

Approximate Infrared Emissivity Calculations for HCl at Elevated Temperatures*

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(Received November 15, 1960)

IN a recent paper,¹ Plass has presented the results of infrared emissivity calculations for HCl at elevated temperatures. The data were obtained through the use of machine computations by employing the best available spectroscopic data. We wish to point out that numerical values in good accord with Plass' spectral absorption coefficients may be obtained, when the weak-line approximation holds, by utilizing the results of a relatively simple analytical treatment to the harmonic oscillator approximation. Our method is similar to an analysis first used by Kivel, Mayer, and Bethe² in emissivity calculations on the ultraviolet bands of NO. This method of treatment for electronic band systems has been refined recently by Keck, Camm, Kivel, and Wentink³ in order to account for the influence of vibrational structure on emissivities.

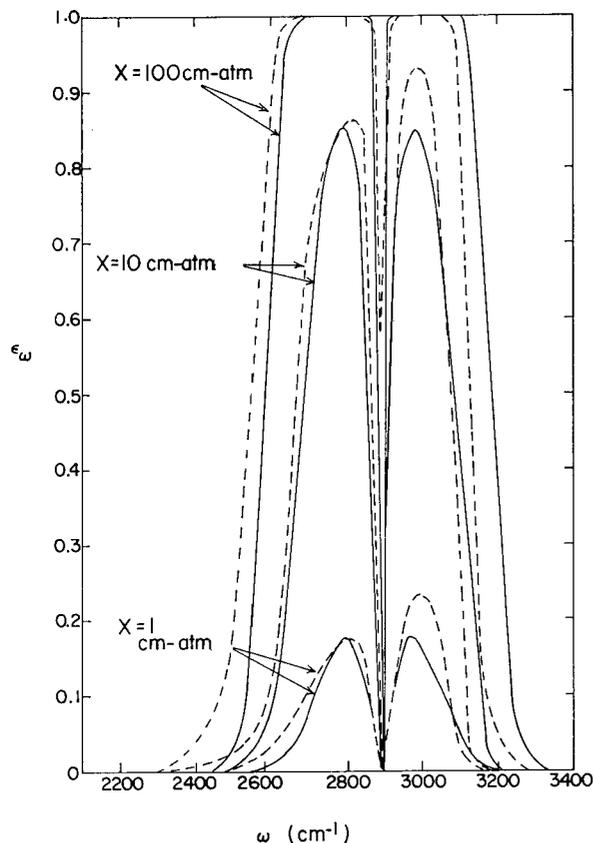


FIG. 1. Comparison of spectral emissivities in the weak-line approximation obtained by numerical calculations¹ (dotted curves) and spectral emissivities obtained by using Eq. (3a) (solid curves) for various optical depths at 600°K.

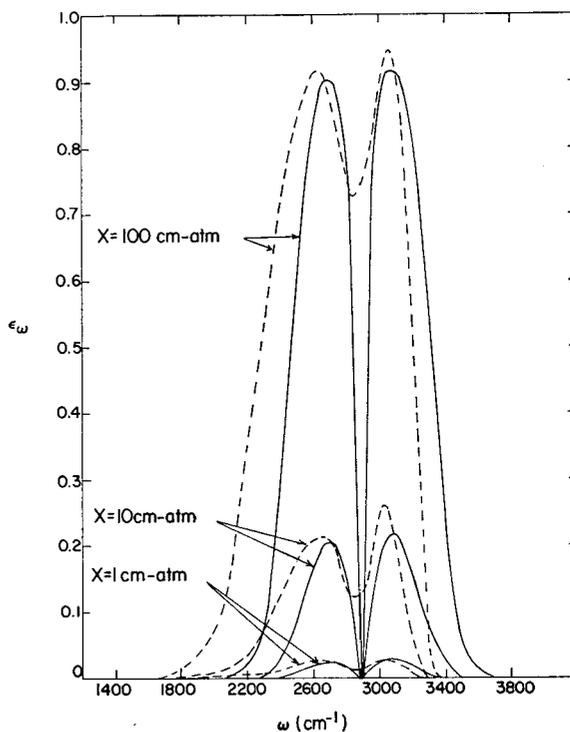


FIG. 2. Comparison of spectral emissivities in the weak-line approximation obtained by numerical calculations¹ (dotted curves) and spectral emissivities obtained by using Eq. (3a) (solid curves) for various optical depths at 2400°K.

Consider⁴ transitions between the ground state with vibrational quantum number n'' and rotational quantum number j'' and the upper state n' , j' . Then

$$hc\omega \simeq (\epsilon_{n'} - \epsilon_{n''}) \pm 2j'hcBe,$$

where ω is the observed wave number for the transition $(n'', j'') \rightarrow (n', j')$ if $\epsilon_{n'}$ and $\epsilon_{n''}$ are the corresponding vibrational energies. If the dominant contributions are made by the higher rotational energy levels, then

$$\epsilon_{j'} \simeq (j')^2 hcBe = [\omega/2Be - (\epsilon_{n'} - \epsilon_{n''})/2hcBe]^2 hcBe$$

and⁵

$$\frac{df_{n', n''}}{d\omega} = \frac{1}{2} f_{n', n''} \frac{|hc\omega - (\epsilon_{n'} - \epsilon_{n''})|}{2BekT} \times \exp\left\{-\frac{[hc\omega - (\epsilon_{n'} - \epsilon_{n''})]^2}{4hcBekT}\right\}. \quad (1)$$

In Eq. (1), $f_{n', n''}$ is the total f number for the $n' \rightarrow n''$ transition, k is the Boltzmann constant, and T denotes the temperature.

It is convenient to write

$$f_{n', n''} = f_{n'-n'', 0} \chi^2_{n', n''}, \quad (2)$$

where $f_{n'-n'', 0}$ is the f number for the transition from the ground state that falls in the same spectral region as the transition $n' \rightarrow n''$. Since⁶

$$P_{\omega_{n', n''}} \approx \frac{\pi e^2}{mc^2} \frac{N_{n''}}{p} \frac{df_{n', n''}}{d\omega} (1 - e^{-hc\omega/kT}),$$

where $P_{\omega_{n', n''}}$ is the spectral absorption coefficient at the wave number ω produced by the vibrational transition $n' \rightarrow n''$ (e and m denote, respectively, the electronic charge and mass; $N_{n''}/p$ represents the total number of molecules in the ground vibrational state per unit volume per unit pressure), we find for the spectral absorption coefficient P_{ω} the following explicit relation:

$$P_{\omega} = \sum_{n''} P_{\omega_{n', n''}} \approx \frac{1}{2} \frac{\pi e^2}{mc^2} f_{n'-n'', 0} \frac{N_T}{p Q_v} \frac{hc}{2BekT} [1 - \exp(-hc\omega/kT)] \\ \times \sum_{n''} \chi^2_{n', n''} [\exp(-\epsilon_{n''}/kT)] |\omega - \omega_{n', n''}| \\ \times \exp\left[-\frac{hc(\omega - \omega_{n', n''})^2}{4BekT}\right], \quad (3)$$

where N_T/p is the total number of molecules of the emitting species per unit pressure per unit volume. Equation (3) takes a particularly simple form to the harmonic oscillator approximation since only the transitions $n' \rightarrow n'-1$ are allowed in emission,

$\omega_{n', n''} \approx \omega_0 = \text{constant}$, $\epsilon_{n''} = (n'' + \frac{1}{2})hc\omega_0$, $\chi^2_{n', n''} = n' = n'' + 1$. Thus

$$P_{\omega, \text{h.o.}} = \frac{1}{2} \frac{\pi e^2}{mc^2} f_{1,0} \frac{N_T}{p Q_v} [1 - \exp(-hc\omega/kT)] [\exp(-hc\omega_0/2kT)] \\ \times [1 - \exp(-hc\omega_0/kT)]^{-2} \frac{hc|\omega - \omega_0|}{2BekT} \left[\exp - \frac{hc(\omega - \omega_0)^2}{4BekT} \right], \quad (3a)$$

where the subscript h.o. identifies results that are applicable to the harmonic oscillator approximation and $\omega \approx \omega_0$ for harmonic transitions.⁷

Spectral emissivities

$$\epsilon_{\omega} \approx 1 - \exp(-P_{\omega, \text{h.o.}} p l),$$

computed by the use of Eq. (3a), are compared with Plass' data in Figs. 1 and 2.⁸ Reference to Figs. 1 and 2 shows that Eq. (3a) represents an acceptable approximation for the spectral absorption coefficient.

* Supported by the Office of Naval Research under contract.

¹ V. R. Stull and G. N. Plass, "Spectral emissivity of hydrogen chloride from 1000-3400 cm^{-1} ," Publ. No. U-461. (Aeronutronic, Newport Beach, California, May 15, 1959).

² B. Kivel, H. Mayer, and H. A. Bethe, *Ann. phys. (N. Y.)* **2**, 57 (1957).

³ J. C. Keck, J. C. Camm, B. Kivel, and T. Wentink, *Ann. phys. (N. Y.)* **7**, 1 (1959).

⁴ A more complete account of the theoretical treatment will be published elsewhere by S. S. Penner, K. G. P. Sulzmann, and C. B. Ludwig.

⁵ S. S. Penner, *Quantitative Molecular Spectroscopy and Gas Emissivities* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1959), p. 398.

⁶ Reference 4, Eqs. (14-7) and (2-19).

⁷ Equation (3a) is identical with Eq. (11-141) of reference 4.

⁸ In our calculations we used a numerical estimate for $f_{1,0}$ equivalent to that employed by Plass for the sum of the isotopic species HCl^{35} and HCl^{37} . This value is probably somewhat low (cf. reference 4).