Hydrogen dimer features in low temperature collision-induced spectra

M Gustafsson
Applied Physics, Division of Materials Science, Department of Engineering Science and Mathematics, Luleå University of Technology, SE-97187 Luleå, Sweden
E-mail: magnus.gustafsson@ltu.se

Abstract. The absorption of radiation in pure hydrogen (H$_2$) gas around the S(0) and S(1) rotational transitions is computed at 20 K and compared with laboratory data. All transitions involving free state are included in the calculations of the absolute absorption. These calculations are done with an isotropic approximation for the H$_2$–H$_2$ pair potential. Agreement with the experiment is observed around the S(0) transition, while the computational approach appears to be slightly worse around the S(1) transition. The positions for bound-to-bound transitions are computed including the full anisotropic pair potential. The anisotropy seems to be crucial to achieve agreement with the measured bound-to-bound transition frequencies. However, these transitions contribute little to the total absorption. The present computed absolute absorptions will provide improved input for radiative transfer models of planetary atmospheres.

1. Introduction
Despite the weak attraction between hydrogen molecules, if hydrogen gas is sufficiently cool, a significant fraction of the molecules may form weakly bound van der Waals complexes. The importance of these complexes, which are also called dimers, in the absorption spectrum of hydrogen gas has long been recognized. They have been studied both theoretically and experimentally [1, 2, 3, 4], and their influence on Jupiter’s and Saturn’s spectra has been verified [1]. Recently, it has been discovered that a discrepancy on the order of 10% in the absorption coefficient is significant for the analysis of Jupiter’s atmosphere [5]. Therefore, more accurate calculations of absorption data are desired.

The influence of the dimers on the spectrum increases with decreasing temperature. There is a laboratory measurement of the hydrogen spectrum around the rotational transitions S(0) and S(1) at 20 K recorded by McKellar [4] where dimer features are quite pronounced. This temperature is admittedly lower than what is typically considered in modeling of the atmospheres of the giant planets. The measurement provides, however, an excellent testing ground for various computational treatments of the dimer features.

This theoretical study has the purpose to explore the validity of the established treatment [2] of the dimer contributions to the hydrogen spectrum. The contributions are of three different characters.

(i) Free-to-free: This can be computed with proper anisotropic potential accounted for. It has been shown, however, that the influence from the anisotropy is quite small [6, 7]. In this work we have used the isotropic potential approximation (IPA) for this contribution.
(ii) Bound-to-free and free-to-bound: This is only computed in the isotropic potential approximation in this work. Below I will discuss the limitations of this approach and possible ways to include the anisotropy of the pair potential.

(iii) Bound-to-bound: In the laboratory measurement [4] there are one and three bound-to-bound transitions detected in the S(0) and S(1) regions, respectively. For sufficient accuracy the transition frequencies are computed here with the anisotropic potential accounted for.

2. Theory

In this section the method for calculating bound states with a discrete variable representation (DVR) is outlined. It accounts for the complete anisotropic interaction potential of the H₂–H₂ pair. This is the method used for calculations of the bound states in contributions (ii) and (iii) listed above. The calculation of the absorption coefficient is done as described in Ref. [2] where the continuum wave functions are determined with a Numerov integration of the Schrödinger equation. In the present case all bound wave functions and energy levels, whether anisotropic or not, are computed with a DVR. In section 2.1 the DVR method is described for the case of two distinguishable hydrogen molecules, i.e. one para-H₂ and one ortho-H₂, which have even and odd rotational quantum number, respectively. In section 2.2 the appropriate adjustments for the case of two identical molecules will be described and in section 2.3 the selection rules for dipole transitions for hydrogen dimers are reviewed.

2.1. Bound state calculation with DVR, distinguishable molecules

Consider two interacting hydrogen molecules that remain in their electronic ground states. In a space fixed frame of reference the corresponding Hamiltonian is

\[ H(r_1, r_2, R) = H^{H-H}(r_1) + H^{H-H}(r_2) - \frac{\hbar^2}{2m} \nabla_R^2 + V(r_1, r_2, R) \]  

where \( R \) is the vector pointing from the center of one hydrogen molecule to the center of the other, and \( r_i \) is the vector pointing from one atom to the other in molecule \( i = 1 \) or \( 2 \). \( H^{H-H} \) is the rovibrational Hamiltonian of an isolated diatom, \( V \) is the interaction potential, and \( m \) is the reduced mass of the two-body system consisting of molecules 1 and 2. In this study the hydrogen molecules will remain in their vibrational ground state and a rigid rotor potential \( V(\hat{r}_1, \hat{r}_2, \hat{R}) \) is used. Thus the wave function may be expanded in angular basis functions according to

\[ \Psi_{JM}(\hat{r}_1, \hat{r}_2, \hat{R}) = \sum_\beta \frac{1}{R} F^j_\beta(R) Y^J_{M}^{JM}(\hat{r}_1, \hat{r}_2, \hat{R}) \]  

where \( \beta \) is short hand for the quantum numbers \((j_1 j_2 j)\) and \( Y^J_{M}^{JM} \) is the vector coupling function,

\[ Y^J_{M}^{JM}(\hat{r}_1, \hat{r}_2, \hat{R}) = \sum_{m_1 m_2 m_1 m_t} C(j_1, j_2, j; m_1, m_2, m_j) C(j, l, J; m_j, m_t, M) \times Y_{j_1 m_1}(\hat{r}_1) Y_{j_2 m_2}(\hat{r}_2) Y_{l m_t}(\hat{R}), \]  

\( \delta_{\beta \beta'} + V^J_{\beta \beta'}(R) \).
Both $J$ and $M$ are good quantum numbers, and the Hamiltonian is independent of $M$ [8]. For two interacting diatoms it is appropriate to expand the potential energy in angular basis functions according to

$$ V(\hat{r}_1, \hat{r}_2, R) = (4\pi)^{3/2} \sum_{\gamma_1\gamma_2\gamma_3} V_{\gamma_1\gamma_2\gamma_3}(R) \sum_{\alpha_1\alpha_2\alpha_3} C(\gamma_1\gamma_2\gamma_3; \alpha_1, \alpha_2\alpha_3) Y_{\gamma_1\alpha_1}(\hat{r}_1) Y_{\gamma_2\alpha_2}(\hat{r}_2) Y_{\gamma_3\alpha_3}(\hat{R}). \quad (5) $$

Then the integration over all spatial coordinates except for $R$, which was carried out in the derivation of Eq. (4), yields the potential energy matrix element,

$$ V_{\beta\beta'}^J(R) = \sum_{\gamma_1\gamma_2\gamma_3} V_{\gamma_1\gamma_2\gamma_3}(R) e_{\gamma_1\gamma_2\gamma_3}(J_1, J_2, J, J_1', J_2', l, l'; J), \quad (6) $$

where the coefficient, $e_{\gamma_1\gamma_2\gamma_3}$, is given in the appendix of Ref. [6].

The radial Schrödinger equation is solved by implementation of a DVR with uniform grid spacing [9] $\Delta R = (R_{\text{max}} - R_{\text{min}})/N$ and corresponding grid points $R_\alpha = R_{\text{min}} + \alpha \cdot \Delta R$ where $\alpha = 1, 2, ..., (N-1)$. This choice of grid applied to the Hamiltonian in Eq. (4) yields

$$ H_{\alpha\alpha'}^{J\beta\beta'} = \left( E_{0j_1} + E_{0j_2} + \frac{\hbar^2(l + 1)}{2m R_\alpha^2} \right) \delta_{\alpha\alpha'} \delta_{\beta\beta'} + T_{\alpha\alpha'} \delta_{\beta\beta'} + V_{\beta\beta'}^J(R_\alpha) \delta_{\alpha\alpha'} \quad (7) $$

with the kinetic energy matrix

$$ T_{\alpha\alpha'} = \frac{\hbar^2}{2m \Delta R^2} (-1)^{\alpha - \alpha'} \left\{ \frac{\pi^2}{3} - \frac{1}{2\alpha^2} - \frac{2}{(\alpha + \alpha')^2} \right\} \quad (8) $$

and diagonalization of the Hamiltonian (7) yields $(N-1)N_\beta$ eigenstates and eigenergies, $E_k$. $N_\beta$ is the number of angular momentum basis functions in the expansion, Eq. (2).

2.2. Identical molecules

Two homonuclear diatoms of the same species are distinguishable if their individual parities, $(-1)^{j_1}$, are different. This means that para-H$_2$ and ortho-H$_2$ are distinguishable molecules. On the other hand, two para-H$_2$ molecules are identical, as well as two ortho-H$_2$ molecules, and their wave functions have to be symmetrized correctly for exchange of their nuclear skeletons. Nuclear spin zero for both parts, i.e. the para-H$_2$–para-H$_2$ case, is inconsistent with an antisymmetric wave function and thus the para-H$_2$–para-H$_2$ pair comes only in symmetric states, while the ortho-H$_2$–ortho-H$_2$ pair can be both symmetric (+) and antisymmetric (−).

The angular part of the wave function for the case of a para-H$_2$ molecule interacting with an ortho-H$_2$ molecule is the angular momentum coupling function, $Y_{\beta\beta'}^{JM}(\hat{r}_1, \hat{r}_2, \hat{R})$, defined in equation (3). Using this one can construct functions that are symmetric and anti-symmetric under the exchange $(\hat{r}_1, \hat{r}_2, \hat{R}) \rightarrow (-\hat{r}_2, -\hat{r}_1, -\hat{R})$ to be used in calculations involving identical diatoms (see e.g. Ref. [4]). Using those functions potential energy matrix elements, corresponding to those given in Eq. (6) for para-H$_2$ interacting with ortho-H$_2$, can be derived for the case of identical molecules. These are given in the appendix of Ref. [6].

In the present calculations interactions that could produce spin flips are not included. Thus the $(\pm)$ symmetry is conserved in the calculations, much as a para-H$_2$ molecule cannot become an ortho-H$_2$.

2.3. Dipole selection rules

Consider first an H$_2$–H$_2$ complex which does not interact with radiation. Then total angular momentum $J$, total parity $(-1)^{J_1+J_2+l}$, diatomic parity $(-1)^{j_1}$ and symmetry, are all conserved. In dipole transitions, however, only the last two of those four constraints still hold. These are the dipole selection rules for H$_2$–H$_2$ complexes (unprimed and primed means initial and final, respectively):
Table 1. Bound-to-bound transition frequencies, in units cm$^{-1}$, around the S(0) and S(1) transitions in hydrogen predicted in the calculations described in section 2.1 together with those found in the laboratory measurement (exp).

| $j_1$ | $j_2$ | symmetry | $l, J \rightarrow l', J'$ | present calculation, $E_{k'} - E_k$ | exp [4] |
|-------|-------|----------|---------------------------|---------------------------------|--------|
| even  | even  | +        | even, 0 $\rightarrow$ odd, 1 | 352.524 $- (-2.978) = 355.502$ | 355.425 |
| odd   | odd   | -        | odd, 1 $\rightarrow$ even, 0 | 823.826 $- 235.625 = 588.201$ | 588.300 |
|        |       |          | not predicted              |                                 | 588.503 |
| odd   | odd   | -        | odd, 1 $\rightarrow$ even, 0 | 823.826 $- 234.940 = 588.886$ | 588.803 |

- Total angular momentum: $J' = J; J \pm 1$
- $j_i$ and $j'_i$ are both even or both odd for $i=1$ or 2
- Parity must change, and including the previous constraint this implies that $l$ changes from odd to even or vice versa
- In the case of identical molecules the ($\pm$) symmetry is conserved

2.4. Computational details

For the calculations of the bound-to-bound transition frequencies the DVR Hamiltonian in Eq. (7) is diagonalized with the DSYEV routine from LAPACK [10]. The experimental, rovibrational, hydrogen energy levels, $E_{v,j}$, from Ref. [11] and the $H_2$–$H_2$ anisotropic interaction potential by Schäfer and Köhler [12] are implemented. In calculations of absorption coefficients I use the isotropic component of the same potential. For the interaction-induced dipole surface the $ab\ initio$ data from Ref. [13] is used for free-to-free transitions and the data presented in Ref. [2] for free-to-bound and bound-to-free transitions.

3. Results and discussion

Table 1 shows the transition energies between $H_2$–$H_2$ bound states. One and three transitions are found in the experiment [4] in the vicinity of the S(0) and S(1) rotational transitions, respectively. One of the three latter transitions is not predicted in the calculation indicating that the potential energy surface may need improvement. A test calculation with a more recent rigid rotor potential by Milordos and Hunt, which was also used in Ref. [7] yields virtually the same frequency, 355.5 cm$^{-1}$, for the transition close to S(0). On the other hand, that potential predicts no bound-to-bound transitions close to S(1). A test calculation with the Schäfer and Köhler [12] potential and the anisotropy turned off also fails to predict the transitions close to S(1). The transition energies are clearly quite sensitive to the anisotropy of the potential. Note that in each transition the higher of the two levels is a truly bound state because the basis expansion for the corresponding parity does not contain the $j_1 = j_2 = 0$ and $j_1 = j_2 = 1$ functions for para-para and ortho-ortho, respectively, but at least one of the hydrogens must be rotationally excited.

In Fig. 1 an experimental absorption coefficient for pure para-hydrogen at a temperature of 20 K around the S(0) rotational transition is displayed together with calculations. The bound-to-bound transition frequency is indicated while the corresponding absolute absorption is not computed in this work. From the experimental data it is clear that the corresponding absorption is relatively small, however. Adding the free-to-free absorption to the free-to-bound/bound-to-free appears to give an absorption in agreement with the experiment. Fig. 1 shows the corresponding calculation around the S(1) rotational transition for normal-hydrogen. The agreement between the measured and computed absolute absorption is not as good as in Fig. 1. This may indicate that the anisotropy of the potential plays a bigger role when ortho-$H_2$ is involved.
The anisotropy of the potential could be included in the calculations of the free-to-bound/bound-to-free in order to improve the agreement with experimental data. For example it could be done with a scattering calculation with propagation of the dipole matrix element on-the-fly as in Ref. [14]. The area under the absorption curves in both Figs. 1 and 2 are, however, relatively well reproduced by the calculation. Temperatures below 40 K are normally not involved in the modeling of planetary atmospheres and there is often spectral broadening. I conclude that the present method, with isotropic interaction potential, and including free-to-free, free-to-bound, and bound-to-free transitions in the calculations of absolute absorption coefficients, is sufficient for the purpose of modeling of the atmospheres of the giant planets. The present calculation will be extended to higher temperatures so that it may be added to the presently available free-to-free data table [15, 16].

References
[1] Frommhold L, Samuelson R and Birnbaum G 1984 Astrophys. J. 283 L79 – L82
[2] Meyer W, Frommhold L and Birnbaum G 1989 Phys. Rev. A 39 2434 – 2448
[3] Schäfer J and McKellar A R W 1990 Z. Physik D 15 51 – 65 erratum: Z. Physik D 17 (1990) 231
[4] McKellar A R W and Schäfer J 1991 J. Chem. Phys. 95 3081 – 3091
[5] Fletcher L 2016 private communication
[6] Gustafsson M, Frommhold L, Bailly D, Bonanich J P and Brodbeck C 2003 J. Chem. Phys. 119 3081 – 3091
[7] Karman T, van der Avoird A and Groenenboom G C 2015 The Journal of Chemical Physics 142 084305
[8] Green S 1975 J. Chem. Phys. 62 2271 – 2277
[9] Colbert D T and Miller W H 1992 J. Chem. Phys. 96 1982 – 1991
[10] Anderson E, Bai Z, Bischof C, Blackford S, Demmel J, Dongarra J, Du Croz J, Greenbaum A, Hammarling S, McKenney A and Sorensen D 1999 LAPACK Users’ Guide 3rd ed (Philadelphia, PA: Society for Industrial and Applied Mathematics)
[11] Stoicheff B P 1957 Can. J. Phys. 35 730–741
[12] Schäfer J and Köhler W E 1989 Z. Physik D 13 217 – 229
[13] Meyer W, Borysow A and Frommhold L 1989 Phys. Rev. A 40 6931 – 6949
[14] Karman T, Miliordos E, Hunt K L C, Groenenboom G C and van der Avoird A 2015 J. Chem. Phys. 142 084306
[15] Orton G S, Gustafsson M, Burgdorf M and Meadows V 2007 Icarus 189 544 – 549
[16] Richard C, Gordon I, Rothman L, Abel M, Frommhold L, Gustafsson M, Hartmann J M, Hermans C, Lafferty W, Orton G, Smith K and Tran H 2012 J. Quant. Spectroscopy and Rad. Transfer 113 1276 – 1285