

INFLUENCE OF LINE SHIFT ON THE ATMOSPHERIC TRANSMISSION FUNCTIONS ALONG TANGENT PATHS

A.V. Polyakov, Yu.M. Timofeev, M.V. Tonkov, and N.N. Filippov

State University, St. Petersburg

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The atmospheric transmission functions at HCl, HF, and H₂O absorption lines are calculated with and without regard for line center shifts for the case of remote sensing from space. It has been shown that line shift effect for HCl, HF, H₂O, and CH₄ lines has to be taken into account when interpreting the data of spaceborne measurements of the atmospheric transmission along tangent paths with spectral resolution $\Delta\nu \leq 0.01 \text{ cm}^{-1}$. It is shown that additional errors in content of these gases determined when neglecting these effects may range from 2 to 10% and higher.

1. At present, the instrumentation with successively improved spectral resolution (up to 10^{-2} cm^{-1}) (see Ref. 2) is being used to estimate different atmospheric parameters by optical methods in the IR region. Specifically, interferometers with resolution of about 0.01 cm^{-1} have been used in space investigations of atmospheric gas composition (see Refs. 1 and 2). In this connection, consideration of all peculiarities of the radiation transformation inside the atmosphere is of increasing importance. As the theory of collisional line broadening predicts, line centers are shifted with pressure (see Ref. 3). In the context of this theory, the line shape $f(\nu)$ is described by Lorenz shape

$$f(\nu) \sim \frac{1}{\pi} \frac{\alpha p}{(\nu - \nu_0 - \gamma \pi)^2 + \alpha^2 \pi^2}, \quad (1)$$

where α and γ are the half-width and shift of the line, respectively, ν_0 corresponds to the line center, p is pressure.

Analysis of the data presented in Refs. 4 and 5 shows that the ratio γ/α is maximal for HCl and HF and ranges up to 1.2 and 1.5, respectively. The shifts of water vapor lines in the near-IR region were found to be high. The ratio γ/α for methane ranges up to 0.1 and 0.3 in the bands around $3.3 \mu\text{m}$ and $7.7 \mu\text{m}$, respectively. Significant shifts of fundamental NO band and lines from $A \leftarrow X(0, 0)$ band were observed at $\lambda \sim 226 \text{ nm}$. The effect of shift on different optical parameters of the atmosphere was investigated in Ref. 5. In this paper, we present the results of calculation of transmission functions for the case of remote sensing from space along tangent paths.

2. The atmospheric transmission functions $P_{\Delta\nu}(H_0)$ were calculated on the basis of known expression

$$P_{\Delta\nu}(H_0) = \frac{1}{\Delta\nu} \int_{-\infty}^{\infty} \exp \left[- \int_{-\infty}^{\infty} k(\nu, s) N(s) ds \right] d\nu, \quad (2)$$

where $\Delta\nu$ is the spectral interval under consideration, $k(\nu, s)$ is the molecular absorption factor, $N(s)$ is the molecular density of absorbing gas and s is the spatial variable along the radiation propagation path. Factors $k(\nu, s)$ and $N(s)$ are determined by the measurement geometry and aiming height H_0 . We have developed special program providing the accuracy of $P_{\Delta\nu}(H_0)$ calculations no less than 0.1% (0.001). The profiles of gas concentrations and atmospheric state from well known paper (see Ref. 8) were used in our calculations. As pointed out above, the ratio γ/α was observed to be at its maximum in fundamental bands of HCl (2900 cm^{-1}) and HF (4000 cm^{-1}) (see Ref. 6). Therefore, we have investigated in detail the effect of line center shift in these absorption bands.

Figure 1 depicts the differences of monochromatic transmission functions within HCl R5 absorption line shape for different aiming heights (here $\Delta P(\nu, H_0) = P^{(1)}(\nu, H_0) - P^{(2)}(\nu, H_0)$, $P^{(1)}$ and $P^{(2)}$ are the transmission functions calculated with and without regard for the line center shifts). The analysis of the curves presented in Fig. 1 and the results of $\Delta P(\nu, H_0)$ calculations for other HCl spectral lines enable us to draw the following conclusions:

a) The peaks in the differences of the monochromatic functions in HCl lines reaches 0.02–0.04 at aiming heights $H_0 \in [10–20] \text{ km}$.

b) The difference $\Delta P(\nu, H_0)$ changes its sign within the line shape. Neglect of this factor underestimates and overestimates the monochromatic transmission function at $(\nu - \nu_0) < 0$ and $(\nu - \nu_0) > 0$, respectively.

c) $\Delta P(\nu, H_0)$ curves are symmetric about the origin of the coordinates. The latter two of these peculiarities testify to the fact that at finite spectral resolution the line center shift effect on the transmission function decreases. So, at $\Delta\nu \geq 0.02–0.03 \text{ cm}^{-1}$ this effect is negligible.

d) The monochromatic function differences have a peak at $|v - v_0| \approx 0.005 \text{ cm}^{-1}$. As the aiming height decreases (and the pressure increases), the spectral region where $\Delta P(v, H_0)$ is high moves to the line shape wings.

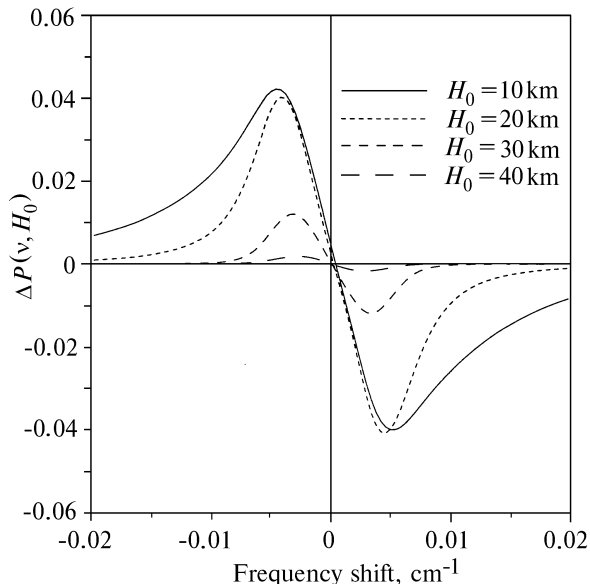


FIG. 1. Differences of monochromatic transmission functions in R5 HCl absorption line shape at different aiming heights.

Similar numerical calculations were performed in HF absorption line. The line shift effect in HF lines was found to be close to but lower than that for HCl

lines. In particular, the maximal differences of the monochromatic transmission functions along a tangent path for HF absorption lines do not exceed 0.02–0.03 (R3 and R4 lines).

Investigation of the line shift effect on transmission functions at finite spectral resolution is most interesting. As an illustration, the results obtained at typical for ATMOS and DOPI interferometers spectral resolution of $\Delta v = 0.01 \text{ cm}^{-1}$ (see Refs. 2 and 7) are given in Table I. The table lists maximal differences $|\Delta P_{\Delta v}(v, H_0)|$ at different values of $S = v - v_0$, where v_0 corresponds to the center of measurement spectral range. Analysis of the data presented in Table I and a large body of other calculations enable us to draw the following conclusions:

1) At spectral resolution $\Delta v = 0.01 \text{ cm}^{-1}$ maximal differences of transmission functions calculated with and without regard for the line shifts can range up to 3.3% (0.033) in HCl R5 line and 2.5% (0.025) in R3 and R4 HF lines, respectively. Differences in the most intense HCl and HF lines comprise, on the average, 1–2%.

2) The differences $|\Delta P_{\Delta v}(v, H_0)|$ depend on the position of the measurement spectral range with respect to the line center. The differences have peaks at $S = \pm 0.005 \text{ cm}^{-1}$ and are negligible as $S = 0$ or if the measurements are performed in the line wings.

3) $\Delta P_{\Delta v}(v, H_0)$ are opposite in sign in short- and long-wave wings of the absorption line shape.

4) The differences are maximal at aiming heights 10–20 km. Out of that height range $|\Delta P_{\Delta v}(v, H_0)|$ does not exceed 1%.

TABLE I. Maximal differences of the transmission functions at absorption lines of HCl R-branch (as percentage of absolute transmission, value).

S, cm ⁻¹	Absorption lines identified										
	R0	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
-0.020	0.1	0.6	0.8	0.8	0.9	0.7	0.3	0.2	0	0	0
-0.015	0.1	0.8	1.1	1.1	1.4	1.3	0.8	0.4	0	0	0
-0.010	0.2	1.2	1.5	1.9	2.4	2.4	1.8	1.0	0.4	0	0
-0.005	0.2	0.9	1.2	1.6	2.5	3.3	3.1	2.0	1.0	0.4	0.1
0	0	0	0	0.1	0.2	0.3	0.4	0.4	0.2	0.1	0.1
0.005	0.1	0.8	1.1	1.4	2.2	3.1	2.9	1.9	0.8	0.3	0
0.010	0.1	1.0	1.5	1.8	2.4	2.6	2.1	1.9	0.5	0.1	0
0.015	0.1	0.7	1.0	1.2	1.4	1.4	0.9	0.4	0.1	0.1	0
0.020	0	0.5	0.7	0.8	0.7	0.4	0.8	0.7	0.5	0.1	0

As mentioned above, significant shifts the H₂O absorption line centers were recorded in the near-infrared spectral range (see Refs. 4 and 5). The differences of monochromatic transmission functions along a tangent path calculated for H₂O line at $v = 13947.2608 \text{ cm}^{-1}$ with and without regard for the line shifts (for the line to be investigated $\gamma/\alpha = 0.51$) are plotted in Fig. 2. One can see that the differences

range up to 14% ($H_0 = 10 \text{ km}$) and exceed 4% at aiming heights 8–12 km. Similar effects were observed in some other H₂O absorption lines in the spectral range under consideration. Notice that according to the data available from literature similar line shift effect on the transmission functions could be also expected in methane absorption lines.

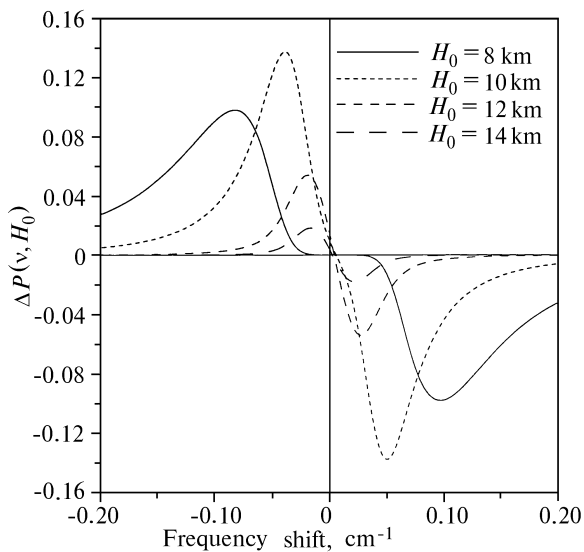


FIG. 2. Differences of monochromatic transmission functions at H₂O absorption line at $\nu_0 = 13947.2608 \text{ cm}^{-1}$ for different aiming heights.

3. Let us estimate the influence of line shift neglect on the errors in determination of gas composition of the atmosphere using the transmission method from space (see Ref. 1). Let us introduce the coefficient R , describing in linear approximation the relation between absolute errors in calculations of transmission functions along a tangent path and relative errors in determination of absorbing gas concentration

$$R = \frac{\Delta N}{N} / \Delta P_{\Delta\nu}(\nu, H_0). \quad (3)$$

The value R varies from 1.9 (minimal value) to 3–5 depending on the regime of solar radiation absorption (weak or high absorption). It should be kept in mind that coefficient R also depends on the method the transmission function is measured and interpreted. Thus, if the data on gas content are obtained from the analysis of equivalent bandwidth of discrete spectral lines, for example, from integral absorption in HCl and HF lines, additional errors in HCl and HF content determination due to the neglect of the line shifts does not exceed 0.2%.

If spectral dependences of the transmission functions along a tangent path are used (as is done in the interpretation methods currently in use) the additional errors in determining HCl and HF content can comprise 2–10% depending on the absorption line used, spectral resolution ($\Delta\nu = 0.01 \text{ cm}^{-1}$) and the aiming height.

Many current methods of the transmission functions interpretation are based on minimizing the spectral differences of measured and estimated

parameters. In this case and taking into account opposite signs of the spectral differences $\Delta P_{\Delta\nu}(\nu, H_0)$ (see Figs. 1 and 2) one can state that the neglect of the line shifts leads to R values calculated from Eq. (3) even exceeding those presented above.

Thus, the main conclusion from this paper is that when interpreting results of measuring atmospheric transmission obtained in the case of remote sensing from space at spectral resolution $\Delta\nu \leq 0.01 \text{ cm}^{-1}$, the shift of line centers of fundamental HCl and HF bands, H₂O absorption bands in the near infrared spectral range and, perhaps, in CH₄ absorption bands have to be taken into account. Otherwise, obtained data on concentration of above gases can contain additional errors ranging up to 2–10% and more.

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REFERENCES

1. Yu.M. Timofeev, *Izv. Akad. Nauk SSSR, Fiz. Atmos. Okeana* **25**, No. 5, 451–469 (1989).
2. C.B. Farmer, *Microchim. Acta* **IV**, No. 5, 189–214 (1987).
3. R.M. Goody and J.L. Yung, *Atmospheric Radiation* (Oxford Univ. Press, second ed., 1989), 519 pp.
4. A.D. Bykov, Yu.N. Ponomarev, and L.N. Sinitsa, *Atmos. Oceanic Opt.* **5**, No. 9, 604–608 (1992).
5. H.D. Hollweg, V.S. Kostsov, G. Schlüssel, P. Schlüssel, Yu.M. Timofeev, M.V. Tonkov, A.V. Polyakov, and N.N. Filippov, *Interaction at mm Optical Frequencies. Part II: Specific Atmospheric Absorption and Emission Features: Investigations and Modeling*. Berichte aus dem Zentrum für Meeres und Klimaforschung, Reihe A: Meteorologie, Hamburg, 1995. Nr.18 (Contract No.10603/93/NL/NB. Final Report), 224 pp.
6. A.S. Pine and J.P. Looney, *J. Mol. Spectrosc.* **122**, No. 1, 41–45 (1987).
7. Yu.M. Timofeev, L.I. Dlugoborskaya, V.S. Kostsov, and V.M. Osipov, *Issled. Zemli iz Kosmosa*, No. 1, 12–24 (1995).
8. G.P. Anderson, J.H. Chetwynd, S.A. Cloud, E.P. Sheettle, and F.X. Kneizus, *AFGL Atmospheric Constituent Profiles (0–120 km)* (AFGL-TR-86-0110, AFGL, 1986), 43 pp.
9. L.S. Rothman, R.R. Gamache, R.H. Tipping, et al., *J. Quant. Spectrosc. Radiat. Transfer* **48**, 469–507 (1992).