A computational study of hydrogen dimers in giant-planet infrared spectra

Magnus Gustafsson¹, Leigh N Fletcher² and Glenn S Orton³

¹ Applied Physics, Division of Materials Science, Department of Engineering Science and Mathematics, Luleå University of Technology, 97187 Luleå, Sweden
² Department of Physics and Astronomy, University of Leicester, University Road, Leicester, LE1 7RH, UK
³ Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA
E-mail: magnus.gustafsson@ltu.se

Abstract. The absorption due to $\text{H}_2$–$\text{H}_2$ complexes is investigated theoretically. The potential and dipole surfaces for the complex are taken from the literature. Quantum dynamical calculations of the roto-translational absorption spectrum are performed. Special attention is paid to the fine features due to hydrogen dimers, $(\text{H}_2)_2$, at the centers of the collision-induced rotational $S(0)$ and $S(1)$ transitions. The computed absorption coefficients are used to analyze the spectra of the four giant planets of our solar system.

1. Introduction
Absorption of electromagnetic radiation due to a rotational transition in a hydrogen molecule is dipole forbidden. Yet, in laboratory experiments hydrogen gas absorbs radiation at frequencies corresponding to rotational transitions if the density is high, or if the absorption path length is long. The absorption is due to transient dipoles, which are induced in collisions between hydrogen molecules. In the giant planets, where competing absorbers are rare, the resulting collision-induced, or interaction-induced, absorption is the main opacity in some regions of the spectrum. The collisional pairs are in proximity for a short time, leading to broad spectral features. Two hydrogen molecules can also form bound states, so-called dimers. These are weakly bound, and play a small role in gas at room temperature where chemical equilibrium implies a small population of bound states. In the giant planets, however, the temperature is often lower, and spectral features due to dimers have indeed been observed in missions like Voyager, Spitzer, and Cassini. Since the bound states are longer lived than the collisional complexes, the dimer features are generally more narrow than the conventional collision-induced structures. The dimer absorption has been investigated both in the laboratory [1, 2] and theoretically [3, 4]. Below we briefly present a refined method for the computation of the absorption in hydrogen gas, including all free and bound contributions. More details of this work may be found in Ref. [5].
Table 1. Bound state energies in cm$^{-1}$ for two interacting para-hydrogen molecules ($j_1$ and $j_2$ are both even) with total angular momentum $J \leq 3$. The energy relative to the lowest allowed asymptote for the respective state is given in parentheses. The anisotropic Schäfer-Köhler potential, indicated with SK, from Ref. [6] has been used in this work. Values computed with the potential used in Ref. [7] are indicated with HM (Hunt-Miliordos). The isotropic part of the SK potential has been used for the values in the last column. The sole dipole allowed bound-to-bound transition in the vicinity of S(0) is indicated with an arrow.

| $J$ | parity ($l$) | symmetry ($ε$) | $E$ [SK]       | $E$ [HM]       | $E$ [SK iso]     |
|-----|-------------|----------------|----------------|----------------|-----------------|
| 0   | even        | +              | $-2.98$ ($-2.98$) | $-2.36$ ($-2.36$) | $-2.95$ ($-2.95$) |
| 0   | odd         | +              | $707.60$ ($-1.18$) | $708.09$ ($-0.68$) | $707.39$ ($-1.39$) |
| 1   | odd         | +              | $352.52$ ($-1.87$) | $353.09$ ($-1.30$) | $353.00$ ($-1.39$) |
| 2   | odd         | +              | $353.15$ ($-1.23$) | $353.63$ ($-0.76$) | $353.00$ ($-1.39$) |
| 3   | odd         | +              | $352.85$ ($-1.53$) | $353.37$ ($-1.01$) | $353.00$ ($-1.39$) |

2. Method for computation of absorption coefficients

The calculations of the absorption coefficients are divided according to the absorption mechanism. The most exact quantum dynamical calculation is carried out for the bound-to-bound transitions. Here the full anisotropic potential [6] is accounted for and the bound state energies and wave functions are computed with a discrete variable representation [8] for the radial coordinate, and a rotational basis set for the angular coordinates. The hydrogen molecules are assumed to remain in their vibrational ground state. Some of the computed eigen energies are presented in tables 1 and 2. The energy values in parenthesis, which are the actual binding energies of the bound states, are converged to a 2% level. A recent potential energy surface (HM) turns out to be insufficient in reproducing the observed bound-to-bound transitions around S(1) and thus we have decided to use the SK potential.

Table 2. As in table 1 but for two interacting ortho-hydrogen molecules ($j_1$ and $j_2$ are both odd) with total angular momentum $J \leq 1$. Two bound-to-bound transitions are supported by the anisotropic SK potential, but not by HM or SK-iso.

| $J$ | parity ($l$) | symmetry ($ε$) | $E$ [SK]       | $E$ [HM]       | $E$ [SK-iso]    |
|-----|-------------|----------------|----------------|----------------|-----------------|
| 0   | even        | +              | $233.93$ ($-3.06$) | $234.57$ ($-2.42$) | $234.03$ ($-2.95$) |
| 0   | odd         | +              | $235.95$ ($-1.04$) | $236.39$ ($-0.60$) | $235.60$ ($-1.39$) |
| 0   | even        | $-$            | $823.83$ ($-0.20$) | $-$             | $-$              |
| 1   | odd         | +              | $235.40$ ($-1.59$) | $235.92$ ($-1.07$) | $235.60$ ($-1.39$) |
| 1   | even        | $-$            | $234.01$ ($-2.98$) | $234.61$ ($-2.38$) | $234.03$ ($-2.95$) |
| 1   | odd         | $-$            | $234.94$ ($-2.05$) | $235.50$ ($-1.48$) | $235.60$ ($-1.39$) |
| 1   | odd         | $-$            | $235.62$ ($-1.36$) | $236.16$ ($-0.83$) | $235.60$ ($-1.39$) |

The total angular momentum is $J = j_1 + j_2 + l$, where $j_1$ and $j_2$ are the dumbbell angular momenta of each of the two hydrogen molecules, and $l$ is the end-over-end angular momentum of the complex. The corresponding quantum numbers are $J, j_1, j_2,$ and $l$, and these are used to label the dimer states in tables 1 and 2. Note that $J, j_1,$ and $j_2$ are good quantum numbers in
Figure 1. The absorption coefficient, normalized by the square of the hydrogen density, around the S(0) transition for equilibrium hydrogen at 77 K. The circles labeled “Birnbaum” and the line labeled “McKellar” represent measurements from Refs. [9] and [4], respectively. The latter experiment was done with a number density of 2.63 amagats. Reproduced with permission from Ref. [5].

Figure 2. Same as Fig. 1 but around the S(1) transition, at a temperature of 20 K, and with normal hydrogen. McKellar’s measurement [10] was taken at a pressure of 40 Torr, corresponding to a number density of 0.72 amagats. Reproduced with permission from Ref. [5].

the calculations with the full anisotropic calculation. In the isotropic approximation \( l \) is a good quantum number, that is why there are only two eigen energies in the columns labeled SK-iso, corresponding to \( l=0 \) and \( l=1 \). Symmetry (\( \epsilon \)) has to be accounted for. The former is (+) if the overall wave function is even with respect to exchange of any two nuclei in the \((H_2)_2\) complex, and (−) if it is odd. The parity is even/odd for even/odd values of \( l \).

For transitions involving continuum states we have decided to use the isotropic potential approximation. It has been shown that the anisotropy has only a small effect on the free-to-free contribution to the interaction-induced absorption [11, 7]. We have extended this to also include the bound-to-free and free-to-bound transitions. The continuum states are computed with the Numerov algorithm [12] and the bound states are computed with a discrete variable representation. The formulas used for the calculation of the corresponding absorption coefficients are the same, or equivalent to, those given in Ref. [2].

3. Results
In order to convince ourselves that the method outlined in section 2 is adequate we compare the computed absorption with laboratory measurements in Figs. 1 and 2. Acceptable agreement is observed, considering that the magnitude of the absolute absorption is difficult to calibrate in the experiment, and that there is some uncertainty in the potential and dipole data that goes into the calculation. In addition, the experimental dimer features may be pressure broadened.

We have computed absorption coefficients at

- 223 frequencies, from 0.1 cm\(^{-1}\) to 2400 cm\(^{-1}\)
- 8 para-\(H_2\) to ortho-\(H_2\) fractions, from 0.25 to 1.0
- 10 temperatures, from 40 K to 400 K

and the values are available as supplementary material in Ref. [5]. The dimer features decrease rapidly in strength with increasing temperature, more rapidly than the rest of the collision-induced features. This has the effect that in an observed planetary spectrum the dimer features

\[ \frac{\alpha}{\rho^2} \text{[cm}^{-1} \text{amagat}^{-2}] \]
Figure 3. Spectral fits to the S(0) and S(1) lines detected on the four giant planets, using Cassini data for Jupiter and Saturn and Spitzer data for Uranus and Neptune. The spectral models with and without bound-to-bound transitions are shown in blue and red, respectively. For details on the spectral retrieval model, including the temperature-pressure profile, see Ref. [5]. Reproduced with permission from Ref. [5].
will appear as enhanced absorption if the sensed region has a temperature that falls with increasing altitude. This is the case for example in the troposphere. In the stratosphere, on the other hand, the temperature increases with increasing altitude. Thus the dimer features appear as depleted absorption, or emission, if the observations sense stratospheric altitudes.

Fig. 3 displays model spectra, based on those absorption coefficients, compared with high-resolution observations. The emitted radiation is given as a brightness temperature, i.e. essentially as emission intensity. The observations of Jupiter and Saturn have better certainty around the S(0) transition (panels a and b) than around S(1) (panels e and f). The bound-to-free and free-to-bound absorption can clearly be identified around the S(0) transition at 351 cm$^{-1}$ and 357 cm$^{-1}$. This is the best resolved observation of those features to date. They are also seen in the observations of Uranus and Neptune (panels c and d). In Jupiter and Saturn the dimer features are seen as enhanced absorption as the observations sense a region in the upper troposphere. And in Uranus and Neptune the dimer features are seen as emission, since the observations in these cases sense higher altitudes, in the lower stratosphere.

The S(1) dimer features in Uranus and Neptune (panels g and h) are quite faint. In this case the sensed region is around the tropopause, in the transition between the troposphere and the stratosphere. Here the temperature gradient is close to zero and this is the reason for the faintness of the dimer features.

We have assumed that the spectral regions shown in Fig. 3 are completely dominated by H$_2$ and He interaction-induced absorption. There could potentially be features from water around the S(0) line and carbon dioxide around the S(1) line, but the observations do not show this. Furthermore, there are no notable features from hydrocarbons.

4. Conclusion
We have refined the available interaction-induced absorption data set for hydrogen. Dimer contributions are included, and simulations of planetary spectra show that these are crucial for satisfactory agreement with observations. Overall the required amount of out-of-equilibrium ortho/para-hydrogen fractions is lowered when the new absorption data is used as input in the simulations. There is still room for improvement in the quantum dynamical treatment. In particular, it could be investigated whether inclusion of the anisotropic potential in the bound-to-free and free-to-bound calculations would further improve the agreement in Fig. 2.

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