

THE IR BROAD-BAND SPECTRAL CHARACTERISTICS OF WATER VAPOR IN THE TEMPERATURE RANGE 300–2000 K

O.K. Voitsekhovskaya, N.V. Kuz'mina, and N.N. Trifonova

*Institute of Atmospheric Optics,
Siberian Branch of the Academy of Sciences of the USSR
Institute of Physics, Belorussian Academy of Sciences
Received November 20, 1989*

Direct calculations aimed at analyzing the propagation of light through thermally inhomogeneous gases require that the parameters of the spectral absorption lines (PSL's) be known within a wide temperature range. An initial version of a databank on high-temperature PSL's has been compiled at the Institute of Atmospheric Optics, Tomsk.

This paper outlines the problems of the completeness and reliability of a databank of H₂O PSL's. The control procedure is based on calculations of the broad-band characteristics, such as spectral trends of the averaged absorption coefficient and the temperature dependence of the integral intensity of the H₂O band systems at 6.3, 2.7, and 1.87 μm , with subsequent comparison with the experimental data.

INTRODUCTION

One of the principal directions of ecological studies is IR remote sensing of the composition of exhausts from industrial enterprises and power plants. Important aspects of this problem are the calculation of the exhaust gas self-emission and the need for an adequate account of reabsorption of these emissions into the atmosphere.

The empirical techniques that have been widely used up to now, along with various band models,¹ and the Curt is-Godson technique^{2,3} no longer satisfy the demands on the accuracy of such computations. It seems most expedient to develop new techniques, predominantly employing the approach of direct (line-by-line) calculations, already very popular for modeling at normal temperatures. Such techniques are not limited in their spectral resolution, and are compatible with the capabilities of any possible measurement instrumentation. Obviously, what is needed in the way of initial information for the design of such techniques is data on the spectral line parameters (SLP), reliable over a wide range of temperatures (300–3000 K).

The presently available SLP atlases⁴ contain reliable data only for normal conditions. This means that such atlases include only those spectral lines that display intensities exceeding certain minimal levels at normal temperatures (296 K). Meanwhile, repopulation of energy levels takes place in a molecule at higher temperatures, so that an ever increasing contribution to the emission (absorption) of radiation is produced by the so-called "hot" lines, which correspond to transitions between high vibra-

tional and rotational quantum numbers. These are so far absent in SLP atlases for normal temperatures.

THE EFFECT OF "HOT" LINES IN CALCULATIONS OF THE WATER VAPOR ABSORPTION COEFFICIENTS

The most abundant exhaust gas from power plants is water vapor, which is highly concentrated in combustion products and is active in the IR range. The necessity of accounting for "hot" lines when computing radiation from heated volumes of water vapor has been repeatedly stressed in literature.

The authors of Refs. 6–8 attempted to use the SLP atlas⁴ to compute the emissivity $\bar{\epsilon}_v$ and transmissivity $\bar{\tau}_v$ of water vapor in the temperature range 500–1500 K by transforming the SLP values taken at 300 K to higher temperatures. This was done using the well-known relationships.³ Comparison of the values of $\bar{\epsilon}_v$ and $\bar{\tau}_v$ thus obtained with the experimental data demonstrates that the SLP values contained in these banks are only fit for computing the emissions of gases at temperatures up to 600 K. At higher temperatures the SLP's from these atlases satisfactorily describe only the center part of the absorption line. Meanwhile, around 1500 K even this information appears insufficient. Therefore, to account for radiation from heated volumes of molecular gases, dedicated SLP banks should be compiled for high temperatures. At normal temperatures the main attention must be given to analyzing the intensity distribution over the rotational structure of a vibrational band, while the total intensity of the

band is determined from the experiment in Refs. 4 and 5. Since the total intensities of the vibrational transitions are unknown for $T > 300$ K and, all the more so for highly excited states, the conventional approach is inapplicable here. In Ref. 9 a detailed description of the solution is given of the problem of computing the positions of the line centers and transition intensities between highly excited vibrational states. On the basis of rather complete data on the total intensities of the water vapor bands for low vibrational states wave functions of these states were found that relate the matrix elements of the water vapor molecule dipole moment $\langle V'|M|V \rangle^2$ (in the basis of harmonic oscillator wave functions) to the coefficients of the expansion of the dipole moment in the normal coordinates. Starting from the experimental values of $\langle V'|M|V \rangle^2$ (for 300 K), an inverse electrooptical problem was solved and the derivatives of the dipole moment were found. These computations were extrapolated to transitions with high rotational quantum numbers, and an atlas of fine structure lines was compiled for hot gases, including water vapor. To this end, an information retrieval system for high resolution spectroscopy was constructed at the Institute of Atmospheric Optics of the Siberian Branch of the USSR Academy of Sciences.¹⁰

EVALUATION OF THE RELIABILITY OF THE H₂O SPECTRAL DATA

To use SLP's from the above-described databank in applied problems, one has to analyze their completeness and confidence level. The usual technique in this case is to compare the computed parameters with those experimentally measured in high-resolution spectra. Despite the high confidence level of such control for parameters of separate lines, it is not suitable for an overall check of the bank. As a rule, high-resolution spectra are taken within very narrow spectral ranges, and positive results from such comparisons obtained for a given spectral range do not at all guarantee high accuracy of SLP's extrapolated to adjacent spectral domains. Thus, experimental data on the H₂O spectral characteristics measured in broad-band intervals (much wider than the half-width of an individual spectral line) are needed for an overall check of such high-temperature SLP's. The experience we gained in such comparisons demonstrated that in the process it was possible to check for the presence of systematic errors in the SLP computation algorithm itself, and also in the initial data on the total intensities of the vibrational transitions. In their temperature dependences, and even in individual archival data on the energies of the individual vibrational - rotational states employed in calculations.

When calculating high temperature SLP's⁹ the most difficult stage is the correct evaluation of the total Intensity of a vibrational transition $S_{v'v}(T)$. It

is obvious that the summation $S_{\Sigma}(T)$ for a given system of vibrational-rotational ($V-R$) bands (6.3 μm , 2.8 μm , etc.)

$$S_{\Sigma}(T) = \sum_{v'v} S_{v'v}(T) \quad (1)$$

and the determination of the total intensity of the band system $\alpha(T)$, given by

$$\alpha(T) = 11 \text{ m} \int_{\nu_1}^{\nu_2} K_{\nu}(T) d\nu, \quad (2)$$

where $K_{\nu}(T)$ is the spectral absorption coefficient, and ν_1 and ν_2 are the boundaries of the given $V-R$ band system (as obtained from processing of experimental data), are but two approaches to determining one and the same value.

The experimental determination of $\alpha(T)$ for H₂O is based on processing measurement data on the average transmissivity $\bar{\tau}_{\nu}$ (for $T < 1000$ K), or on the average emissivity $\bar{\epsilon}_{\nu}$ (for $T > 1000$ K) of homogeneous layers of hot water vapor, using the formula

$$\alpha(T) = 11 \text{ m} \int_{\nu_1}^{\nu_2} \ln \frac{\epsilon(\nu)}{u} d\nu. \quad (3)$$

Here u is the absorbing mass of the given layer (in atm · cm). Formula (3) also holds for finite values of u when the approximation of an optically thin layer ($Su \ll 1$) holds.¹ Then ϵ_{ν} and u are related to each other by the expression

$$\epsilon_{\nu} = K_{\nu} u, \quad (4)$$

The results of computing using the algorithms in Refs. 5 and 9 are compared in Fig. 1, with the experimentally determined values of $\alpha(T)$ borrowed from various sources for systems of $V-R$ bands (6.3, 2.7, 1.87 μm). The high scatter of the values of $S_{\Sigma}(T)$ is explained by experimental error, which, first of all, includes an uncertainty in the temperature of the radiating gas, violations of the approximation of an optically thin layer, and the impossibility of accounting for the degree of overlap of various $V-R$ -band systems.

As a source of heated water vapor, the authors of Refs. 10–13 used hydrogen-oxygen burners. During such experiments it was rather difficult to provide for homogeneity of the heated gas volume, and also to control the gas temperature T and absorbing mass u . Following the authors' estimates, the uncertainty in the values of T leads to errors in $\alpha(T)$ from 10% (Refs. 10 and 11) to 20% (Refs. 13, 16, and 18).

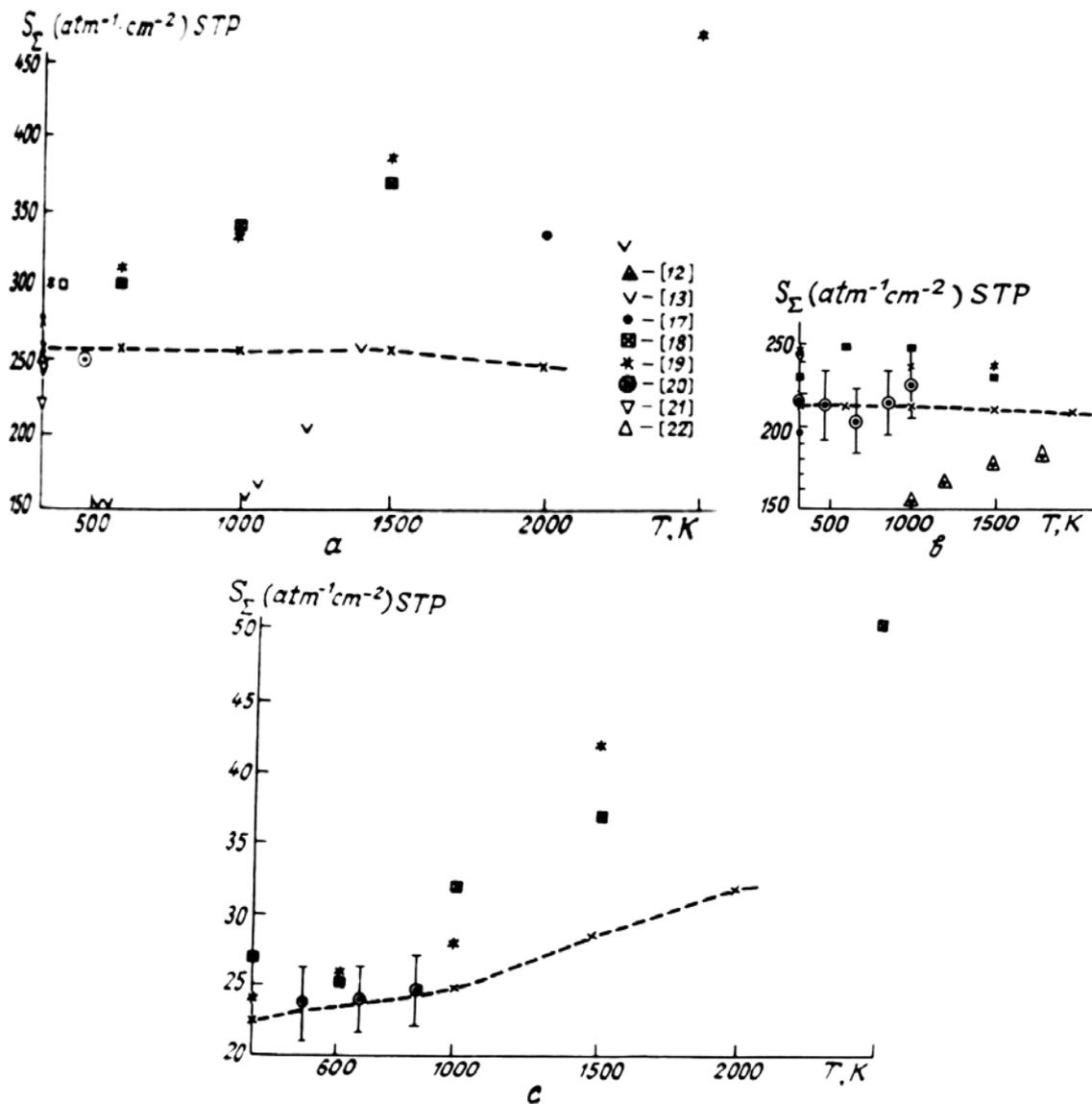


FIG. 1. Temperature dependence of the total intensities for H_2O band systems: $a - 6.3 \mu\text{m}$, $b - 2.7 \mu\text{m}$, $c - 1.87 \mu\text{m}$. Crosses – the authors' computations; for references on experimental data see Fig. 1.

The next source of error consists in applying formula (3) to the processing of the measured values of $\bar{\epsilon}_v$ in those spectral ranges where the condition $Su \ll 1$ is not actually satisfied. In such a situation the true value of the emissivity is lower than the corresponding "optically thin layer" estimate (4), so that formula (3) underestimates the integral $\alpha(T)$ in comparison with its actual value. Accounting for the fact that the principal part of the integral $\alpha(T)$ is formed in the band center, where the optically-thin limit is violated at even quite small u , we see that the error thus introduced can be rather significant. Such an error also shows in the anomalous total intensity vs. temperature dependences obtained for the band systems of $6.3 \mu\text{m}$ in Refs. 15 and 19 and for

the band system of $2.7 \mu\text{m}$ in Ref. 12. Moreover, this deviation is higher for a comparatively cool gas. Apparently, this effect may be explained if one recalls that for a constant geometrical size of the burner deviations from the approximation of an optically thin layer will be lower at higher temperatures.

Finally, another source of error in the determination of the total intensity $\alpha(T)$ is uncertainty in the position of the band boundaries ν_1 and ν_2 , and in the average value of the absorption coefficients at the band edges. Such ambiguities are produced by overlapping of the vibrational-rotational band systems. When processing experimental data using formula (2), it is assumed that the absorption band contour at the band edges displays an exponential

dependence on frequency. Then the band edges can be obtained by extrapolating the contour into the overlapping domain. The error in the determination of $\alpha(T)$ increases at higher temperatures since the degree of overlap increases then due to higher occupancies of the upper energy levels.

The above-enumerated measurement errors in $\alpha(T)$ have led to a considerable scatter of the total intensities at $T = 300$ K (Ref. 9), and also have left open the problem of the exponential temperature dependence of S_{Σ} for the various bands. As demonstrated in Ref. 14, the values of S_{Σ} for the 6.3 and 2.7 μm bands do not depend on temperature, while for the band at 1.87 μm we have $S_{\Sigma}(2000 \text{ K})/S_{\Sigma}(3000 \text{ K}) = 1.45$, which agrees quite well with our computations.

However, Ferriso et al.¹⁵ cite a private correspondence with Benedict on the existence of a temperature dependence of S_{Σ} for the 6.3 μm band of H_2O :

$$S_{\Sigma} = 250 + 0.05 \cdot T \text{ at } \text{m}^{-1} \cdot \text{cm}^{-1} \text{ at STP.}$$

Indeed, summation over the V - R bands using the data in the tables of Refs. 15 and 18 produces results that exceed the results of our computations for all the bands (see Fig. 1).

Moskalenko et al.¹⁹ also noted an increase in the total intensity in the 6.3 μm range by 32% in the 300–2200 K range. The same study revealed¹⁹ that the total intensity insignificantly decreased (by approximately 10%) for the 2.7 μm band system in the 300–2200 K range, which does not contradict the results of our computations if one accounts for possible experimental errors. However, it was stated¹⁷ that the temperature dependence of the total intensity in the 6.3 μm band is explained exclusively by the contribution from the adjacent rotational band, the total intensity of the latter being higher by an order of magnitude. Thus, on the one hand, the mechanism of the temperature dependence of S_{Σ} is still not identified, while, on the other hand, an experiment is lacking which would unequivocally demonstrate that the total intensity of the 6.3 μm band increases with temperature due to an overlapping rotational band.

CALCULATIONS OF THE DEPENDENCE OF THE ABSORPTION COEFFICIENT

While comparison of the total intensities discloses systematic errors in the calculated values of $S_{V,V}(T)$ in order to find systematic errors in the parameters of individual vibrational-rotational lines one has to compute another broad-band characteristic, i. e., the average absorption coefficient

$$\bar{\kappa}_{\nu}(T) = \frac{1}{\Delta\nu} \int \kappa_{\nu} d\nu. \quad (5)$$

A typical averaging integral for H_2O is $\Delta\nu = 25 \text{ cm}^{-1}$. It is easy to demonstrate that this average absorption coefficient is approximately (to the accuracy of the contribution from the line wings) determined by the sum \sum_1 of the line intensities covered by this

interval $\Delta\nu$ and also depends on the intensities and contours $\Phi(\gamma_1, \nu - \nu'_1)$ of the lines external to the given integral, whose contribution we will denote by the sum \sum'_1 . Then the values we are computing

and the exact value $\bar{\kappa}_{\nu}(T)$ are related by the relation

$$\begin{aligned} \frac{1}{\Delta\nu} \sum_1 S_1 &= \bar{\kappa}_{\nu}(T) + \frac{1}{\Delta\nu} \sum_1 S_1 \int_{\nu \in \Delta} \Phi(\nu - \nu_1) d\nu - \\ &- \frac{1}{\Delta\nu} \sum'_1 S'_1 \int_{\nu \in \Delta} \Phi(\nu - \nu'_1) d\nu. \end{aligned} \quad (6)$$

Analysis of expression (6) demonstrates that the difference between $\frac{1}{\Delta\nu} \sum_1 S_1$ and $\bar{\kappa}_{\nu}$ in the center of the vibrational-rotational band is of the order of a few per cent. In the interval between the individual V - R bands where the effect of line wings is important^{2,3} the value of the absorption coefficient is completely determined by the contributions from "external" lines, and estimate (6) loses its meaning.

The experimental determination of the absorption coefficient was conducted according to the same scheme, simultaneous with the measurement of the total intensities $\alpha(T)$, i. e., the value $K_{\text{exp}}(u)$ is calculated according to relation (3), where ν_1 and ν_2 are the end-points of an interval with width $\Delta\nu$ (this technique is outlined in Refs. 15 and 18). Below we briefly describe the technique for determining $\bar{\kappa}_{\nu}$ employed in Ref. 18, the results of which (Ref. 18) are given in Fig. 2 and adopted as the experimental baseline.

Since in certain spectral ranges an optically thin layer is difficult to realize for the H_2O molecule, the determination of $\alpha(T)$ was carried out using a series of $\bar{\epsilon}_{\nu}$ and $\bar{\tau}_{\nu}$ values measured at various optical depths.^{15,18} The measurement data were processed using a two-parameter technique based on a statistical band model. According to this model the transmissivity $\bar{\tau}_{\nu}$ averaged over the spectral range $\Delta\nu$; may be written as

$$\bar{\tau}_{\nu} = \exp\left[-\frac{1}{\Delta\nu} \sum W_1\right], \quad (7)$$

where W_1 is the equivalent width of the i th spectral line, which for the Lorentz contour is equal to

$$W_1 = 2\pi\gamma_1\chi_1 \exp\left[-\frac{\chi_1}{2}\right] \left[I_0(\chi_1) + I_1(\chi_1)\right], \quad (8)$$

Here $\chi_1 = \frac{S_1 u}{\pi\gamma_1}$, and I_0 and I_1 are the modified Bessel functions. Assuming an exponential distribution of the line intensities, the actual sum W_1 is replaced by the two-parameter approximation

$$\frac{1}{\Delta\nu} \int W_1 = \bar{K}u \left[1 + \frac{\bar{K}u}{4\bar{\gamma}/d}\right]^{-1/2}, \quad (9)$$

where the second parameter $\bar{\gamma}/d$ is called the ratio of the average line half-width to the average line-to-line distance. The parameters \bar{K} and $\bar{\gamma}/d$ are obtained by the method of least squares from the series of measurements at various optical thicknesses. Since formula (9) only approximately describes our sum for intermediate values of u (the average deviation of this value is 10%, and reaches 40% in certain spectral intervals), additional errors are possible in the values of \bar{K} .

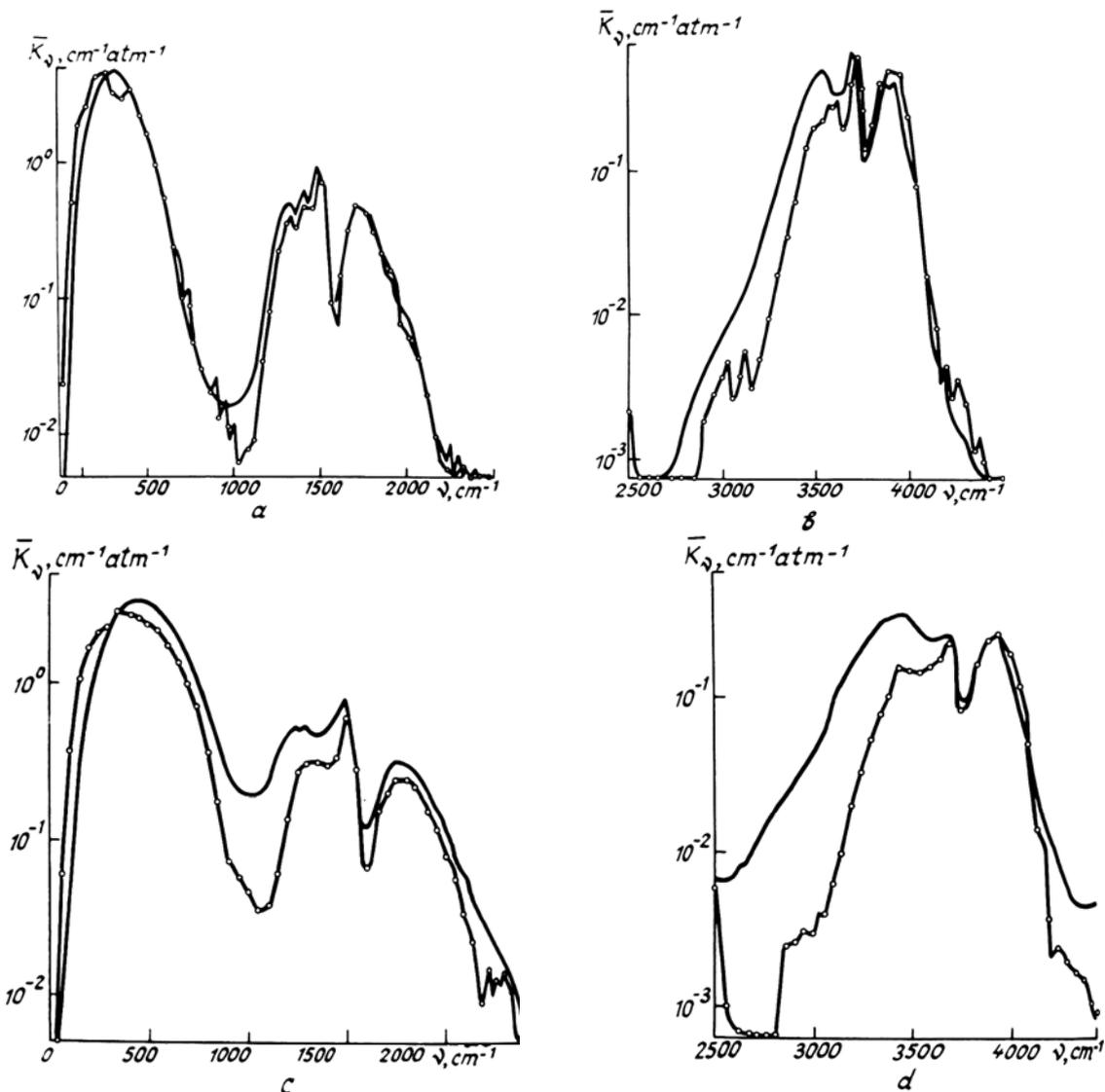


FIG. 2. Spectral trend of the H₂O absorption coefficient. Solid line – experiment; circles – authors' calculations. At $T = 1000$ K: a – 6.3 μm , b – 2.7 μm bands; at $T = 2000$ K: c – 6.3 μm , d – 2.7 μm bands.

Calculations of the average absorption coefficients from the obtained fine structure SLP's for H₂O show good agreement with experiment for the band centers. In the band wings to the left of the

band center the difference between the calculated and measured values increases and reaches an order of magnitude in the H₂O transparency windows.

Such a picture is explained by the form of Eq. (6) since the wings of individual lines give the main contribution to the absorption in these transparency windows.

Further updating of the water vapor spectral lines database around 2000 K is planned in the following directions:

1) a more comprehensive account of the effect of intramolecular interactions on the intensity of individual $V-R$ lines in the 2.7 and 1.87 μm ranges;

2) updating of the Initial values of the total intensities for the vibrational bands of H_2O ($T = 300$ K) that are used to construct the dipole moment function;

3) extending the range of both the vibrational and the rotational quantum numbers for the lines included in the database;

4) computation of line half-widths taking account of their temperature dependence.

To assess the reliability of the database of calculated SLP values, they should, in perspective, be directly compared to the results of field experiments on the transmissivity and emissivity functions. This would require the use of a line shape that would simultaneously describe both the far wings and the line center. Meanwhile, even the Lorentz line shape allows one to differentiate between the continuum (due to the wings of distant lines) and selective (due to the line center) components, and examine the temperature dependence of the intramolecular interaction potential.

REFERENCES

1. R.M. Goody, *Atmospheric Radiation* [Russian translation], Mir, Moscow (1966), 522 pp.
2. V.E. Zuev, *Propagation of Visible and Infrared Waves in the Atmosphere*, Sov. Radio, Moscow (1970).
3. V.E. Zuev, *Propagation of Laser Radiation in the Atmosphere*, Radio i Svyaz', Moscow (1981).
4. A. Chedin, N. Husson, N. Scott, et al., *The GEISA Data Bank, 1984 Version. — Laboratoire de Hétérolog. Dynamique du CNRS*, 1986; L. R. Brown, C. B. Farmer, C. P. Risland, and R. A. Toth, *Appl. Opt.* **26**, 5154–5182 (1987).
5. O.K. Voitsekhovskaya, Yu.S. Makushkln, N.N. Trifonova, and V.N. Cherepanov, *Computational Programs for Calculating $V-R$ Line Centers and Intensities of Asymmetric Rotor Type. GOS-FAP (State Fund of Computer Programs)*, No. P004348, (1984), 64 pp.
6. J.M. Hartmann, L.R. Leone, and J. Taine, *J. Quant. Spectrosc. Radiat. Transfer* **32**, 119–127 (1984).
7. A.A. Soufiani, J.M. Hartmann, and J. Taine, *J. Quant. Spectrosc. Radiat. Transfer* **33**, 243–257 (1985).
8. L.R. Leone, J. Taine, and S. Marbot, *J. Quant. Spectrosc. Radiat. Transfer* **35**, 345–347 (1986).
9. O.K. Voitsekhovskaya, *Atm. Opt.* **3**, No. 7, in press (1990).
10. O.K. Voitsekhovskaya, A.V. Rozhina, and N.N. Trifonova, *Information System for High-Resolution Spectroscopy*, Nauka, Novosibirsk (1988), 150 pp.
11. C.C. Ferriso and C.B. Ludwig, *J. Chem. Phys.* **41**, 1668–1674 (1964).
12. C.C. Ferriso and C.B. Ludwig, *J. Quant. Spectrosc. Radiat. Transfer* **4**, 215 (1964).
13. C.B. Ludwig, C.C. Ferriso, and C.N. Abeyta, *J. Quant. Spectrosc. Radiat. Transfer* **5**, 281–290 (1965).
14. J.C. Breeze and C.C. Ferriso, *J. Chem. Phys.* **42**, 402–406 (1965).
15. C.C. Ferriso, C.B. Ludwig, and A.L. Thomson, *J. Quant. Spectrosc. Radiat. Transfer* **6**, 241–273 (1966).
16. Y. Ben Aryeh, *J. Quant. Spectrosc. Radiat. Transfer* **7**, 211–224 (1967).
17. C.W. Von Rosenberg, N.H. Pratt, and N.D. Bray, *J. Quant. Spectrosc. Radiat. Transfer* **10**, 1156–1169 (1970).
18. C.B. Ludwig, *Appl. Opt.* **10**, 1057–1073 (1971).
19. N.I. Moskalenko, Ya.A. Il'in, N.K. Pokotilo, S.A. Sementsov, and V.T. Pushkin, *Zh. Prikl. Spektrosk.* **34**, 475–480 (1981).
20. R. Goldstein, *J. Quant. Spectrosc. Radiat. Transfer* **4**, 343–352 (1964).
21. C.Y. Maclay, *J. Chem. Phys.* **43**, No. 1, 185 (1965).
22. J.M. Jaffe and W.S. Benedict, *J. Quant. Spectrosc. Radiat. Transfer* **3**, 87 (1963).
23. A. Goldman and V.P. Oppenheim, *Appl. Opt.* **5**, No. 6, 1073 (1964).