CONTRIBUTION OF THE DIKE EFFECT TO ATMOSPHERIC TRANSMISSION FUNCTIONS AT HCl, HF, AND H_2O ABSORPTION LINES

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The atmospheric transmission function is calculated for IR radiation propagated along tangent paths at HCl, HF, *and* H_2O *absorption lines, both including and ignoring the Dike effect (line narrowing). The differences in the monochromatic transmission functions for Galatry and Voigt lineshapes reach* 1–2% *for* HCl *and* HF *lines and* 5–8% *for water vapor lines near* 2.5 μm. *Additional errors in determining* HCl, HF, *and* H_2O *content from satellite measurements of the atmospheric transmission at spectral resolution* $\Delta\nu \le 0.01$ cm^{-1} *can reach* 0.8–2.0; 2.0–5; 10–25%, *respectively.*

In atmospheric optics, the influence of molecules' motion on the formation of the absorption line contour is usually taken into account by the Doppler or Voigt lineshapes.[1] However, the situation is considerably more complicated with the allowance for the fact that the molecules' velocities change at collisions. This leads to the so-called Dike effect,[2] i.e., narrowing of the Doppler lineshape due to molecular collisions. In the spectra of IR absorption, the effect was first observed quadrupole absorption lines[3] of hydrogen, and then in the dipole absorption.[4–6] The Dike effect was comprehensively studied in laboratory experiments[7–9] for vibrational-rotational bands of HF and HCl mixed with inert the gases, N_2, and air.

A considerable narrowing of lines can be observed if the mean free path of molecules is less than the wavelength of absorbed radiation, and the collisional broadening is not large. For atmospheric problems, this effect can be significant in calculating the spectra of main components of the atmosphere because small values of the collisional broadening coefficient are characteristic just for weak lines corresponding to transitions between highly excited rotational levels.

There are several methods available for calculating the lineshape allowing for the Dike effect.[10] The Galatry method seems to be the most popular. It uses weak collision model that leads to the following lineshape:

$$f(x, y, z) = \frac{1}{\alpha_D\sqrt{\pi}} \times$$

$$\times \operatorname{Re} \int\limits_0^\infty \exp\left\{-(ix+y)t + \frac{1}{2z^2}[1 - zt + \exp(-zt)]\right\} dt, \quad (1)$$

where $x = (\nu - \nu_0)/\alpha_D$; $y = \alpha_L/\alpha_D$; $z = \beta/\alpha_D$; $\alpha_D = \nu_0\sqrt{kT/\pi m}$ is the Doppler width; $\alpha_L = \alpha_{0L}p$ is the Lorentz halfwidth; $\beta = \beta_0 p$ is the narrowing parameter; k is the Boltzmann constant; T and p are temperature and pressure of the gas. It follows from Eq. (1) that in order to describe the line narrowing, the additional parameter, $\beta_0 = kT/2\pi cmD_0$, is to be introduced. According to theoretical findings,[10] this parameter depends, first of all, on gas temperature, molecular mass, and the diffusion coefficient D_0; the latter, in its turn, is determined by the intermolecular potential. Often a strong collision model is used that leads to the Rautian contour[11]

$$R(x, y, z) = \operatorname{Re}[W(x, y + z)]/[1 - \sqrt{\pi z}W(x, y + z)] , \quad (2)$$

where $W(x, y)$ is the complex probability function

$$W(x, y) = \frac{i}{\pi} \int\limits_{-\infty}^{\infty} \frac{\exp(-\xi^2)}{iy + x - \xi} d\xi.$$

The account for the correlation between the change of translational velocity of molecules and the disturbance of their rotational states leads to further complication of the expressions and to line assymetry especially in the presence of a displacement.

The influence of the Dike effect on optical characteristics of the atmosphere was analyzed in Refs. 12–14. Armstrong[13] compared the transmission functions for the Voigt and Dike lineshapes (a particular case of the Galatry contour when neglecting the collisional broadening) with the results obtained using Galatry contour (which was considered to be exact) for CO_2 lines at spectral resolution $\Delta\nu = 0.0025$ cm^{-1} (analysis of laser radiation propagation). The maximal influence of the Dike effect did not exceed 4.3% and could be masked by selection of line parameters; the latter explains why the effect is often imperceptible. Rodgers[14] paid attention to the

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influence of the Dike effect on equivalent line widths when the Voigt and Galatry lineshapes are used. In particular, analysis yielded a relation describing the influence of the Dike effect $\varepsilon = 100\,[(w_G - w_V)/w_V]$ on equivalent line widths w_G and w_V for the Galatry and Voigt contours, and useful for estimations

$$-1.1/r \le \varepsilon \le 1.3/r(\%),$$

where $r = y/z$ is the dimensionless parameter independent of pressure. Estimations[14] demonstrate that, for many molecules, the value r is 1.6–4.0 and, consequently, Dike's effect does change the equivalent width by no more than 1%. This conclusion is of practical importance because the measured equivalent widths are used in some cases for ground-based, airborne, and space-based experiments to obtain information about the atmospheric gas composition. However, it should be noted that the value of the parameter r is rather small (for instance, r can reach 0.36 for H_2O lines).[14] It is shown in Ref. 8 that the parameter r falls within the range 0.1–0.5 for HF (mixed with Ne and Ar) absorption lines. In these cases, the influence of Dike effect on the equivalent line widths can reach 3.6% for H_2O and 10% for HF. Of course such errors cannot be treated as small, especially, when interpreting optical measurements.

The influence of lineshapes on the solution of inverse problem on reconstructing vertical profiles of absorbing gas content from ground-based measurements is analyzed in Ref. 15 Additional errors in determining profiles of CO_2 and CH_4 content may vary from 2 to 60% depending on height and interpretation methods applied.

The primary goal of this paper is to study the influence of the Dike effect on the atmospheric transmission functions measured on tangent paths from space. The importance of this study is caused by a wide use of the transparency method in the studies of the atmospheric gas composition.[16]

As was already mentioned, significant values of the narrowing parameter β_0 were observed for the absorption lines of HCl and HF fundamental absorption bands.[8] Table I presents maximum relative differences (%) in absorption coefficients of different HCl and HF lines. The differences were calculated using Galatry and Voigt lineshapes. Maximum differences reach 22.5% for HF and 14.5% for HCl, but they are observed for weak absorption lines in the atmosphere even on tangent paths of radiation propagation (P9 for HF and R10 for HCl). According to our calculations, maximum influence of the Dike effect is at pressure of 0.01–0.1 atm, i.e., in the atmospheric layer at 16–30 km height.

The spectral behavior of the difference of monochromatic transmission functions ΔP for tangent paths (sighting observation height h_0 = 20 km) and two lineshapes (Galatry and Voigt) is presented in Fig. 1 for different HCl absorption lines. The maximum value of the difference (1.3%) is observed at the line R6 center and when $|V - V_0| \sim 0.005$ cm^{-1} for the line R4.

TABLE I. Maximum differences in the absorption coefficients of Voigt and Galatry lineshapes for different absorption lines of HCl *and* HF (%)

Line identification	HF		HCl	
	P-branch	R-branch	P-branch	R-branch
0	7.3	–	4.5	–
1	5.8	5.2	1.9	3.2
2	5.0	5.1	3.5	3.6
3	4.9	5.1	3.1	3.3
4	5.5	7.3	4.2	5.7
5	8.6	9.6	4.3	5.3
6	12.2	10.6	5.4	6.6
7	14.7	12.7	6.7	7.4
8	18.5	14.8	8.3	9.5
9	22.5	–	9.9	9.9
10	–	–	11.8	14.5

As follows from Fig. 1, the influence of Dike effect is noticeable in a relatively narrow spectral interval within ± 0.01 cm^{-1} from the line center. The differences between the line center and the neighbourhood $|V - V_0| \approx 0.005$ cm^{-1} have different signs. The latter enables one to conclude that, at the spectral resolution of measurements $\Delta V > 0.02$ cm^{-1}, the influence of the Dike effect on the transmission functions at HCl lines is negligible. The study of differences of monochromatic transmission as functions of height, for HCl lineshapes, demonstrates that their maximum values are observed for sighting heights ~20 km.

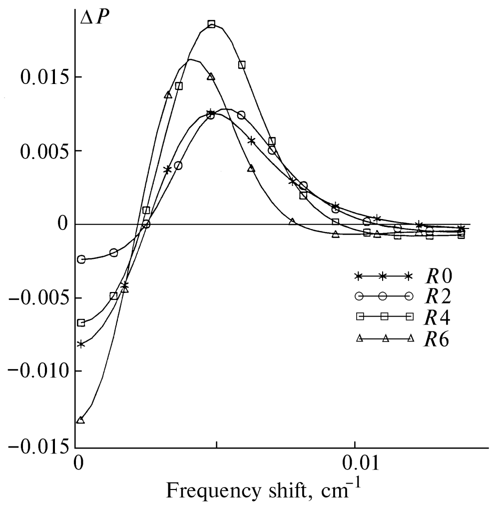

FIG. 1. SPectral dePendences of differences between the monochromatic transmission functions for Voigt and Galatry lineshaPes for different HCl *lines at the sighting height* h_0 = 20 km.

Similar features in the spectral and height behavior of the differences between monochromatic transmission for Galatry and Voigt lineshapes were discovered for HF absorption lines. Here, maximum differences in transmission functions reach 2%. The study of the influence of the lineshapes on transmission at a finite spectral resolution is most practical.

Table II presents the maximum differences between the transmission functions on tangent paths for different HCl and HF lines. These data are presented for the spectral resolution ΔV = 0.01 cm^{-1} (at different positions of measurement intervals with respect to line centers) what corresponds to satellite interferometers ATMOS and DOPI.[17,18]

TABLE II. Maximum differences between the transmission functions for Galatry and Voigt lineshaPes for different HCl *and* HF *lines (%)*

Displacement $\Delta\nu$ from the line center, cm^{-1}	Line identification						
	$R0$	$R1$	$R2$	$R3$	$R4$	$R5$	$R6$
0.000	0.2/0.8	0.3/0.6	0.3/0.3	0.3/0.4	0.3/0.4	0.2/0.2	0.1/0.1
0.005	0.2/0.6	0.3/0.5	0.3/0.05	0.3/0.3	0.4/0.1	0.3/0.1	0.2/0.0
0.010	0.2/1.0	0.2/1.0	0.2/0.8	0.2/0.6	0.3/0.4	0.2/0.1	0.2/0.0
0.015	0.1/0.3	0.1/0.3	0.1/0.2	0.1/0.1	0.1/0.1	0.1/0.0	0.1/0.0

Note: Numerator and denominator correspond to HF and HCl lines, respectively.

The calculated results presented show that the maximum differences in the transmission functions for absorption line contours (Voigt and Galatry) reach 0.4% for HCl and 1% for HF. These values are observed when the center of the measurement interval is displaced by 0.005 cm^{-1} (HCl) and 0.01 cm^{-1} (HF) with respect to the absorption line centers.

Although there are no direct experimental data about the narrowing parameter β_0 for H_2O absorption lines at present, one can estimate the effect by indirect data. In Ref. 19, the Dike effect was studied for the lines of the doublet $14_{1,15} \leftarrow 15_{0,14}$ and $14_{0,14} \leftarrow 15_{1,15}$ of the band ν_2 in mixtures of H_2O with Ar, N_2, O_2, and air, and for the line $11_{2,10} \leftarrow 12_{1,11}$. In these experiments, the doublet was not resolved neither at low pressure under Doppler broadening (~4 mbar), nor under the collisional broadening (~1000 mbar). Nevertheless, the doublet was partially resolved at the intermediate pressure 85 mbar that indicates to the significance of the Dike effect. A good agreement between the calculated Voigt profile and the experimental profile of the line with empirically selected Doppler width equal to 0.0004 cm^{-1} was observed for the line $11_{2,10} \leftarrow 12_{1,11}$ at pressure of 163 mbar (see Ref. 13). At the same time, the theory predicts the value of the Doppler width to be equal 0.0019 cm^{-1}. Based on these results one can conclude that the influence of the Dike effect for water vapor lines must manifest itself under atmospheric conditions. We chose the narrowest absorption lines of water vapor in near 2.5 μm for the quantitative analysis. In order to make calculations we had to set the value of the parameter β_0. The value D_0 for water vapor in the air equals ~0.24 cm^2/s at 1 atm (STP). This value yields β_0 - 0.03 cm^{-1}/atm that coincides with the value obtained from thermodynamic data for HF lines in argon,[9] within the limits of the estimation accuracy. It should be noted that this value satisfactorily predicts the value of Dike effect using the Galatry lineshape.

Figure 2 presents the differences between monochromatic transmission functions calculated for Voigt and Galatry lineshapes, for H_2O absorption line $14_{0.14} \leftarrow 13_{0.13}$ of the band ν_3 at ν_0 = 3990.271 cm^{-1} with the broadening coefficient 0.0096 cm^{-1}/atm (see Ref. 20) and different sighting heights. One can see that the differences reach ~0.08 (8% of the absolute transmittance) for the sighting observation height h_0 = 10 km. The maximum values of the difference are observed at the center of the line (for h_0 = 12 km) and at a frequency shift of 0.01 cm^{-1} from the line center (h_0 = 10 km).

Figure 2 demonstrates that, if spectral resolution of measurements $\Delta V \geq 0.02$ cm^{-1}, the influence of Dike effect is negligible due to different signs in the transmittance deviations near the line center ν_0 and in the line wing. However, the influence of Dike effect reaches ~5% for the considered H_2O absorption line at spectral resolution $\Delta V \leq 0.01$ cm^{-1}.

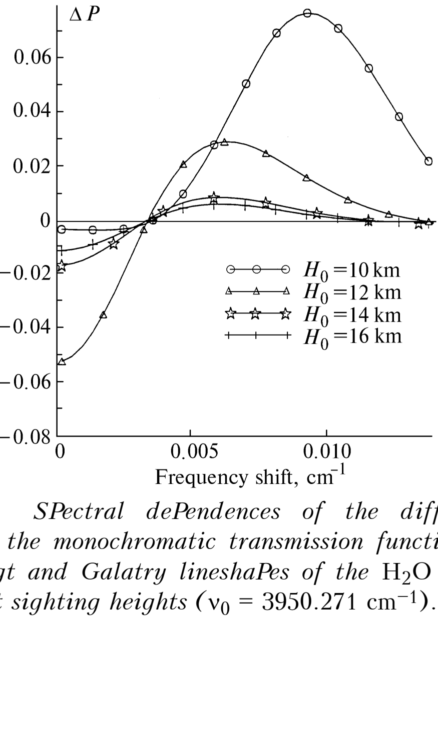

FIG. 2. SPectral dePendences of the differences between the monochromatic transmission functions for the Voigt and Galatry lineshaPes of the H_2O *line at different sighting heights* (ν_0 = 3950.271 cm^{-1}).

Let us estimate the influence of Dike effect on the accuracy of remote satellite measurements of the atmospheric gas composition by a simple method presented in Ref. 21. As was mentioned above, the correlation coefficient R between the absolute errors of the transmittance calculations on tangent paths and relative error of determining the mixture composition falls within the range 1.9–5 depending on the regime of solar radiation absorption. Therefore, additional errors in determining HCl content can reach 0.8–1.0%; 1.0–5% for HF and 10–15% for H_2O.

Thus, the main conclusion of the paper is that, interpretation of the atmospheric transparency change in the IR range on tangent paths measured from space with the spectral resolution $\Delta\nu \le 0.01\ cm^{-1}$, should at least estimate possible contribution from the Dike effect into the radiation absorption, and take it into account for some HCl, HF, and H_2O lines. Our results also demonstrate that experimental study of the Dike effect for different absorption bands of the atmospheric gases is important.

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