Computational Model of Collision Induced Absorption Spectra of H_2–H_2 Complexes in the Second Overtone Band of Hydrogen at Temperatures from 20 to 500 K.

Aleksandra Borysow *

Niels Bohr Institute for Astronomy, Physics and Geophysics;

Copenhagen University Observatory, DK-2100 Copenhagen, Denmark

and Yi Fu †

Michigan Technological University; Houghton, MI 49931, USA

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*On professional leave of absence from Michigan Technological University, e–mail address: aborysow@nbi.dk

†Current address unknown

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Address for the correspondence:

Aleksandra Borysow

Niels Bohr Institute for Astronomy, Physics and Geophysics,

Copenhagen University Observatory

Juliane Maries vej 30

DK-2100 Copenhagen

Denmark

Phone: (+45) 35-32-59-81

Fax: (+45) 35-32-59-89

e-mail: aborysow@nbi.dk

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Abstract

We present a numerical method to compute the collision induced rotovibrational absorption spectra (RV CIA) of H_2–H_2 complex in the second overtone band of hydrogen, at temperatures from 20 to 500 K. The spectral region of the second overtone corresponds approximately to $\sim$0.86–0.77μm, and is often referred to as the (3-0) band. Model spectra closely reproduce the latest quantum mechanical results (Fu *et al.* 1997) which are found to agree with experimental CIA spectra typically within 20-30%. The numerical procedure described in this paper uses simple analytical model lineshapes and can generate the RV CIA spectra of H_2–H_2 with simplicity. A FORTRAN program, utilising the presented method is available at http://www.astro.ku.dk/~aborysow/programs/. This work is of interest for modelling of the atmospheres of the outer planets, especially those of Neptune and Uranus, in the near-infrared region of the spectrum.

1 Introduction

1.1 Collision Induced Absorption

Nonpolar hydrogen molecules do not absorb electromagnetic radiation in the infrared region of the spectrum on their own. However, at sufficiently high gas densities, collisionally interacting H_2–H_2 pairs absorb significantly in the broad vicinity of rotovibrational (RV) lines of H_2 due to dipoles induced by intermolecular interactions (Welsh, 1972). Three main mechanisms contribute to the induced dipole: the polarisation of one H_2 molecule in the quadruple field of another H_2 molecule; electron exchange in the H_2–H_2 supermolecule at near range; and the dispersion interaction. Collision–induced absorption (CIA) spectra of H_2–H_2 pairs are of considerable interest for studies of the stellar (Borysow, 1994; Borysow and Jørgensen, 1999, to appear), as well as the planetary atmospheres (Trafton 1966; 1967; 1989; 1995; Conrath *et al.*, 1989 and Hanel *et al.*, 1992). The second overtone band of the rotovibrational CIA of H_2–H_2 pairs, typically referred to as the $\sim$0.8 μm band, or the (3-0) band, is associated with two cases, a "single" vibrational transition $v_1 = 0 \rightarrow 0, v_2 = 0 \rightarrow 3$ (or $v_1 = 0 \rightarrow 3$, $v_2 = 0 \rightarrow 0$) and the "double" vibrational transitions, $v_1 = 0 \rightarrow 1, v_2 = 0 \rightarrow 2$ (or $v_1 = 0 \rightarrow 2$ and $v_2 = 0 \rightarrow 1$), where v_i are the vibrational quantum numbers of two interacting H_2 molecules (i =1, 2). The second overtone band appears at the borderline between the near infrared and the visible spectral region, roughly between 11,000 and 13,500 cm^{-1}.

Our choice of temperatures is dictated by the potential planetary needs, and cover the temperature range from that of the cold upper atmospheric layers to that of the deep hot regions of H_2 rich atmospheres.

Existing models of the rototranslational (RT) CIA spectra of H_2–H_2 pairs (from 40 to 300 K) (Borysow et al., 1985), the RV CIA of H_2–H_2 pairs in the fundamental band (from 20 to 350 K) (Borysow, 1991; Borysow, 1993) and in the (2-0) band (from 20 to 500 K) (Zheng and Borysow, 1995) closely represent the existing laboratory measurements and permit dependable predictions of the spectra over a wide range of frequencies and temperatures. This work presents a new numerical model of the RV CIA spectra of H_2–H_2 pairs in the second overtone band at temperatures from 20 to 500 K. In this paper we will give a detailed description of the analytical method used to reconstruct the spectra. A FORTRAN program incorporating the presented procedures is available from aborysow@nbi.dk.

1.2 Historical background

The diffuse feature at 0.826 μm in the spectrum of Uranus was first observed by Kuiper (1949). It was later on identified by Herzberg (1952), based on laboratory measurements, as being the $S_3(0)$ line of the H_2-H_2 second overtone band. This discovery confirmed that H_2 is the major constituent of Uranus' atmosphere. The second overtone, despite its relative weakness in comparison with the lower H_2 overtones, was the strongest one accessible to the ground observations at that time.

Below, we will briefly review the historical development in obtaining a reliable model of the second overtone. Whereas we will cite the basic work concerned with an analysis of Uranus' and Neptune's atmospheres, which relied on

CIA spectra of the second (and also the third) H_2 overtones, we will restrict our review to early attempts in CIA modelling of second overtone band, and will only briefly mention basic discoveries related to planetary research. In this section we are concerned with sketching the background for contrasting the model presented here, with the synthetic models used until now.

Poll (1971) first computed the *integrated* absorption coefficients of various roto-vibrational spectral lines belonging to the second overtone band. He based his work on the then newly computed polarizability and quadrupole moments matrix elements. His theory was thus strictly classical as far as the origin of the induced dipole moments. His work presented the first, simple analysis of the H_2 abundance in Uranus atmosphere.

Soon after, Belton and Spinrad (1973) attempted to compute simple synthetic spectra of the second overtone band, using parametric model lineshape available at the time, and using the information available for the $S_3(0)$ line alone (as the rest of the CIA band was obscured by the strong CH_4 lines). All roto-vibrational lines have been represented by *the same*, one parameter lineshape profile, whose half width was related to temperature as $\sim \sqrt{T}$. Such crude treatment certainly could not secure accurate results, as confirmed by the authors. However, their analysis, even though adopting such simple synthetic spectrum, used, for the first time, the full frequency range of the (3-0) CIA profile, as opposed to the integrated intensity. It allowed the authors to draw more conclusions, or better, to formulate more precisely the issues regarding the uncertainty of their analysis, and point at possible ways to analyse the atmospheres of Uranus and Neptune more conclusively.

Few years later, Trafton (1976) made new, higher resolution observations of spectra of Uranus in both the second, and third CIA overtone bands of hydrogen. Subsequently he fitted the synthetic spectra to the observed spectrum. His work presents a more comprehensive analysis of the atmosphere of Uranus, than the earlier works, and draws more definitive conclusions regarding the atmospheric structure, as far as distribution of clouds in the atmosphere. Trafton's synthetic model of the second overtone CIA band resembles the one proposed by Belton and Spinrad. However, in his work, Trafton used slightly modified analytical profiles to represent the CIA spectral lines and more importantly, he used more realistic parameters, based on his more accurate line measurements. However, also this time, all the roto-vibrational lines was presented by the same model lineshape. As before, the model covered full frequency range, and offered temperature dependent spectra (where, however, only the spectral width varies with temperature).

Baines and Bergstralh (1986) attempted new synthetic modelling of CIA spectra in the second overtone. As far as the quality of the model, they attempted a very simple model, which utilised *one* single, two parametric, BC model lineshape to be used to *fit* the whole experimental spectral band at 85 K (i.e. all spectral lines), following the method outlined by McKellar and Welsh in their original paper (1971). As previously, the model assumed only quadrupole induced terms contributing to the observed spectrum of the second overtone. Although it appears to be a very crude model, their results appear quite reasonable, though their fit (and thus, the model) is unfortunately restricted to one temperature only (85 K). Nevertheless, their work further advanced the analysis of Uranus atmosphere and refined understanding of the the distribution of the Uranian haze.

Summarising, after examining previous attempts of modelling of CIA spectra, one can conclude that an accurate, temperature dependent, multi-parametric model, based on physical principles, will certainly be highly beneficial for further work on the atmospheres of all H_2-rich atmospheres.

1.3 Significance for the planetary studies

In this section we briefly review the anticipated significance of the new, improved model, having in mind the current interest in studies of planetary atmospheres, which involve the second overtone band.

The (3-0) RV CIA band contributes to the visible and the near-infrared spectra of all the Jovian planets, but it plays the largest role in determining the spherical albedo of Uranus and Neptune. For Jupiter and Saturn, clouds produce an effective reflecting surface at pressures less than 1 bar. For Uranus and Neptune, however, the global cloud is much deeper: at >2 bars for Uranus, and at >5 bars, or absent altogether for Neptune. Hence, the $S_3(0)$ and $S_3(1)$ dipole transitions at 0.826 and 0.817μm are much more prominent.

The second overtone (3-0) of H_2-H_2 (and also of H_2-He) CIA band is also significant because it is the strongest band accessible to high quantum efficiency CCD detectors, sensitive from 0.33 to 1.1 μm, which allow for high resolution spectral observations from ground based telescopes. The (3-0) spectral region is more observationally accessible because the telluric and the CH_4 absorptions are weaker at this spectral range. Previous attempts to model the (3-0) CIA described in the previous section, tried to derive the vertical haze distribution near 0.82μm. This is needed in order to interpret spectra of other lines and to derive accurate ratios of D/H and other species. The properties of and depth probed by the haze in the infrared and at the (3-0) band (near visible) wavelength regions are different because the haze cross section varies with wavelength; so the two spectral regions are complementary rather than redundant for such haze studies.

The large width of the CIA band is useful for modelling the atmospheric absorption spectra inbetween the strong CH_4 lines. The $S_3(0)$ and $S_3(1)$ lines are particularly important because they fall in a relatively rare spectral window between regions of strong methane absorption. In particular, for the 0.830μm window, $S_3(0)$ of the H_2 feature limits the depths to which one can probe into the atmospheres of Uranus and Neptune.

The use of the (3-0) and the lower overtones may help derive the temperature profile at various atmospheric depths, because CIA spectra are strongly dependent upon temperature. For example, the present estimate of the temperature of Uranus' atmosphere is currently confused by the uncertain ortho-to-para H_2 ratio, which is likely to deviate from the equilibrium value due to dynamical effects such as caused by the latent heat transfer during ortho/para H_2 conversion. Temperatures are presently deduced from the H_2 quadrupole lines and at Uranus' low temperature only the first two rotational levels of H_2 are strongly populated. The new model, giving independent estimate of the intensities of the dipole $S_3(J)$ lines, may help resolving the confusion between the temperature, and the ortho/para ratio, since line intensities are dependent in a different way on each parameter (T, ortho/para ratio).

The first overtone (2-0) is partly hidden by strong CH_4 absorption. The second overtone, which probes the Uranus and Neptune atmospheres much deeper than does the fundamental band, provides therefore complementary information on deeper atmospheric levels. The (3-0) CIA $S_3(0)$ & $S_3(1)$ transitions also overlap the hydrogen's $S_3(0)$ and $S_3(1)$ quadrapole transitions, which have been used in studies of the vertical structure of these atmospheres. Existing uncertainties in the strength of the H_2 CIA absorption at these wavelengths therefore compromised the accuracy of these studies. Improved estimates of the temperature-dependent intensities and widths of the (3-0) CIA band will allow the development of better models of the vertical structure of these atmospheres.

In addition, the WFPC2 Science Team has recently acquired Hubble Space Telescope WFPC2 images of Neptune at 0.826 and 0.830μm to further constrain the vertical structure of that planet's atmosphere. Improved model of (3-0) CIA data will be particularly important for that study.

2 Line Shape Theory - Formulas

The absorption coefficient at an angular frequency $\omega = 2\pi\nu$ (s^{-1}) arising from collision-induced dipoles in H_2–H_2 pairs can be written as (Meyer et al., 1989b):

$$\alpha(\omega) = \frac{2\pi^2}{3\hbar c} n^2\, \omega\, [1 - \exp(-\hbar\omega/kT)]\; g(\omega), \tag{1}$$

where α denotes an absorption coefficient (in cm^{-1}) and n is the number density of the gas. It is customary that the frequency is expressed in wavenumbers $\tilde{\nu}$

(cm^{-1}) as $\omega = 2\pi c\tilde{\nu}$, or $\tilde{\nu} = \lambda^{-1}$, with λ being the wavelength (cm) and ν, the frequency (s^{-1}). The density ϱ is usually expressed in units of amagat. For hydrogen n is very nearly equal to ϱN_L, with $N_L = 2.68676{\cdot}10^{19}$ cm^{-3} amagat^{-1} being Loschmidt's number. $\hbar$ denotes the Planck's constant, k is the Boltzmann constant, c is velocity of light, and T is temperature in Kelvin degrees.

The spectral density function $g(\omega)$ is given by

$$g(\omega) = \sum_{\lambda_1\lambda_2\Lambda L} \sum_{v_1 j_1 v_1' j_1' v_2 j_2 v_2' j_2'} (2j_1 + 1)\ P_{v_1 j_1}\ C(j_1\lambda_1 j_1'; 00)^2$$
$$(2j_2 + 1)\ P_{v_2 j_2}\ C(j_2\lambda_2 j_2'; 00)^2\ G^{j_1 j_1' j_2 j_2'}_{\lambda_1\lambda_2\Lambda L}(\omega - \omega_{v_1 j_1 v_1' j_1'} - \omega_{v_2 j_2 v_2' j_2'}), \tag{2}$$

where v_1, j_1 and v_2, j_2 are initial roto-vibrational, molecular states of the two interacting molecules, and a prime denotes their final states.

Isotropic interaction potential is assumed in our quantum mechanical computations. Whereas the real interaction potentials are not rigorously isotropic, such an approximation has given accurate results for molecules as small as hydrogen for the hydrogen CIA bands previously studied. Within the isotropic potential approximation $g(\omega)$ is a simple superposition of the purely translational spectral functions $G^{j_1 j_1' j_2 j_2'}_{\lambda_1\lambda_2\Lambda L}(\omega)$ (Eq. 2) shifted by the sums of molecular rotovibrational frequencies $\omega_{v_1 j_1 v_1' j_1'}$ and $\omega_{v_2 j_2 v_2' j_2'}$, which may be positive, negative, or zero. We should have in mind that whereas we explicitly denote the j_i dependence of the $G(\omega)$ functions, they are also dependent upon the vibrational transitions. In our case these are two transitions, (3-0)&(0-0) and (2-0)&(1-0). The $C(j_i\lambda_i j_i'; 00)$ are Clebsch-Gordan coefficients, and the non-negative integers λ_1, λ_2, Λ and L are the dipole expansion parameters (Meyer et al., 1989a; Meyer et al., 1989b). $P_{v_1 j_1}$ and $P_{v_2 j_2}$ are the population probabilities (Boltzmann factors) of the rotovibrational states (v, j) of the first and the second molecule, which can be written as:

$$P_{vj}(T) = \frac{g_j \exp(-E_{vj}/kT)}{\sum_{\mathrm{v}J} g_J \,(2J+1)\, \exp(-E_{\mathrm{v}J}/kT)}. \tag{3}$$

The nuclear statistical weights for molecular states of hydrogen in thermodynamic equilibrium are $g_j = 1$ and 3 for even and odd j, respectively. E_{vj} are the rotovibrational energies of the H_2 molecule, which we take from (Fink et al., 1965). The rotovibrational molecular transition frequencies are defined as $\omega_{vjv'j'} = (E_{v'j'} - E_{vj})/\hbar$.

In the computations of the collision-induced second overtone band of H_2–H_2 pairs, we considered two different vibrational transitions: single, $v_1 = v_2 = 0$, $v_1' = 0$, $v_2' = 3$ (and $v_1' = 3$, $v_2' = 0$), and double vibrational transitions, $v_1 = v_2 = 0$, $v_1' = 1$, $v_2' = 2$ (and $v_1' = 2$, $v_2' = 1$). For a given vibrational transition, spectral functions $G_{\lambda_1\lambda_2\Lambda L}(\omega)$ generally depend upon the initial, and the final rotational quantum numbers of both hydrogen molecules (Meyer et al., 1989a; Meyer et al., 1993). We thus denote them from now on as $G^{j_1 j_1' j_2 j_2'}_{\lambda_1\lambda_2\Lambda L}(\omega)$. The obvious dependence of $G_{\lambda_1\lambda_2\Lambda L}(\omega)$ upon vibrational quantum numbers is assumed throughout. For ease of notation, we suppressed the indices v_1, v_1' and v_2, v_2' as we are dealing with the second overtone band only. When it will be necessary, we'll indicate whether we refer to single, or to double vibrational transitions. At low temperatures the initial vibrational state of each molecule is always the ground state ($v_1 = v_2 = 0$). The final states are either $v_1' = 0$, $v_2' = 3$ (or $v_1' = 3$, $v_2' = 0$) for the single vibrational transition or $v_1' = 1$, $v_2' = 2$ (or $v_1' = 2$, $v_2' = 1$) for the double vibrational transitions.

For each vibrational transition and dipolar $\lambda_1\lambda_2\Lambda L$ term, functions $G^{j_1 j_1' j_2 j_2'}_{\lambda_1\lambda_2\Lambda L}(\omega)$ are found to be approximately of the same shape for all rotational transitions, while their zeroth moments (integrated intensities) are strongly j-dependent. As a result, spectral lineshapes $G^{j_1 j_1' j_2 j_2'}_{\lambda_1\lambda_2\Lambda L}(\omega)$ for a given vibrational transition can be obtained for a rotational transition characterised by $j_1 j_1' j_2 j_2'$, in the following way:

$$G^{j_1 j_1' j_2 j_2'}_{\lambda_1\lambda_2\Lambda L}(\omega) \simeq \left[\frac{M^{j_1 j_1' j_2 j_2'}_{0;\lambda_1\lambda_2\Lambda L}}{M^{j_1=j_1'=j_2=j_2'=0}_{0;\lambda_1\lambda_2\Lambda L}} \right] \; G^{j_1=j_1'=j_2=j_2'=0}_{\lambda_1\lambda_2\Lambda L}(\omega), \tag{4}$$

where the indices $\lambda_1\lambda_2\Lambda L$ denote the dipolar term and where $M^{j_1 j_1' j_2 j_2'}_{0;\lambda_1\lambda_2\Lambda L}$ and $M^{j_1=j_1'=j_2=j_2'=0}_{0;\lambda_1\lambda_2\Lambda L}$ denote the zeroth translational spectral moments defined as

$$M^{j_1 j_1' j_2 j_2'}_{0;\lambda_1\lambda_2\Lambda L} = \int_{-\infty}^{\infty} G^{j_1 j_1' j_2 j_2'}_{\lambda_1\lambda_2\Lambda L}(\omega)\; d\omega = 4\pi \int_0^{\infty} g(R)\, |\beta^{j_1 j_1' j_2 j_2'}_{\lambda_1\lambda_2\Lambda L}(R)|^2\, R^2\, dR. \tag{5}$$

In above equation R is the intermolecular distance, and $g(R)$ is the radial distribution function. The $\beta^{j_1 j_1' j_2 j_2'}_{\lambda_1\lambda_2\Lambda L}(R)$ functions used in this work have been taken from Table II in the paper by Fu *et al.* (1998, submitted) . The intermolecular potential required for the computation of the distribution function $g(R)$ is taken as $\langle 00|V(R)|00\rangle$ from Table VII of Meyer et al. (1993).

The line profiles $G^{j_1=j_1'=j_2=j_2'=0}_{\lambda_1\lambda_2\Lambda L}(\omega)$ (Eq. 4) for both single and double vibrational transitions can be accurately approximated by simple analytical functions $\Gamma_{K_0}(\omega)$ (Borysow et al., 1985) or $\Gamma_{BC}(\omega)$ (Birnbaum and Cohen, 1976).

Lineshapes $\Gamma_{BC}(\omega)$ and $\Gamma_{K_0}(\omega)$ are known from the RT CIA studies, to describe quantum mechanical profiles $G(\omega)$ fairly well. We use the same profiles here, even though our spectra are RV, and not RT, CIA bands. The reason for that is that we use the *same* initial, and final intermolecular H_2-H_2 interaction potential (as is strictly appropriate for RT CIA only). These two model lineshapes are suitable when the detailed balance condition is identically satisfied, which is not exactly the case for RV bands. For mode details the reader is referred to . Moraldi et al. (1988), Birnbaum and Borysow (1991), Borysow (1991) and Zheng and Borysow (1995). Analytical model lineshapes, 'BC' and 'K_0' are expressed below. The $\Gamma_{BC}(\omega)$ model is given as (Birnbaum and Cohen, 1976):

$$G(\omega) = \Gamma_{BC}(\omega) \; = \; M_0 \; \times \; \frac{1}{\pi} \frac{\tau_1}{1 + (\omega \tau_1)^2} \exp(\tau_2/\tau_1 + \tau_0 \, \omega) \; z \, K_1(z) \tag{6}$$

with $z = [(\tau_1^{-2} + \omega^2)(\tau_2^2 + \tau_0^2)]^{1/2}$, $\tau_0 = \hbar/2kT$.

The Γ_{K_0} model is given as (Borysow et al., 1985):

$$G(\omega) = \Gamma_{K_0}(\omega) = M_0 \; \times \; \frac{\tau_1}{\pi} \; \exp(\tau_1/\tau_2 + \tau_0 \, \omega) \; K_0(z) \tag{7}$$

with $z = [(\tau_2^{-2} + \omega^2)(\tau_1^2 + \tau_0^2)]^{1/2}$, $\tau_0 = \hbar/2kT$.

For the quadrupole–induced terms, i.e. those with $\lambda_1, \lambda_2, \Lambda, L = 2023$, 0223, and 2233 we have chosen Γ_{BC} lineshapes as reproducing best the quantum profiles $G(\omega; T)$. For the overlap–type terms, i.e. those with $\lambda_1, \lambda_2, \Lambda, L = 0001$ and 0221, Γ_{K_0} model lineshapes turned to be more adequate. Both BC and K0 are three parameters lineshapes, depending on (M_0, M_1, M_2). For a weak term 2021, we were able to compute only two spectral moments. We suspect that the reason for this difficulty lies in a strange behaviour of the $\beta_{\lambda_1 \lambda_2 \Lambda L}(R)$ functions, see Figs. 2 and 3 of Fu *et al.* (1998, submitted) . Since this two term contributes less than 5% of the total absorption spectrum, we decided to include it, but model it with a simpler, two parameter model lineshape (M_0, τ), which, in this paper, we'll call the $\Gamma_{K_1}(\omega)$ model (Borysow and Borysow, 1987).

It is expressed as follows:

If we define

$$\tau_0 = \hbar/(2kT)\,;\ \tau = \sqrt{3\tau_0(M_0/M_1)};\ \ \tau_3 = \sqrt{\tau^2 + \hbar/(2kT)^2},$$

and $z = \mid \omega \mid \times \tau_3$,

then, for $z = 0$:

$$G(\omega) = \Gamma_{K_1}(\omega) = M_0/\pi \times \exp\left[\hbar\omega/(2kT)\right] \times (\tau/\tau_3)^2 \times \tau,$$

and if $z \neq 0$ then:

$$G(\omega) = \Gamma_{K_1}(\omega) = M_0/\pi \times \exp\left[\hbar\omega/(2kT)\right]\ \times (\tau/\tau_3)^2\ \times\ \tau\ \times K_1(z). \qquad (8)$$

The functions $K_1(z)$ and $K_0(z)$ in Eqs. **??** designate the modified Bessel functions of the first, and the zeroth order respectively for which accurate approximations for numerical work exist (Abramowitz and Stegun, 1972). In the equations above, M_n denotes the quantum mechanical n-th moment $M_{n;\lambda_1\lambda_2\Lambda L}^{j_1=j_1'=j_2=j_2'=0}$.

3 Results

Quantum mechanical spectral moments $M_{n;\lambda_1\lambda_2\Lambda L}^{j_1=j_1'=j_2=j_2'=0}$ $(n = 0, 1, 2)$ have been computed at selected temperatures between 20 and 500 K, using the sum formulas (Moraldi *et al.*, 1984) . Both single, and double vibrational transitions, have been included.

To obtain these moments, the information about the vibrational state averages of the potential is required. The zeroth quantum moments depend only upon the potential of the initial state, $\langle 00|V(R, r_1, r_2)|00\rangle$. However, for the M_1

and M_2 moments, functions that specify the vibrational average of the potential for the final states are also needed (Moraldi et al., 1987), when one or both hydrogen molecules remain in the excited state. Functions $\langle 03|V(R,r_1,r_2)|03\rangle$ and $\langle 12|V(R,r_1,r_2)|12\rangle$ represent the final vibrational state averages of the H_2–H_2 interaction potential for single vibrational transition and double vibrational transitions. These functions are, however, not available for our computations, and we will use the same function $V_{00} = \langle 00|V(R,r_1,r_2)|00\rangle$, column 2 of Meyer *et al.* (1993) as initial and final intermolecular potential function instead.

Total of nine different, non-negligible spectral components are included in our computations: $\lambda_1\lambda_2\Lambda L$ = 0001, 2023, 0223 2021, and 0221 for single vibrational transition, and $\lambda_1\lambda_2\Lambda L$ = 2023, 0223, 2021, and 0221 for double vibrational transitions. All other non-accounted terms contribute together at the level of 3% of the total absorption and are here neglected.

The RV CIA spectra corresponding to the transitions $v_1 = 0 \rightarrow v_1' = 3$; $v_2 = 0 \rightarrow v_2' = 0$, and $v_1 = 0 \rightarrow v_1' = 1$; $v_2 = 0 \rightarrow v_2' = 2$, are exactly identical to those of $v_1 = 0 \rightarrow v_1' = 0$; $v_2 = 0 \rightarrow v_2' = 3$, and $v_1 = 0 \rightarrow v_1' = 2$; $v_2 = 0 \rightarrow v_2' = 1$. Therefore, we consider only the first two (out of four) cases, and multiply the results by a factor of 2. Our goal is to construct the RV CIA spectra from Eqs. 1 and 2 by modelling the spectral functions $G^{j_1j_1'j_2j_2'}_{\lambda_1\lambda_2\Lambda L}(\omega)$ using Eqs. 4, 6, 7 and 8.

Model lineshapes $G(\omega)$ have originally been designed and tested for free-free transitions only. Two bound states ($v = 0$, $l = 1$ and 2) exist for H_2–H_2 pair (van der Waals dimer), and thus produce bound-free and bound-bound transitions. While we can not model these sharp transitions, we account for them by including bound states in the spectral moments M_n. Our spectra are thus the low resolution spectra. Having in mind the uncertainties related to the input, see Sec. 4, we think that our bound-bound and bound-free features would not be enough dependable to be described by our model.

While the quantum mechanical $M_{0;\lambda_1\lambda_2\Lambda L}^{j_1=j_1'=j_2=j_2'=0}$ have been used for the computations of $G_{\lambda_1\lambda_2\Lambda L}^{j_1=j_1'=j_2=j_2'=0}(\omega)$, (i.e. for $\Gamma_{K_0}(\omega)$, Γ_{K_1} and $\Gamma_{BC}(\omega)$) we have employed the semi-classical formulas (Moraldi et al., 1984; Hartye et al., 1975) for $M_{0;\lambda_1\lambda_2\Lambda L}^{j_1j_1'j_2j_2'}$ (including $M_{0;\lambda_1\lambda_2\Lambda L}^{j_1=j_1'=j_2=j_2'=0}$) for the purpose of scaling (Eq. 4) only. The semi-classical $M_{0;\lambda_1\lambda_2\Lambda L}^{j_1j_1'j_2j_2'}$ were computed from Eq. 5 using the j-dependent, induced dipole functions $\beta_{\lambda_1\lambda_2\Lambda L}^{j_1j_1'j_2j_2'}(R)$ (Fu *et al.*, 1998, submitted) and the semi-classical radial distribution function $g(R)$ (see Appendix, Eq. 11). However, it can be seen from Eq. 5 that $g(R)$ affects $M_{0;\lambda_1\lambda_2\Lambda L}^{j_1j_1'j_2j_2'}$ and $M_{0;\lambda_1\lambda_2\Lambda L}^{j_1=j_1'=j_2=j_2'=0}$ in the same way, and therefore Eq. 4 can be expected to give good results at low temperatures because we use the *ratio* of $M_{0;\lambda_1\lambda_2\Lambda L}^{j_1j_1'j_2j_2'}/M_{0;\lambda_1\lambda_2\Lambda L}^{j_1=j_1'=j_2=j_2'=0}$ and not the absolute values of the moments. We have used semi-classical quantities in Eqs. 4 and 5 over the entire temperature range of our computations. In fact, the results are found to be highly satisfying. Whereas the zeroth moments (quantum mechanical vs. semi-classical) at the lowest temperature examined (40 K) differ typically by not more than 10% (for various terms, and various rotational – vibrational lines), the abovementioned *ratios* were found to differ by not more than 0.1–0.3% at the lowest temperature. Since the absolute values of the zeroth moments differ even less with increasing temperature, (typically only by 1% at 100 K, and vanishingly at higher temperatures), naturally the ratios follow the same tendency (and differ by less then 0.01–0.03% already at

100 K).

The parameters of the model lineshapes have been obtained from the first three quantum spectral moments M_n $(n = 0, 1, 2)$ which we computed at the temperature range from 20 to 500 K. Next, they were fitted to a parametric, temperature dependent function:

$$\log_{10} \Re(T) = B_0 + B_1 \log_{10} T + B_2 \left(\log_{10} T\right)^2 + B_3 \left(\log_{10} T\right)^3. \qquad (9)$$

In the above equation $\Re$ denotes M_0, and the time parameters τ_1, τ_2 or τ, of either function $\Gamma_{BC}(\omega)$, $\Gamma_{K_0}(\omega)$, or Γ_{K1}. The parameters B_0, B_1, B_2, B_3 are given in Tables 1 and 2 for single, and double vibrational transitions, respectively. The units of the parameters listed in the tables are: M_0 in $erg \cdot cm^6$; and τ_1, τ_2, τ in s. Thus, at any temperature between 20 and 500 K, the RV model lineshape parameters (and therefore the model lineshapes for $G_{\lambda_1\lambda_2\Lambda L}^{j_1=j_1'=j_2=j_2'=0}(\omega)$) are known. After a simple scaling procedure, Eq. 4, one obtains spectral functions $G_{\lambda_1\lambda_2\Lambda L}^{j_1 j_1' j_2 j_2'}(\omega)$ for all rotational transitions. The RV CIA spectra can next be easily computed from Eqs. 1 and 2.

3.1 Comparison of the model with experimental data

The model presented in the previous section has been computed based on the same quantum mechanical theory, and the same input as presented by Fu et al. (1998, submitted) and by Brodbeck et al. (1998, submitted). The only difference is that while in the previous papers we computed quantum mechanical line profiles $G(\omega; T)$ numerically, we have replaced them here by model lineshapes, whose parameters are based on the quantum mechanical spectral moments. Our model presented here reproduces well the quantum mechanical results at the temperatures presented in Fu et al. (1998, submitted) and in Brodbeck et al. (1998, submitted) . The differences, however, between each theoretical spectrum and experimental data are quite substantial. There are many reasons why it may be so, with the main reason being the extreme weakness of the second overtone which makes it equally difficult to be measured, as to be accurately computed. The computational difficulty lies in deriving dependable, accurate collision induced dipole moments, which would cover the required range of internuclear distances between H atoms in the H_2 molecules. It is not an easy task. The details about how such dipoles were obtained can be found in our writeup placed on WWW, at http://www.astro.ku.dk/~aborysow/H2_dipole_CIA_LT/index.html. The discussion of the complications related to our *ab initio* computations of the induced dipoles can be found therein and in our papers cited above.

In principle, the collision induced absorption coefficients for a given roto-vibrational band, depend upon sums of squares of roto-vibrational matrix elements such as:

$$\beta_{\lambda_1,\lambda_2,\Lambda,L}(R) = < v_1 j_1 v_2 j_2 | A_{\lambda_1,\lambda_2,\Lambda,L}(R, r_1, r_2) | v_1' j_1' v_2' j_2' >, \tag{10}$$

where we used, $v_1(r_1), v_2(r_2) = 0$; $v_1'(r_1)$ =3, $v_2'(r_2)$=0, (or $v_1'(r_1)$=0, $v_2'(r_2)$=3) for single vibrational transition, and $v_1'(r_1)$=1, $v_2'(r_2)$=2, (or $v_1'(r_1)$=2, $v_2'(r_2)$=1) for double vibrational transition. j_i denotes initial and final rotational states of both hydrogen molecules (i=1, 2). $A(R, r_1, r_2)$ denotes the collision induced dipole functions, characteristic for each spherical term $\lambda_1\lambda_2\Lambda L$, depending upon intermolecular distance R, and two internuclear distances r_i, see, for example (Meyer et al., 1993).

Our model of RV CIA for the second overtone band, naturally assumes v dependence corresponding to (3-0) and (2-0)&(1-0) vibrational transitions. The j dependence, which we accounted for, gives, however, results which are not superior to the results which *neglect* j-dependence. In fact, both theoretical results do not give good agreement with measurements. The reasons for such discrepancy still remains unknown. It can be traced to accuracy of the dipole moments, and to the other assumptions we were forced to make, refer to Sec. 4. It is our intention to give the best model possible, which is based on current theory. Whereas using non-j-dependent results is physically incorrect, we decided to present both results, and compare them with existing experiments. Our computer model will allow the user to choose which variant is preferred, especially if one works in a selected, narrow spectral range, where one method may be better than the other.

Fig. 1 presents the comparison between our model and the measurements of the hydrogen second overtone band by McKellar and Welsh (1971) at 85 K for normal hydrogen. We show model intensities both with, and without j-dependence (where we take the ratio of Eq. 4 to be equal to unity). McKellar and Welsh do not comment on their experimental errors. They may, however, easily exceed 10%, as those are standard error-bars for the much more intense CIA bands. In this paper, we shall assume them to be at least 15%.

Figs. 2 and 3 show the experimental results of the second overtone band, measured recently by Brodbeck et al. (1998, submitted) obtained at 77.5 K and 298 K, respectively. Normal H_2 is used, and the presented spectra are the *binary* spectra (i.e. the higher order contributions in density have been taken away).

Fig. 4 presents model results of the second overtone band intensities at temperatures of 50 K, 100 K, 150 K, and 250 K, for equilibrium hydrogen. We present results both, with- and without j-dependence. That gives the future user the best insight into the possible range of uncertainties in the intensities given by the model.

A user-friendly FORTRAN program has been developed utilising the described method, from which the RV CIA spectra of H_2–H_2 pairs in the second overtone band can be easily obtained with the desired temperature and the frequency range as the input. The program is useful for modelling of the planetary atmospheres, and is available at http://www.astro.ku.dk/~aborysow/programs/.

4 Approximations

An isotropic interaction potential is assumed in the quantum mechanical computations. Whereas it is not rigorously correct, such an approximation provided accurate results for molecules as small as hydrogen. It is yet to be shown if the same approximation is not too crude when vibrational states as high as v=3 are concerned, and if the anisotropy of the interaction can indeed be ignored also in this case.

We also neglected the v dependence of the interaction potential between two H_2 molecules. Such v dependent potential is not available for the vibrational states involved in this work. Again, it is hard to estimate how much uncertainty such an assumption introduces. Unlike for the fundamental band, and the first overtone band, where v dependent potentials are known, and hence accounted for, we are using the same intermolecular potential for the initial and final states. Our tests, however, performed for the first overtone band spectra indicate that the effect of neglecting the v dependence in the potential does not cause dramatic changes, when the entire absorption spectrum is considered.

In addition, the intercollisional interference is neglected here; this many body effect, which appears even at low densities, causes a (pressure-broadened) dip to occur at the center of the $Q_3(j)$ rotovibrational band ($\Delta j = 0$) as seen in experimental spectra (Brodbeck et al., 1998, submitted) . The intercollisional dip is almost symmetric at low temperatures. Its width is roughly proportional to $\sqrt{T}$ (T being the temperature) and proportional to the gas density. The intensity of the dip decreases with the decreasing temperature. Except for this narrow frequency region, the presented model describes the absorption within roughly 20–30%, but often more closely, depending on the frequency range, see Figures 1, 2 and 3.

5 Final Remarks

The model presented in this paper is based on physical input, i.e. on the "first principles". One can note, however, that the present model reproduces the experimental results with lesser accuracy (Fu et al., 1998, submitted; Brodbeck et al., 1998, submitted) than it was observed for the CIA spectra of H_2-H_2

at lower overtones (Borysow et al., 1985; Borysow, 1991; Borysow, 1993). As described in our original paper (Fu et al., 1998, submitted), the difficulties in reproducing accurately the experimental data arise equally severely on the experimental, and the theoretical sides.

One could postulate that since our model is not as dependable as the previous ones, one might have chosen an alternative route and instead of calculating the parameters from first principles, try to fit these parameters directly to the experimental data at 85, 77.5 and 298 K (McKellar and Welsh, 1971; Brodbeck et al., 1998, submitted). However, it would be an extremely difficult task, and possibly unmanageable, to fit all 9 non-negligible dipolar $\lambda_1, \lambda_2, \Lambda, L$ terms at once, and to derive a set of unique parameters. In addition, the interpolation/extrapolation method of those parameters, as a function of temperature, would be highly uncertain.

An alternative approach, successfully used by us in the past, in modelling CIA by molecular systems like N_2-N_2 (Borysow and Frommhold, 1986), N_2-CH_4 (Borysow and Tang, 1993), or CH_4-CH_4 (Borysow and Frommhold, 1987) relied on the concept of finding the unique set of temperature *independent* parameters describing the induced dipole terms, by fitting the full range of existing experimental data. Having found such a unique set to represent the dipoles, we then used basic theory to predict the spectra, together with the new input, at any desired temperature, also those different from these where experimental results are known. This method worked well when fewer $\lambda_1\lambda_2\Lambda L$ terms were present, and when each of them contributed at a somewhat different frequency region. This situation could secure more or less unique set of fitted parameters.

In view of as many as nine terms to account for, which, in addition, contribute at the same frequencies, and due to the limited number (and possibly also accuracy) of experimental data, both abovementioned approaches seemed unrealistic or unmanageable at present. What seems to have been done by earlier researchers, trying to obtain the "synthetic" spectra of the second overtone, was to fit either the early astrophysical measurements, or, later on, the only existing laboratory measurement (McKellar and Welsh, 1971), but using only *one* model lineshape. It has never been explained, how the spectrum as complex as the (3-0) band, involving nine different dipolar terms, two sets of vibrational transitions, could possibly be fit by *one* model lineshape of one, or two parameters (the differences between the models relied mainly on the choice of the model lineshape and/or on the value of the parameter(s)). Whereas such procedures did provide (Belton and Spinrad, 1973; Trafton, 1976; Baines and Bergstralh, 1986) quite satisfactory models, they could not be extrapolated to temperatures other than that of the fit, or if so, then with a great caution and uncertainty. Early models were highly unphysical, and therefore unreliable and impractical for use in radiative transfer analysis, which requires dependable predictions of the spectrum at a wide range of temperatures *and* frequencies.

These considerations led us to believe that by presenting the current model, we do make a step forward, even if the model is not as accurate as it might have been expected, based on our previous experience.

Appendix

Semi-classical distribution function, $g(R)$

In Equation 11, one must integrate the square of the dipole function, weighted with the radial distribution function, $g(R)$. The classical form of $g(R)$ is well known, $g(R) = \exp(-V(R)/kT)$ with k being the Boltzmann factor, and T the temperature (in K). However, the H_2-H_2 collisional pair should be viewed as a highly quantum mechanical system. Due to its small reduced mass one needs (especially at low temperatures) to include quantum corrections to the expression for $g(R)$. The semi-classical results obtained for the zeroth spectral moment, agree remarkably well with the quantum mechanical computations. The Wigner-Kirkwood quantum corrections, up to $\mathcal{O}(\hbar^2)$, to $g(R)$ are given by Moraldi *et al.* (1984) :

$$g(R) = \exp(-V/kT)\left[1 + \frac{\hbar^2}{24\mu(kT)^2}\left(-2V'' - \frac{4V'}{R} + \frac{(V')^2}{kT}\right)\right], \qquad (11)$$

where μ is the reduced mass of the H_2 pair. The quantities V, V', V'' denote, at a given intermolecular distance R, values of the interaction potential, and its first and second derivative, respectively.

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Table 1: Parameters of Eq. 9 for single vibrational transition $v_1v_1'v_2v_2' = 0003$. Superscripts of τ_1, τ_2, and τ stand for 'BC', 'K_0' and 'K_1' model lineshapes. M_0 in $erg \cdot cm^6$; τ_1, τ_2 and τ in s.

$\Re$	B_0	B_1	B_2	B_3
		$\lambda_1\lambda_2\Lambda L = 0001$		
M_0	-64.6632	-3.79051	1.69722	-0.237117
$\tau_1^{K_0}$	-11.8974	-1.19800	0.604604	-0.140778
$\tau_2^{K_0}$	-19.6454	12.8185	-7.74865	1.474260
		$\lambda_1\lambda_2\Lambda L = 2023$		
M_0	-64.7965	-3.18043	1.22891	-0.120397
τ_1^{BC}	-12.1305	-0.469693	-0.0484486	0.00534555
τ_2^{BC}	-12.6634	-0.1798	-0.134118	0.0170518
		$\lambda_1\lambda_2\Lambda L = 0223$		
M_0	-64.5628	-2.90725	1.1752	-0.156739
τ_1^{BC}	-10.5700	-2.77937	1.12265	-0.16634
τ_2^{BC}	-12.6675	0.297043	-0.267489	0.00264082
		$\lambda_1\lambda_2\Lambda L = 2021$		
M_0	-70.1186	1.67553	-1.51323	0.37531
τ^{K_1}	-14.4108	3.35085	-2.03575	0.327846
		$\lambda_1\lambda_2\Lambda L = 0221$		
M_0	-64.5327	-3.42757	1.39377	-0.156109
$\tau_1^{K_0}$	-12.3188	-0.386058	-0.0590297	0.0152675
$\tau_2^{K_0}$	-7.49955	-4.75913	1.50426	-0.201579

Table 2: Parameters of Eq. 9 for double vibrational transitions $v_1v_1'v_2v_2' = 0102$. Superscripts of τ_1, τ_2, and τ stand for 'BC', 'K_0' and 'K_1' model lineshapes. M_0 in $erg \cdot cm^6$; τ_1, τ_2 and τ in s.

$\Re$	B_0	B_1	B_2	B_3
		$\lambda_1\lambda_2\Lambda L = 2023$		
M_0	−64.5732	−2.93532	1.13392	−0.123712
τ_1^{BC}	−11.9119	−0.595612	0.0174677	−0.00576595
τ_2^{BC}	−12.5616	−0.179975	−0.129425	0.0152609
		$\lambda_1\lambda_2\Lambda L = 0223$		
M_0	−64.5689	−2.97008	1.15348	−0.127921
τ_1^{BC}	−11.8130	−0.741825	0.115793	−0.0310663
τ_2^{BC}	−12.6915	0.0680707	−0.291291	0.0527647
		$\lambda_1\lambda_2\Lambda L = 2233$		
M_0	−65.7947	−2.84093	1.09193	−0.122333
τ_1^{BC}	−11.7945	−0.712328	0.0745054	−0.0117238
τ_2^{BC}	−12.5353	−0.159049	−0.129466	0.0104684
		$\lambda_1\lambda_2\Lambda L = 2021$		
M_0	−65.8634	−3.26495	1.30463	−0.145022
τ^{K_1}	−12.0872	−0.251777	−0.140516	0.0232436
		$\lambda_1\lambda_2\Lambda L = 0221$		
M_0	−65.1641	−4.97074	2.15157	−0.244661
$\tau_1^{K_0}$	−13.5173	1.39961	−1.01606	0.183536
$\tau_2^{K_0}$	−9.8152	−4.75287	2.21046	−0.376787

FIGURE CAPTIONS:

Figure 1.

Comparison between the present model and the CIA spectra of normal hydrogen for the second overtone band measured (squares) by McKellar and Welsh (1971) at 85 K. Solid and dotted lines indicate model *with*, and *without* j-dependence, respectively.

Figure 2.

Comparison between the present model and the CIA spectra of normal hydrogen for the second overtone band at 77.5 K measured (crosses) by Brodbeck et al. (1998, submitted). Experimental error bars are marked. Solid and dotted lines indicate the model *with*, and *without* j-dependence, respectively.

Figure 3.

Comparison between the present model and the CIA spectra of normal hydrogen for the second overtone band at 298 K measured (crosses) by Brodbeck et al. (1998, submitted). Experimental error bars marked. Solid and dotted lines indicate the model *with*, and *without* j-dependence, respectively.

Figure 4.

Model results of the CIA RV intensities in the second overtone band, at temperature of 50 K (solid line), 100 K (dotted line), 150 K (short dashed line), and 250 K (long dashes). Thicker lines correspond to results assuming j-dependence, and corresponding thin lines show results without j-dependence. Equilibrium hydrogen is assumed.