The binary collision-induced second overtone band of gaseous hydrogen: Modelling and laboratory measurements

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Abstract

Collision-induced absorption (CIA) is the major source of the infrared opacity of dense planetary atmospheres which are composed of nonpolar molecules. Knowledge of CIA absorption spectra of H_2-H_2 pairs is important for modelling the atmospheres of planets and cold stars that are mainly composed of hydrogen. The spectra of hydrogen in the region of the second overtone at 0.8 μm have been recorded at temperatures of 298 and 77.5 K for gas densities ranging from 100 to 800 amagats. By extrapolation to zero density of the absorption coefficient measured every 10 cm^{-1} in the spectral range from 11100 to 13800 cm^{-1}, we have determined the binary absorption coefficient. These extrapolated measurements are compared with calculations based on a model that was obtained by using simple computer codes and lineshape profiles. In view of the very weak absorption of the second overtone band, we find the agreement between results of the model and experiment to be reasonable.

1 Introduction

Accurate knowledge of certain collision-induced absorption continua of molecular pairs such as H_2-H_2 is a prerequisite for most spectral analyses and modelling attempts of atmospheres of planets and cold stars. Dense, natural atmospheres, even those composed of nonpolar molecules, do absorb infrared radiation in various rotovibrational bands that may be forbidden by dipole selection rules in the isolated molecules. Collision-induced absorption arises from intermolecular interactions of two (or more) molecules; it is a supermolecular process that has been studied in great detail in various dense gases, especially in hydrogen (Welsh, 1972).

Collision-induced rototranslational (RT) bands are known in the far infrared and microwave regions, and rotovibrational (RV) bands, including various overtone bands, exist in the infrared and visible spectral regions (Frommhold, 1993). The astrophysical significance of CIA has long been recognized (Herzberg, 1952; Trafton, 1964; Field et al., 1966). Supermolecular absorption determines significant features of planetary atmospheres, such as the vertical temperature profile, the high-altitude haze distribution and offers opportunities for the determination of abundance ratios of helium and hydrogen, and of ortho- and para-H_2. Equally important are the collision-induced opacities for modelling the cool, dense stellar atmospheres (Linsky, 1969; Borysow, 1994).

For the analyses of such spectra, absorption profiles need to be known accu-

rately as function of frequency, density and temperature for the molecular pairs (and eventually triplets) normally encountered in such atmospheres. Most significant information of that kind is obtained by laboratory measurements of the absorption by compressed gases, but the use of laboratory spectra for the modelling of planetary atmospheres is not straightforward. The problem of interpolating (or extrapolating) the absorption coefficients measured in the laboratory at a number of fixed temperatures to the temperatures of the atmospheres cannot be done without sacrificing much of the precision of the measurement. Temperatures of interest to the planetary scientist do not generally coincide with temperatures that are conveniently used in the laboratory, which requires reliable theoretical calculations.

In recent years, a new approach has been developed that is based on a numerical integration of Schrödinger's equation, using accurate dipole and potential models as input for a rigorous computation of supermolecular absorption. For several important molecular systems (H_2-H_2 and H_2-He, for various RT and RV bands) the computational results thus obtained were shown to be consistent with almost all relevant laboratory measurements of such absorption spectra (Frommhold, 1993). Significant progress has also been made to represent the computed collision-induced spectra in a form of relatively simple, analytical expressions that model the absorption quite accurately as function of frequency, gas density and temperature.

In this paper we present new measurements and analyze the CIA spectra for

H_2-H_2 interaction in the second overtone region near 0.8 μm at ambient and at liquid nitrogen temperatures. The spectra were recorded with a Fourier-Transform (FT) spectrometer by using two high-pressure absorption cells. From these results we extracted the binary absorption coefficients in the frequency range from 11100 to 13800 cm^{-1}. The experimental and data reduction procedures have been described in detail previously (Brodbeck *et al.*, 1998) and are briefly presented in the next section. Model spectra (Fu and Borysow, 1998) closely reproducing the quantum calculations are compared with our experimental data. This work is of interest for modelling the atmospheres of the major planets. Indeed, the analysis of the corresponding spectra in the second and the third overtone regions suffered from the lack of precise H_2 collision-induced band profiles.

2 Experimental Results

Few experiments were devoted to the second overtone band of H_2 (Herzberg, 1952; Hunt, 1959; McKellar, 1971; Reddy, 1995), as it is very difficult to measure accurately this weak absorption band which requires very long optical path lengths and/or high gas densities

The set of infrared experiments has been carried out on a Bruker IFS 66V FT spectrometer with a resolution (full width at half maximum) of 0.5 cm^{-1}. Two high-pressure absorption cells constructed of stainless steel and equipped with sapphire windows contained the hydrogen gas were used to record the absorption

profiles at ambient (298 K) and low (77.5 K) temperature. This work only deals with normal hydrogen, i.e., with an ortho-para H_2 abundance ratio equal to 3:1. The densities ρ of H_2 were obtained (in amagat (Am) units) from the initial pressure and temperature of the gas by using EOS tables (Johnson, 1982).

The absorption coefficient $k(\nu)$ at the wavenumber ν (cm^{-1}) is obtained from a measurement of incident and transmitted intensity I_0 and I_t, respectively, according to

$$k(\nu) = \ell^{-1} \ln\left(\frac{I_0(\nu)}{I_t(\nu)}\right), \tag{1}$$

where ℓ is the optical path length. For each absorption measurement $I_t(\nu)$ of the cell filled with hydrogen at the pressure P, a background spectrum $I_0(\nu)$ was recorded either with the cell emptied or filled with the same pressure P of helium, because the deformation of the cell under pressure may slightly change the radiation intensity.

In the case of binary collisions, the intensity of collision-induced absorption varies as the square of the density. Assuming that binary collisions are predominant in our experimental conditions, we thus define an absorption coefficient normalized by the squared gas density as

$$\alpha(\nu) = k(\nu)/\rho^2. \tag{2}$$

In Figs. 1 and 2 we present few spectra chosen among twelve at room temperature and fourteen at low temperature, respectively. Each figure shows three spectra $\alpha(\nu)$ obtained at different densities. It can be seen that the band profiles, $\alpha(\nu)$,

vary significantly with density ρ. Since in the binary regime $\alpha(\nu)$ is invariant of density, the variations of profiles observed in the figures indicate that the effects of many-body collisions are not negligible at the used gas densities. Thus the spectra under study were smoothed, and their absorption coefficients $\alpha(\nu)$ were determined at frequency spacing of 10 cm^{-1} with the help of a spline interpolation technique.

To derive, from our measurements, the binary absorption coefficients $\alpha_0(\nu)$ of H$_2$ in the second overtone region, it was thus necessary to extrapolate the data of $\alpha(\nu)$ to $\rho = 0$. For each frequency ν considered, we studied the variation of α with the density as a linear, and as a quadratic dependence such as

$$\alpha(\nu) = \alpha_0(\nu) + \alpha_1(\nu)\rho, \tag{3}$$

and

$$\alpha(\nu) = \alpha_0(\nu) + \alpha_1(\nu)\rho + \alpha_2(\nu)\rho^2. \tag{4}$$

From consideration about the relative errors on $\alpha_0(\nu)$, we have finally derived smooth values of the binary absorption coefficients $\alpha_0(\nu)$ of H$_2$ in the second overtone band region as follows:

(i) for the spectra at 298 K we have only considered the linear extrapolations;

(ii) for the spectra at 77.5 K we have mainly considered the linear extrapolations in a limited density range (up to 550 Am).

The results of the binary absorption coefficient $\alpha_0(\nu)$, along with the estimated

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uncertainties, are shown in Figs. 3 and 4 and are compared with the results obtained from the model described hereafter.

3 Computational model

Based on the quantum mechanical theory presented in our recent papers (Fu *et al.*, 1998; Brodbeck *et al.*, 1998), we have attempted to construct a computational model of the CIA in the second overtone range of hydrogen (roughly 11000 – 14000 cm^{-1}). Its purpose is, while reproducing available measurements as well as possible, to enable planetary scientists to make predictions of the absorption intensities of this CIA band at temperatures between 20 to 300 K.

Collision induced absorption intensities depend upon the interaction induced dipole moments and the intermolecular interaction potential. In our computations we assumed an isotropic interaction potential, and we neglected its dependence upon vibrational states v of two colliding H_2 molecules. We have used extended induced dipole moments database (see Tables I,II,V on WWW[1] and Fu *et al.* (1998)) which allowed us to compute CIA spectra for the second overtone band. Accordingly, we were able to account fully for the v, j dependence of essential dipole functions, with j denoting the rotational molecular state.

Basically, we have followed the same procedures as outlined in Fu *et al.* (1998), with the difference that instead of the exact quantum mechanical translational

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[1]http://www.astro.ku.dk/~aborysow/ H2_dipole_CIA_LT/

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profiles, $G^{(so)}_{\lambda_1,\lambda_2,\Lambda,L}(\omega;T)$, we have used carefully selected analytical model line-shapes. For the quadrupole–induced terms, i.e. those with $\lambda_1,\lambda_2,\Lambda,L = 2023$, 0223, and 2233 we have chosen BC (Birnbaum and Cohen, 1976) lineshapes as reproducing the quantum profiles, $G(\omega;T)$, best. For the overlap–type terms, i.e. those with $\lambda_1,\lambda_2,\Lambda,L = 0001$ and 0221, K0 (Borysow et al., 1985) model lineshapes turned to be more adequate. Both BC and K0 are three parameters lineshapes. For a very weak term, 2021, we were able to compute only two parameters, and thus we adopted a new lineshape, which we decided to call K1 (Borysow and Borysow, 1987).

The parameters of all above-mentioned lineshapes have been obtained from the three (or only two, in case of K1 lineshape) lowest quantum mechanical spectral moments, $M^{(so)}_{i,\lambda_1,\lambda_2,\Lambda,L}$, $(i = 0, 1, 2)$. Similarly to how we computed our quantum mechanical CIA intensities at 77.5 K and at 298 K, also in the model we accounted for the j-dependence of the transition matrix elements of collision induced dipole moments responsible for the 0-3 and (0-1)&(0-2) vibrational transitions. The construction of the current model is equivalent to that used by us before, see for example Zheng and Borysow (1995), which describes similar model for the first overtone band.

We have written a Fortran program (Y. Fu, 1998, copyright, (Fu and Borysow, 1998), to be available via e-mail from A. Borysow[2]). The program corresponds to

[2]aborysow@nbi.dk

the described model, and to the results presented here. Required input includes the frequency range and temperature only. The model agrees very well with exact quantum mechanical results. However, just as it can be seen from comparison of our theory with experimental data, also the model agrees with those data within 30%, or even worse at few selected frequencies. The reason for such a weak agreement remains uncertain, but can be traced to the seriousness of our assumptions and to the accuracy of our dipole moments; for discussion refer to Fu *et al.* (1998) and Brodbeck *et al.* (1998).

In Figs. 3 and 4, we present the comparison of the model with our new experimental data. We also present (Fig. 5) current model predictions of the CIA absorption intensities at few selected temperatures of potentially planetary interest.

Certainly, an advantage of a model based on (fixed) physical input data, such as dipole moments and interaction potential function, gives predictions of intensities at various temperatures other than experimental data, which follow physical laws and may be more dependable than those of any *ad hoc* model obtained from simple parametric fitting of the measured data. However, due to the obvious weaknesses of the presented model we are attempting to improve it semi-empirically, so that it fits the experimental data more precisely, and yet still follows the quantum theory. When such a model is obtained, we plan to publish it and disseminate its improved version.

Acknowledgements

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Figure Captions

Figure 1. Measured absorption spectra of H_2 at 298 K for three densities: (—) 234.3 Am, (- - -) 438.5 Am, ($\cdots$) 549.5 Am.

Figure 2. Measured absorption spectra of H_2 at 77.5 K for three densities: (—) 347.5 Am, (- - -) 663 Am, ($\cdots$) 809.7 Am.

Figure 3. Comparison of our extrapolated measurements of $\alpha(\nu)$ at 298 K and their estimated error bars with the calculated results from the model (o).

Figure 4. Comparison of our extrapolated measurements of $\alpha(\nu)$ at 77.5 K and their estimated error bars with with the calculated results from the model (o).

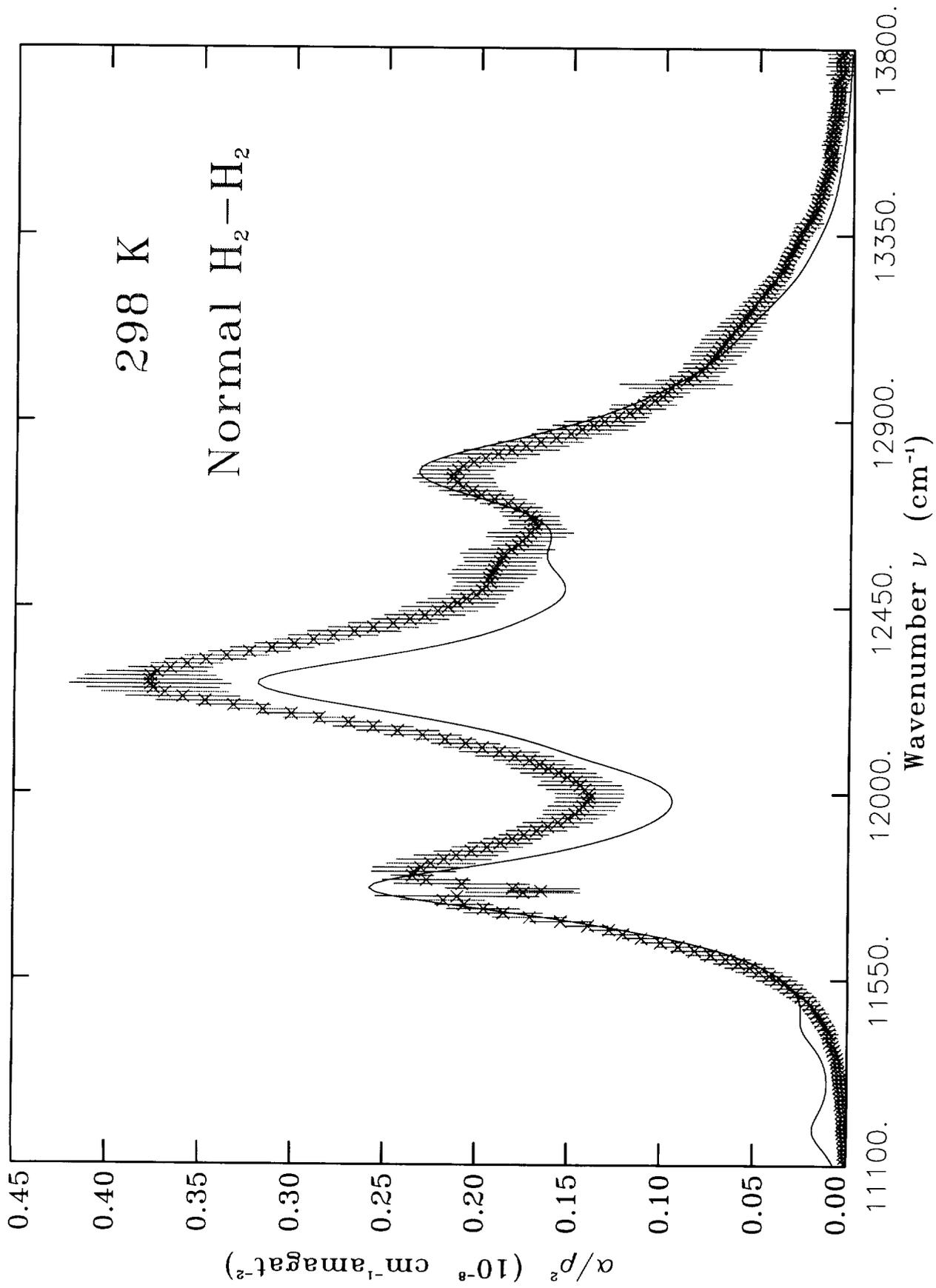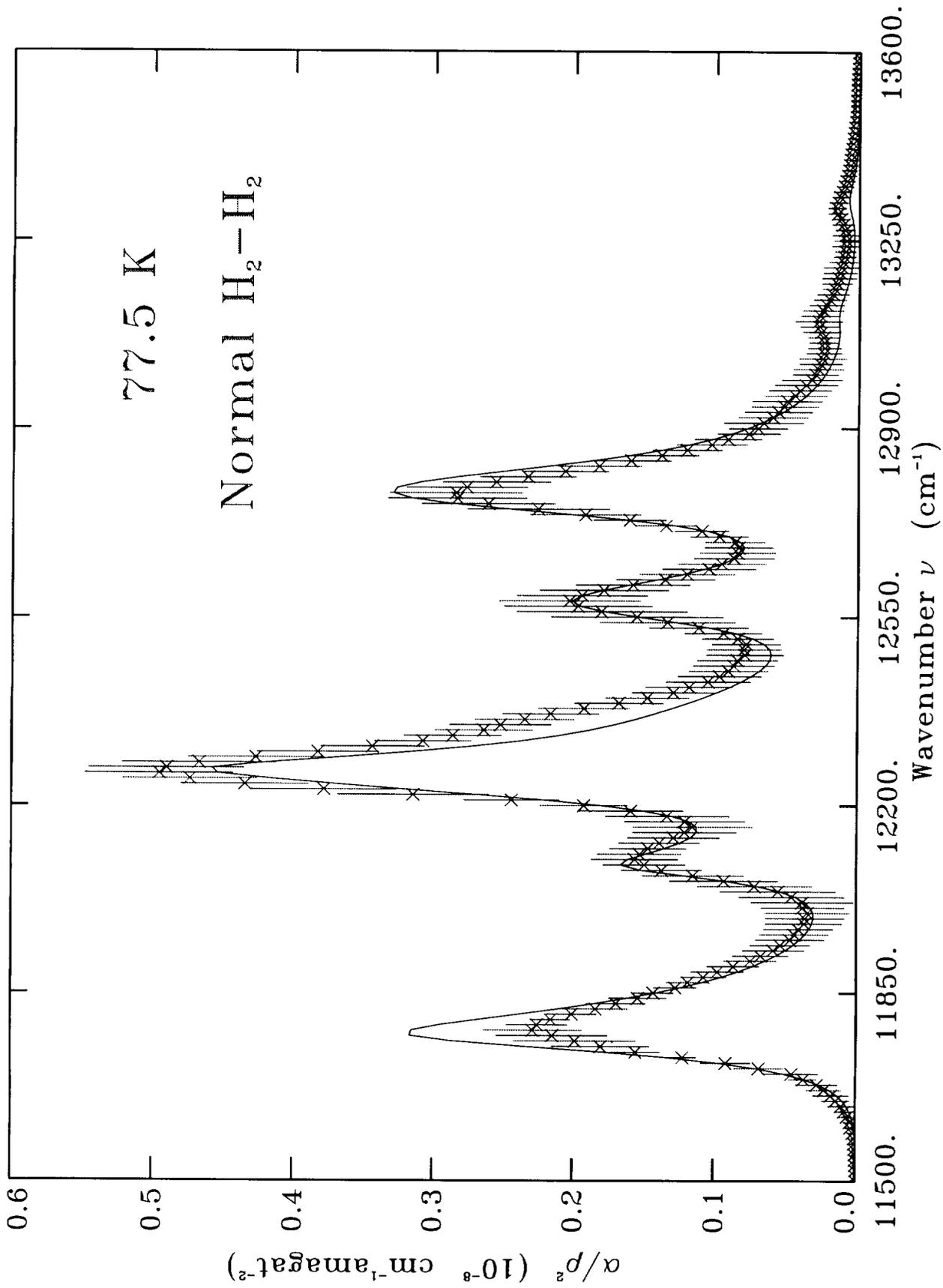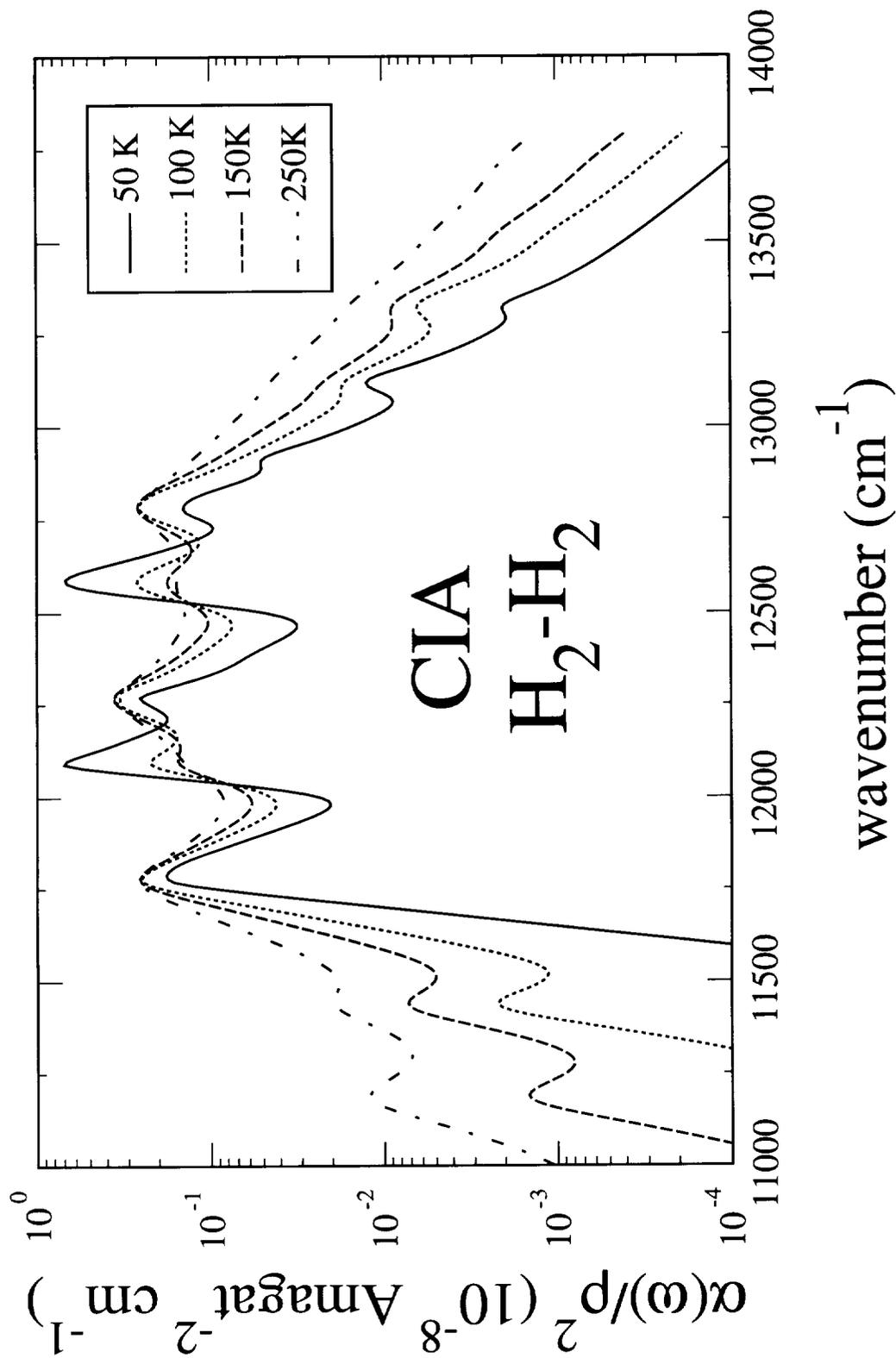Figure 5. Computed results of H_2 at 50, 100, 150, and 250 K from the model.

Fig 3

77.5 K

Normal H_2-H_2

α/ρ^2 (10^{-8} cm^{-1}amagat^{-2})

Wavenumber ν (cm^{-1})

Fig. 4

CIA
H₂-H₂

Fig 5