

NEW BREAKTHROUGH IN FAR-WING LINE SHAPES:

APPLICATION TO CO₂ AND H₂O

R. H. Tipping
Department of Physics and Astronomy
University of Alabama
Tuscaloosa, AL 35487

and

Q. Ma
Department of Applied Physics
Columbia University and
Institute for Space Studies, Goddard Space Flight Center
New York, NY 10027

ABSTRACT

Within the formalism developed previously for the calculation of the far-wing line shape for molecular systems, most of the computer resources were used to diagonalize the anisotropic potential-energy matrix whose size is determined by the number of states included. For systems of interest in atmospheric studies, e.g. CO₂ and H₂O, this limited the number of states that could be included and the accuracy attainable. Recently, a new formalism has been developed in which the eigenfunctions of the orientations of the system are chosen as the basis functions. Both the anisotropic interaction and the dipole moment function are diagonal in this system and as many states as desired can be included. In this new formalism the sums over the initial and final states of the system become integrals over the orientational variables. By choosing reasonable resolutions of the integrands, one can carry out the calculations within modest computational time. Results for self- and foreign-broadened CO₂ and H₂O have been obtained. Using these results one can then easily calculate the corresponding far-wing absorption, and new results will be presented and compared with experiment.

INTRODUCTION

In order to make forward calculations of the effects of the Earth's atmosphere on the transmission of radiation and to use these to extract useful atmospheric profiles from measurements, one must have a transmission code (for instance, a line-by-line code such as FASCOD3, or lower resolution codes such as MODTRAN or LOWTRAN) and a molecular data base (for instance, HITRAN96). This data base must contain information on the frequencies and intensities for all the transitions of interest for the atmospheric species, together with information about the line shape. For many applications one can assume pressure-broadened Lorentzian line

shapes (or possibly Voigt profiles) and one must then know the temperature-dependent half widths and pressure shifts. However, in some cases, the above information is not sufficient to calculate accurate synthetic spectra; in particular, in the regions of Q-branches or in the far wings of the rotational or vibration-rotational bands. In the former case, the phenomenon of line-mixing¹ must be included, while in the latter case, the significant deviation of the true line shape from a Lorentzian shape must be known.² In practice, most of the radiation codes truncate the wings of the Lorentzian line shapes (e.g. at $\pm 25 \text{ cm}^{-1}$ from the line center) and incorporate the remaining absorption that varies smoothly with frequency as a "continuum" correction. In this regard, the self- and N_2 -broadened continua are the most important and lead to significant improvements in the modeling.³ In the present work, we outline some recent theoretical calculations of the far-wing line shape and calculate the corresponding absorption for CO_2 and H_2O to illustrate the importance of these types of calculations.

THEORY

Before presenting the results, we present a brief description of the theory. The absorption coefficient $\alpha(\omega)$ per unit volume at frequency ω (cm^{-1}) for a gas at temperature T is given by

$$\alpha(\omega) = \frac{4\pi^2 n_a \omega}{3\hbar c} \tanh(\beta\hbar\omega/2) [F(\omega) + F(-\omega)] \quad (1)$$

where $\beta = 1/kT$ and n_A is the number density of absorbers. The spectral density $F(\omega)$ is the Fourier transform of the dipole moment correlation function

$$F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(t) e^{-i\omega t} dt \quad (2)$$

$$C(t) = \text{Tr} [\rho \mu^\dagger(0) \cdot \mu(t)], \quad (3)$$

where

$$\vec{\mu}(t) = e^{iHt/\hbar} \vec{\mu}(0) e^{-iHt/\hbar} \quad (4)$$

and

$$\rho = \frac{e^{-\beta H}}{\text{Tr} [e^{-\beta H}]} \quad (5)$$

By introducing the Liouville operator L for the total Hamiltonian, H , defined by

$$L \vec{\mu}(t) = [H, \vec{\mu}(t)] / \hbar , \quad (6)$$

one can formally write the spectral density as

$$F(\omega) = \frac{1}{\pi} \text{Re Tr} \int_0^{\infty} \vec{\mu}^\dagger(0) \cdot \sqrt{\rho} e^{i(\omega - L)t} \sqrt{\rho} \vec{\mu}(0) dt . \quad (7)$$

Then for the far-wing case, one makes the quasistatic approximation in which the translational motion is treated classically. Furthermore, assuming that all the lines have the same (band-average line shape), one can write $F(\omega)$ in the form⁴

$$F(\omega) = \pi^{-1} \sum_{\omega_{ij} > 0} e^{-\hbar(\omega - \omega_{ij})/2kT} \left\{ \frac{1}{(\omega - \omega_{ij})^2} \chi(\omega - \omega_{ij}) + \frac{1}{(\omega + \omega_{ij})^2} \chi(\omega + \omega_{ij}) \right\} . \quad (8)$$

The χ functions can be calculated from first principles from knowledge of the interaction potential. In the present work, this is carried out by a multi-dimensional integration.⁵

RESULTS

The results for the line shape function $\chi(\omega)$ for $H_2O - H_2O$ for $T = 296$ K is shown in Fig. 1. As can be seen from Eq. (8) above, if the shape were Lorentzian in the far wing, $\chi(\omega)$ would be a horizontal line; clearly this is not the case as the far wing shape falls off exponentially with frequency displacement. Furthermore, it is super-Lorentzian in the near wing. In Fig. 2 we compare the corresponding theoretical absorption (denoted by the Δ) to the experimental laboratory results of Burch et al.⁶ for the high frequency wing of the pure rotational band. This region is important in the atmosphere because the Earth's blackbody curve peaks in this region. As can be seen, there is substantial agreement over several orders of magnitude, and given the difficulty of measuring the very weak absorption near the minimum around 1000 cm^{-1} , one sees that the agreement is very good overall. Because the empirical "continuum" corrections in the existing radiative transfer codes are based primarily on this data, one concludes that the theoretically calculated continuum is in good agreement with the current models. Similar comparisons for $CO_2 - CO_2$ at two different temperatures are shown in Fig. 3 and compared to laboratory measurements denoted by the + symbol) in the high-

frequency wing of the ν_3 band. This spectral region is important in the retrieval of CO_2 abundances and distribution. Also shown are the results for the absorption calculated assuming a Lorentzian shape (dashed line). It is clear from this figure that one calculates far too much absorption in the wing of the band by using the Lorentzian shape, and that for accurate modeling in this spectral region, one needs to use a more accurate line shape for CO_2 .

CONCLUSIONS

In order to calculate accurate absorption in the wings of the pure rotational and vibration-rotational bands, one has to utilize a line shape that deviates substantially from that of the Lorentzian shape which gives good results only near the band centers. For atmospheric spectra, this is important for H_2O and CO_2 bands as these dominate the infrared spectral absorption. These line shapes can then be used to calculate the "continuum" correction necessary in radiative transfer codes in order to get agreement between atmospheric spectra and synthetic spectra. Until recently, such corrections had to be made using empirical data and often had to be extrapolated to atmospheric conditions. Recently, by calculating the line shape within the quasistatic approximation by carrying out multidimensional integrals, one can now obtain accurate theoretical results which can be used to refine the empirical continuum corrections.

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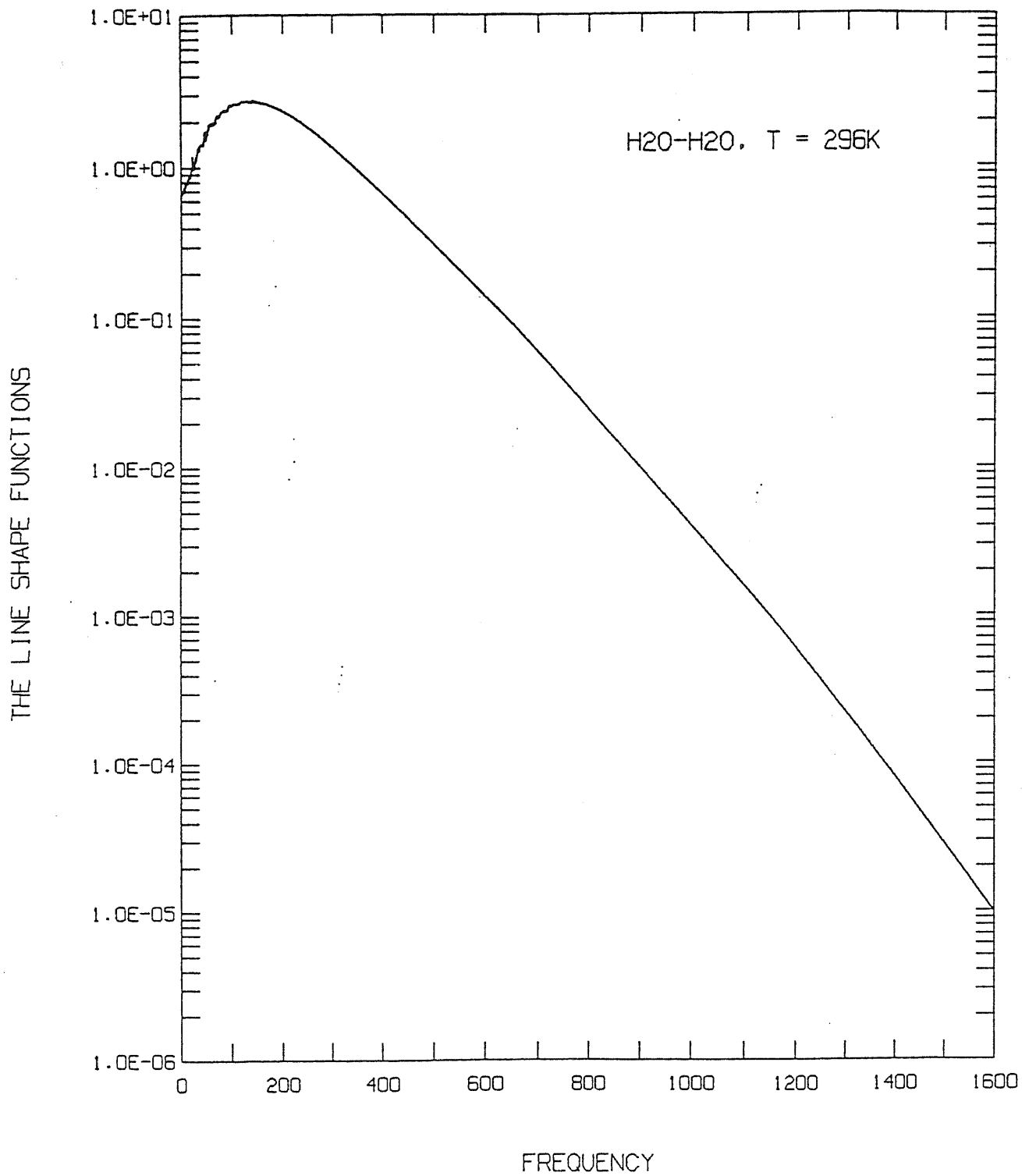


Figure 1. The band-average line shape function for H₂O - H₂O.

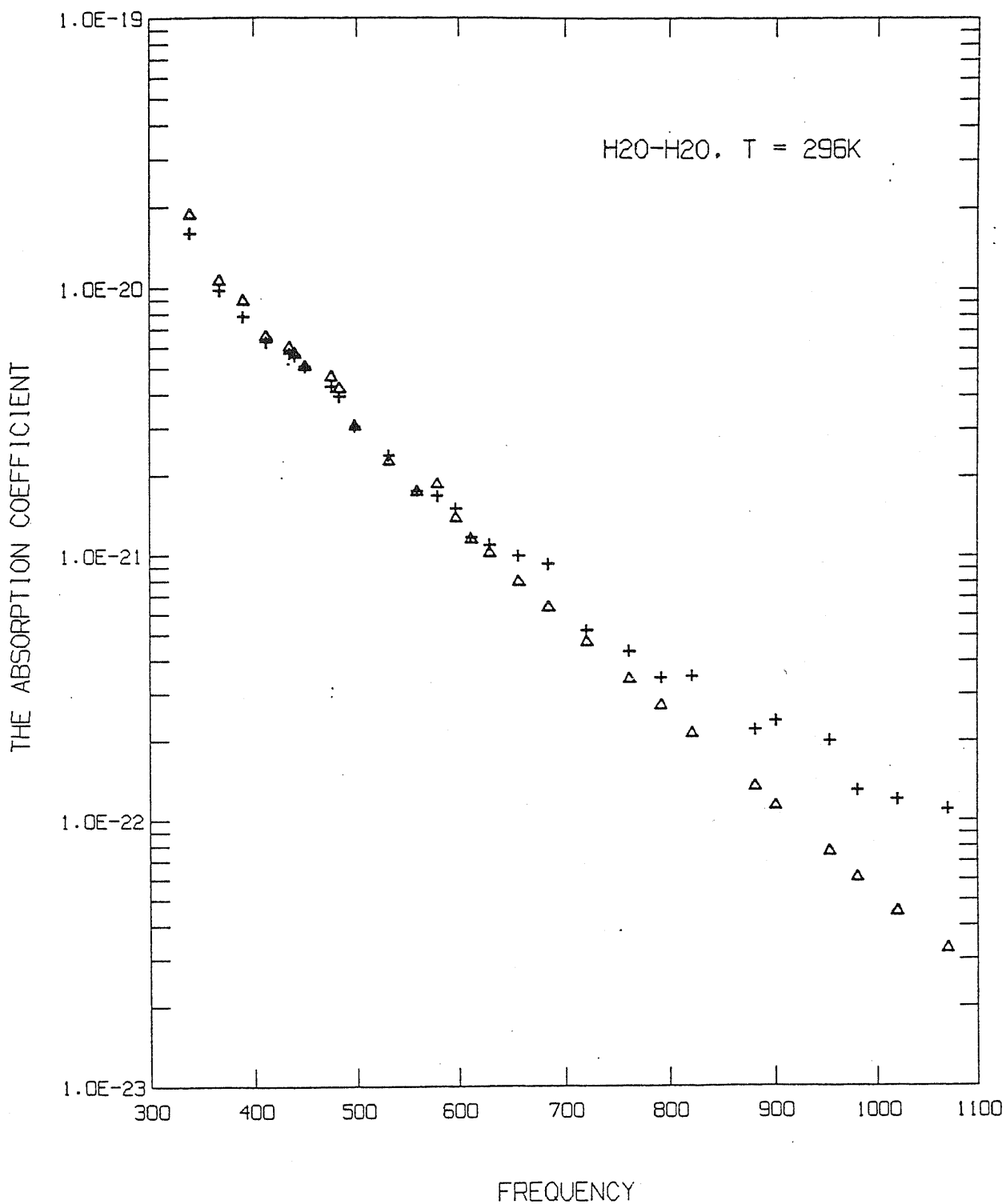


Figure 2. The absorption coefficient $\alpha(\omega)$ in units of $\text{cm}^2 \text{ molecule}^{-1} \text{ atm}^{-1}$ versus frequency in cm^{-1} for $\text{H}_2\text{O} - \text{H}_2\text{O}$ at $T = 296 \text{ K}$.

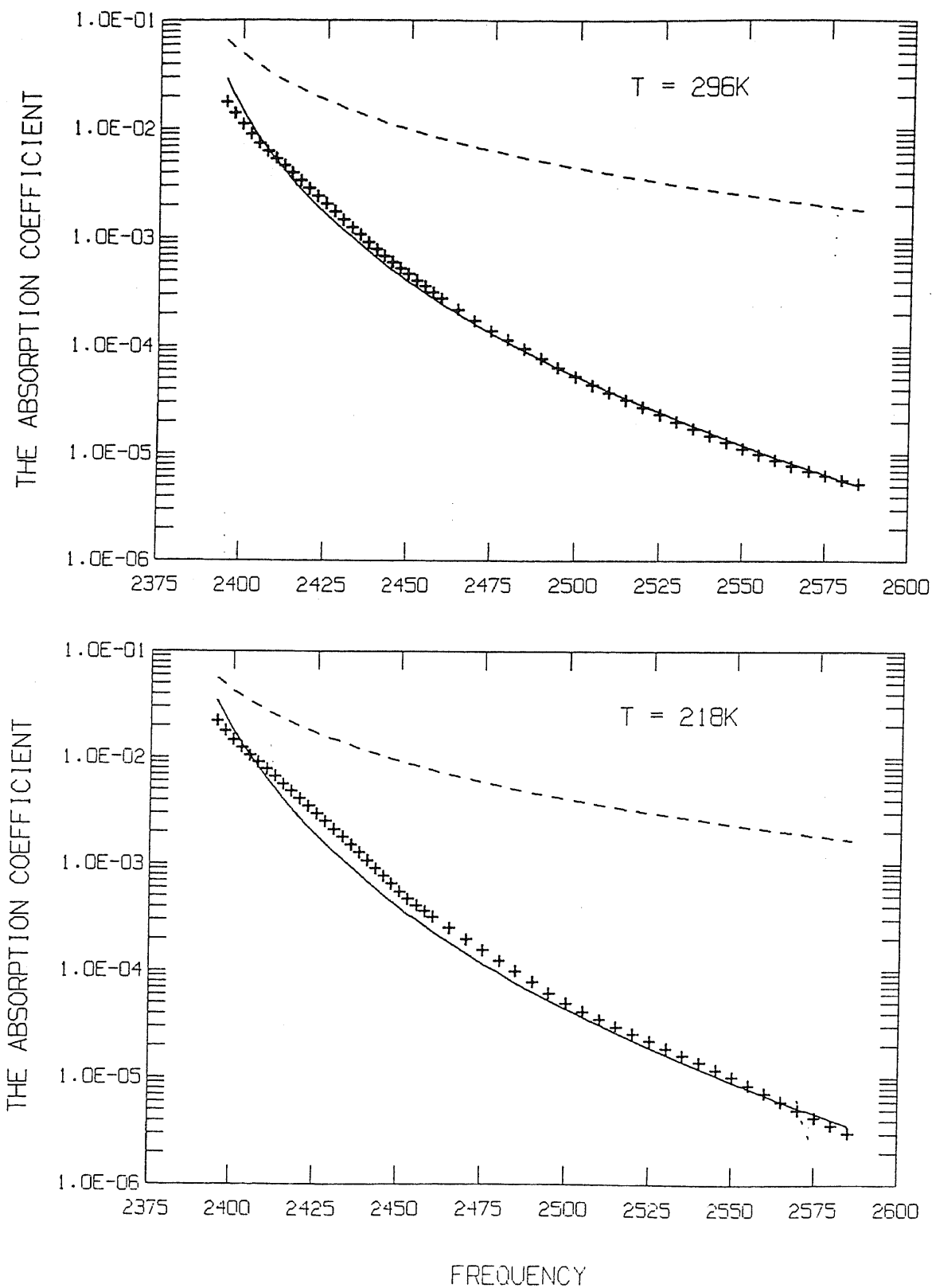


Figure 3. The absorption coefficient $\alpha(\omega)$ in units of cm^{-1} amagat $^{-2}$ versus frequency in cm^{-1} for $\text{CO}_2 - \text{CO}_2$ at two temperatures.