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Non-equilibrium Emissivity of Carbon Dioxide near 4.3μ

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Summary

Calculation of the emissivity of the 4.3μ band of carbon dioxide is made for samples of the gas which are not in vibrational equilibrium. The method is based on an equilibrium calculation and requires specification of the vibrational, rotational and translational temperatures. It is assumed that the vibrational modes are in mutual equilibrium. These calculations were used in conjunction with shock tube experiments to study the vibrational relaxation region of shock waves but are generally valid for uniform samples.

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1. Introduction.

The emissivity of the 4.3μ band of carbon dioxide has been calculated by Malkmus (1963) for uniform samples of the gas in equilibrium. The results show reasonable agreement with experimental data. Blom and Pratt (1968) showed that the rotational energy level population distribution should be taken into account when calculating temperatures from band-reversal experiments on shock wave vibrational relaxation regions. Their calculations, which do not require explicit knowledge of the emissivity, were based on the optically thin approximation with no overlapping lines.

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It is shown in the present paper that for uniform non-equilibrium gas samples the method of Malkmus can be modified to calculate the emissivity of the 4.3μ band for optically thick samples with overlapping lines.

Hot samples of carbon dioxide produced in a shock tube emit spectral bands of infrared radiation associated with the vibrational and rotational energy modes of the molecule. A very strong band, associated with the asymmetric stretching mode of vibration, is centred at 4.3μ . For typical shock tube diameters and working pressures the gas samples produced are optically thick near this wave length. To calculate the total radiation emitted in this spectral band self-absorption effects are taken into account in calculating the spectral emissivity. The product of the spectral emissivity and Planck black body function is then integrated over the spectrum. Usually each band is so narrow that the black body function may be taken as constant during the integration.

Details of experiments measuring the emitted radiation from vibrational relaxation regions were presented in a separate paper by Hodgson and Hine (1969). Here it is intended to explain in more detail how the emissivity of the vibrationally relaxing gas was calculated.

2. The Emissivity at Equilibrium.

In the calculation of the equilibrium emissivity of the 4.3μ band Malkmus (1963) used the harmonic oscillator model to calculate the spectral line intensities, the anharmonic oscillator, including the first-order rotation-vibration interaction approximation to determine the spectral line positions, and the statistical model of a spectral band. The statistical model was used according to several approximations.

The integrated line intensity of absorption of a line in the vibrational band of a diatomic molecule was derived by Stull and Plass (1960) using the harmonic approximation. The result was of the form*:

$$S = S(n,j,T), \quad (1)$$

where n is the vibrational quantum number of the lower energy state involved in the transition, j is the rotational quantum number and T the temperature. Using the anharmonic oscillator model with first-order rotation-vibration interaction approximation, Malkmus and Thomson (1962) gave the wave number of a line in the band

$$\omega = \omega(n,j) \quad (2)$$

which is a quadratic function of j . The equation can be solved to give

$$j = j(n,\omega) \quad (3)$$

* Only the relevant functional dependence of the important spectroscopic parameters will be indicated here as the expressions are long and contain several spectroscopic constants. The derived expressions required for the calculations are given in the next section for the non-equilibrium situation.

There are two solutions of Equation (2), one of which can be eliminated (Hodgson (1966)) as it has very little effect on the emissivity. Moreover the effect is localised to that part of the band where the rotation-vibration interaction approximation is most likely to be insufficient. A spectral line exists only when j is an integer but as there is a high density of lines, and the mean value of j is large, the rotational quantum number may be considered as a continuous variable to a good approximation, particularly as we are interested in low-resolution spectroscopy only.

Direct substitution of j into Equation (1) gives

$$\bar{S} = \bar{S}(n, \omega, T), \quad (4)$$

where the bar indicates that the rotational quantum number has been treated as a continuous variable. \bar{S} is then the mean integrated line intensity at the wave number ω . In practice no such line may exist though spectral lines are very close to ω .

Thus, for a given temperature we can determine the mean integrated line intensity of a line in the vibrational band of a diatomic molecule for a particular vibrational transition, indicated by n . Several component bands (one for each value of n) will be superposed with a slight displacement towards longer wave lengths due to anharmonicity.

The similarity of the 4.3μ band of carbon dioxide to the vibrational band of a diatomic molecule was noted by Malkmus. The 4.3μ band is associated with the asymmetric stretching mode of vibration, which produced dipole moment changes parallel to the ground state axis of the molecule. It follows that the band is similar to the band of a diatomic molecule. However because there are four vibrational energy modes in carbon dioxide the quantum number n is replaced by four quantum numbers and consequently there will be many more spectral lines in this band. The smoothing of the rotational quantum number should therefore be more realistic. The effect of the very weak central Q-branch is ignored.

For carbon dioxide the mean line intensity of absorption then has the dependence:

$$\bar{S} = \bar{S}(n_1, n_2^l, n_3, \omega, T), \quad (5)$$

where n_1 , n_2 and n_3 are the quantum numbers associated with the symmetric stretching, bending and asymmetric stretching modes, respectively, and l is the (internal) quantum number of rotation associated with the bending mode which is degenerate.

Carbon dioxide is peculiar in that the energy levels of the n_1 and n_2 modes contain a Fermi resonance. The characteristic temperature of the n_1 mode is almost exactly twice the characteristic temperature of the n_2 mode. It also happens that the anharmonic correction terms are similarly related by a factor of two (Herzberg (1962)). Since the 4.3μ

band is caused by a unit change in n_3 while n_1 and n_2 remain unchanged during the photon interaction, it is convenient to re-group the quantum numbers of the non-participating modes into a new quantum number,

$$\bar{n} = 2n_1 + n_2, \quad (6)$$

then all states with the same value of \bar{n} have the same energy. The effects of this re-grouping and the internal rotational quantum number can be readily accounted for in the degeneracy factor. Equation (5) becomes

$$\bar{S} = \bar{S}(n, n_3, \omega, T). \quad (7)$$

The absorption coefficient of a sample of gas is given, according to the weak line approximation to the statistical model (Plass (1958)), by

$$K(\omega, T) = \sum_{\bar{n}=0}^{\infty} \sum_{n_3=0}^{\infty} \frac{\bar{S}(\bar{n}, n_3, \omega, T)}{\bar{d}(\bar{n}, n_3, \omega)}. \quad (8)$$

$\bar{d}(n, n_3, \omega)$ is the average line spacing in each component band, determined by substituting for the rotational quantum number j in the same way as for $\bar{S}(\bar{n}, n_3, \omega, T)$. The rotational line separation depends only on intramolecular properties and is independent of temperature.

In the strong line approximation to the statistical model, assuming that the lines have the Lorentz lineshape with half width α_L ,

$$K(\omega, T) = \sum_{\bar{n}=0}^{\infty} \sum_{n_3=0}^{\infty} 2 \left(\frac{\alpha_L}{pL} \right)^{\frac{1}{2}} \frac{|\bar{S}(\bar{n}, n_3, \omega, T)|^{\frac{1}{2}}}{\bar{d}(\bar{n}, n_3, \omega)}, \quad (9)$$

where p is the pressure and L the geometric length of the uniform gas sample. In both cases the emissivity is given by

$$\epsilon(\omega, T, p, L) = 1 - e^{-pLK(\omega, T)} \quad (10)$$

Since neither the weak nor the strong line versions of the statistical model completely describes a molecular band which is optically thick near its centre, Malkmus (1963) proposed a mixed approximation for obtaining the best results. Both the weak and strong line approximations over-estimate the absorption coefficient (Plass (1960)), so that the smaller of the two coefficients obtained will be the most accurate. Applying the same argument to the component bands, corresponding terms in the summations given in Equations (8) and (9) are compared. The lower one gives the contribution of the component band more accurately. By summing over the smaller terms a better value is obtained for the emissivity. Following Malkmus (1963) this will be referred to as the weak-strong approximation.

Comparisons of the results of this calculation with experimental data have been given by Malkmus (1963) and in general it is found that the calculated value of the emissivity overestimates the experimental emissivity by 20 per cent. However it is important to note that the incremental temperature dependence of the emissivity is given more accurately than this for limited variations of the pressure. Thus in the relaxation regions of shock waves the error in the calculated emissivity relative to the emissivity of the gas at equilibrium will be much smaller than 20 per cent.

3. The Emissivity of Non-Equilibrated Gas Samples.

Extension of the calculation outlined in the previous section to apply to uniform samples of carbon dioxide which are not in equilibrium is fairly straight forward. Translational (T_T), rotational (T_R) and vibrational (T_V) temperatures were defined and the algebraic operations carried out as for the equilibrium situation (Malkmus (1963)). No excited electronic states exist in carbon dioxide so there is no requirement for an electronic temperature. In this way each energy mode of the molecule is considered to have its energy level population described by a Boltzmann distribution but a different distribution is ascribed to each mode.

In principle we could define vibrational temperatures for each mode of vibration but this would lead to difficulties in interpretation of the experimental results of measurements of radiant emission from shock wave relaxation regions. Instead we make the assumption that the vibrational modes are in mutual equilibrium. Serious inadequacies of this assumption would have manifested themselves in the relaxation measurements described by Hodgson and Hine.

The mean integrated line intensity of absorption is given by

$$\bar{S}(\bar{n}, n_3, \omega, T_T, T_R, T_V) = A(\bar{n}, n_3, \omega, T_T, T_R, T_V) |B(\bar{n}, n_3, \omega)| e^{-c(\bar{n}, n_3, \omega, T_R)}, \tag{11}$$

where

$$A(\bar{n}, n_3, \omega, T_T, T_R, T_V) = \alpha(\bar{n}, n_3, T_T, T_V) \left(\frac{\omega}{\omega(\bar{n}, n_3)} \right) \left(\frac{B_e hc}{kT_R} \right) \frac{(1 - e^{-\frac{hc\omega}{kT_V}})}{hc\omega(\bar{n}, n_3) (1 - e^{-\frac{hc\omega(\bar{n}, n_3)}{kT_V}})}, \tag{12}$$

$$B(\bar{n}, n_3, \omega) = \left[\frac{B_e}{\alpha_3} - (n_3 + 1) \right] - \sqrt{\left[\frac{B_e}{\alpha_3} - (n_3 + 1) \right]^2 - \frac{1}{\alpha_3} [\omega - \omega(\bar{n}, n_3)]} \tag{13}$$

and/

and

$$c(\bar{n}, n_3, \omega, T_R) = \frac{hc}{kT_R} \left[\frac{B_e}{\alpha_3} - (n_3 + 1) \right] \left[2\{B_e - \alpha_3(n_3 + 1)\} B(\bar{n}, n_3, \omega) - \left(1 + \frac{\frac{1}{2}\alpha_3}{B_e - \alpha_3(n_3 + 1)}\right) (\omega - \omega(\bar{n}, n_3)) \right]. \quad (14)$$

$$\alpha(\bar{n}, n_3, T_T, T_V) = \frac{T_0 \alpha(0, 0, T_0, T_0)}{T_T} (n_3 + 1) \frac{N(\bar{n}, n_3, T_V)}{N(\bar{n}, n_3, T_0)} \times \frac{1 - \exp(-hc\omega(\bar{n}, n_3)/kT_V)}{1 - \exp(-hc\omega(0, 0)/kT_V)} \quad (15)$$

In these equations:

- h is Planck's constant,
- c is the velocity of light,
- k is Boltzmann's constant,
- $\omega(\bar{n}, n_3)$ is the central frequency of the component band defined by (\bar{n}, n_3) (Herzberg (1962)),
- $\alpha(\bar{n}, n_3, T_T, T_V)$ is the integrated band intensity of absorption of a component band for $n_3 \rightarrow n_3 + 1$ and n constant,
- $\alpha(0, 0, T_0, T_0)$ is the integrated band intensity of absorption of the component band for the transition $n_3 = 1$ to $n_3 = 0$ with $n = 0$ at a reference temperature T_0 . (Weber, Holm and Penner (1952)),
- $N(\bar{n}, n_3, T_V)$ is the fractional population of the vibrational energy level (\bar{n}, n_3) at T_V ,
- B_e is the rotational line separation constant (Herzberg), and
- α_3 is the rotation-vibration interaction spectroscopic constant for the asymmetric stretching mode (Herzberg).

The average line spacing $\bar{d}(\bar{n}, n_3, \omega)$ is given by

$$\bar{d}(\bar{n}, n_3, \omega) = 2 \sqrt{\left[B_e - \alpha_3 (n_3 + 1) \right]^2 - \alpha_3 (\omega - \omega(\bar{n}, n_3))} \quad (16)$$

In equation (12) the term $(B_e hc/kT_R)$ is derived from the rotational partition function and with Equation (14) defines the variation in intensity of rotational lines in a particular component band.

The integrated band intensity of absorption $\alpha(\bar{n}, n_3, T_T, T_V)$ depends on the translational temperature simply because it is defined (according to the usual notation of spectroscopists) in terms of a pressure unit. At constant pressure the number of molecules is inversely proportional to translational temperature. The vibrational energy level populations depend on the vibrational temperature; so also do the exponents of Equation (15). In Equation (12) the exponents stem from the energy level populations involved in the transition, since the vibrational energy changes dominate the transitions the vibrational temperature has been used here.

The anharmonic correction terms depend only on the intramolecular properties of the molecule and these are independent of temperature, as are the spectral line positions and spacings defined by Equations (13) and (16).

In the case of the strong line approximation, Equation (9), we must also consider the Lorentz line width α_L , which depends on the frequency of molecular collisions and hence on the molecular velocity and translational temperature. The collision cross-section was assumed to be independent of temperature and was calculated from the experimental data of Kaplan and Eggers (1956).

For calculations of the total emitted radiant intensity the Planck black body function is required and for non-equilibrium samples this depends on the vibrational temperature for vibrational bands.

4. Results and conclusion.

Computations were made on the Manchester University Atlas machine and energy levels up to 2eV were considered.

In the vibrational relaxation region of shock waves the rotational temperature is essentially equal to the translational temperature since the rate of relaxation of rotational energy modes is about 10^3 times that of vibrational modes. For this reason computations were restricted to cases where $T_T = T_R$. However cases where the rotational and translational temperature are less than the vibrational temperature are plotted here since such situations may exist in expansion waves. The independent effect of the vibrational temperature and the rotational and translational temperatures are demonstrated in Figs. 1 and 2.

In Fig. 1 the vibrational temperature is kept constant at 800°K. The translational temperature is varied between 600°K and 1600°K, and the emissivity is plotted for a gas sample 0.203m long, having a density of 0.0171 amagat. It can be seen that the band broadens due to increased population of the higher energy rotational states, which on de-excitation produce spectral lines in the wings of the component bands. The rotation-vibration interaction term, which spreads the P-branch and causes a band head in the R-branch, causes the broadening to be more prominent at the long-wavelength edge of the band. In the R-branch the increase in intensity of the lines in the wings of the band causes a general increase in the emissivity since these spectral lines are very close together. Thus the peak value of the emissivity moves to shorter wave lengths, though the band spreads towards longer wave lengths.

The cusp near 2350 cm^{-1} is the division between the P and R-branches of the component band for which $\bar{n} = 0$ and n_3 changes from 1 to 0, i.e. the cusp is at the centre of this component band. The prominence of this cusp decreases as the rotational temperature increases since the lines in the wings of higher component bands overlap this spectral region. Such cusps appear at the centre of all component bands derived using this spectral band model, but since the higher component bands are weaker (for the temperature range of interest here) their cusps are less prominent.

Due to anharmonicity effects, which reduce the vibrational energy level separation as the vibrational energy increases, component band centres exist at longer wavelengths for higher vibrational energies. Thus all the other cusps appear in the P-branch of the lowest energy band. In the spectral region 2295 cm^{-1} to 2320 cm^{-1} several cusps exist and the nett effect is that the emissivity is slightly reduced. As the rotational temperature increases the cusps become wider and the effect is to reduce the emissivity slightly in this region. However it must be pointed out that this effect may not be realistic since these cusps do not really occur because the Q-branches which, though weak, have been completely ignored.

For Fig. 2 the rotational and translational temperatures are maintained at 1200°K , with the density and path length identical to those for Fig. 1. The vibrational temperature is varied from 800°K to 1600°K . The emissivity is seen to be a more sensitive function of vibrational temperature than rotational and translational temperature, particularly near the long wavelength end of the band. The spreading of the band to larger wavelengths is due to anharmonic effects in this case, since higher vibrational levels become increasingly well-populated at higher vibrational temperatures. The cusp near 2350 cm^{-1} disappears as it is overshadowed by the R-branches of higher component bands. The effect of the cusps of the higher component bands can be seen as a slight reduction in emissivity at the shoulder of the P-branch, which becomes less important as the vibrational temperature increases and more component bands are present. In this case the peak value of the emissivity moves towards longer wavelengths.

In Fig. 3 the integrated emissivity,

$$\int_{\Delta\omega_{\text{band}}} \epsilon(\omega, \rho, L, T_T, T_V) d\omega ,$$

is plotted for $L = 0.203 \text{ m}$ and the density $\rho = 0.0171 \text{ amagat}$. It can be seen that the net effect of any increase in temperature is to increase the integrated emissivity but the effect of the rotational and translational temperature is only about 30 per cent of that of the vibrational temperature. The integrated emissivity, according to the optically thin approximation would be independent of temperature having the value of 330 cm^{-1} for these gas samples. As the temperature increases the emissivity, as computed here, tends towards this value. Blom and Pratt found that the rotational energy level population distribution does not affect emission/absorption intensity ratio measurements of temperature provided

the whole spectral band is within the band width of the filter. This is the case for no self-absorption (optically thin gas), except when the emission/absorption ratio is unity, i.e. reversal conditions exist exactly. The present results include the effects of self-absorption and overlapping spectral lines but require explicit knowledge of the rotational and vibrational temperatures rather than their ratio. This is because a further variable, the geometric length of the gas sample, is required to calculate the effects of self-absorption.

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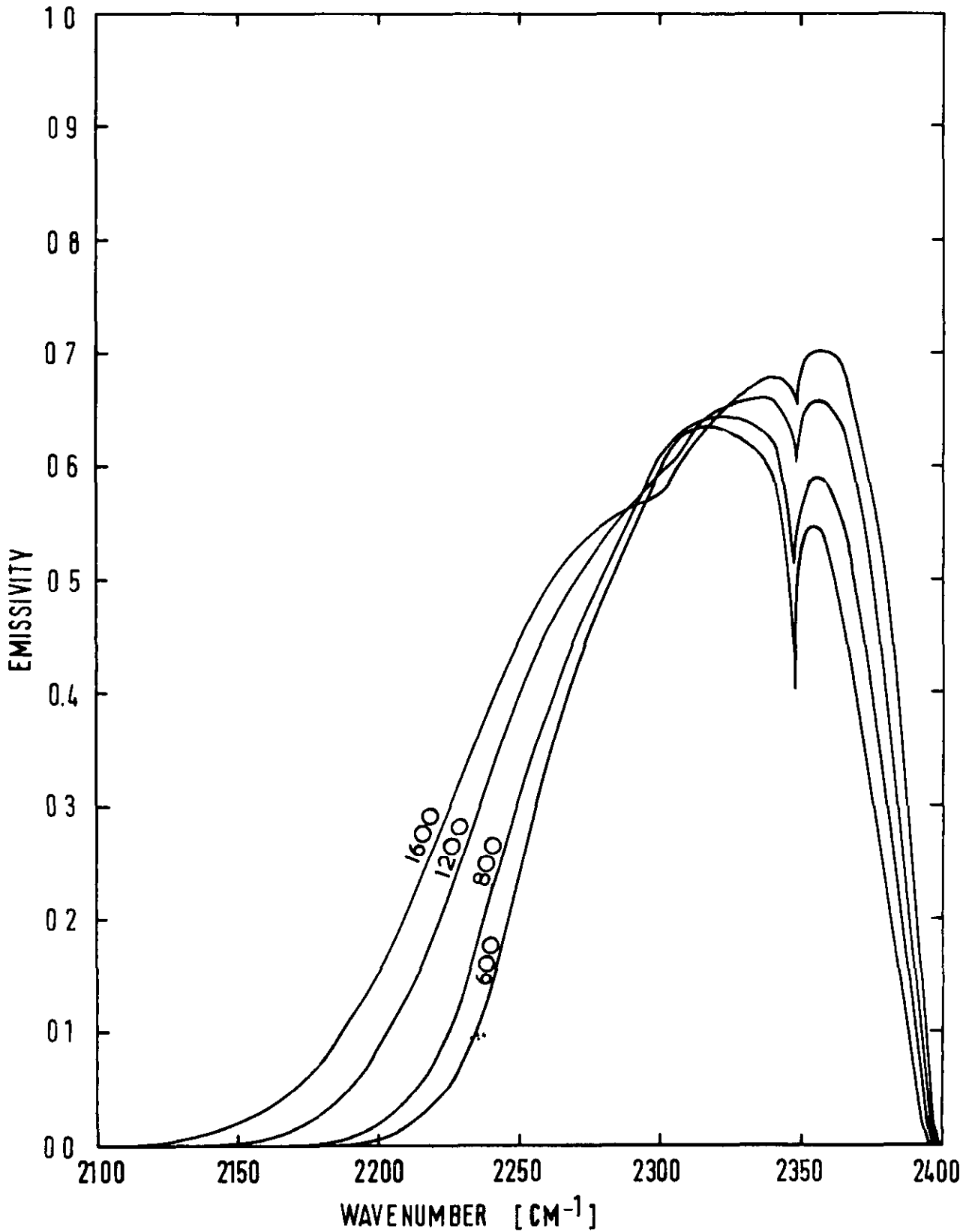


FIG.1

$T_V = 800^\circ\text{K}$,
 CO_2 DENSITY = 0.0171 AMAGAT,
PATH LENGTH = 0.203 M,
 $T_T = T_R$ INDICATED ON DIAGRAM.

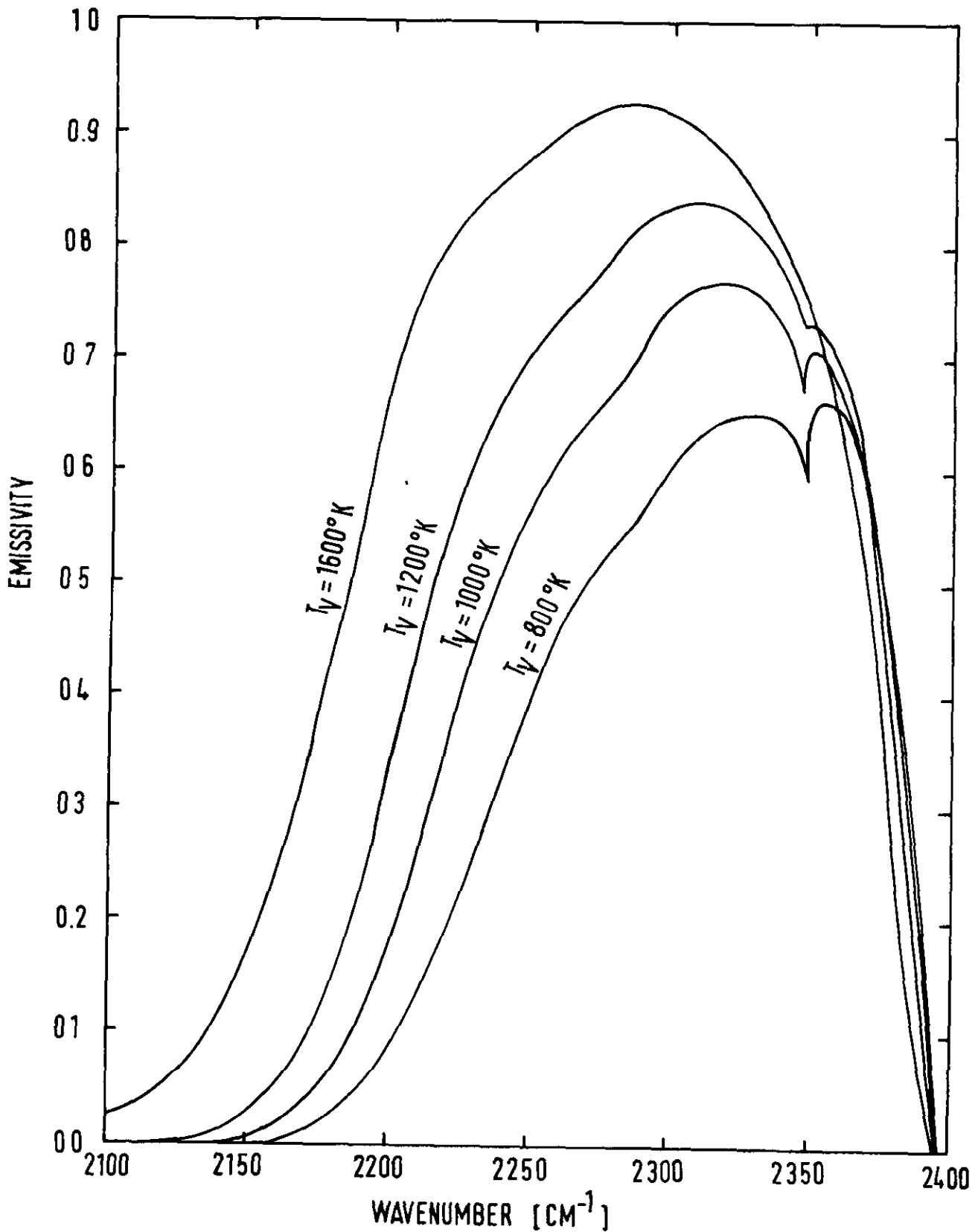


FIG 2.

$T_T = T_R = 1200^\circ\text{K}$
 CO_2 DENSITY = 0.0171 AMAGAT
PATH LENGTH = 0.203 M

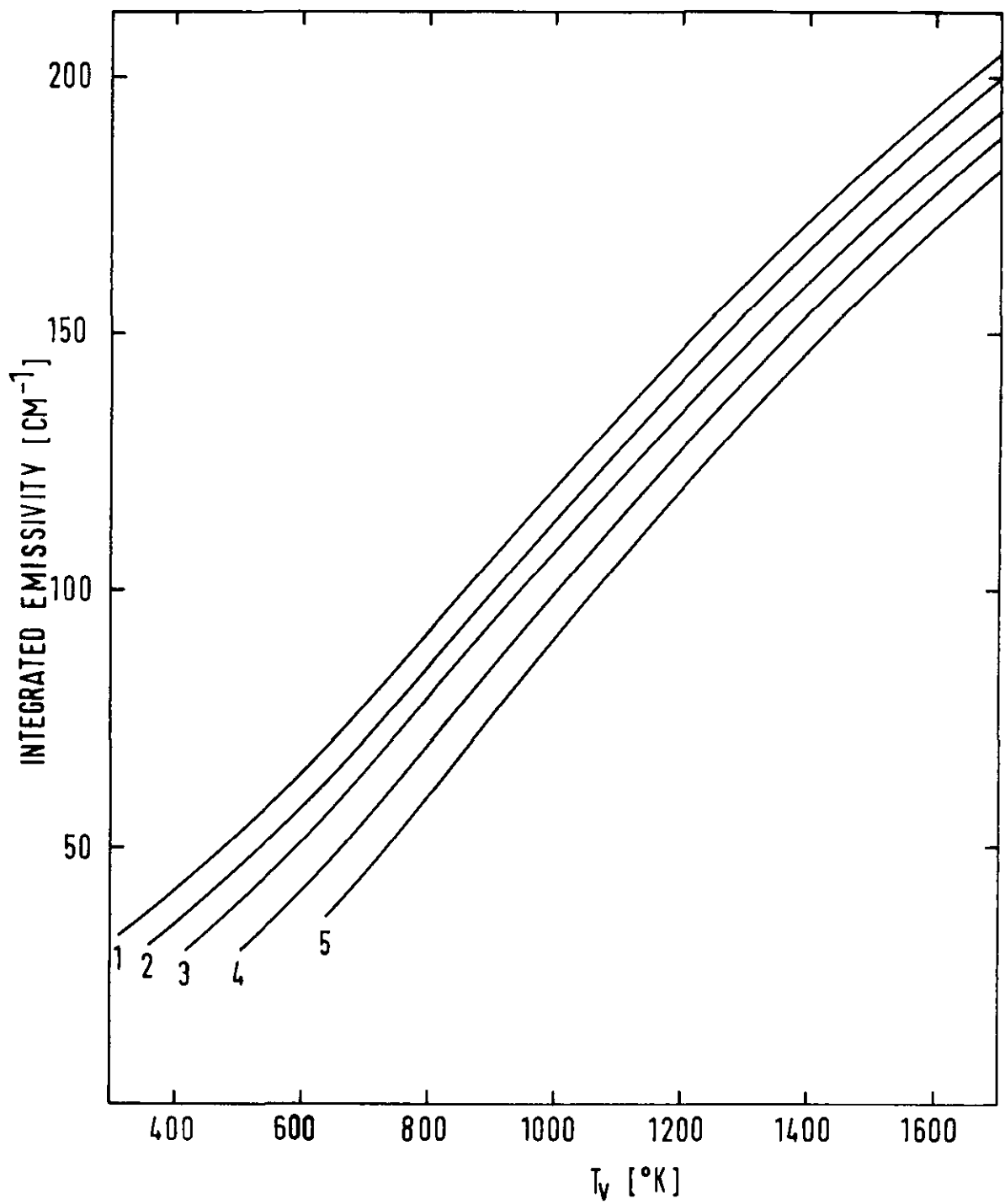


FIG 3

| | | |
|----------|-------------------------------|---|
| CURVE 1 | $T_T = T_R = T_v + 400^\circ$ | } CO_2 DENSITY = 0.0171 AMAGAT PATH LENGTH = 0.203 M |
| CURVE 2 | $T_T = T_R = T_v + 200^\circ$ | |
| CURVE 3 | $T_T = T_R = T_v$ | |
| CURVE 4. | $T_T = T_R = T_v - 200^\circ$ | |
| CURVE 5 | $T_T = T_R = T_v - 400^\circ$ | |

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