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CALCULATION OF RADIATION CHARACTERISTICS OF DIATOMIC AND SOME TRIATOMIC MOLECULES

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A mathematical model and a software package that permit calculation of the chemical composition of complex mixtures in a wide range of temperatures and densities are developed. A thermodynamic databank for a large number (about 300) of molecules and radicals up to pentatomic ones inclusive is set up. The chemical composition is determined in the approximation of local thermodynamic equilibrium. A mathematical model and a software package for calculating electron-vibration-rotation spectra of diatomic molecules are proposed. A databank of optical characteristics of molecules makes it possible to calculate spectra of about 50 of the most important molecules. The calculation is performed in the approximation of Morse potential–nonrigid rotator. A version for calculating spectra in the approximation of the Rydberg–Klein–Reese potential is also set up.

Earlier in [1–3] the authors studied methods for calculating the coefficients of absorption and emission in a plasma. At temperatures lower than 1 eV spectra of atomic gases have a very characteristic form. Strong absorption begins only at the first threshold of ionization and in resonance lines. Absorption from excited levels is very low because of their low population. Bremsstrahlung absorption is also practically absent because of the small number of electrons in the plasma. Thus, before the first photoabsorption threshold we observe a frequency window in which the absorption is several orders of magnitude lower than on the threshold. However it is precisely in this frequency region (infrared, visible) that absorption spectra of di- and triatomic molecules are generally found. Even low concentrations of molecules lead to a substantial spectral change in the frequency windows. For this reason it is important to allow for absorption in the molecular spectrum at temperatures lower than 1 eV. In this work, consideration is given to computational methods and obtained results for absorption spectra of mixtures that contain air and nitrogen, carbon, silicon, and sulfur oxides in the temperature range where they exist as applied to problems of entry of meteorites into the earth's atmosphere, eruptions of volcanos, and others in which these characteristics can be significant and can be of interest.

The problem of calculating molecular spectra consists of two independent problems: finding the concentrations of different molecules of the mixture for the prescribed temperatures and densities and calculation of absorption and emission spectra in these molecules once their concentrations are determined. Determination of the chemical composition of a gaseous mixture is a more difficult problem than calculation of the ionization composition in a plasma. Finding the ion concentrations in a plasma under conditions of local thermodynamic equilibrium (LTE) can be considered to be a rather trivial problem that reduces to solving a system of Saha equations. In a gaseous mixture, the problem is complicated by the wide variety of different molecules and radicals. Unlike Saha equations, we have to solve a system of nonlinear algebraic equations of large dimensionality, which involves significant computational difficulties. First of all, difficulties with convergence of iterations arise when a system of nonlinear equations is solved. A second, no less important problem is that of distinguishing between true and false solutions since, apart from absolute minima (true solutions), there are numerous local minima.

To bypass these difficulties, use is often made of another method. The system of nonlinear algebraic equations that correspond to an equilibrium state is replaced by a system of unsteady-state kinetic equations. In this case, a system of equations in which the concentrations of different sorts of molecules depend explicitly on

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time is solved. Starting with arbitrary molecular concentrations, we can find the equilibrium solution in the limit of large time intervals. However, this computational procedure has serious limitations. In solving such systems, we must know a large set of rates of all kinds of chemical reactions. As a rule, these data are exclusively empirical in very narrow temperature intervals and are by no means represented for all chemical reactions. Furthermore, the rigidity of the kinetic equations, i.e., the significant difference (by several orders of magnitude) in the rates of different chemical reactions is a serious problem in this approach. These two facts restrict substantially the applicability of the method. Commonly, it is employed for relatively simple chemical compositions.

The authors of this work dwelled on realization of the first approach, i.e., solving the system of nonlinear algebraic equations. To do this, two procedures were employed successively. First, an estimating solution where for each chemical element the molecule with the maximum content of this element was determined and normalization to the number of atoms of the latter was found. The computational error amounts to ~50% since the presence of many molecules with approximately the same content of the indicated chemical element simultaneously in the gaseous mixture is highly improbable. It is important to note that this approximate solution is already quite similar to the true solution, and therefore in this case the problem of false extrema is eliminated. In the second step, the system of nonlinear algebraic equations was linearized relative to the approximate solution found. Next, this system was solved iterationally by the methods of perturbation theory with rather rapid convergence. This computational method does not restrict, in practice, the selection of the number of molecules allowed for.

As a test, the authors calculated a complex chemical mixture containing oxygen and nitrogen in large quantity, carbon and hydrogen to a lesser extent, and impurities of sulfur, chlorine, fluorine, and certain metals in small quantities. Conceptually, this is a typical environmental problem associated with determination of atmospheric pollution in various technogenic (technology-induced) accidents of various scales and natural terrestrial disasters (eruptions of volcanos). In the calculations, we allowed for all kinds of forms of molecules that consist predominantly of light elements, but ones no higher than pentatomic. Even with these restrictions we found more than 150 molecules and radicals of all kinds in a given gaseous mixture. Unfortunately, the method proposed has its limitations of applicability, too. The presence of LTE in the gaseous mixture is invariably assumed in calculations. In other words, the gaseous mixture invariably is able to come to equilibrium in times that are much smaller than the times of macroscopic processes. The rate of chemical reactions decreases sharply with temperature, and there can come a point where the time in which equilibrium is established exceeds the characteristic rate of change of the temperature. In this case, the equilibrium chemical composition will not correspond to the actual composition. The lower limit of applicability of the equilibrium approximation is usually several hundred degrees (this depends on the form of the molecules allowed for).

The given computational procedure has the corresponding software and makes it possible, within the framework of the indicated approximations, to calculate the chemical compositions of rather complex mixtures. For calculations, detailed databanks are available that contain equilibrium constants in a wide temperature interval and required thermodynamic functions such as pressure, internal energy, enthalpy, etc. These quantities were taken from handbooks [4]. About 300 molecules are listed in the databank. This list is being supplemented as necessary. For some diatomic molecules (first of all, these are positive or negative radicals), the necessary characteristics are absent in the handbooks used. In this case, the required thermodynamic functions were calculated using the methods of quantum mechanics. This will be pointed out below in discussing the methods for calculation of optical characteristics. Figure 1 presents a calculation of the chemical composition of air in the temperature interval of 1000–10,000 K as an example. Different oxides, in addition to nitrogen and oxygen molecules, appear as the temperature increases, but they dissociate rapidly as the temperature increases further. In addition to neutral atoms and molecules, there are positively and negatively charged atoms and molecules. The difficulty of graphical representation of a large number of curves made it impossible to present a calculation of a more complex mixture.

Absorption and emission spectra were calculated not for all the molecules present in a gaseous mixture but only for diatomic and some triatomic molecules. This substantial limitation has objective and subjective explanations. Among the first reasons is the fact that precisely diatomic molecules have the maximum temperature interval of existence. They are presented most for temperatures of 1000 to 10,000 K. The upper temperature bound

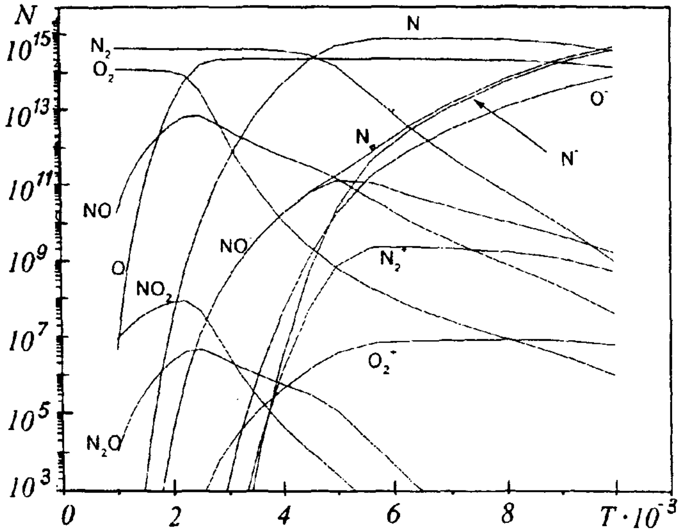


Fig. 1. Molecular composition of air at high temperatures. N, cm^{-3}; T, K.

for triatomic molecules generally does not exceed 2000–3000 K. Multiatomic molecules exist at much lower temperatures, where radiation processes can be considered negligible in the overall balance of the system's energy. Among the subjective reasons is the fact that spectra of multiatomic molecules are inadequately studied, and their known spectra are only minor empirical fragments.

In our calculations, we allowed for absorption and emission spectra for a large number of different diatomic molecules and some triatomic molecules. The existence domain of diatomic molecules lies in the interval of 1000–10,000 K. In this case, the main part of the radiation can be found in the infrared, visible, and ultraviolet ranges. The spectrum is governed by the set of electronic-vibrational-rotational transitions. Precise quantum-mechanical consideration of this problem is difficult, and therefore semiempirical models are employed most frequently. Then usually use is made of the experimental structure of the electron therms of a molecule and of the main characteristics of the vibrational-rotational structure of the levels – the frequency of harmonic vibrations, the anharmonicity, the rotational constant, etc.

The structure of vibrational-rotational levels can be calculated within the framework of the semiempirical approximation of Morse potential–nonrigid rotator [5]. For many molecules, the Morse potential makes it possible to calculate an anharmonic structure of vibrational levels that is close to the experimental structure. These entities can differ significantly only near the dissociation threshold. The Morse-potential approximation also enables us to calculate with a satisfactory degree of accuracy the probabilities of discrete vibrational transitions between various electron states – Franck–Condon factors and photodissociation probabilities. First, we calculate a complete set of vibrational wave functions, including the continuous spectrum, for each electron state. Next, we employ these functions to calculate all kinds of matrix elements that govern the transition probabilities. For some electron states, the Morse potential describes the experimental structure of vibrational levels with an insufficient degree of accuracy. The matter is that, in the Morse-potential approximation, three quantities – the frequency of vibrations ω_e, the anharmonicity $\omega_e x_e$, and the dissociation potential D_e – are related by $\omega_e x_e = \omega_e^2/4D_e$. For real potentials, this relation is not invariably fulfilled. In particular, for the Schumann–Runge electronic transition in an oxygen molecule in the upper electron state the value of D_e found exceeds the experimental value. This can bring about errors in calculating Franck–Condon factors and especially photodissociation probabilities.

If the Morse-potential approximation is unacceptable, in these cases use is commonly made of the so-called Rydberg–Klein–Reese (RKR) potential [6]. This potential is governed by the set of classical reversal points for each value of the vibrational energy E_v. Since for each value of the energy we must know two reversal points, to determine them the vibrational energies E_v themselves and dE_v/dv are used. The method for determining the reversal points is nonlocal and requires knowledge of the entire set of quantities indicated. If in some region of the potential the levels are perturbed (for example, due to predissociation) the RKR method can yield large errors, and this fact limits its applicability. There are different versions of this method, but all of them have known limitations of applicability. The authors of this work proposed a simple modification of the RKR method. The region of near reversal points that govern repulsion between atoms is localized in a narrow interval. In calculation of a number of molecular characteristics, accurate determination of a far reversal point is more important. Then we can determine with a sufficient degree of accuracy the set of near reversal points by the Morse potential. To determine the branch of the potential that describes attraction between atoms, use is made of the set of experimental values of vibrational energy levels E_v and the Bohr–Sommerfeld quasiclassical quantization condition. This simplification enables us to calculate the potential for any number of energy levels, thus circumventing the difficulties described above. The rotational constant of a molecule B as a function of the vibrational quantum number v can serve as the figure of merit for the indicated potential. The value of $B(v)$ calculated by the procedure described above is in good agreement with experimental data. In our calculations, we allowed for the vibrational-rotational interaction governed primarily by the rotational constant as a function of the vibrational quantum number v. It is precisely by ths that the "nonrigid rotator" model is governed. We should note that allowance for nonrigidity can alter substantially the form of the absorption bands. Such experimental characteristics as the energies of electron terms, the frequencies of fundamental vibrations, anharmonicities, etc. were taken from handbooks [7].

Adoption of the Morse or RKR approximation makes it possible to calculate the detailed vibrational-rotational structure of the levels. This, in turn, permits determination of statistical sums of molecules for a set temperatures of with a good degree of accuracy. Knowing the statistical sums and the dissociation potential, we can calculate equilibrium constants and necessary thermodynamic functions for molecules for which these data are missing from the handbooks.

Commonly, use is made of experimental values of electron-transition strengths. A procedure for determining these quantities from sums of vibrational-rotational components is presented in [6] in sufficient detail. Generally speaking, the electron-transition strength depends on the internuclear distance or on the magnitude of the vibrational quantum. To allow for this effect, the approximation of the R centrode is adopted. The R centrode $R_{v_1 v_2}$ is determined by the integral of the vibrational wave functions of the upper and lower electron states:

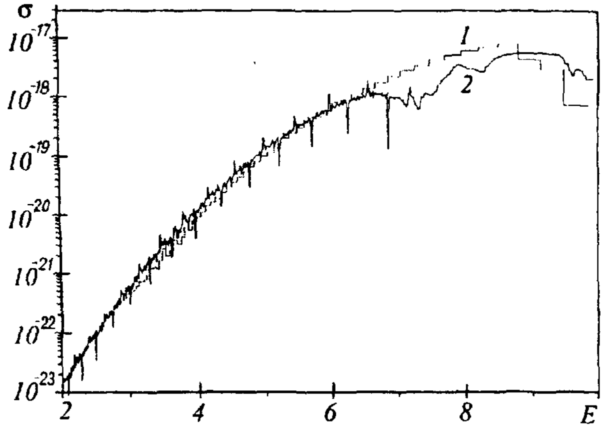
$$R_{v_1 v_2} = \frac{\int \psi_{v_1} r \psi_{v_2} dr}{\int \psi_{v_1} \psi_{v_2} dr} .$$

The electron-transition strength as a function of the quantum numbers v_1 and v_2 can be represented by a function of $R_{v_1 v_2}$. The corresponding functions for numerous electron transitions are given in [6]. They were employed in our calculations.

In calculating rotational transitions, one often proceeds from a simplified description of the rotational band. In our works, such simplifications are not used. For rotational transitions, we calculate Henle–London factors [8] in explicit form, which permit detailed allowance for individual P, Q, and R components of the transition and accurate determination of the band's edge.

Calculations were performed for the diatomic molecules O_2, N_2, NO, CN, CO, OH, CH, SiO, and SO and a number of others. Their list was governed by the range of problems in which they were presumed to be used. In this case, it was of interest to study the optical characteristics of the earth's atmosphere, the vapor of meteorite material, and volcanic gases. For each of these molecules, allowance was made for 3–5 electron states and 5–10 electron transitions. We took the experimental electron-transition strength in the R-centrode approximation. Figures 2–5 present absorption spectra of systems of bands of a number of molecules. The selection of precisely these molecules is not random. It governs the composition of the atmosphere at high temperatures and was studied by many authors. In particular, these figures make a comparison with existing data [5]. The degree of agreement obtained is quite satisfactory. In a number of cases, the spectra of this work have a more detailed vibrational-structure resolution.

In calculating optical properties we take into account both atomic and molecular components. In the temperature interval of 1000–3000 K, allowance for absorption of multiatomic molecules, primarily triatomic ones, is important. Of them, the water molecule is of greatest interest. This is governed by the fact that water is a most important component of atmospheric air and many mixtures. One variant of meteorite material is ice, and most of



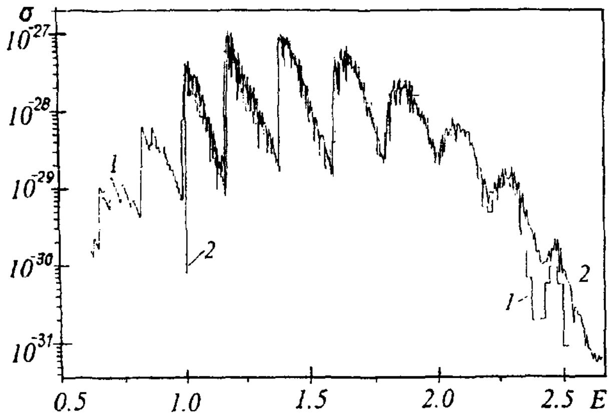


Fig. 2. Absorption of an O_2 molecule, the Schumann–Runge system of bands (T = 4000 K): 1) data of [5]; 2) present work. σ, cm^2; E, eV.

Fig. 3. Absorption of an N_2 molecule, the first positive system of bands (T = 1000 K): 1) data of [5]; 2) present work.

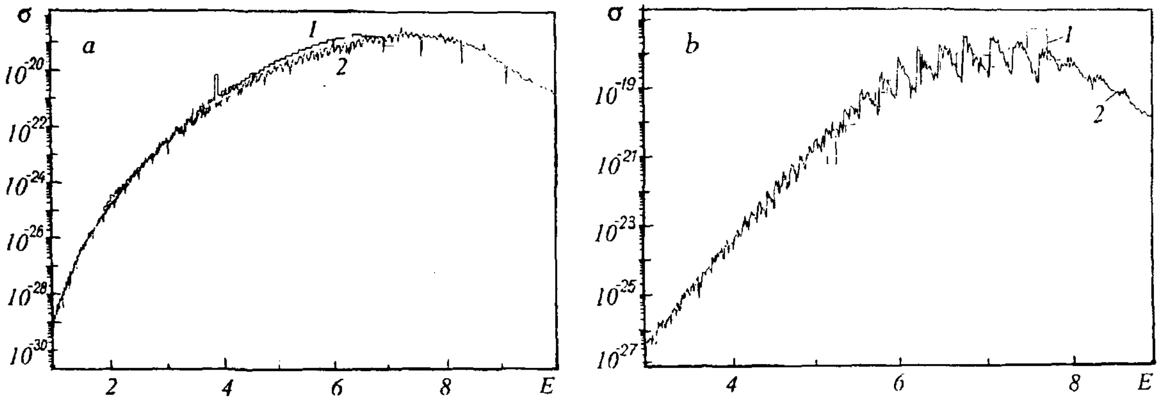
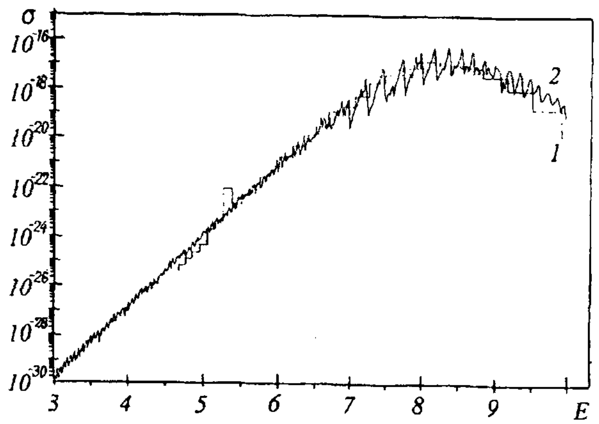


Fig. 4. Absorption of an NO molecule [a) β-system of bands, T = 3000 K; b) δ-system of bands, T = 4000 K]: 1) data of [5]; 2) present work.

the earth's surface, against which a meteorite's impact occurs, is the World Ocean. Water vapor is also a most important component of the ejection of many volcanos. This is the reason for the great interest in studying spectra of water.

Water has a rather high dissociation potential, which determines the existence domain of this molecule up to temperatures of 4000 K. Calculation of absorption and emission spectra of water was limited to allowance for vibrational-rotational transitions for the ground electron state. Electronic transitions were not allowed for in the calculations. The vibrational-transition strength was taken from experiment. It should be noted that, for asymmetric triatomic molecules, we are unable to construct the Morse-type potential, which makes it possible to calculate with a satisfactory degree of accuracy the structure of vibrational levels and vibration probabilities. The reason is the strong interaction between the individual modes. Therefore one always restricts himself only to allowance for experimental values of vibrational-transition strengths, even when they are presented inadequately. In our calculations, we used results of the widely known databank HITRAN-92 [9]. For a water molecule, we allowed for about 90 different vibrational transitions from the ground state that lie in the region of frequencies from 500 cm^{-1} to the visible region and a number of "hot" bands from excited states. Incorporation of these bands enabled us to allow for absorption processes up to temperatures of 4000 K.

A water molecule is an asymmetric rotator with a high degree of asymmetry. For this reason, the rotation spectra of water have an extremely disordered and irregular character. The structure of rotational energy levels of a symmetric rotator can be expressed analytically. We can represent the wave function of an asymmetric rotator as a linear combination of functions of a symmetric rotator. Then, to calculate rotational energy levels, we need to



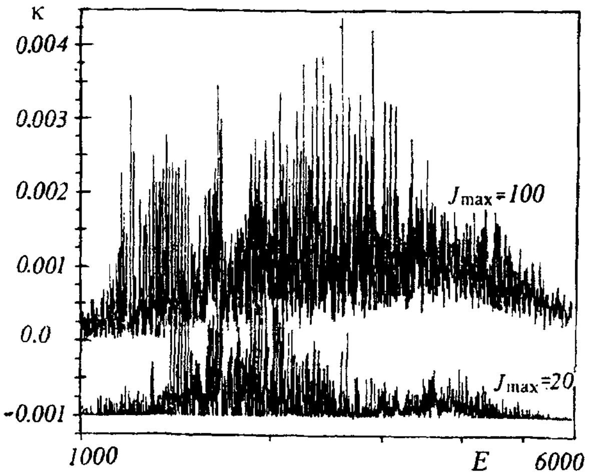
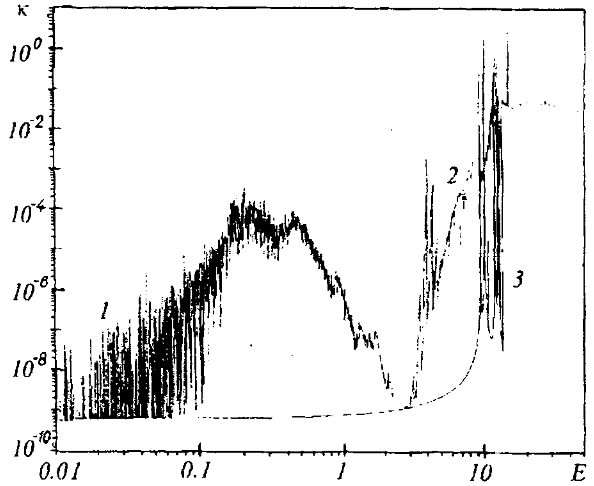


Fig. 5. Absorption of a CO molecule, the fourth positive system of bands ($T = 3000$ K): 1) data of [5]; 2) present work.

Fig. 6. Absorption spectrum of water vapor (T = 4000 K and $N = 10^{18}$ cm^{-3}) (the plot for $J = 20$ is reduced by 0.001). κ, cm^{-1}.



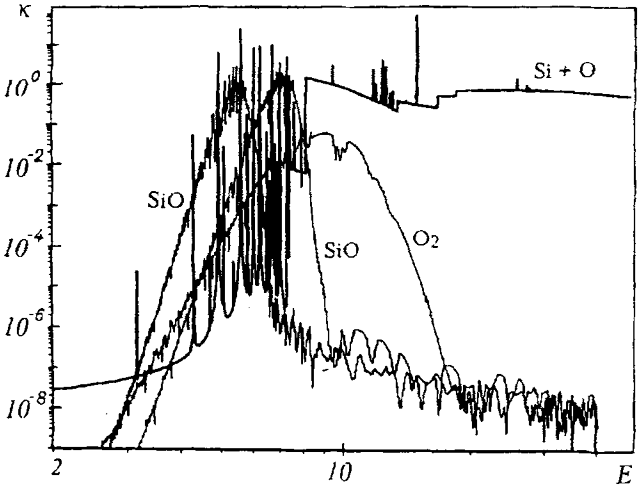


Fig. 7. Absorption spectrum of water vapor with allowance for molecular and plasma components (T = 0.2 eV and $N = 10^{18}$ cm^{-3}): 1, 2) tri- and diatomic molecules, respectively; 3) absorption on atoms. E, eV.

Fig. 8. Absorption spectrum of quartz plasma with allowance for the molecular component (T = 0.2 eV, $N = 10^{17}$ cm^{-3}).

solve a system of secular equations of dimensionality $2J + 1$ [10]. The degree of detail of the calculated spectrum depends on the number J allowed for. One often restricts himself to allowance only for J = 10–20 since the difficulties in solving the secular equations increase substantially with the number J. In our calculations, $J = 100$ was used. Figure 6 presents rotation spectra of water with $J_{max} = 20$ and $J_{max} = 100$. It can be seen that in the second case the spectrum is much more complex. To calculate transition probabilities, we must formulate selection rules for rotational transitions. They allow transitions with $\Delta J = 0, \pm 1$, which corresponds to Q, R, and P branches. In addition to the indicated rules, there are selection rules for parity in successive rotation about two axes by 180°. We distinguish A, B, and C transitions depending on the direction of the dipole moment of the transition along a moment of inertia of the molecule. The relative intensities of the rotational transitions of a symmetric rotator are determined by the Henle–London factors [8]. If the wave function of an asymmetric rotator is represented as a linear combination of functions of a symmetric rotator, the relative intensities of the rotational transitions can be found numerically in terms the corresponding Henle–London factors.

SO_2- or NO_2-type molecules have a much lower degree of asymmetry. For this reason, their rotation spectra have a more regular character.

When the contour of a spectral line is calculated it is sufficient to restrict oneself to allowance for the Doppler and Lorentz contours. Calculation of the Doppler width presents no difficulty. The Lorentz contour is formed by several mechanisms of broadening, the principal one of which is an impact mechanism. The quantum mechanical method for calculating the impact width is difficult, and therefore the method of standard conditions is used. The impact width γ_0 is measured experimentally at $P_0 = 1$ atm and $T_0 = 273$ K. For other temperatures and pressures, a simple recalculation is performed [11]:

$$\gamma = \gamma_0 \frac{P}{P_0} \left(\frac{T_0}{T}\right)^{1/2} .$$

Figures 7 and 8 give total absorption coefficients of water and quartz, which are of interest as the most probable meteorite materials. It can be seen that the spectrum of water consists of three characteristic segments: a complex vibration-rotation spectrum of the water molecule in the longwave region, spectra of the diatomic molecules H_2, O_2, and OH, and spectra of O and H atoms in the ultraviolet part of the spectrum. The quartz spectrum is governed by SiO and O_2 molecules and Si and O atoms. The two most important systems of bands are presented for the SiO molecule, and the Schumann–Runge bands are presented for the oxygen molecule. Absorption by Si_2 and SiO_2 molecules was not allowed for since they have a low dissociation potential, and their region of life is limited to low temperatures.

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NOTATION

ω_e, frequency of vibrations; $\omega_e x_e$, anharmonicity; D_e, dissociation potential; E_v, vibrational energy level; v, vibrational quantum number; B, rotational constant; $R_{v_1 v_2}$, R centrode; ψ_v, vibrational wave function; r, internuclear distance; J, rotational quantum number; γ, line width; P, pressure; T, temperature; N, concentration of particles; E, quantum energy; σ, absorption cross section of one molecule; κ, absorption coefficient. Subscripts: e, electron; v, vibrational quantum number.

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