# Grating Infra-Red Measurements at Oblique Incidence. Line Width in the Spectrum of $N_2O$*

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IN a report on line breadth, it is essential to establish at the outset a common understanding of the term. It pertains, of course, to the curve of absorption coefficient, not to the absorption line itself. Thus, 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, where broadening by thermal collisions is the principal agent in shaping an absorption line, 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

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

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 of the curve of absorption coefficient at half its height. Along with $J$, $D_0$ plays an important role in the problem of radiative transfer, since the energy absorbed depends upon it. For example, 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]

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. It is possible, however, to secure a good approximation to the width from the line itself, provided that the latter is weak. For, if the line is weak and has been corrected for finite slits, it follows that $A=1-T\cong k(\nu)\cdot t$; and since $k(\nu)$ stands in association with the constant multiplier $t$, the width of $k(\nu)$ is also sensibly that of $A$, the weak line. Such estimates of width are conservative, and the true width will be slightly smaller. In this paper, true-line width will be thus closely approximated by the breadths of weak lines corrected for finite slits.

An examination of the literature of infra-red spectra reveals half-widths of about $\frac{1}{2}$ cm$^{-1}$, although Lorentz broadening indicates widths approximately an order of magnitude smaller at normal pressure and temperature. Supporting this requirement is an indirect observation of line breadth in CO, by Matheson,[2] who found $D_0\cong 0.1$ cm$^{-1}$. Matheson determined the fractional absorption $A$ from the rise in temperature of a mass of CO transmitting a beam of radiation of spectral width $\Delta\nu$. From the intercepts of the plot $A\Delta\nu/t$ *vs.* $t$, which provided information regarding $J$ and the square root of $JD_0$, both $J$ and $D_0$ were determined.

If infra-red absorption lines are indeed as narrow as one or two-tenths cm$^{-1}$, then to get within a single line and explore it for width will require exceedingly narrow slits, narrower than the line itself. That is to say, if a line possesses a half-breadth of 0.1 cm$^{-1}$, one may hope to explore it with a slit of half-width 0.05 cm$^{-1}$, whereas a slit of half-width 0.5 cm$^{-1}$ would provide a line shape characteristic of the slit rather than of the true line. Correction of line width for finite slits is trustworthy only if the slits are relatively narrow; that is, approximately half the apparent width of the line, or smaller.

The spectral width of a slit depends upon the

* Presented at the Chicago Meeting of the American Physical Society, December 1–2, 1944, under the title: *Measurements of line width in the infra-red spectra of* $CO_2$, $N_2O$, and $NH_3$.

[1] D. M. Dennison, Phys. Rev. **31**, 503 (1928).

[2] L. A. Matheson, Phys. Rev. **40**, 813 (1932).

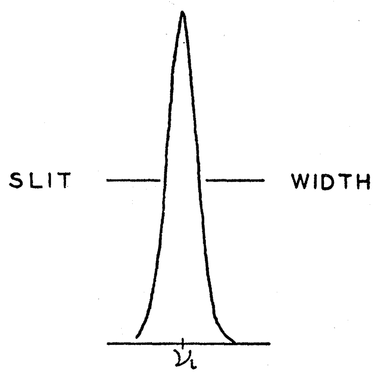


FIG. 1. The observed central image. Throughout the work described in this paper, the slit opening was determined by observation of the central image and checked by thickness gauge measurements.

dispersion available even more importantly than upon the actual slit opening. The intensity distribution within the spectral interval transmitted by 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 a spectrometer setting $\nu_i$. The width of the slit is the width of the slit distribution function at half height. The dependence of slit width on the slit opening and the dispersion is readily obtained from the equation

$$\lambda = K \sin \vartheta,$$

where $K$ is the spectrometer constant, and $\vartheta$ is the angle through which the grating is turned from the position in which it serves merely as a mirror to reflect undispersed radiation from the entrance to the exit slit. It follows that

$$d\tilde{\nu} = -(1/K) \cot \vartheta \csc \vartheta d\vartheta,$$

where $d\vartheta$ is the angle subtended by each slit, and $d\tilde{\nu}$ is the slit width as defined above. Figure 2 is a plot of $d\tilde{\nu}$ *vs.* $\vartheta$ for a grating with 2400 lines per inch and $d\vartheta = 1$ minute of arc; that is for an actual slit width of 0.3 mm in a spectrometer of one-meter focal length. The rapidity with which $d\tilde{\nu}$ decreases with increasing $\vartheta$ is due in appreciable measure to the $\cos \vartheta$ term ($d\tilde{\nu} = -(K/\lambda^2) \times \cos \vartheta d\vartheta$), which is ordinarily quite unimportant in the performance of infra-red spectrometers, since the gratings are customarily used at angles smaller than 30° (about 10 mu for a 2400 line grating), and $\cos \vartheta \sim 0.9$. Under these circumstances $d\tilde{\nu} \geq \sim 0.6$ cm$^{-1}$. If, on the other hand, it were possible to extend the use of the 2400 line to between 18 mu and 19 mu, $\vartheta \sim 65°$, the width of the slit would be reduced to $\sim 0.06$ cm$^{-1}$, a full order of magnitude. The method of oblique incidence is thus available for securing the narrow slits so essential in the measurement of line width, provided sufficient energy remains to enable discrimination between signal and noise. The rate at which energy is received by the thermopile varies as the square of the slit width, and the shift from 10 mu to 18 mu, therefore, implies a reduction in energy of one-hundred fold, other things being equal. Actually, reflection (central image) losses may be greater. Moreover, the cross section of the beam intercepted by the grating may be reduced. Despite this considerable reduction in energy, oblique incidence observations have proved feasible, and the technique has been succesfully applied to the problem of line widths. The spectra of $CO_2$, $N_2O$, $H_2O$, and $NH_3$, amongst others, have been examined, and the lines of all have been found to be narrow indeed.

Only the work on $N_2O$ will be considered in detail in this paper. It constitutes a critical test

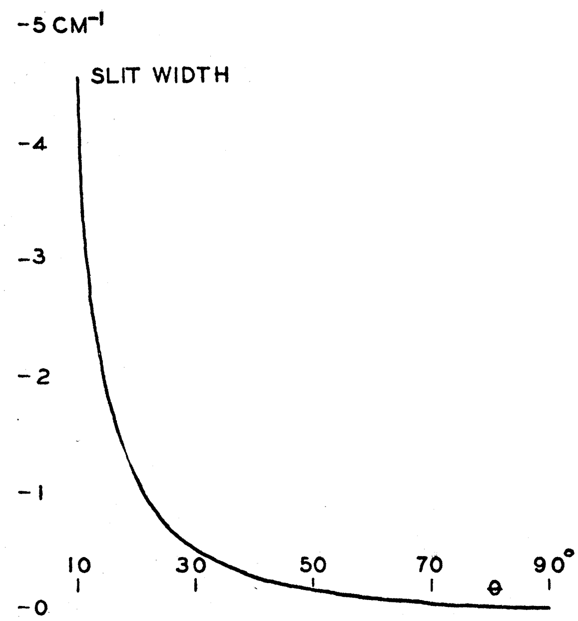


FIG. 2. Slit width, per minute of arc slit opening, as a function of grating position, for a grating with 2400 lines per inch.

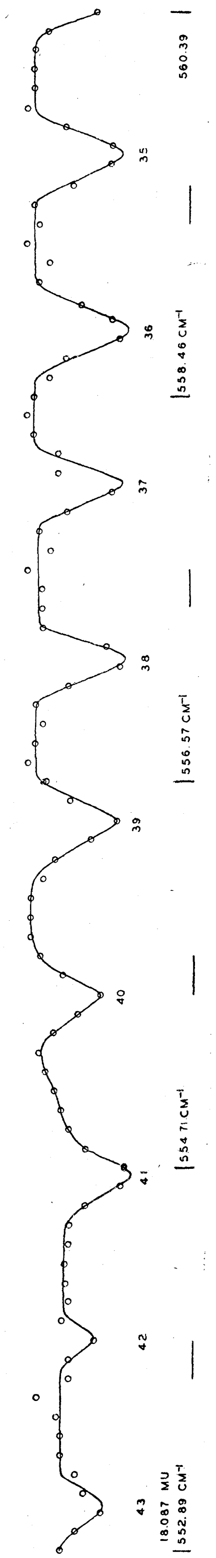


FIG. 3. Rotation-vibration lines in $\nu_2$ of $N_2O$.

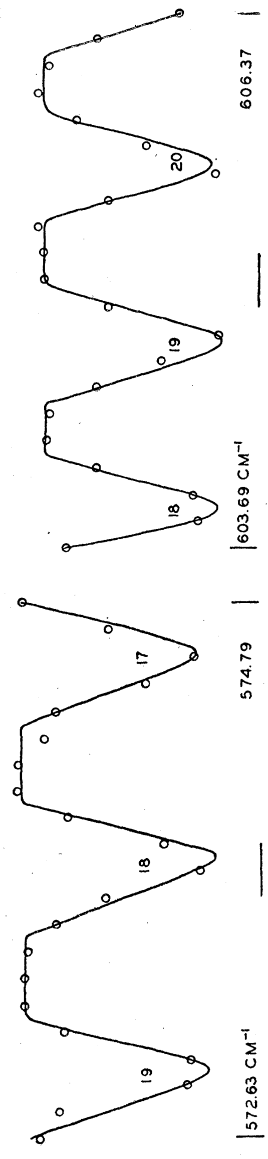


FIG. 4. Rotation-vibration lines in $\nu_2$ of $N_2O$.

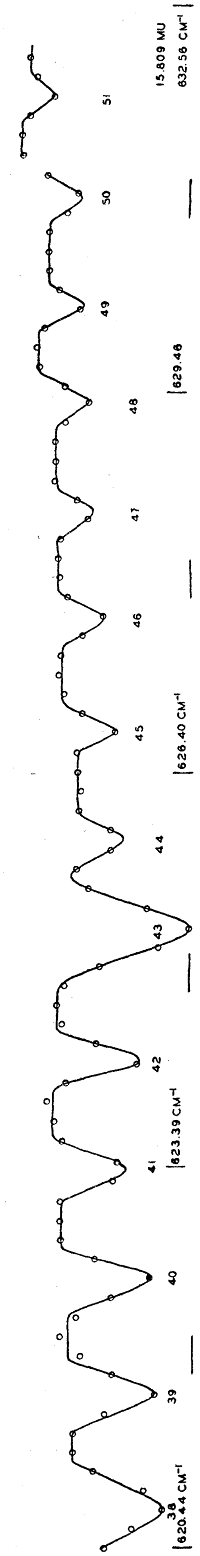


FIG. 5. Rotation-vibration lines in $\nu_2$ of $N_2O$, No. 43 a blend.

of the method, since its lines are but 0.8 $cm^{-1}$ apart,[3] and before it is possible successfully to explore an individual line, it must first be clearly separated from its neighbors. The fundamental $\nu_2$ of $N_2O$, with center at 17 mu was selected for observation. It extends from below 15 mu to beyond 18 mu; and it was examined with a 2400-line grating and slits subtending one minute of arc. The slit width thus varied from 0.15 $cm^{-1}$ at the short wave-length limit of the band to 0.09 $cm^{-1}$ at the long wave-length limit. Nearly one hundred lines were observed in the band, all of them—even the intense ones—well separated and narrow.[4] Some of the weaker lines (at the ends of the band) appear in Figs. 3–5. They were measured at a pressure of 30 cm Hg and a path length of 12.5 cm. The points are one minute of arc apart ($\sim$0.1 $cm^{-1}$), and each point is the average of ten independent observations. Even prior to correction for finite slits, it is evident that the lines are narrow. An average of the weak lines 43, 42, 41, and 40 of the $P$-branch yields an apparent half-width of 0.09 $cm^{-1}$, and an average of the lines 47, 48, 49, 50, and 51 in the $R$-branch yields an apparent half-width of 0.10 $cm^{-1}$. These values are decidedly smaller than those heretofore reported for infra-red lines by direct observation.

At the 18 mu end of the band, where the apparent line breadth is double the slit width, the true line though dominant, may, nevertheless, be importantly affected by the slit. At the 15 mu edge of the band, where the slit is three-quarters the apparent width of the line, the correction for slit effects is not only greater, but somewhat uncertain, and will not be seriously considered here. For the extreme $P$-branch lines a significant correction for slit width is readily obtained from the simple theory of slit influence. The following calculation, based on a paper by Dennison,[5] is due in part to Dr. H. M. Foley.

Because of the finite slits, the fractional transmission must be described with the aid of the slit distribution function. The observed central image, Fig. 1, is closely approximated by, and justifies the use of, the triangular slit distribution function

$$\rho(\nu_i)=\frac{\nu-\nu_i}{(2S)^2}+\frac{1}{2S},$$

from $\nu=\nu_i-2S$ to $\nu=\nu_i$, and

$$\rho(\nu_i)=-\frac{\nu-\nu_i}{(2S)^2}+\frac{1}{2S},$$

from $\nu=\nu_i$ to $\nu=\nu_i+2S$.

Here $S$ is the half-width of the slit and $\nu_i$ is the setting of the spectrometer. The fractional transmission is given by

$$T(\nu_i)=\frac{\int_{\nu_i-2S}^{\nu_i+2S}\rho(\nu)e^{-k(\nu)\cdot t}d\nu}{\int_{\nu_i-2S}^{\nu_i+2S}\rho(\nu)d\nu};$$

and the fractional absorption by

$$A(\nu_i)=1-T(\nu_i)=\frac{\int_{\nu_i-2S}^{\nu_i+2S}\rho(\nu)(1-e^{-k(\nu)\cdot t})d\nu}{\int_{\nu_i-2S}^{\nu_i+2S}\rho(\nu)d\nu}.$$

Assuming weak absorption, we may set

$$e^{-k(\nu)t}\simeq 1-k(\nu)\cdot t.$$

The fractional absorption is then given by

$$A(\nu_i)=\frac{\int_{\nu_i-2S}^{\nu_i+2S}t\rho(\nu)k(\nu)d\nu}{\int_{\nu_i-2S}^{\nu_i+2S}\rho(\nu)d\nu}.$$

If we make the further reasonable assumption of uniform background over the spectral interval occupied by the line, it follows that the fractional absorption at the point $\nu_i$ is proportional to

$$\int_{\nu_i-2S}^{\nu_i+2S}\rho(\nu)k(\nu)d\nu.$$

[3] E. K. Plyler and E. F. Barker, Phys. Rev. **38**, 1827 (1931).

[4] The entire band was shown at the meeting of the American Physical Society, Chicago, December 1–2, 1944.

[5] See reference 1.

We have, therefore,[6]

$$A(\nu) \propto \frac{1}{2\pi(2S)^2} \log \left\{ \frac{[1+(\nu-\nu_0)^2]^2}{[1+(\nu-\nu_0-2S)^2][1+(\nu-\nu_0+2S)^2]} \right\} + \frac{1}{\pi(2S)} \{\tan^{-1}(\nu-\nu_0+2S) - \tan^{-1}(\nu-\nu_0-2S)\} + \frac{\nu-\nu_0}{\pi(2S)^2} \{\tan^{-1}(\nu-\nu_0+2S) + \tan^{-1}(\nu-\nu_0-2S) - 2\tan^{-1}(\nu-\nu_0)\}.$$

Numerical solution of this equation for the frequencies at which the absorption is half the maximum value yields the curve of Fig. 6. The values of the coordinates as calculated are listed in Table I, where both $S$ and $D$, the *apparent* half-width of the line, are given in terms of $D_0$ as unity. The values computed from the equation are thus actually ratios, and they have been plotted as such in Fig. 6.[7] It is more convenient to plot $D/D_0$ as a function of the observable $D/S$, and this curve is shown in Fig. 7. For the $N_2O$ lines near 18 mu, $D/S=2$, and $D/D_0=1.35$. Thus, from $D=0.09$ cm$^{-1}$, we find $D_0(N_2O) = 0.067$ cm$^{-1}$.[8]

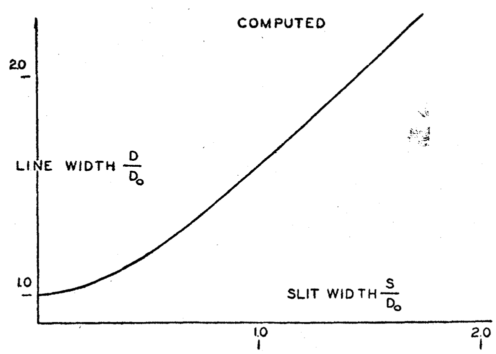


FIG. 6. Apparent line half-width as a function of slit half-width.

TABLE I.

| $S$ | $D$ |
|---|---|
| 0.15 | 1.012 |
| 0.25 | 1.050 |
| 0.50 | 1.210 |
| 1.00 | 1.664 |
| 2.00 | 2.550 |

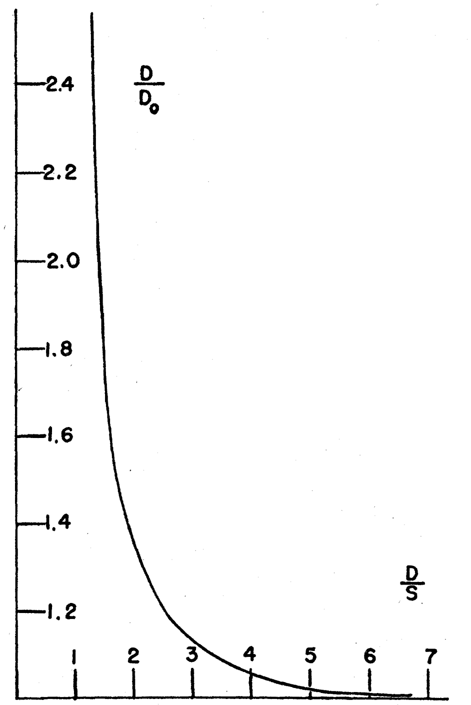


FIG. 7. Apparent line half-width, in units of true line half-width, as a function of apparent line half-width, in units of the slit half-width.

[6] For convenience, the line is assigned a half-width of unity, and the intensity is normalized to unity. That is, $D_0=1$, $J=1$.

[7] Figure 6 is well approximated by the curve

$$\frac{D}{D_0} = \left[1+1.76\left(\frac{S}{D_0}\right)^2\right]^{\frac{1}{2}},$$

and the general form of the curve is not particularly sensitive to the assumptions of small absorption and triangular slit function.

[8] In another half-width determination, of a broader line to be reported on later, an alternative estimation of the correction for slit width was employed. $D$ was measured as a function of $S$ for a variety of slit widths extending down to $2S=0.06$ cm$^{-1}$, and the curve extrapolated to $S=0$, where $D=D_0$. This is the experimental equivalent of the numerical analysis underlying Figs. 6 and 7. The experimental curve and Fig. 6 are in good agreement. This method of correction is particularly valuable when the lines are somewhat broader than in $N_2O$ so that extrapolation begins only after the slit width has been reduced to about one-fifth of the apparent line width.