Approximate Infrared Emissivity Calculations for HCl at Elevated Temperatures

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I
n 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 Bethe 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 Wentink in order to account for the influence of vibrational structure on emissivities.

Consider transitions between the ground state with vibrational quantum number \( n'' \) and rotational quantum number \( j'' \) and the upper state \( n', j' \). Then

\[
\hbar \omega \approx (\varepsilon_{n''} - \varepsilon_{n'}) \pm 2 j' \hbar \omega \Omega,
\]

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

\[
\varepsilon_{n''} (j'') = \hbar \omega (2j'' + 1) / \sqrt{2} \hbar \Omega,
\]

and

\[
\frac{df_{n''}}{d \omega} = \frac{1}{2B \hbar \Omega} \left( \frac{\varepsilon_{n''} - \varepsilon_{n'}}{\hbar \omega} \right) \left( 1 - e^{-\hbar \omega / kT} \right)^{-1},
\]

In Eq. (1), \( f_{n''} \) 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

\[
\frac{df_{n''}}{d \omega} = \frac{1}{2B \hbar \Omega} \left( \frac{\varepsilon_{n''} - \varepsilon_{n'}}{\hbar \omega} \right) \left( 1 - e^{-\hbar \omega / kT} \right)^{-1},
\]

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

\[
P_{w''} = \sum_{n''} \sum_{n'} \frac{1}{2 \hbar \Omega} \left( \frac{\varepsilon_{n''} - \varepsilon_{n'}}{\hbar \omega} \right) \left( 1 - e^{-\hbar \omega / kT} \right)^{-1} \left[ \exp \left( -\frac{\hbar \omega}{kT} \right) \right]

\times \sum_{n''} \frac{\chi_{n''}}{\chi_{n'}} \left[ \exp \left( -\frac{\hbar \omega}{kT} \right) \right] \left[ \exp \left( -\frac{\hbar \omega}{kT} \right) \right],
\]

where \( N_{w''} / p \) 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 \( n'' \rightarrow n' \rightarrow 1 \) are allowed in emission, \( \omega_{n''} \approx \omega_{n'} \approx \omega_{n''} = \omega_{n''} = \omega_{n''} = \omega_{n''} + 1 \). Thus

\[
P_{w''} \approx \frac{1}{2 \hbar \Omega} \left( \frac{\varepsilon_{n''} - \varepsilon_{n'}}{\hbar \omega} \right) \left( 1 - e^{-\hbar \omega / kT} \right)^{-1} \left[ \exp \left( -\frac{\hbar \omega}{kT} \right) \right]

\times \left[ \exp \left( -\frac{\hbar \omega}{kT} \right) \right] \left[ \exp \left( -\frac{\hbar \omega}{kT} \right) \right],
\]

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

Figure 2. Comparison of spectral emissivities in the weak-line approximation obtained by numerical calculations (dotted curve) and spectral emissivities obtained by using Eq. (3) (solid curve) for various optical depths at 2400°K. April 1961 LETTERS TO THE EDITOR
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

$$\omega \approx 1 - \exp(-P_{n, h.o.} \phi),$$

computed by the use of Eq. (3a), are compared with Plass' data in Figs. 1 and 2.\(^7\) Reference to Figs. 1 and 2 shows that Eq. (3a) represents an acceptable approximation for the spectral absorption coefficient.

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4 A more complete account of the theoretical treatment will be published elsewhere by S. S. Penner, R. G. P. Sulzmann, and C. B. Ludwig.
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 $f_2$, equivalent to that employed by Plass for the sum of the isotopic species HCl\(^{35}\) and HCl\(^{37}\).

Photoelectric Measurement of Polized Light by Means of an ADP Polarization Modulator.

I. Photoelectric Polarimeter

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A SENARMONT compensator has been made that uses a crystal of ammonium dihydrogen phosphate (ADP) as a retardation plate. The arrangement is shown in Fig. 1. An alternating voltage is applied across the ADP crystal, which voltage causes the azimuth of the transmitted linearly polarized light to oscillate in synchronism with the applied voltage. The optical system of Fig. 1, not including the polarization polarizer, is named the polarizing azimuth vibrator (PAV) of Senarmont type.

Another type of PAV can be made with a different arrangement, shown in Fig. 2. This type is named the PAV of circular polarizer type. The two kinds of PAV affect the principal rays in the same way, but they differ in the way that they affect oblique rays; the conoscopic patterns are different.

Fig. 1. The polarization azimuth vibrator of Senarmont type. The element $P$ is a linear polarizer, $X$ is an ADP crystal with electrodes on both surfaces, and $Q$ is a quarter-wave plate.

Fig. 2. The polarization azimuth vibrator of circular polarizer type. As in Fig. 1, $P$ is a polarizer, $X$ is an ADP crystal, and $Q_1$ and $Q_2$ are quarter-wave plates.

A photoelectric polarimeter has been made that uses a PAV, as shown in Fig. 3. The transmitted light flux is calculated to be

$$F' = \frac{1}{2} F_0 \left( 1 + \cos 2\theta \cos \phi \right) \sin 2\phi \sin 2\phi,$$

where $\theta$ is the azimuth angle of the polarizer and $\phi$ is the angular retardation of the ADP.

Fig. 3. A photoelectric polarimeter. The servo system rotates the polarizer $P$ so that its rotation compensates the rotation produced by the material under study.

It is now supposed that the angle $\phi$ varies sinusoidally in time

$$\phi = K \sin \omega t,$$

and that $\theta$ is so small that sine is equal to $\phi$, and cosine is represented by $1 - \frac{1}{2} \phi^2$. Then

$$F' = \frac{1}{2} F_0 \left( 1 + \cos 2\theta - \frac{1}{2} K^2 \sin 2\omega t - K E \sin 2\phi \sin 2\phi \right).$$

In this expression the first and second terms on the right represent the DC outputs, the third term is an AC signal with twice the driving frequency, and the last term has the fundamental frequency and is proportional to $\sin \theta$. This signal is amplified by a frequency selective circuit and is fed to a balancing motor that rotates the polarizer so as to make $\theta$ zero.

A PAV is a kind of half-shade device. The optimum half-shade angle $\phi$ is a function of the extinction constant of the optical system, and is usually in the range from 0.5° to 3.0°. Accuracy of the polarimeter has been found to be about 1 min of angle.

This polarimeter has the following advantages:

1. The half-shade angle is easily adjusted to the desired value.