Programs and database for calculation of spectral characteristics of atoms and molecules in the visible, UV, and IR regions for simulation of high-temperature processes in gas media

A.S. Abaturov, E.A. Gavrilin, M.B. Kiselev,
N.N. Naumova, S.B. Petrov, and A.P. Smirnov

Rastr Public Corporation, St. Petersburg

A suit of programs and database of initial atomic and molecular fundamental constants and spectroscopic parameters for mathematical simulation and calculation of optical characteristics of gases at the temperature of 200–10000 K and pressure of 10^{-5}–10.0 atm at any averaging intervals in the spectral region of 0.1–25.0 μm is described. The most essential difference of this suit from the majority of earlier developed software packages is in the possibility of calculating fine and hyperfine structure parameters of rotational-vibrational-electronic molecular spectra in a wide temperature and pressure ranges. Some examples of positions of rotational lines, lambda-doubling, Hönl–London factors and the results of testing the emission spectrum of the NO molecule ($Å^2\Sigma^+ - Õ^2\Pi$) at $Õ$ = 4600 K calculated with the use of the code we have developed are presented.

Programs and databases of the initial data for calculation of spectra of heated gas media in wide spectral ranges are being developed for a few decades. They differ in the composition of components, the set of input and output parameters, and domains of practical application (see, for example, Refs. 1–3).

This paper describes briefly the suit of applied programs and a database of the initial parameters for calculation (on a PC) of spectral characteristics of gases at high temperatures in the UV, visible, and IR regions in simulating optical phenomena in continuum mechanics, radiant heat exchange between bodies moving in planetary atmospheres, as well as when processing recorded spectra of heated gases, solving problems of radiant heat exchange in the power production, high-temperature chemistry, and other fields and various processing plants.

The suit includes a set of algorithms describing optical properties of atoms and molecules, banks of the initial data including spectroscopic constants of neutral and ionized particles, databank of basic physical constants and algorithm for their conversion into different systems of units, libraries of programs and archives. It contains initial data for calculation of the parameters of fine and hyperfine structure in electronic, vibrational, and rotational spectra of diatomic molecules, absorption coefficients and cross sections, and emissivity of various heated gaseous substances, as well as cross sections of deceleration absorption, photodissociation, and photoionization with the temperature from 200 to 10000 K, pressure from 10^{-5} to 10 atm, and wavelength from 0.1 to 25.0 μm with arbitrary spectral averaging intervals under conditions of local thermodynamic equilibrium and non-equilibrium conditions, when the state of the medium is determined by different (electronic,

vibrational, and rotational) temperatures. The output parameters are spectral distributions of absorption coefficients and cross sections, as well as emissivity of atomic and molecular particles under various external conditions. In developing the codes, we used reference data, results of original papers, and information published in scientific journals.

Calculations of absorption coefficients and cross sections or emissivity of atoms and atomic ions involve the following basic constants: line position (wave number), oscillator strength and strength (intensity) of a spectral line, energies and statistical weights of the lower and upper levels of an atomic transition.[4]

The set of basic spectroscopic constants in calculation of parameters of fine and hyperfine structure of molecular spectra includes: Dunham coefficients, minimum energies of the corresponding electronic state, vibrational frequencies of molecules, anharmonic constants, rotational constants of the corresponding state, rotation-vibration interaction constants, constants of spin-orbit and spin-rotation interaction, a constant characterizing the spin-spin interaction, etc.[5,6]

The position of rotational spectral lines in vibrational-electronic transitions is determined by the contributions of the electronic, vibrational, and rotational components. The electronic and vibrational contributions to the spectral line position can be expressed through the Dunham coefficients.[7] The rotational contribution that determines the fine and hyperfine spectral structure depends on characteristics of the upper and lower electronic states of a transition, multiplicity of the upper and lower states, and Hund's cases for the upper and lower states.[5]

An example of calculation of the fine-structure parameters for the (1 – 1) vibrational band of the electronic transition $Å^2\Sigma^+ - Õ^2\Pi$ in the NO molecule

is depicted in Figs. 1–3. Rotational branches of vibrational bands that are marked by different color in the program are indicated to the right on the figures. The positions of rotational lines in 12 branches of the (1–1) band of the electronic transition $\mathrm{\mathring{A}}^2\Sigma^+ - \mathrm{\bar{O}}^2\Pi$ of the NO molecule is shown in Fig. 1.
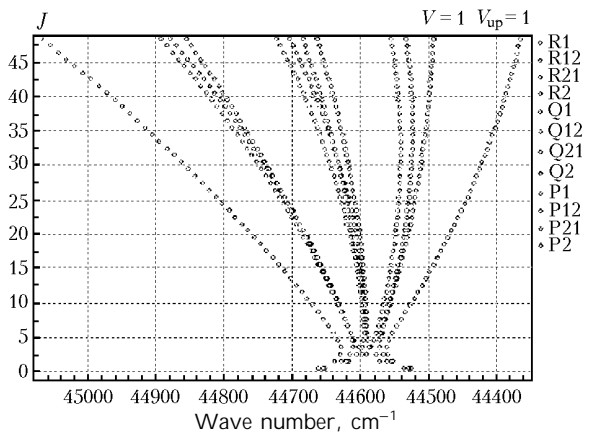
Fig. 1. Positions of rotational lines in the electronic transition $\mathrm{\mathring{A}}^2\Sigma^+ - \mathrm{\bar{O}}^2\Pi$ (1 – 1) of the NO molecule.
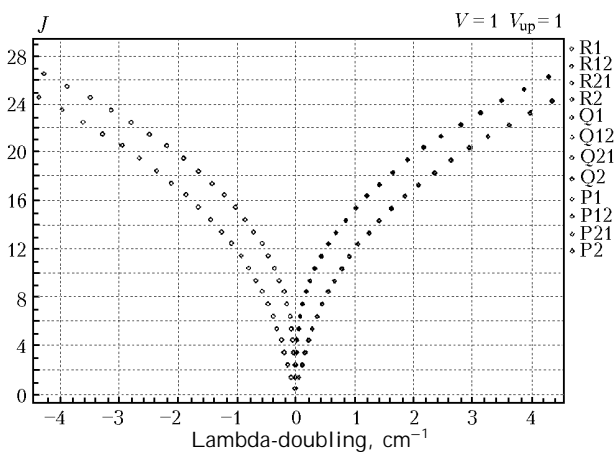
Fig. 2. Dependence of lambda-doubling on rotational quantum numbers J for the transition $\mathrm{\mathring{A}}^2\Sigma^+ - \mathrm{\bar{O}}^2\Pi$ (1–1) of the NO molecule.
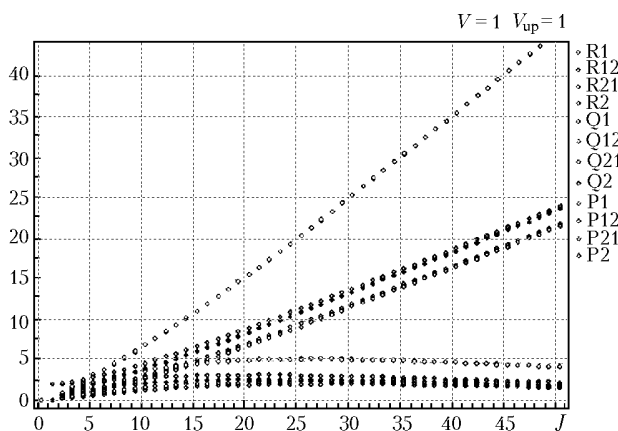

Fig. 3. Calculated dependence of Hönl–London factors on the rotational quantum number J for the transition $\mathrm{\mathring{A}}^2\Sigma^+ - \mathrm{\bar{O}}^2\Pi$ (1–1) of the NO molecule.

The program allows calculating to be performed of the positions of rotational lines in electronic spectra of molecules taking into account and neglecting lambda-doubling of states.[5] The values of lambda-doubling for electronic states are calculated by equations from Ref. 10. The dependence of lambda-doubling on rotational quantum numbers for the NO molecule in the $\mathrm{\mathring{A}}^2\Sigma^+ - \mathrm{\bar{O}}^2\Pi$ (1–1) transition is depicted in Fig. 2.

The intensity distribution in rotational-vibrational-electronic molecular spectra is determined by the electronic transition strengths,[8] Franck–Condon factors,[9] and Hönl–London factors.[10] The calculated dependences of the Hönl–London factors on rotational quantum numbers for the transition $\mathrm{\mathring{A}}^2\Sigma^+ - \mathrm{\bar{O}}^2\Pi$ (1–1) of the NO molecule are shown in Fig. 3.

Integral absorption coefficients of rotational lines in electronic spectra of diatomic molecules (line intensities) were calculated by the equation from Ref. 11 with allowance for the Voigt line profile.

For a comparison of calculated results with the results of other authors, the suit includes a testing program. Figure 4 compares the emission spectrum of the NO molecule ($\mathrm{\mathring{A}}^2\Sigma^+ - \mathrm{\bar{O}}^2\Pi$) calculated by our program (curve *1*) with the experimental spectrum[12] of NO fluorescence excited by a laser in a shock wave at $\mathring{O} = 4600$ K and the pressure of 100 Torr (curve *2*). Assignment of the vibrational bands is presented in Ref. 12. The intensities of both of the spectra are given in relative units.
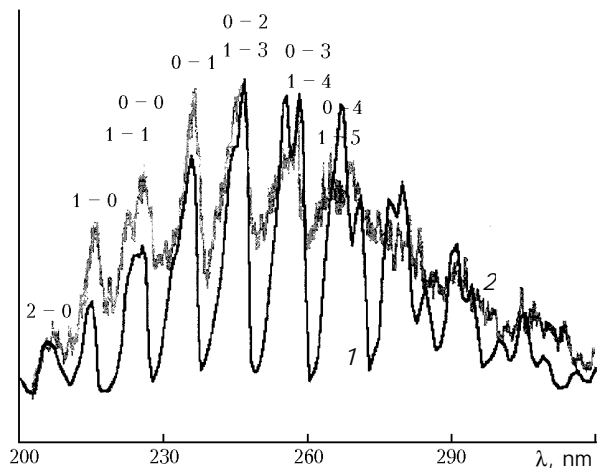

Fig. 4. Comparison of the calculated emission spectrum of the NO molecule ($\mathrm{\mathring{A}}^2\Sigma^+ - \mathrm{\bar{O}}^2\Pi$) (curve *1*) with the measured spectrum of NO fluorescence excited by a laser in a shock wave at $\mathring{O} = 4600$ K and the pressure of 100 Torr (curve *2*) (Ref. 12).

References

1. L.A. Kuznetsov and S.T. Surzhikov, "*Atlas of spectral absorption cross sections of electronic and vibrational systems of bands of diatomic molecules,*" Preprint No. 603, Institute for Problems of Mechanics, Moscow (1997), pp. 1–102.
2. K.L. Stepanov, L.K. Stanchits, and Yu.A. Stankevich, Zh. Prikl. Spektrosk. **67**, No. 2, 238–243 (2000).

3. S.T. Surzhikov, "*Spectral and narrow band directional emissivity of light-scattering and non-scattering volumes,*" Paper of the American Inst. Aeron. Astron. (New York, 2002), AIAA 2002−3324, pp. 1−15.

4. G. Herzberg, *Atomic Spectra and Atomic Structure* (Prentice Hall, New York, 1937).

5. G. Herzberg, *The Spectra and Structures of Simple Free Radicals: An Introduction to Molecular Spectroscopy* (Dover, New York, 1971).

6. K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (D. Van Nostrand, 1979).

7. V.P. Glushko, ed., *Thermodynamic Properties of Individual Substances*. Reference Book (Nauka, Moscow, 1978), Books 1−2.

8. L.A. Kuznetsov, N.E. Kuz'menko, Yu.Ya. Kuzyakov, and Yu.A. Plastinin, *Probabilities of Optical Transitions of Diatomic Molecules* (Nauka, Moscow, 1980), 319 pp.

9. N.E. Kuz'menko, L.A. Kuznetsova, and Yu.Ya. Kuzyakov, *Franck−Condon Factors of Diatomic Molecules* (IMU, Moscow, 1984), 344 pp.

10. I. Kovac, *Rotational Structure in the Spectra of Diatomic Molecules* (Akademiai Kiado, Budapest, 1969), 289 pp.

11. S.T. Surzhikov, *Computational Experiment in Development of Radiative Models of Mechanics of Emitting Body* (Nauka, Moscow, 1992), 159 pp.

12. U.E. Meier, G.A. Raich, D.R. Crosley, G.P. Smith, and D.J. Eckstrom, Appl. Phys. Â **59**, No. 3, 138−141 (1991).