

Atmospheric spectroscopy in the Institute of Atmospheric Optics. 30 years of formation and development

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Main physical aspects of the scientific program of the Spectroscopy Department of the Institute of Atmospheric Optics are presented.

The founder of the spectroscopic school of the Institute of Atmospheric Optics, Academician Vladimir Evseevich Zuev, whose scientific interests began with classical molecular spectroscopy (his candidate's thesis (1954) was devoted to intermolecular interaction in the quinone-phenol system), made several interesting works on atmospheric spectroscopy^{1,2} already in the 50s (before the Institute was opened in 1969). He solved some complicated problems arising in adaptation of the data of laboratory measurements of the absorption function to specific atmospheric conditions. Critical analysis of the models of absorption bands has demonstrated the fallibility of argumentation of the "square root law," which was popular at that time, as a possible approximation of spectrally integrated absorption. The almost heuristic method of describing the absorption function of an inhomogeneous medium by introducing the weighted-mean pressure was rigorously grounded. But the main methodological result of the state project developed under the leadership of V.E. Zuev (measurement of integral transmittance of the ground atmospheric layer for estimation of operation efficiency of an infrared radar) is clear understanding of the fact that the field of application of purely empirical information is too narrow and that it is necessary to develop what was later called a "complex approach to the problem on propagation of visible and IR radiation in the real atmosphere."

Wide penetration of methods, ideas, and results of classical molecular spectroscopy into atmospheric spectroscopy was a significant element of this approach. And it is very significant that the high professional level just in the field of classical spectroscopy (both theory and experiment) was the inherent part of fulfillment of this program. Without discussing the corresponding examples now, let us present an illustration on this subject, as a digression.

Traditionally, from the 30s, after Natalia Aleksandrovna Prilezhaeva came in Tomsk, it was quite fairly called the center of Siberian spectroscopy. However, in the 60s, due to various subjective and objective reasons (the science was actively developed in

Novosibirsk and Krasnoyarsk; the Siberian Branch of the Academy of Sciences was surely the "center of attraction" for talented youth, etc.), the leadership of Tomsk became at least doubtful. For instance, at the spectroscopic conference that was held on board a ship going along Yenisei, only three (!) Tomsk scientists took part without any reports (!). Now spectroscopists can hardly imagine such a situation: the Institute of Atmospheric Optics is nowadays a permanent organizer of regular international symposiums, schools, and conferences with various programs, wide representation of Russian and foreign colleagues, and already settled reputation. More than ten doctor's theses, the great number of published monographs (let us mention Refs. 3-22 among them), numerous papers and reports, constructive participation in international scientific cooperation, regular defenses of candidate's theses are clear evidences of stability of the spectroscopic field in the Institute's activity. This list can be supplemented by a high rating of the doctor's councils: defenses of theses by colleagues from Moscow, Saint-Petersburg, Minsk, Novosibirsk, and other acknowledged spectroscopy centers have become quite usual events.

Another necessary digression is a little excursus into the history of atmospheric spectroscopy; here I would like to describe the background against which the specific results should be considered.

The salient feature of atmospheric spectroscopy is the necessity to deal with spectrally integral fluxes of visible and IR radiation in the atmosphere with all its thermodynamic and meteorological realities. Such characteristics are included in the radiation block of climatic models; they appear in geophysical applications of atmospheric optics and serve as initial information in the passive sounding of the atmosphere (for instance, by outgoing radiation), and so on. In fact, the subject of study is characteristics of the type

$$\int d\omega K(\omega, \mathbf{r}) \exp\left(-\int dl \kappa(\omega, \mathbf{r})\right), \quad (1)$$

where κ is the spectral (for the frequency ω) coefficient of molecular absorption at the point \mathbf{r} . Appearance of \mathbf{r}

is evident since κ depends on pressure, temperature T , and concentration of an absorbing gas, which vary from point to point in the general case. Further, K can either be connected with the Planck function (in problems studying medium emission) or play the part of an instrumental function; certainly, combination of both the factors is also possible. Finally, $\int dl(\dots)$ is the integral over the beam trajectory in the geometric-optics approximation. Equation (1) is often associated with the absorption function

$$A(x) = \frac{1}{\Delta\omega} \int_{\omega_1}^{\omega_2} \{1 - \exp[-x \kappa(\omega)]\} d\omega, \quad (2)$$

$$\Delta\omega = \omega_2 - \omega_1$$

of a homogeneous medium of thickness x .

The main salient feature of Eqs. (1) and (2) is $\int d\omega(\dots)$: the change in the medium temperature, being the consequence of radiative transfer, is caused by the whole spectrum. The next problem is overlapping of bands for

$$\kappa(\omega) = \sum \kappa_j(\omega) \quad (3)$$

with summation over all gases that absorb radiation at the frequency ω . It is quite evident that if A_j given by Eq. (2) are known for $\kappa = \kappa_j$, Eq. (2) cannot be calculated directly with Eq. (3) through A_j . It is also evident that information on Eq. (2) for all points of an inhomogeneous path does not permit one to construct Eq. (1) because $\int d\omega$ and $\int dl$ are not commutative.

Certainly, the function K introduces additional difficulties, especially, because Eq. (1) falls under the integral $\int dr$ in solution of the radiative transfer equation. In the "ante-computer" epoch, the predominant approach referred to empirical information about the function (2) in combination with approximating, very witty, procedures (models of absorption bands, reduction to the problem for a homogeneous medium by introducing the weighted-mean pressure, etc.) of the consequent transition to Eq. (1). It seemed that the use of computers removed all the problems because in fact we "merely" deal with integrals, and Eq. (1) can be directly calculated from

characteristics of spectral lines (the line-by-line procedure). The databases containing information on the lines of atmospheric gases were created,* as well as the methods for calculating Eq. (1) with allowance for the aerosol component of the atmosphere together with its turbulence, etc. This was supported by formation of new problems connected with propagation of almost monochromatic high-intensity laser radiation in the atmosphere.^{23,24}

However, a little later some unexpected problems began to arise. It proved that the giant number of spectral lines generates not only technical difficulties. Attempts to overcome them led to a nearly paradoxical situation: teams dealing with the corresponding calculations had to compare final (and allegedly accurate) results and to ascertain differences, sometimes considerable. (The physical problem was, in fact, replaced by a computer game.) By the same reason, the radiation blocks of climatic models prove to be so cumbersome that their practical significance becomes doubtful. Note, by the way, that radical reduction of radiation blocks, preserving the necessary accuracy, is nowadays one of the main problems of atmospheric optics.

There is one more, rather delicate, matter. The problem for κ is accompanied by numerous approximations and assumptions; it is rich in empirical constants. However, finally, detailed components of the κ structure are not needed due to $\int d\omega$. In other words, first we obtain clearly excessive information at the cost of some approximations, and then we must shake off it by new approximations (!?). Certainly, it seems necessary to turn to actions such as "kinetic equations."

Finally, it proved that significant physical facts connected with "atmospheric windows," i.e., frequency regions where the value of κ is determined by the periphery of a spectral line profile, remain beyond the scope of direct calculations with nearly forced approximations applied to the spectral line profile. However, just these spectral regions are decisive for the radiation budget of the Earth as a planet. All these facts caused "renaissance" of the former ideas on solution of Eqs. (1) and (2), but, certainly, taking into account the new capabilities given by modern computers. An example on this subject, namely, "exponential series," is considered below.

Now let us briefly characterize elements of a large-scale program of investigations in classical molecular spectroscopy. From the very beginning, spectroscopy in the Institute was considered as not a mere "supplier" of

*The Automated Information System on the Parameters of Spectral Lines of Atmospheric Gases compiled in the Institute of Atmospheric Optics was among the first databases of such a type. The Optical Model of the Molecular Atmosphere should also be mentioned; in this system the absorption coefficients are presented as functions of the altitude for laser wavelengths and climatic models of the atmosphere.

data for problems of atmospheric optics, but as a basis for a new level of their solution. The causal chain (to answer the question A, one has first to answer the question B, and so on) has induced examination of the principal aspects of spectroscopy. The program, whose implementation took several years, consisted of very detailed studies of spectra of atmospheric gases (Yu.S. Makushkin, Vl.G. Tyuterev, L.N. Sinitsa, O.N. Ulenikov, V.I. Perevalov, V.I. Starikov, A.D. Bykov, et al., who are former and active contributors of the Institute), their nonlinear spectroscopy (Yu.N. Ponomarev, V.P. Lopasov, V.P. Kochanov, et al.), line contours (M.R. Cherkasov, V.V. Fomin, L.I. Nesselova, O.B. Rodimova, S.D. Tvorogov, et al.). We restrict ourselves to only illustrative excursus in the corresponding results.

The very significant place in this subject belongs to the study of high-excited rotational-vibrational spectra of light-weight molecules (first of all, H₂O, then HDO, H₂S, H₂, etc.). The problem itself is very interesting: it includes seeking for numerous nonlinear resonances, examination of consequences from interference of quantum states, and very unclear problem on a quantum analog for chaos of classical nonlinear systems, etc. The specific features of the subject (weak intensities of spectral lines and small distances between them) require the use of sophisticated experimental techniques. The experimental techniques presented at the Institute include laser spectrophotometry, photo-acoustic spectroscopy, intracavity laser spectroscopy (the last two are also used in the study of nonlinear spectroscopic effects), laser spectroscopy of fluorescence and Raman scattering. The practical result is thousands of new lines and tens of bands recorded in the 800–16000 cm⁻¹ region (resolution of 10⁻²–10⁻⁴ cm⁻¹, sensitivity (by κ) of 10⁻⁷–10⁻⁹ cm⁻¹).

Here, as a digression, it is quite necessary to come back to the time of origination of experimental laser spectroscopy in the Institute. Very soon the researchers understood that the problems of atmospheric optics urgently require creation of adequate laser systems. And, for this purpose, they had to go to the heart of laser physics, study corresponding processes, and invent very sophisticated experimental procedures. As a result, the ruby and glass-neodymium lasers designed at the Institute had unique, for that time, performance characteristics: short pulse duration, capability of frequency tuning, etc. (At that time it was experimentally observed that the anti-Stokes wave several times exceeded in intensity the Stokes wave. This fact seemed to be improbable at that time but, unfortunately, then it was left.)

The next achievement was the alexandrite laser also having unique performance characteristics. Later the department of spectroscopy had included the laser specialization directed to developing metal vapor lasers; these lasers have then found wide application in atmospheric optics. A remarkable example on this

subject is development of the laser system selectively tuned to detecting radioactive iodine isotopes. It is based on the Cu-vapor laser: absorption bands of iodine radionuclides lie inside its yellow and green lines. Practical significance of such a system is evident because of the necessity to monitor gas plumes of radiochemical industry.

Let us come back to the problem of highly excited states. Certainly, such a subject is a quite natural continuation of spectroscopy of low-lying states. Peculiarities of transitions between highly excited states give an opportunity to understand fine details of intramolecular interactions. The characteristic example is the proof of existence of the local resonance between highly excited states in the H₂O spectrum. It is accidental, to some extent, because it couples highly excited vibrational states (with large Δv) belonging to different polyads of interacting states; it is connected to a strong centrifugal effect manifesting itself at excitation of a large-amplitude bending vibration.

Another example is the shift of a line center by buffer gas pressure. Difficulties in its calculation are generated by the fact that the shift is a difference between two almost equal values (by the way, the line halfwidth is their sum), and sometimes calculations cannot predict even its sign. So, such fine details become significant as the difference between the molecular parameters of the upper and lower states, bending of the trajectory of the mass centers of molecules at their collision, overestimation (in comparison with the analysis of halfwidths) of contributions of different terms from the Coulomb energy of intermolecular interaction.

The aspects discussed well complement the experimental results on nonlinear spectroscopy of atmospheric gases. Measurements are very demonstrative that show how the saturation effect vanishes as the shifted frequency grows with the following appearance (for other physical causes) of dependence of the absorption coefficient on the intensity of laser radiation in the anomalously far (hundreds of halfwidths) line wing. The fact is also interesting that polarization of laser radiation influences the saturation effect. This influence and field narrowing are clearly observed at linear polarization; however, they are both absent at circular polarization. This regularity is still to be understood.

In the same context, let us mention a cycle of papers dealing with a frequency region that is intermediate between the Doppler and dispersion line contours. Here, some salient features were also discovered, for instance, the dependence of the Dicke effect on quantum numbers.

The "pure" theoretical spectroscopy in the Institute's research is presented by the theory of effective Hamiltonians, that is, a some physical alternative for purely computer solution of the quantum problem of an isolated molecule. Recall that the subject is rotational-vibrational spectra with the electronic

problem left unsolved (it can hardly be solved even with modern computers). This lack of knowledge is compensated for by introducing empirical parameters. The number of such parameters is as high as several hundreds, and this generates very specific problems.

The term "effective Hamiltonian" is associated with the unitary transformation from the initial rotational-vibrational Hamiltonian H of an isolated molecule to the operator $H' = \Omega H \Omega^{-1}$ using a certain procedure (called a contact transformation) of constructing the unitary operator Ω . This procedure is certainly oriented to the structure of H . If, for instance, $H = H_0 + \lambda H_1 + \lambda^2 H_2 + \dots$ with the unperturbed part H_0 and the perturbation parameter λ , we have

$$\Omega = \dots \exp i\lambda^2 S_2 \exp i\lambda S_1, [iS_1, H_0] = H_1, \text{ etc.}$$

Mathematics of super-operators, computer systems of analytical calculations, and others are popular techniques in this case. It is evident that H and H' have the same eigenvalues, and the eigenfunctions can be calculated after Ω is constructed. The pragmatic sense of this action is that H' must be simpler than H , since the unitary transformation converts it to the quasi-diagonal form. Further, the numerous parameters entering into the Hamiltonian (we have already said about their inevitable appearance) have, on the one hand, clear physical sense (they are connected with the corresponding intramolecular interactions), but, on the other hand, quite expectable ambiguity of H' can lead to very different values (with even different signs) depending on the way or stage at which Ω is constructed.

One of main results obtained at the Institute is a principal solution to the problem discussed, or a sort of the "theory of perturbations" which turns a primitive approximation into a quite physical method.

Strictly speaking, just this generated the following applications, and one of them is the system for global processing of carbon dioxide spectra, which allows reconstruction of the whole spectrum from measurements of the limited number of sufficiently strong lines. (By the way, they are just the lines that are detected most reliably.) Similar spectroscopic information is also collected and carefully classified for the ozone spectrum. The part of carbon dioxide and ozone in atmospheric radiative processes is well-known so there is no need to comment the significance of classical spectroscopy for atmospheric spectroscopy.

Light molecules introduce their own additional, and significant, problems (atmospheric spectroscopy actually deals with) because of strong interaction between vibrations of nuclei and rotation of a molecule as the whole. So, the seemingly evident system "harmonic oscillator + rigid rotator" becomes inefficient, because the perturbation parameter λ involves not only anharmonic character of vibrations and non-rigidity of the rotator, but also the interaction between vibrational and rotational degrees of freedom. So, because of physical reasons, the zeroth

approximation in the theory of perturbations should be changed for it include the non-harmonic (i.e., without expansion in terms of normal coordinates) potential of high-amplitude vibrations, torsion-rotational interaction, etc.

So, the convergence of the effective Hamiltonian as a series of the theory of perturbations becomes problematic, and the procedures for summation of divergent series should be applied. As it often occurs, understanding of the mathematical nature of divergence implies understanding of physical aspects of the problem. The method of generating functions presents a possibility to advance in overcoming these difficulties.

Another fundamental field in the Institute's research is spectroscopy of intermolecular interactions which determine the contour of spectral lines. (We have already cited some results of this scope.)

The problem of the contour, under sufficiently general assumptions, reduces to analysis of an expression in the form

$$F(\omega) = \int_0^{\infty} dt \exp(i\omega t) \text{Sp } \rho M S^{-1} M S,$$

where t plays the part of time; $S(t)$ is the evolution operator for two interacting molecules; ρ is the Gibbs density matrix of this system; M is the dipole moment of a molecule that directly absorbs light (at the frequency ω). As for the physical content, F is the parameter proportional to the probability that the quantum system consisting of two molecules absorbs a radiation quantum.

Generally speaking, $F(\omega)$ is a tangle of problems (solving one of them, one must remember about solving others): calculation of $\int dt$, solution of the Schrödinger

equation for colliding molecules (usually one deals with intramolecular quantum degrees of freedom at the classical centers of masses), statistical averaging by collision parameters which enters into Sp, construction of the classical potential of intermolecular interaction V which determines the dynamics of mass centers, and, finally, calculation of matrix elements of the operators under the Sp sign. Every specific theory of the contour is a compromise combination of approximations for each of the listed problems. Differences, in fact, arise in analysis of the contour periphery, since for the line center any approach gives the dispersion contour with corrections, if needed, for Doppler broadening and interference of quantum states (the latter is very seldom).

The version proposed by us starts from the asymptotic estimation of $\int dt(\dots)$ by the formal parameter "large shifted frequency." The method of the stationary phase proves to be applicable, and the equation for a stationary point has the form of the law of conservation of energy at absorption of a quantum

by a pair of interacting molecules. (This is significant, because if "mathematical rules of the game" find their clear physical sense, the asymptotic method is applicable, so to say, "on the verge of a foul.") After this, the quantum problem is radically simplified: it is reduced to only calculation of eigenvalues of the Hamiltonian of a pair of molecules and, in practice, to calculation of the term due to intermolecular interaction to be added to the sum of energies of isolated molecules. The classical problem is also localized: it becomes sufficient to deal with a section of the trajectory in the vicinity of a stationary point, and this section can be approximated by a straight line. The statistical averaging is now merely integration with the Gibbs distribution function for V over the parameters of this straight line. Actually, all the known experimental facts on light absorption and emission in wings of spectral lines and bands can be interpreted (and not only qualitatively, but also quantitatively, what is more important) within the frames of this scheme. It should necessarily be emphasized that specific analysis verifies the leading part of the classical potential of intermolecular interaction for events at the periphery of a contour.

We have already noted that the combination of fine physical problems of classical molecular spectroscopy and traditional problems of atmospheric spectroscopy is the principal and most important characteristic of the scientific program of the Institute. This complex approach has formed the basis for original spectroscopic ideas in the problem of laser sounding of the atmosphere, and some examples are presented to illustrate the subject.

The method of differential absorption was supplied by reliable specific numerical information for sounding H_2O , O_3 , and other gases. Besides, it was shown that errors (for the case of water vapor sounding at the wavelength of 694.38 nm of a ruby laser) due to ignoring the line shift achieve 10–12% for altitudes above 10 km and exceed 30% for altitudes above 20 km.

Spectroscopic details are sometimes of a decisive factor in solving the inverse problem of laser sounding. Besides, they are very significant when "inverting" information on outgoing radiation obtained from space. This list can be complemented by capabilities of laser fluorescent spectroscopy: detection of OH radical and determination of temperature from the ratio of two fluorescence signals.

Spectroscopic results are also significant for the problem of studying the "nature" of some geophysical phenomenon. A good illustration is the problem on the cause of "excessive" absorption of solar radiation in the atmosphere due to water vapor. It should be noted here that the solution to this problem is sought at the "level of hypothesis."

First of all, let us note that the theory of spectral line contour quite clearly asserts that this additional absorption cannot be treated as the spectroscopic continuum formed by far wings of lines. Under any

allowable variations of the contour, deviations from atmospheric measurements (that are comparable with purely laboratory measurements) toward smaller values achieve several orders of magnitude. Analysis of data on spectral transparency of the aerosol component of the atmosphere (visibility, character of the humidity dependence) has led to the hypothesis of fractal scattering, especially, taking into account that carbon particles are the necessary component of the real atmosphere. An interesting problem arises: Maxwell equations with boundary conditions on a surface with fractal dimension: "catchers for photons" are possible just there.

Another hypothesis discussed is induced by the results of the study of high excited states: very weak, but numerous and closely spaced lines can create a continuum (to be more precise, quasi-continuum), and just the continuum can be responsible for "excessive" absorption. Recently a hypothesis appeared that the cause of the effect should be sought in the influence of the weak electric field of the atmosphere on spectroscopic processes. It is quite evident that in all the ways the results of pure spectroscopy determine the initial point in consideration.

However, the most convincing evidence of fruitful combination of classical and atmospheric spectroscopy is the problem of the atmospheric window, i.e., the 8–12 μm region.

First let us recall the thoroughly studied spectroscopic properties of this frequency region. This region is characterized by existence of non-selective (continuum) absorption due to water vapor, and the corresponding coefficient is $\kappa = apP + bp^2$, where $a = a(\omega)$, $b = b(\omega)$, and p and P are, respectively, the partial pressure of water vapor and total pressure. Here $bp^2 \gg apP$, in spite of $P \gg p$; and $\partial\kappa/\partial T > 0$ for atmospheric temperatures. A somewhat paradoxical methodical content of the problem reduces to the fact that all the known hypotheses on the origin of the long-wave continuum, namely, wings of water vapor rotational bands, water dimers, ionic clusters, fine aerosol (there exists even an attempt to treat the continuum as a quantum-optics effect), are indistinguishable in their consequences as applied to the listed regularities: all of them can be interpreted (qualitatively, but usually invoking numerical estimates) within the frames of any hypothesis. However, geophysical consequences of the assumptions discussed are very different. This is very important, as the atmospheric window plays one of the leading parts in formation of the radiative budget of the Earth as a planet.

The way out of the situation (which seems to be deadlock) is, in fact, rather evident: the assumptions should be expanded to adjoined fields (light emission, nonlinear optics), where their results differ radically and direct experiments fully solve the problem. The corresponding program was implemented in the Institute of Atmospheric Optics.

Let us begin with the problem on the emission coefficient χ entering into the transfer equation. In the semi-classical electrodynamics, the medium emission is explained by quantum fluctuations of the equilibrium dipole moment, and the fluctuation-dissipation theorem together with Maxwell equations states that local thermodynamic equilibrium (i.e., the relation $\chi = B\kappa$ with the Planck function B) takes place if and only if spatial dispersion is absent in the imaginary part of the permittivity ϵ . However, the above-mentioned theory of the contour quite definitely (mathematically rigorously) asserts the existence of this effect in band wings. (Here it is worth mentioning that electrodynamics usually treats the spatial dispersion $\text{Re } \epsilon$.) The physical nature of the effect is in general quantum and statistical regularities of non-resonant interaction between the field and a molecule: this condition is quite different from resonances often analyzed in spectroscopy. A natural consequence is violation of the local thermodynamic equilibrium, and this fact is reliably verified in experiments.

Another argument, similar in its significance, comes from nonlinear spectroscopy. We have already emphasized the part of classical potential of intermolecular interaction in formation of the contour periphery and, according to the quantum-mechanics rules, V is the average over intramolecular variables with ρ and the Coulomb energy. In a strong laser field, ρ depends on the field intensity J , and the causal chain, which was already presented, implies the nonlinear effect $\kappa = \kappa(J)$.

It is remarkable that nonlinear spectroscopy usually studies resonance processes on almost necessarily isolated lines; whereas here the condition of "large shifted frequency" is necessary, just as the "band wing" when the sum of a great number of lines works as an amplifier of weak non-resonant interaction at quantum transitions. Experimental data have demonstrated the isotopic dependence of the effect: $\kappa(J)$ for H_2O and D_2O is different, but absorption of a weak field by both isotopes is the same. Another interesting fact is the opposite field dependence of relaxation time in the resonant and non-resonant cases.

All the above-stated facts can be quantitatively interpreted within the frames of the theory of line contour, and this is quite definitely indicative of line wings as a cause of longwave continuum. In fact, it is evident that other hypotheses on its nature cannot explain (even qualitatively) these additional experimental results.

Another example in the context of the program "classical and atmospheric spectroscopy" is the experimentally detected diffuse absorption band of water vapor in the UV part of the spectrum (250–320 nm). It is interesting that this band must complete the "ozone shield" protecting the Earth from hard solar radiation, which is dangerous for living organisms. However, the spectroscopic origin of this band is still unclear.

Now let us come back to pragmatic problems of atmospheric spectroscopy which were mentioned while discussing Eqs. (1)–(3).

We have already mentioned the difficulties in calculations of κ , which are generated by the giant number of lines in spectra of atmospheric gases. The theory of a spectral line contour proves the existence of a way to overcome them. It is based on a very simple idea. Let the absorption coefficient be written in the form

$$\kappa = \sum_{\alpha \subset \Delta\omega(\omega)} \kappa_\alpha(\omega, \omega_\alpha) + \sum_{\alpha \notin \Delta\omega(\omega)} \kappa_\alpha(\omega, \omega_\alpha) \equiv \sigma(\omega) + \beta(\omega).$$

Here $\kappa_\alpha(\omega, \omega_\alpha)$ is the absorption coefficient of a line centered at ω_α ; $\Delta\omega(\omega)$ is the interval near ω within which the contour is disperse. The function β formed by line wings proves to be very smooth function of ω and T , so the full information about it does not occupy much place in computer memory. So, only several lines forming the term σ should be added to the "background" of β .

An outstanding place in the spectroscopic program of the Institute, in the section "Atmospheric spectroscopy," is occupied by the method of "exponential series." Its mathematical essence is that the peaked function $\kappa(\omega)$ in Eq. (2) looking like a "fence" of spectral lines (with a large number of peaks and dips) is replaced by a monotonic function $s(g)$ so

$$\text{that the integral (2) coincides with } \int_0^1 dg \exp(-s(g)).$$

Thus the possibility appears to apply an appropriate quadrature formula with a small number of terms and write the exponential series

$$1 - F(x) = \sum_v c_v \exp(-x s(g_v))$$

with abscissas g_v and ordinates c_v of the chosen quadrature formula.

The initial idea of such a rearrangement of the lines forming $\kappa(\omega)$ was proposed as early as in 1936 by V.A. Ambartsumyan, and then for a long time it was developed nearly intuitively. Understanding that the formal implementation must be connected with the Laplace transformation of the function $F(x)$ was a remarkable landmark; but even after this the problem was discussed "at the physical level of the rigor." Simultaneously, the Dirichlet series existed in mathematical literature; application of the corresponding results allowed development of much more favorable "mathematical climate" and, as a consequence, it opened see new potentialities of exponential series.

In this connection, two facts should be noted; first, the procedure of constructing $s(g)$ directly from databases of spectroscopic information and, second, the exact procedures for solving the problems that are generated by Eqs. (1)–(3); and already within them the efficient approximate techniques appear. Their

practical significance is in radical reduction of the radiation block; there are examples demonstrating that calculations can be reduced by orders of magnitude with the required accuracy preserved.

In fact, one can assert that the exponential series is an illustration of very fruitful combination of classical spectroscopy, "pure" mathematics, and capabilities presented by computer. All the elements of this symbiosis are similarly necessary. We have already said about the part of mathematical results; implementation of the algorithm for constructing $s(g)$ is unthinkable without a computer; but the main point is that rational allowance for just physical features of a line contour and spectrum (position of lines, their intensity distribution) makes the problem realistic. And we again assert the importance of classical spectroscopy for atmospheric spectroscopy.

The exponential series successfully harmonize with the idea to apply methods of nonlinear dynamics to qualitative analysis of nonlinear differential equations describing relations between thermodynamic characteristics of the atmosphere and radiative fluxes in it. Such analysis separates just the characteristic points for which this detailed and very cumbersome calculation invoking complicated n -dimensional models of the atmosphere is needed. The spectroscopic factor is also evident: just the dependence of Eq. (1) on T determines the nonlinear character of the equations with all the following consequences.

Thus, the paper presents main physical fields of the spectroscopic program of the Institute of Atmospheric Optics. The "humanitarian" style of the presentation corresponds to the aim of this paper in the issue devoted to the 30th anniversary, that is, to demonstrate that the spectroscopic school originated in the Institute has its own methodical approach, set of problems to be solved, and fundamental results. The key point in the characteristic of this school is treatment of atmospheric spectroscopy as a part of classical molecular spectroscopy, as well as firm conviction that general results of classical spectroscopy for the basis for successful solution of the problems of atmospheric spectroscopy. Practically speaking, this is just the realization of the complex approach, i.e., the idea constantly propagandized and put in practice by Academician Vladimir Evseevich Zuev.

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