# Absorption Line Width in the Rotation Spectrum of Atmospheric Water Vapor*

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Grating measurements at oblique incidence are employed as a means of obtaining the narrow slits essential to the direct observation of line width. Correction for the finite width of slit is small. It is accomplished by empirical extrapolation to zero slit in one instance, and by numerical estimation of slit influence in another. The absorption coefficient half-width at half-height for the atmospheric water vapor lines at 18.64 mu and 15.99 mu is found to be 0.12 $cm^{-1}$ and 0.11 $cm^{-1}$, respectively.

FOR a spectrometer of unlimited resolving power the fractional transmission of radiation through an absorption line is given by the expression,

$$T=e^{-k(\nu)\cdot t},$$

and the fractional absorption by $A=1-T$. By the width of the line is meant the width of the absorption coefficient $k(\nu)$. In the infra-red, broadening by thermal collisions is the principal agent in shaping an absorption line, and the absorption coefficient has the Lorentz dispersion form

$$k(\nu)=\frac{J}{\pi}\frac{D_0}{(\nu-\nu_0)^2+D_0^2},$$

where $\nu_0$ marks the center of the line, and

$$J=\int_{-\infty}^{+\infty}k(\nu)d\nu$$

is the total intensity of the line. The distance from $\nu_0$ to the point at which $k(\nu)$ falls to half its maximum value is $D_0$, the half-width of the line, that is, half the width at half the height of the curve of absorption coefficient. $J$ and $D_0$ are important in the problem of radiative transfer. In an absorption line of moderate depth the rate at which energy is absorbed is proportional to

$$(JD_0t)^{\frac{1}{2}},$$

where $t$ is the length of path.[1]

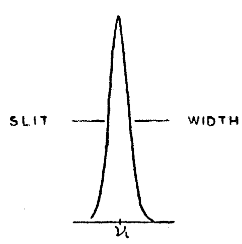


FIG. 1. The intensity distribution within the spectral interval transmitted by the exit slit of a spectrometer with equal entrance and exit slits.

For the purpose of measuring widths, the curve of absorption coefficient can always be obtained from the absorption line following correction of the latter for the finite slits of the spectrometer. This correction can be made directly for a line of any strength by using a graduated series of slits and extrapolating the curve of apparent line width *versus* slit width to zero slit width. The correction can also be made indirectly by application of the simple theory of slit influence to a line of moderate depth.[2] Both methods will be applied to atmospheric water vapor—the empirical to the line at 18.64 mu, the numerical to the line at 15.99 mu.

Infra-red lines are generally exceedingly narrow. It has been shown, for example, that the directly observed absorption line half-width in $N_2O$, at a pressure of 30 cm Hg, even prior to correction for slit width is but 0.09 $cm^{-1}$.[2] The need for narrow slits is evident, since one may hope to explore a line significantly only if the slit is narrower than the line.

The spectral width of a slit depends more importantly upon the available dispersion than upon actual slit opening. The intensity distribution within the spectral interval transmitted by

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[1] D. M. Dennison, Phys. Rev. **31**, 503 (1928).
[2] Arthur Adel and E. F. Barker, Rev. Mod. Phys. **16**, 236 (1944).

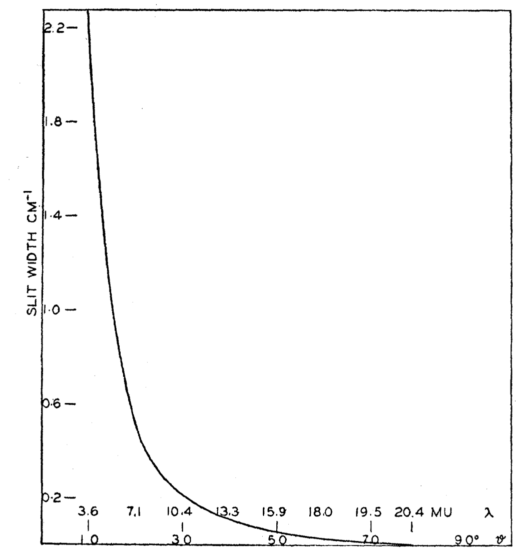


FIG. 2. Effective slit width as a function of wave-length or grating angle for the spectrometer $\lambda_\mu = 20.764 \sin\theta$, with 2400 line grating and slits of angular width one minute of arc.

the exit slit of a spectrometer with equal entrance and exit slits is shown in Fig. 1. This is the frequency pattern received by the thermopile at the frequency setting $\nu_i$. The width of the slit is the width of the slit distribution function at half-height. The functional dependence of spectral slit width on slit opening and dispersion can be obtained from the spectrometer equation

$$\lambda = 2a \cos\tfrac{1}{2}\varphi \sin\vartheta,$$

where $a$ is the grating constant, $\varphi$ is the angle between the incident and diffracted beams, and $\vartheta$ is the angle between the grating normal and the bisector of $\varphi$.

For entrance and exit slits of equal angular width $d\varphi$ the spectral slit width is given by

$$d\tilde{\nu}_L = \frac{10^4 \cdot d\varphi}{2K_\mu \sin\vartheta}(\cot\vartheta - \tan\tfrac{1}{2}\varphi)\ \text{cm}^{-1},$$

where

$$K_\mu = 2a \cos\tfrac{1}{2}\varphi\mu.$$

$d\tilde{\nu}_L$ must not be confused with $d\tilde{\nu}_C$, the spectral interval which sweeps past a point in the exit slit when the grating turns through a small angle $d\vartheta = d\varphi$; for the grating sweeps the spectrum across the exit slit faster than would a mirror a ray of light, that is,

$$d\tilde{\nu}_C = \frac{10^4 d\vartheta}{K_\mu \sin\vartheta}\cot\vartheta > 2d\tilde{\nu}_L,$$

when $d\vartheta = d\varphi$, the slit width. $d\tilde{\nu}_L$ may also be written

$$d\tilde{\nu}_L = \frac{10^4 \cdot d\varphi}{2K_\mu \sin\vartheta}\,\frac{\cos(\vartheta + \frac{1}{2}\varphi)}{\sin\vartheta \cdot \cos\frac{1}{2}\varphi},$$

from which it is clear that $d\tilde{\nu}_L = 0$ at grazing incidence, that is, when $\vartheta + \frac{1}{2}\varphi = \frac{1}{2}\pi^{(r)}$, and remains very small at oblique incidence.

In the experiment described in this paper a grating with 2400 lines per inch was used, thus making $2a = 127/6$ mu. From the spectrometer constant, $K_\mu = 20.764$ mu, it is found that $\frac{1}{2}\varphi = 11°\ 20'$. Figure 2 is a plot of $d\tilde{\nu}_L$ *versus* $\vartheta$ (or $\lambda$) for a grating with 2400 lines per inch and an angular slit width of one minute of arc, according to the equation

$$d\tilde{\nu}_L = 0.07\frac{\cot\vartheta - 0.2004}{\sin\vartheta}\text{cm}^{-1}.$$

The technique of oblique incidence has been applied to the atmospheric water vapor lines at 15.991 mu, 16.667 mu, 18.018 mu ($7_4 - 6_0$), and 18.64 mu ($6_5 - 5_1$). All are extremely narrow and essentially of the same width. Only the two at 15.991 mu and 18.64 mu will be treated in detail. The line at 18.64 mu was examined with a variety of slit widths ranging from 0.62 cm$^{-1}$ to 0.061 cm$^{-1}$. The reduction appears in Fig. 3,[3]

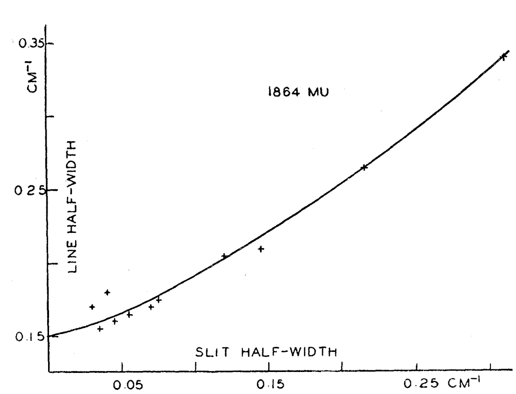


FIG. 3. Observed dependence of absorption line width on spectrometer slit width.

[3] Line half-width is here plotted against slit half-width.

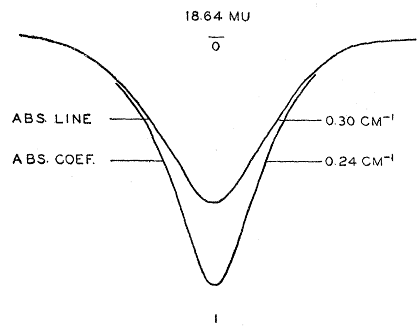


FIG. 4. The atmospheric absorption line at 18.64$\mu$ and its absorption coefficient.

which has the form indicated by theoretical considerations.[4] The extrapolation to zero slit is short and can certainly lead to a value no greater than 0.15 cm$^{-1}$ for the half-width at half-height, at the observed fractional absorption of 56 percent. The line, and the curve of $k(\nu)\cdot t$ deduced from it, appear in Fig. 4. $k(\nu)\cdot t$ and $k(\nu)$ possess the same half-width, since $t$ is a constant factor. The half-width at half-height of $k(\nu)$ is 0.12 cm$^{-1}$.

It also seems worth while to correct for finite slits by computing the effect of slit-width on apparent line width, in contrast to the empirical extrapolation just concluded. The elementary theory of slit influence has been applied to the problem of line width[2,5] in $N_2O$. Figure 5 is taken from this work. Here the apparent half-width of the line, in units of true half-width, is plotted against the apparent half-width, in units of slit half-width. The abscissa is an observable. Thus $D/D_0$ may be read from the curve, $D$ being known, $D_0$ follows. It is assumed in this analysis that the line is weak so that line half-width and absorption coefficient half-width are sensibly equal.[6] The atmospheric water vapor

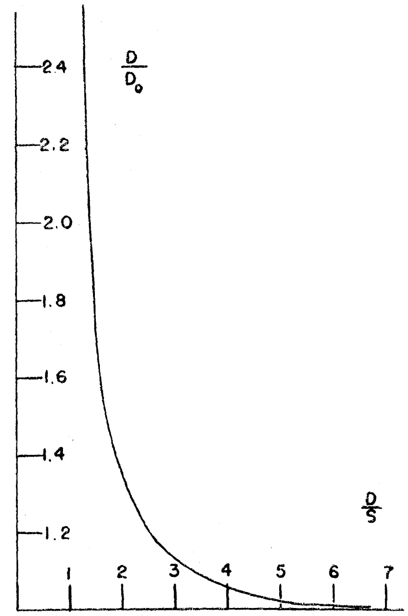


FIG. 5. Infra-red absorption line width in units of absorption coefficient width as a function of absorption line width in units of slit width.

line at 15.991 mu was observed to have a half-width at half-height of 0.145 cm$^{-1}$, at a time when the maximum absorption was 39 percent, and the slit half-width was 0.075 cm$^{-1}$. Since $D/S=2$, $D/D_0=1.35$, and $D_0=0.11$ cm$^{-1}$, in substantial agreement with the value obtained for the line at 18.64 mu.

Since this work was done, in the summer of 1944,[7] several investigators have determined the half-width of the water vapor line $(6_{-5}-5_{-1})$ at $\lambda$1.35 cm in the microwave region. See, for example, G. E. Becker and S. H. Autler,[8] who found values of 0.087 cm$^{-1}$ and 0.107 cm$^{-1}$ for low and high density of water vapor, respectively, in good agreement with the results given in this paper.

[4] See Fig. 6, reference 2.

[5] The author takes this opportunity to correct a small error in the work on $N_2O$. $d\tilde{\nu}_C$ rather than $d\tilde{\nu}_L$ was used to compute slit width, and, as a result, the line half-width was overcorrected to 0.07 cm$^{-1}$. By using the true slit half-width of 0.02 cm$^{-1}$, the apparent line half-width of 0.09 cm$^{-1}$ for $N_2O$ is reduced to 0.08 cm$^{-1}$, true line half-width.

[6] For an observed central absorption of 39 percent the line is of moderate strength rather than weak, and the computed half-width will be conservative, that is, slightly too large.

[7] Div. 14, NDRC. Report No. 320, October 10, 1944; and an unpublished letter to Professor G. E. Uhlenbeck, dated February 1, 1945.

[8] G. E. Becker and S. H. Autler, Phys. Rev. **70**, 300 (1946).