

SPECTRAL CHARACTERISTICS OF CARBON DIOXIDE IN THE REGION 2 – 6 μm AT TEMPERATURES 300 – 3000 K

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Database including the spectral line parameters of carbon dioxide determined in a wide range of temperatures is described. An estimate of reliability of data is given based on computation of wideband spectral characteristics of emission and absorption. Temperature dependences of integrated intensities of the system of the CO₂ bands, mean absorption coefficients, and emissivity calculated with the use of exact formulas for spectral characteristics and those measured independently have shown a good agreement.

The analysis of absorption and emission spectra of hot gases mainly of carbon dioxide is necessary for treating the composition of fuel and the products of its combustion, the regimes of action of different thermal cells, and high-temperature ovens and the development of the ecological control equipment. It seems that the most accurate calculations of the above characteristics should use the database containing parameters of vibrational-rotational lines of carbon dioxide including information about the entire set of lines needed for computations in large temperature intervals. The databases available include the numerical values of parameters of spectral lines whose strengths at normal temperature (296, 300 K) are not smaller than some quantity S_{\min} . However, the temperature increase leads to the qualitative changes in a molecular spectrum since because of a redistribution of the level populations a number of lines disappear below the boundary S_{\min} while at the same time, a number of "hot" lines due to transitions from high energy states appear above this threshold. To describe and predict the parameters of these lines the resonance effects should be taken into account. Such an account was performed when creating the database containing spectral line parameters of carbon dioxide at temperatures $T = 1200\text{--}3000$ K, which is one of the constituent parts of the information system on high resolution spectroscopy developed at the Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences.¹

This paper presents estimates of the reliability of the CO₂ line parameters as well as an analysis of the adequacy of the spectral characteristics calculated using the developed database to experimental data.

PROCEDURES FOR COMPUTING CO₂ ROTATIONAL LINE PARAMETERS

The procedure of computation of rotational structure of CO₂ spectrum was given in Ref. 1. The empirical energies of vibrational levels, the integrated intensities of vibrational transitions, and the effective rotational and centrifugal constants are used in this approach as the initial input data.² However, these values are unknown at high temperatures and the problem on accurate calculation of characteristics of vibrational transitions is brought to the foreground. Theoretical studies of the problem have been made in a number of publications, here we point out only the theses.^{3,4}

Analysis of the results obtained by various authors allowed us to formulate the optimal (and saving the

computation time) procedure for determining the spectral line parameters of carbon dioxide in the absorption bands formed by transitions from levels with large ($V \sim 10$) values of vibrational quantum numbers determining thus the absorption and emission at temperatures up to ~ 3000 K. In this paper the inverse spectroscopic problem on determination of the rotational and centrifugal constants and the components of effective dipole moment of CO₂ up to and including the terms of the third order was solved. We used the effective Hamiltonian,⁵ which was constructed on the subspace of vibrational wave functions of the resonantly coupled states. The set of integrated intensities and levels of vibrational transitions corresponding to the vibrational quantum numbers $V = 1 - 5$ at $T = 256$ K given in Ref. 2 was used as the initial experimental information for the inverse spectroscopic problem. Then, the algorithm for computation of wave functions, integrated intensities of vibrational transitions, and effective rotational and centrifugal constants for high energy states was directly extrapolated onto the vibrational numbers up to $V \sim 20$.

The perturbation of rotational states due to Fermi resonance was analyzed in Ref. 6. It was shown there that this resonance could be considered as a purely vibrational one correct up to the terms of the third order. This means that the intensity distribution over the rotational structure of a vibrational band of a linear triatomic molecule could be calculated according to nonresonant procedure¹ taking resonances into account only when determining the integrated intensity of the vibrational band. Note, that the procedure proposed in this paper is not the only possible one. At present, the direct numerical diagonalization, and variational methods of calculating the wave functions and energies based on the complete rotational-vibrational Hamiltonian are used (see, e.g., Ref. 7). However, computational difficulties (the use of big $\sim 500 \times 500$ matrices) make this way to be too cumbersome. Thus, for temperatures ~ 2000 K the contributions of 1.2×10^6 lines in the 2.0 μm band have to be considered.

GENERAL APPROACH TO THE ESTIMATION OF THE SPECTRAL DATA RELIABILITY

A successful use of wideband spectral characteristics (for spectral intervals much wider than the half-width of an individual spectral line) for the control of reliability of the high resolution spectral information was demonstrated in Ref. 8 in application to a water vapor molecule. When

preparing the paper⁸ it appeared advisable to pay attention to a certain order of operations (beginning with general characteristics and passing to the more specific data):

1. To compare the temperature dependence of the sum of intensities of individual vibrational transitions for a given system of vibrational-rotational bands with the corresponding experimental dependence. It is the most rapid and simple way to make such estimates since for each sequence of vibrational-rotational bands it is necessary to calculate only one temperature dependence. Such an intercomparison enables one to find the upper boundary, which is rather strict, of the temperature interval where the database is adequate.

2. To compare the calculated absorption coefficients averaged over wide spectral intervals with corresponding experimental values in the entire temperature range under consideration. However, it should be taken into account that some additional errors are introduced into the absorption coefficients and integrated intensity data when processing the experimental data. The analysis of sources of such errors was given in Ref. 8.

3. To compare the calculated and measured spectra of the emissivity ϵ_v and the transmission function τ_v of homogeneous gas layers. This stage is most difficult since the spectral characteristics should be calculated not only for a set of temperatures but also for a wide set of absorbing masses. The absorption and emission spectra provide the most reliable experimental information and, in addition, at this last stage the temperature and pressure dependences of spectral line half-widths used in calculations are verified.

In what follows, the results of the analysis of reliability of the calculated spectral characteristics are given.

TEMPERATURE DEPENDENCES OF INTEGRATED INTENSITIES OF A SEQUENCE OF VIBRATIONAL BANDS

Three systems of the CO₂ absorption bands, which are produced by transitions with definite differences of vibrational quantum numbers fall within the spectral region 2 – 6 μm (see Table I).

The temperature dependences calculated in this paper for the three band systems are shown in Fig. 1 by dashed lines. The results of a number of independent measurements¹⁰⁻²¹ are denoted in Fig. 1 by different signs.

TABLE I. The CO₂ absorption bands in the spectral region 2 – 6 μm .

System of bands, μm	ΔV_1	ΔV_2	Δl	ΔV_3
4.3	0	0	0	1
2.7	0	2	0	1
2.0	0	4	0	1
	1	2	0	1
	2	0	0	1

The important advantage of the constructed high temperature database on the CO₂ line parameters is the account for the Fermi and Darling-Dennison resonances. However, the data presented in the figures show that the resonances contribute only to the spectral dependence, whereas within the band system the compensation of resonance effects takes place if an integrated total intensity is determined. This fact was noted earlier and the calculations⁹ made as long ago as 1966 using the harmonic oscillator approximation quite well agreed to the corresponding experimental data. It should be kept in mind, however, that since the wave functions of the CO₂ vibrational states were constructed by an extrapolation

over the vibrational quantum numbers, one should necessarily be sure that there are no disagreements to the experiment, what is well illustrated by Fig. 1.

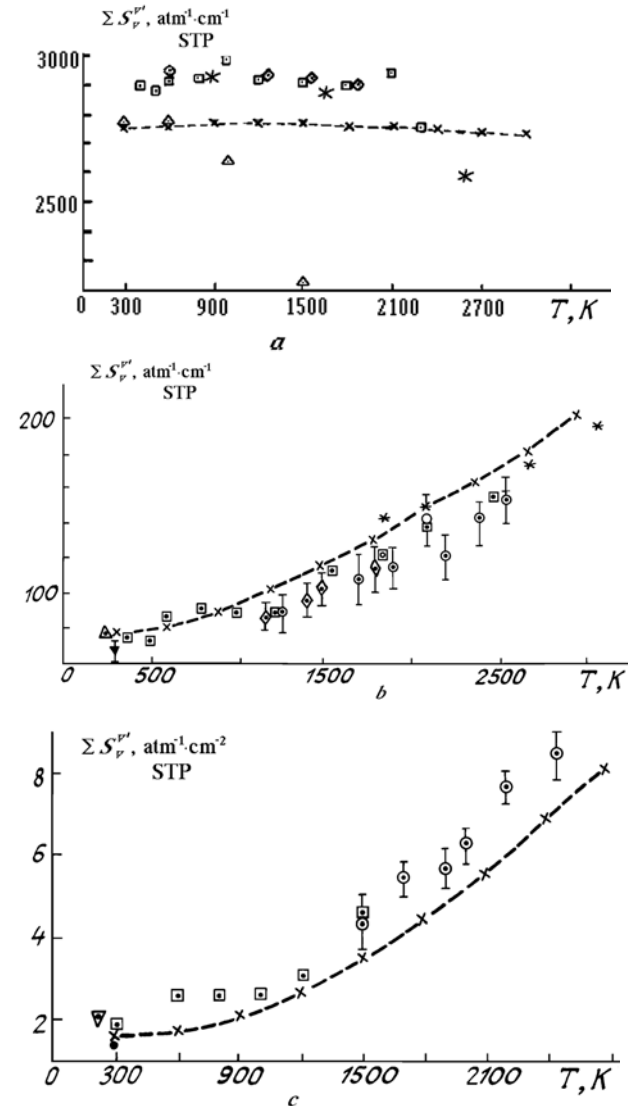


FIG. 1. Temperature dependences of integrated intensities of the CO₂ band sequences. a) 4.3 μm , b) 2.7 μm , and c) 2 μm ; dashed line denotes our calculation. Experimental results: \square – Ref. 2, $-$ Ref. 10, $*$ – Refs. 11 and 12, \diamond – Refs. 13 and 14, \odot – Refs. 15 and 16; \blacktriangledown – Ref. 17, Φ – Ref. 18, \bullet – Ref. 19, ∇ – Ref. 20, and \blacktriangledown – Ref. 21.

ANALYSIS OF SPECTRAL DEPENDENCES OF THE CO₂ ABSORPTION COEFFICIENT AT HIGH TEMPERATURES

Systematic errors in characteristics of individual vibrational-rotational lines are normally revealed in calculations of the absorption coefficients averaged over fairly wide spectral intervals. As in the previous paper⁸ we use for calculations the approximate relation

$$K_v = \sum_{i=0}^N S_i / \Delta v, \tag{1}$$

where S_i is the intensity of an individual line and N is the number of lines within a chosen spectral interval $\Delta\nu$. In the transmission windows, that is, in the spectral regions between the groups of absorption bands, relation (1) obviously underestimates the absorption because the effect of line wings is not taken into account in this approach.

Considerable spread should be noted in numerical data on spectral characteristics given by the authors of experimental studies of the CO₂ spectra at high temperatures. This is caused by unavoidable errors connected with photometry, determination of concentrations in a gas mixture, determination of the thickness and homogeneity of the absorbing layer, the control of thermodynamic conditions, and the correct account for the instrumental function.

We have compared our calculations only with those experimental data that were obtained at $T > 1200$ K, because, according to our estimates, at lower temperatures the main contributions to the absorption come from the lines being well investigated at room temperatures. This circumstance allowed us to essentially shorten the set of necessary experimental data on the CO₂ absorption coefficients.²²⁻²⁶

In their study Berman et al.²² used the approximation of the optically thin layer for determining the absorption coefficient within the 4.3 μm band from the measurements of spectral density of the brightness of a gas flow at the output of a plasmatronic installation: $\epsilon = K_\nu U$, where U is the emitting mass of CO₂. In our calculations for this case the averaging was performed over the interval of 16 cm^{-1} that is equal to the width of the instrumental function.²² Figure 2 shows a satisfactory agreement between the present results and the experimental data²² at temperatures of 2600 K and 1650 K.

Some results of extensive experimental studies of light absorption by pure CO₂ and in mixtures with other gases were given in Refs. 26 and 27. Figure 3 shows the values of the averaged absorption coefficients. The agreement between our calculations and independent experimental data should be noted for 2.7 μm absorption band, as an example.

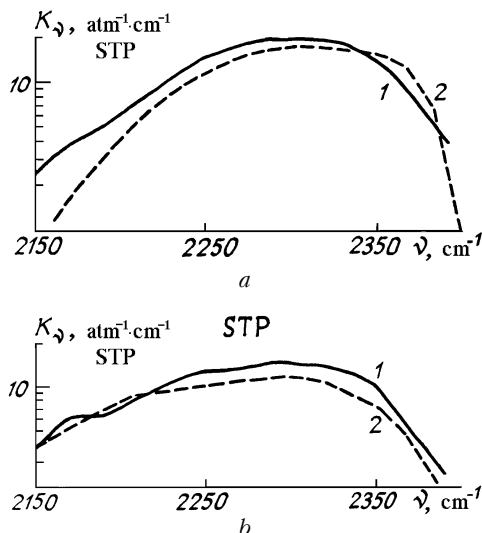


FIG. 2. Spectral dependence of the CO₂ absorption coefficient within the 4.3 μm band; 1) experimental data from Ref. 22 and 2) our calculations; a) $T = 1650$ K and b) $T = 2600$ K.

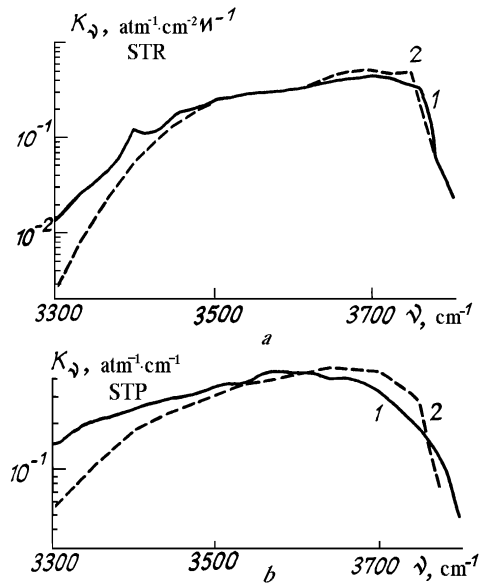


FIG. 3. Spectral dependence of the CO₂ absorption coefficient within the 2.7 μm band; 1) experimental data from Refs. 26 and 27 and 2) our calculations; a) $T = 1500$ K and b) $T = 2500$ K.

CHARACTERISTICS OF THE CO₂ EMISSION AT HIGH TEMPERATURES

The emission intensity of a gas was calculated by the formula

$$J(\Delta\nu, T) = \int_{\nu_1}^{\nu_2} B(\nu, T) \cdot \epsilon(\nu, T) d\nu,$$

where $B(\nu, T)$ is the Planck function, $\epsilon(\nu, T) = 1 - \exp \times [-K_\nu(\nu, T) \cdot U]$ is the spectral emissivity of a gas. In the case of thermodynamic equilibrium $\epsilon(\nu, T)$ is equivalent to the absorption function of a molecular medium. It is important, when calculating the emissivity characteristics, to take the value of optical depth to be close to the experimental one. Thus, for example, Copalle and Vernisch²⁴ measured the CO₂ concentration using a gas chromatography technique whereas the emissivity characteristics were measured at the temperature of 2900 K, what, naturally, excluded the use of chromatography to measure CO₂ concentrations at such a high temperature. For this reason it remains unclear, how the thermal molecular dissociation has been accounted for. Since the relative velocity of colliding molecules increases with temperature, the probability of transfer of large quanta, capable of initiating the dissociation, also increases. In calculations we used the values of dissociation coefficients for a CO₂ molecule (the ratio of the number of dissociated molecules to their total number) taken from Ref. 28 (see the temperature dependence in Fig. 4). Then it follows that at $T \sim 3000$ K almost every other molecule is dissociated. Therefore, when calculating the CO₂ emissivity under conditions given in Ref. 24 we multiplied the given value of optical depth by the dissociation coefficient. As a result a satisfactory agreement was achieved (see Fig. 5) with the experimental spectral emissivity. The calculated values of spectral density of the brightness also agreed with the experimental one quite well.

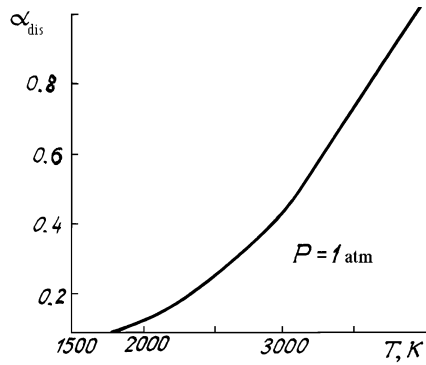


FIG. 4. Temperature dependence of the CO₂ dissociation coefficient.

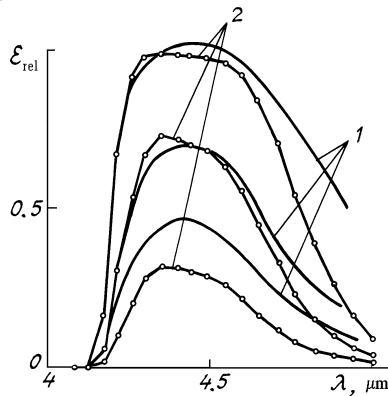


FIG. 5. Emissivity of gas layers with thickness of 2, 6.8, and 21.2 cm at the CO₂ concentration of 0.25 at T = 290° K. 1) Experimental data from Ref. 24 and 2) our calculations.

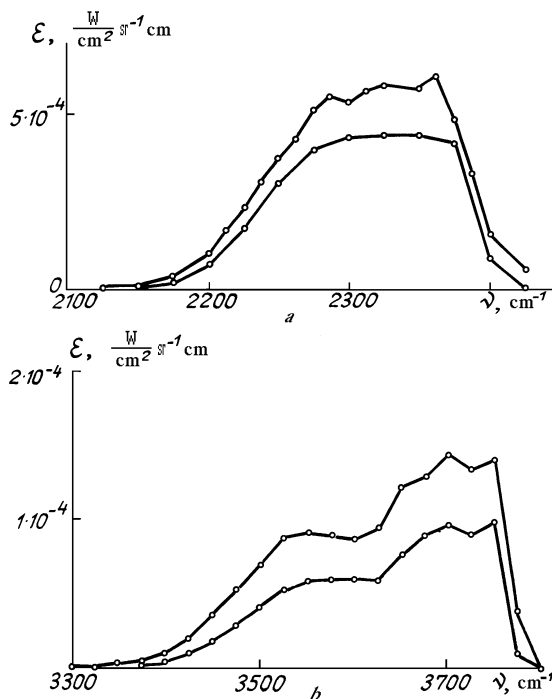


FIG. 6. Spectral density of the CO₂ brightness at T = 1200 K; 1) experiment of Ref. 25 and 2) our calculation. a) The 2.7 micrometers band and the 3 atm-cm optical depth and b) The 4.3 micrometers band and the 0.6 atm-cm optical depth.

CONCLUSIONS

The primary purpose of this paper was to verify the adequacy of an independent theoretical description of the CO₂ spectrum at the temperature T > 1200 K to the experimental results. We did not consider the questions connected with the computational procedures of spectral characteristics of the CO₂ gas at high temperature. Nevertheless, the obtained sets of spectral line parameters can be used to develop different kinds of computational procedures.

REFERENCES

- O.K. Voitsekhovskaya, A.V. Rozina, and N.N. Trifonova, *Information System on High Resolution Spectroscopy* (Nauka, Novosibirsk, 1988), 150 pp.
- L.S. Rothman, *Appl. Opt.* **25**, No. 11, 1795–1896 (1986).
- V.M. Osipov, "Theoretical study of the CO₂ IR spectrum at high pressures and temperatures", Author's Abstract of Cand. Phys.–Math. Sci. Dissert., State University, Leningrad (1971), 18 pp.
- I.Ph. Golovnev, "Radiative characteristics of carbon dioxide", Author's Abstract of Cand. Phys.–Math. Sci. Dissert., Institute of Theoretical and Applied Mechanics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, (1981), 18pp.
- I. Suzuki, *J. Mol. Spectrosc.* **25**, No 4, 479–500 (1968).
- O.K. Voitsekhovskaya, Yu.S. Makushkin, and O.N. Sulakshina, in: *Spectroscopy of Atmospheric Gases* (Nauka, Novosibirsk, 1982), pp. 16–34.
- R.B. Wattson and L.S. Rothman, *J. Mol. Spectrosc.* **119**, No. 1, 83–100 (1986).
- O.K. Voitsekhovskaya, N.N. Kuz'mina, and N.N. Trifonova, *Atm. Opt.* **3**, No. 5, 443–450 (1990).
- J.C. Breeze, C.C. Ferriso, C.B. Ludwig, and W. Malkmus, *J. Chem. Phys.* **42**, No. 1, 402–406 (1965).
- N.I. Moskalenko, Yu.A. Il'in, N.K. Pokotilo, et al., *Zh. Prikl. Spektrosk.* **34**, No. 3, 475–480 (1981).
- A.M. Berman, V.N. Vasil'ev, A.A. Tyuftin, and Yu.V. Denisov, in: *Abstracts of Reports at the Third All-Union Conference of Young Scientists "Theoretical and Applied Optics"*, S.I. Vavilov State Optical Institute, Leningrad (1988).
- A.M. Berman, A.Ph. Kuzin, et al., in: *Tr. Mosk. Energ. Inst. Ser. Prikl. Fiz. Opt.*, No. 177, 112 (1988).
- C.C. Ferriso, *J. Chem. Phys.* **37**, No. 9, 1955–1961 (1962).
- C.C. Ferriso and C.B. Ludwig, *J. Opt. Soc. Amer.* **54**, No. 5, 657–662 (1964).
- J.C. Breeze and C.C. Ferriso, *J. Chem. Phys.* **39**, 2619 (1963).
- J.C. Breeze and C.C. Ferriso, *J. Chem. Phys.* **40**, No. 5, 1276–1282 (1964).
- M. Fukabori, T. Nakazawa, and M. Tanaka, *J. Quant. Spectrosc. Radiat. Transfer* **36**, 265–170 (1986).
- M. Hirono, *J. Phys. Soc. Japan* **55**, No. 11, 3825–3830 (1986).
- K.P. Vasilevskii, L.E. Danilochkin, and V.A. Kazbanov, *Opt. Spektrosk.* **33**, No. 5, 871–875 (1975).
- D.F. Eggers and B.L. Crawford, *J. Chem. Phys.* **19**, 1554 (1951).
- D. Weber, R.L. Holm, and S.S. Ponner, *J. Chem. Phys.* **20**, 1820 (1952).
- A.M. Berman, A.Ph. Kuzin, V.A. Makarov, et al., in: *Tr. Mosk. Energ. Inst. Ser. Prikl. Fiz. Opt.*, No. 223, 32–37 (1989).
- D.K. Edwards, *J. Opt. Soc. Amer.* **50**, No. 6, 617–625 (1960).

24. A. Copalle and P. Vervisch, *J. Quant. Spectrosc. Radiat. Transfer* **33**, No. 5, 465–473 (1985).
25. P.S. Sukanek and L.P. Davies, *ATAA-paper*, No. 77–734, 8 (1977).
26. C.B. Ludwig, W. Malkmus, J.B. Reardon, and J.A. Thomson, *Handbook of Infrared Radiation from Combustion Gases* (NASA–SP–3080, Washington, D.C., 1973), 223 pp.
27. N.I. Moskalenko and Yu.A. Il'in, in: *Proc. of the First All–Union Conference on Atmospheric Optics, Tomsk (1976)*, Part 1, pp. 8–12.
28. G.E. Becker and S.H. Autler, *Phys. Rev.* **70**, 300 (1946).