MATHEMATICAL MODELING OF THE OPTICAL CHARACTERISTICS OF CARBON DIOXIDE*

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UDC 535.33/34

A method of calculating the absorption coefficient in CO_2 rotational–vibrational bands, taking account of the rotational structure, is outlined. Account is taken of the effect of Fermi resonance on the position and intensity of the spectral lines.

To calculate the radiant heat transfer in power installations and also to solve a number of applied problems of laser physics and atmospheric physics, information is required on the spectral and integral characteristics of carbon dioxide over a broad range of temperature and density. The IR spectrum of CO_2 is formed by vibrational–rotational transitions which, grouped in certain regions of the spectrum, form about 10 bands at room temperature. At higher temperatures, the number of vibrational transitions rises sharply and the separation of the individual bands becomes very arbitrary. The most important optical characteristic of the gas is the absorption coefficient. Accurate calculations require a knowledge of the absorption coefficient, taking account of the rotational structure.

The absorption coefficient for an individual line in the case of linear triatomic molecules takes the form

$$k_\nu = \frac{8\pi^3}{3hc} N \frac{(2j+1)}{Q} \exp(-E_{v_1 v_2^l v_3}/kT)\, \nu\, [1-\exp(-hc\nu/kT)]\, |\langle v_1' v_2'^{l'} v_3' j' |\mathbf{R}| v_1 v_2^l v_3 j \rangle|^2\, W(\nu). \tag{1}$$

Thus, to calculate the absorption coefficient, it is necessary to know the energy of the vibrational–rotational states, their wave functions, the form of the dipole-moment operator, and the line shape.

1. In the CO_2 molecule, Fermi resonance has a strong effect on the energy-level structure and the wave-function values. A resonance interaction arises between closely lying states of the same symmetry: $(v_1, v_2^l, v_3) - (v_1 - 1, (v_2 + 2)^l, v_3)$. The part of the anharmonicity potential responsible for the resonance interaction takes the form

$$V_R = C_{122}\xi_1\xi_2^2. \tag{2}$$

The resonance-interaction operator V_R is given in the eigenvector space for the Hamiltonian

$$H_0 + \tilde{V}. \tag{3}$$

This allows perturbation theory to be used for the Hamiltonian in Eq. (3) in the eigenvector space of the Hamiltonian H_0; splitting with respect to l^2 is taken into account. As a result, values of the energy and the wave function are obtained for a state of the type $(0, v^v, v_3)$ which is unperturbed by Fermi resonance. The system of equations for determining the spectroscopic constants from the anharmonicity constants differs from that obtained in [1] in

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*In the present issue (pp. 121-262), papers on the current state and main lines of development in methods of the mathematical modeling of radiation and complex heat transfer are published; this subject was considered at a combined session of the section on radiant heat transfer of the Scientific Council on Mass and Heat Transfer in Technological Processes of the State Committee of the USSR on Science and Technology and the section on heat and mass transfer of the Scientific Council on Complex Problems of Thermophysics of the Academy of Sciences of the USSR (Minsk, Apr. 6-7, 1978). A report of the session is given on p. 261.

Institute of Theoretical and Applied Mechanics, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 36, No. 2, pp. 197-203, February, 1979. Original article submitted July 31, 1978.

0022-0841/79/3602-0121$07.50

the following expressions:

$$X_{22} = 3C_{2222}/2 + (C_{122})^2[-1/2\omega_1 - 1/8(2\omega_2 + \omega_1)],$$
$$X_{ll} = -3C_{2222}/2 + (C_{122})^2/8(2\omega_2 + \omega_1) - B_l,$$
$$X_{12} = C_{1122} - 3C_{111}C_{122}/\omega_1 - (C_{122})^2/2(2\omega_2 + \omega_1).$$

The values of the spectroscopic constants X_{ij} and B_l are taken from [2] and C_{122} from [3]. The values of the anharmonicity constants obtained are given in Table 1.

Further, the eigenvectors $\tilde{\psi}_i$ and eigenvalues $\tilde{E}_i$ of the Hamiltonian

$$H_0 + \tilde{V} + V_R \tag{4}$$

are found in the eigenfunction space $\tilde{\psi}_i^\circ$ of the Hamiltonian in Eq. (3). Let $\tilde{E}_i^\circ$ be the eigenvalues corresponding to the eigenvectors $\tilde{\psi}_i^\circ$. It is quickly evident that the vector subspaces of the form

$$\begin{array}{ll} 0 & (l + 2V_1)^l v_3, \\ 1 & (l + 2v_1 - 2)^l v_3, \\ \cdot & \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ v_1 & l^l v_3 \end{array}$$

are invariant for the operator V_R. Hence, the eigenvectors of the Hamiltonian in Eq. (4) may be found in the form of the linear combinations

$$\tilde{\psi}_i = \sum_{j=1}^{n} C_{ji}\tilde{\psi}_j^0. \tag{5}$$

Substituting Eq. (5) into the Schrödinger equation, a system of equations for the determination of the constants of the expansion is obtained:

$$\sum_{j=1}^{n} C_{ji}\,[(E_j^0 - E)\,\delta_{kj} + (V_R)_{kj}] = 1, \tag{6}$$

and the condition of solvability of this system gives a secular equation for the determination of the energy:

$$\det|(\tilde{E}_j^0 - E)\,\delta_{kj} + (V_R)_{kj}| = 0. \tag{7}$$

The expression for the matrix elements $(V_R)_{kj}$ was theoretically obtained in [4], and the constants were found in [2]. The energies of the levels were found by numerical diagonalization of the matrix; polyads of dimensionality up to n = 11 were taken into account. For example, in Fig. 1 the effect of Fermi resonance on a group of vibrational levels is shown. It is evident that the resonance perturbation may considerably exceed the distance between the levels [5].

2. To find the probability of vibrational–rotational transitions, taking account of the effect of Fermi resonance, it is necessary to find the wave functions in Eq. (5).

For the constant C, the following recurrence relations are obtained

$$C_{mi} = C_{1i}K_m^i; \quad m = 2,\ 3,\ \ldots,\ n,$$
$$K_m^i = -[K_{m-2}^i(V_R)_{m-1,m-2} + K_{m-1}^i(\tilde{E}_{m-1}^0 - E_i)]/(V_R)_{m,m-1}, \tag{8}$$
$$(V_R)_{1,0} = (V_R)_{0,1} = 0;\ K_0^i = 0;\ K_1^i = 1.$$

The conditions of wave-function normalization allow C_{ji} to be determined accurately except for the phase factor. Knowing these coefficients, it is possible to calculate the rotational constants, taking account of Fermi resonance:

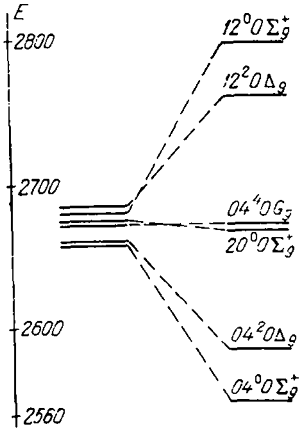

Fig. 1. Effect of Fermi resonance on the shift of the vibrational energy levels. E, cm^{-1}.

TABLE 1. Anharmonicity Constants, cm^{-1}

C_{111}	—28,12	C_{122}	74,52	C_{133}	—117,8
C_{1111}	—1,041	C_{1122}	1,1175	C_{1133}	—5,1555
C_{2222}	0,007822	C_{2233}	—8,891	C_{3333}	—20,51

$$B_i = \sum_j |C_{ji}|^2 \tilde{B}_j^0. \tag{9}$$

Here $\tilde{B}_j^0$ are calculated from the examples given, e.g., in [2]. The effects of Fermi resonance on the constants of l division are taken into account analogously.

The relation between the matrix elements in the laboratory system and the coordinate system rigidly fixed to the molecule takes the form

$$\langle v'j'l'm' | R_q^1 | vjlm \rangle = i^{j-j'} (-1)^{l'-m'} \sqrt{(2j+1)(2j'+1)} \begin{pmatrix} j' & 1 & j \\ -l' & q' & l \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ -m' & q & m \end{pmatrix} \langle v'l' | R_{q'}^1 | vl \rangle . \tag{10}$$

Here R_q^1 and $R_{q'}^1$ are the tensor components of the dipole-moment operator in the laboratory and rotating coordinate systems, respectively. Taking account of degeneracy with respect to m and l allows the right-hand side to be reduced to the form

$$(N_{jl}^{j'l'})^2 | \langle v'l' | R_{q'}^1 | vl \rangle |^2,$$

where $(N_{jl}^{j'l'})$ are the Conwell–London factors and $|\langle v'l' | R_{q'}^1 | vl \rangle|^2$ are the vibrational matrix elements. Using the wave functions found, the final result obtained is

$$(\psi_i | R_{q'}^1 | \psi_l) = (\sum C_{ki} \tilde{\psi}_k^0 | R_{q'}^1 | \sum C_{\varkappa j} \tilde{\psi}_\varkappa^0) = \sum C_{ki}^* C_{\varkappa j} (\tilde{\psi}_\kappa^0 | R_{q'}^1 | \tilde{\varphi}_\varkappa^0). \tag{11}$$

In calculating $\tilde{\psi}_k^0$ by perturbation-theory methods, the second-order approximation was taken into account; in the first approximation, the third and fourth orders of the anharmonicity potential were taken into account, and in the second approximation the third order. In this case the matrix elements in the right-hand side of Eq. (11) take the form

$$(\tilde{\psi}_k^0 | R_{q'}^1 | \tilde{\psi}_\varkappa^0) = (\psi_k^0 | R | \psi_\varkappa^0) + \sum \frac{(\psi_j^0 | V^{(3)} | \psi_\varkappa^0)(\psi_k^0 | R | \psi_j^0)}{(E_\varkappa^0 - E_j^0)} +$$

$$+\sum\frac{(\psi_j^0|V^{(3)}|\psi_k^0)(\psi_j^0|R|\psi_\varkappa^0)}{(E_k^0-E_j^0)}+\sum\frac{(\psi_j^0|V^{(4)}|\psi_\varkappa^0)(\psi_k^0|R|\psi_j^0)}{(E_\varkappa^0-E_j^0)}+\sum\frac{(\psi_n^0|V^{(3)}|\psi_j^0)(\psi_j^0|V^{(3)}|\psi_\varkappa^0)(\psi_k^0|R|\psi_n^0)}{(E_n^0-E_\varkappa^0)(E_j^0-E_\varkappa^0)}-$$

$$-\frac{1}{2}\left[\sum\frac{|(\psi_j^0|V^{(3)}|\psi_\varkappa^0)|^2}{(E_j^0-E_\varkappa^0)^2}\right](\psi_k^0|R|\psi_\varkappa^0)-\frac{1}{2}\left[\sum\frac{|(\psi_j^0|V^{(3)}|\psi_k^0)|^2}{(E_j^0-E_k^0)^2}\right]\times$$

$$\times(\psi_k^0|R|\psi_\varkappa^0)+\sum\frac{(\psi_n^0|V^{(3)}|\psi_j^0)(\psi_j^0|V^{(3)}|\psi_k^0)(\psi_n^0|R|\psi_\varkappa^0)}{(E_n^0-E_k^0)(E_j^0-E_k^0)}+$$

$$+\sum\frac{(\psi_j^0|V^{(3)}|\psi_k^0)(\psi_\sigma^0|V^{(3)}|\psi_\varkappa^0)(\psi_j^0|R|\psi_\sigma^0)}{(E_k^0-E_j^0)(E_\varkappa^0-E_\sigma^0)}+\sum\frac{(\psi_k^0|V^{(4)}|\psi_j^0)(\psi_j^0|R|\psi_\varkappa^0)}{(E_k^0-E_j^0)}, \qquad (12)$$

where the subscripts i, j, k, ... denote the set of quantum numbers (v_1, v_2^l, v_3). The coefficients of the expansion of the dipole moment with respect to the normal coordinates are required for the calculation of the matrix elements; these were found in the form

$$R_{(\xi,\eta)}=R^{(2)}\xi_2+R^{(12)}\xi_1\xi_2+R^{(112)}\xi_1^2\xi_2+R^{(332)}\xi_3^2\xi_2+R^{(222)}\xi_2^3,$$
$$R_{(\xi)}=R^{(3)}\xi_3+R^{(13)}\xi_1\xi_3+R^{(113)}\xi_1^2\xi_3+R^{(333)}\xi_3^3+R^{(223)}\xi_2^2\xi_3. \qquad (13)$$

The values of $\langle v'l'|R|vl\rangle$ for the strongest vibrational transitions were found from experimental data using [6] and the linearity of Eq. (10) with respect to the operator R. Finally, two linear systems of fifth order with respect to the coefficients R^{ijk} were solved. The results calculated for R^{ijk} are given in Table 2.

The matrix elements found allow the integral absorption of the individual vibrational transitions to be calculated. The results obtained in this way for the most important vibrational transitions of CO_2 at T = 300°K are shown in Fig. 2. It is seen that they are grouped in the bands known from experiment. More detailed vibrational-transition structure is shown in Fig. 3.

From the results obtained, choosing the appropriate form of $W(\nu)$ for the lines, the spectral absorption coefficient may be obtained. In the temperature range from 200 to 3000°K at pressures $P > 0.1$ bar and in the frequency range from 500 to 10,000 cm^{-1}, Doppler broadening may be neglected and the contour regarded as dispersional. The half-widths were calculated in accordance with the theory developed in [7, 8] using the results of [9] and taking account of the dependence of the rotational quantum number j. In Fig. 4, as an example, the section of the spectrum with resolved rotational structure is shown.

NOTATION

k_ν, spectral absorption coefficient, taking account of induced emission; N, concentration of CO_2 molecules; j, total moment; Q, vibrational–rotational statistical sum; E, level energy; v_i, v_i', vibrational quantum numbers; h, Planck's constant; c, velocity of light; k, Boltzmann's constant; T, absolute temperature; ν, frequency, cm^{-1}; R, dipole-moment operator; $W(\nu)$ spectral line shape; C_{ij}, anharmonicity constants; ξ, normal coordinates; H_0, Hamiltonian of molecule in the harmonic approximations; $\tilde{V}$, anharmonic potential without resonance

TABLE 2. Coefficients of Expansion of the Dipole Moment with Respect to the Normal Coordinates, 10^{26} $kg^{1/2}\cdot m^{5/2}\cdot sec^{-1}$

$R^{(12)}$	—0,07536	$R^{(222)}$	—0,03958
$R^{(112)}$	0,04349	$R^{(223)}$	0,1119
$R^{(13)}$	5,362	$R^{(3)}$	20,12
$R^{(113)}$	0,8212	$R^{(332)}$	0,03479
$R^{(2)}$	10,996	$R^{(333)}$	0,1632

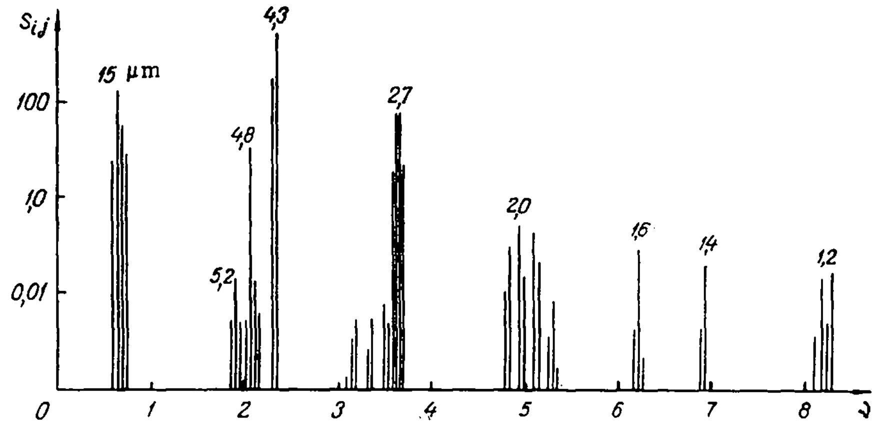

Fig. 2. Vibrational transitions of CO_2 molecules. $\nu \cdot 10^{-3}$, cm^{-1}; S_{ij}, $\mathrm{cm}^{-2} \cdot \mathrm{atm}^{-1}$.

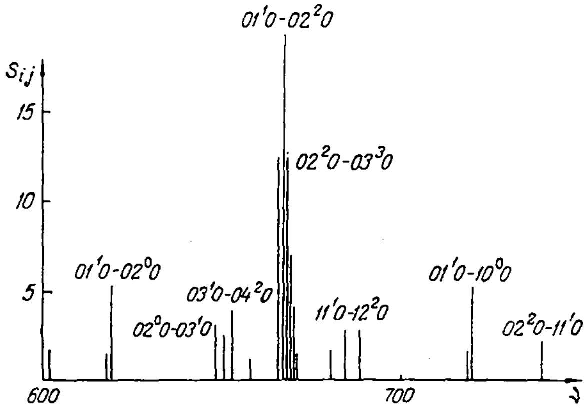

Fig. 3. Vibrational transitions of CO_2 molecule in the vicinity of the 15-µm band. ν, cm^{-1}; S_{ij}, $\mathrm{cm}^{-2} \cdot \mathrm{atm}^{-1}$.

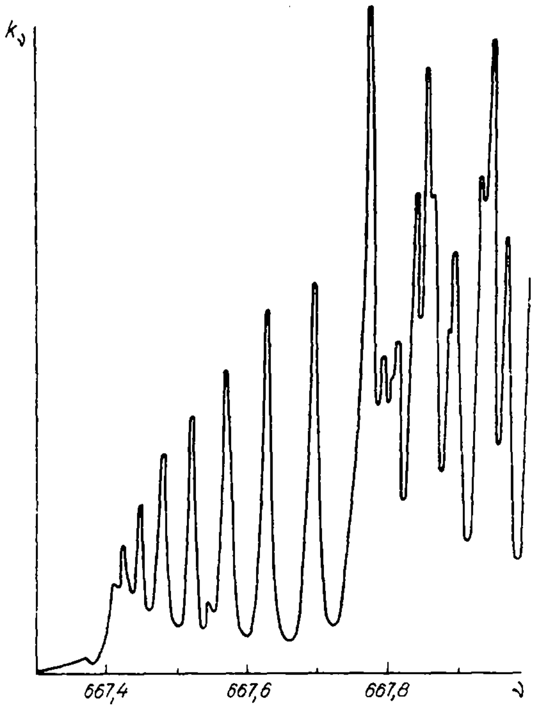

Fig. 4. Example of rotational structure of a section of the CO_2 band in the vicinity of 15 µm. T = 1000°K; ν, cm^{-1}; k_ν, rel. units.

component; ω, frequency of normal oscillations; X, B_l, spectroscopic constants; ψ, wave function; R_{ij}, matrix elements; S_{ij}, integral intensity of vibrational transition.

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METHODS OF CALCULATING MOLECULAR-GAS RADIATION ON THE BASIS OF SPECTRAL-COMPOSITION MODELING

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UDC 535.231.4

A method is proposed for the calculation of the radiation of inhomogeneous molecular gases at low pressures; the method is based on the summation of the equivalent widths of spectral lines and a quasiexponential model of the absorption band.

In many technological processes, the working medium is a molecular gas active in the IR region of the spectrum. At high temperatures of the medium, radiant energy transfer plays an important role as well as the convective mechanism of heat transfer, whereas carbon and metal-oxide particles emit and absorb radiation over the whole spectral region; the absorption of molecular-gas radiation occurs in vibrational–rotational bands, and beyond the limits of the bands the gas is practically transparent.

Each vibrational–rotational band consists of a more or less regular set of individual spectral lines whose characteristics can only be determined from a knowledge of the position, intensity, and contour shape. The bands with the simplest structure are the absorption bands of diatomic molecules, the wave function of which may be written in the first approximation as a superposition of a rigid rotator and a harmonic oscillator, although no difficulties are usually involved in taking account of anharmonic behavior [1]. The spectra of triatomic molecules — both linear (CO_2) and nonlinear (H_2O, SO_2) — are characterized by considerably greater complexity. At high temperatures, theoretical models of symmetric- or antisymmetric-gyroscope type [1, 2] do not give the required accuracy and empirical data play a large role.

However, such detailed information on absorption spectra over a broad range of the parameters determining the thermodynamic state of the radiating medium is not only difficult to obtain but also excessive. At low pressures and temperatures $\gtrsim 10^3$°K, it is necessary to determine the two-parameter function $k_\nu(\rho T)$ — of the order of 10^7-10^8 — describing the spectrum of the gas mixture typical for the combustion products in the range 1-15 μm. It is practically impossible to obtain such a volume of data from experiment, and its use for direct calculations involves a huge consumption of machine time. Therefore, in practice, the calculation of radiant transfer in a selective medium is based on models of the band approximately describing the properties of the real spectrum averaged over a small spectral interval of 10-50 cm^{-1}. The models most often used are the isolated-line model, the regular model, and the statistical (or Goody) model [2-6]. A certain loss of accuracy is involved, but this is compensated by the simplicity and ease of review of the results. In consequence of the great

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Institute of Physics, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 36, No. 2, pp. 204-217, February, 1979. Original article submitted August 30, 1978.

0022-0841/79/3602-0126$07.50