two examples. The first is concerned with the NO and CO molecules. According to Refs. 16 and 17, these molecules are sufficiently stable and dissociate poorly. Thus, at the temperature 3000 K the degrees of dissociation of these molecules are $3.59 \cdot 10^{-3}$ (CO) and $1.54 \cdot 10^{-6}$ (NO). Therefore, within this temperature interval, possible variations of the concentration of these gases may be ignored. As the other example, let us consider the CO_2 molecule. For this molecule at the temperature 3000 K and the pressure 1 atm due to the reaction $CO_2 - CO + \frac{1}{2} O_2$ (Refs. 16 and 17) the dissociation coefficient is 0.439 that means that CO_2 concentration at this temperature decreases almost two times while the concentrations of CO and O_2 molecules increase. Such a change of the gas composition, of course, if the carbon dioxide makes a significant fraction in the gas mixture, must be taken into account. Finally, because of equalizing of the low– and highly–excited state populations, the intensities of transitions from these states are also equalized and, as a consequence, the necessity of calculating the relaxation parameters for such transitions appears. Since at these states the molecular nonrigidity effects are strong it is desirable to take them into account. However, usual obstacle here is either complete absence of or insufficiently accurate information about the second derivatives of the multipole moments with respect to normal coordinates which mainly determine the role of nonrigidity effects.

STRUCTURE OF DATABASE ON NITROGEN AND CARBON OXIDES SPECTRAL LINE PARAMETERS

All known databases on PSL are arranged as strings of a fixed length sorted according to the line center increase (see, e.g., Ref. 18). But in this case the database (DB) of heated gases must contain hundred thousands of strings and will need for a very large external memory. Moreover, it is difficult to predict the temperature from the range 300–3000 K for which the spectroscopic data we are needed. The latter remark is too important, since the quantity of the lines with sufficiently significant intensities vary with temperature.

The simplest way of the DB arrangement is calculation of the PSL within the whole temperature range with some step (approximately 200–300 K), compilation and memorizing the results in the DB with a subsequent interpolation of the intensities, half–widths and shifts to a given temperature. This way allows one to sufficiently quickly make the data retrieval from the DB but requires too much volume of an external memory (dozens of megabytes).

We have also examined the following version. Let parameters of rotational lines be calculated for all energetically efficient vibrational bands that are written (memorized) in an intermediate file in which line sorting according to line center positions is performed with the subsequent erasure of the intermediate file. But this way is inconvenient because of long computation time and necessity to have a large volume of free external memory.

In this paper, in our opinion, the most optimum version of the DB structure is proposed. The database management system has been developed keeping in mind the fact that the time required for computing PSL of CO and NO molecules is comparable with the time of data search and retrieval from an intermediate file. Since parameters of each spectral line are well determined from the quantum identification of the transition under study, as well as by a set of spectroscopic constants of the molecule, not very large file of quantum characteristics of the transitions ordered according to the increase of line center frequencies enables one to calculate other parameters of the lines in any desirable spectral range and for any preset temperature.

To raise the computation speed the intermediate data, for example, the energy levels, are kept in the DB. The block–diagram of the database structure is given in Fig. 1.

As a result the achieved rate of data presentation is equivalent to the rate of data retrieval when the DB operates in a file mode.

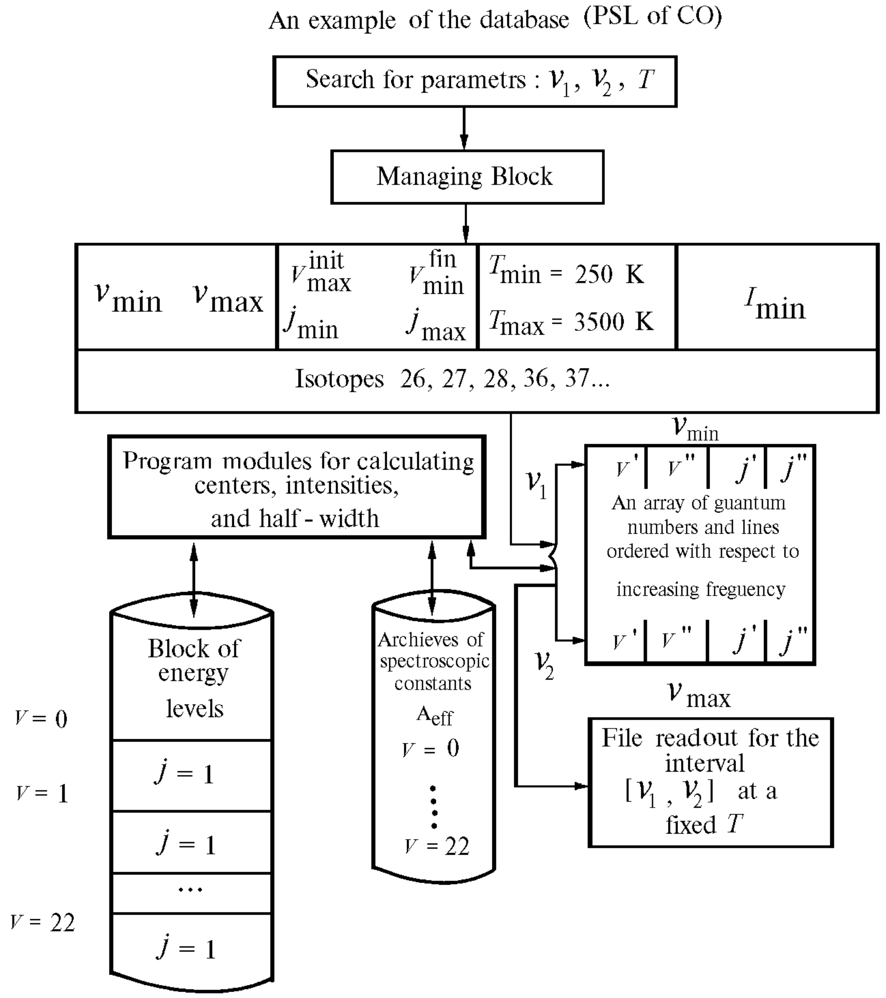

FIG. 1. Block–diagram of the database on the PSL of nitrogen and carbon oxides.

THE PHYSICAL AUTHENTICITY OF THE DB

As in Refs. 6 and 7 the completeness and reliability of the information, which has been used in the formation of the DB, was checked in a few ways. The first one is in calculation of the temperature dependence of the integral intensity in a band sequence with fixed values of $\Delta v = (1, 2, 3)$ which well agrees with experimental data. More rigorous check is done by comparing calculated spectral dependences of the NO and CO absorption coefficients with the experimental ones at different temperatures. The results are shown in Figs. 2 and 3.

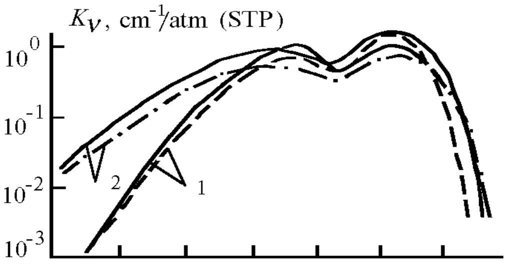

FIG. 2. The CO *absorption coefficient in the band* 4.6 μm *at different temperatures: 1)* $T = 1800$°K *and 2)* $T = 2400$°K; *solid curves are for experiment and dashed and dashed–dotted curves show our calculational data.*

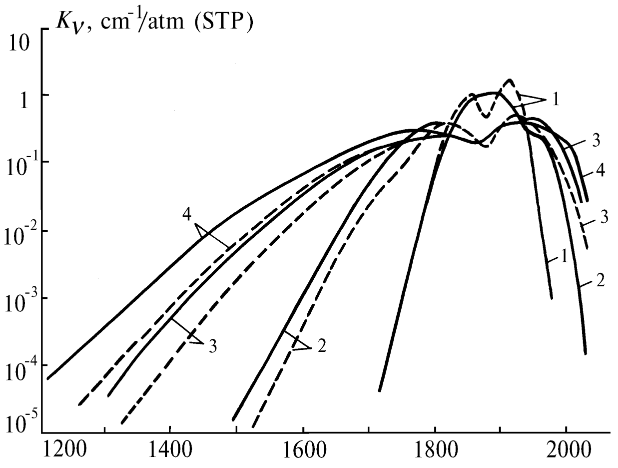

FIG. 3. The NO *absorption coefficient in the sequence of bands near* 5.2 μm *at different temperatures: 1)* $T = 300$°K, *2)* $T = 1200$°K, *3)* $T = 2400$°K, *and 4)* $T = 3000$°K; *solid curve shows experiment and dashed curve shows our calculational data.*

In the case of the NO molecule band wing one can see the discrepancy which may be explained with the model of an optically thin layer.[6,7] Let us note that similar behavior of the absorption coefficient was also observed for the CO_2 and H_2O molecules.[6,7]

For the CO molecule there is no such a discrepancy. This fact confirms once more that line shapes in the wings of absorption bands play an important role because the calculations of the CO molecule spectrum were performed on the basis of semiempirical relations for fitting parameters using the spectra recorded in the temperature range 300–3000 K and therefore the line wing effect in this case virtually was taken into account through the fitting parameters.

REFERENCES

1. S.S. Penner, *Quantitative Molecular Spectroscopy and Gas Emissivities* (Addision–Wesley, Reading, Mass, 1959).
2. V.A. Kamentchikov, Yu.A. Plastinin, V.M. Nikolaev, and L.A. Novitskii, *Radiative Properties of Gases at High Temperatures* (Mashinostroenie, Moscow, 1971), 440 pp.
3. L.A. Kuznetsova, N.E. Kuz'menko, Yu.L. Kuzyakov, and Yu.A. Plastinin, *Probabilities of Optical Transitions of Diatomic Molecules* (Nauka, Moscow, 1980), pp. 319.
4. M. Mizushima, *The Theory of Rotating Diatomic Molecules* (Academic Press., New York, 1975), 365 pp.
5. O.K. Voitsekhovskaya, Atm. Opt. **3**, No. 6, 533–539 (1990).
6. O.K. Voitsekhovskaya, N.V. Kuz'mina, and N.N. Trifonova, Atm. Opt. **3**, No. 5, 443–450 (1990).
7. O.K. Voitsekhovskaya, N.V. Kuz'mina, and N.N. Trifonova, Atm. Opt. **5**, No. 5, 296–300 (1992).
8. G. Guelashvili, D. Villeneuve, R. Farkeno, W. Urban, and J. Verqes, J. Mol. Spectrosc. **98**, No. 1, 64–79 (1983).
9. C. Chackerian and R.H. Tipping, J. Mol. Spectrosc. **99**, No. 2, 431–449 (1983).
10. G. Chandraiach and C.W. Cho, J. Mol. Spectrosc. **47**, 134–147 (1973).
11. C. Amiot and J. Verges, J. Mol. Spectrosc. **81**, 424–444 (1980).
12. C. Amiot, J. Mol. Spectrosc. **94**, No. 1, 150–172 (1982).
13. D. Robert and J. Bonamy, J. Phys. (Paris), **40**, 923 (1979).
14. P.W. Anderson, Phys. Rev. **76**, 647 (1949).
15. C.J. Tsao and B. Curnutte, J. Quant. Spectrosc. Radiat. Transfer **2**, 41 (1962).
16. *Handbook of Chemist* (Khimiya, Moscow–Leningrad, 1963), Vol. 1, 690 pp.
17. *Brief Reference Book of Physical Chemical Quantities* (Khimiya, Leningrad, 1972), pp. 200.
18. L.S. Rothman, A. Goldman, J.R. Gillis, et. al., Appl. Opt. **20**, No. 8, 1323–1328 (1981), ibid., **22**, No. 11, 1616–1627 (1983).
19. C.B. Ludwig, et al., *Handbook of Infrared Radiation from Combustion Gases* (Washington, 1973), 500 pp.