Total transition probability and spontaneous radiative dissociation of B, C, B′ and D states of molecular hydrogen[*]

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Abstract. The total radiative transition probabilities of rovibronic levels of B, C, B′ and D states of molecular hydrogen are calculated with emphasis on the dissociation fraction and the kinetic energy released in the continuum radiation process. The mixing percentages of B, C, B′ and D adiabatic states are also given. The data are calculated with the detailed transition probabilities obtained by Abgrall et al. (1993, 1994). We have included, in the present analysis, results obtained by using a recent ab initio transition moment for D − X which comprises a larger range of internuclear distances. The related data on individual transition probabilities may be obtained on request.

Key words: molecular processes — molecular data

1. Introduction

Molecular hydrogen is the main component of interstellar clouds and atmospheres of outer planets. The knowledge of the electronic transition probabilities and the corresponding wavelengths is critical for the interpretation of the corresponding VUV observations and the recent launch of the FUSE mission, whose wavelength range includes the Lyman and Werner (respectively B − X and C − X transitions) of molecular hydrogen, reinforces the need for accurate data. We have been involved recently in calculations of the discrete transitions between X, the ground electronic state, and the excited levels of B, C, B′, D states up to high values of rotational quantum number (Abgrall et al. 1993a, 1993b, 1994) and we have largely dispatched our results via electronic file

transfer. On the other hand, electronically excited hydrogen can also emit in the continuum of the ground electronic state as first experimentally demonstrated by Dalgarno et al. (1970). In fact, this continuum radiative fluorescence controls dissociation of molecular hydrogen in various astrophysical environments. In diffuse and translucent interstellar clouds, this emission takes place after radiative absorption and controls the transition between atomic and molecular gas (Stephens & Dalgarno 1972; Black & Dalgarno 1977; Abgrall et al. 1992) whereas electronic collisional excitation is the source of excitation in the atmospheres of outer planets (Liu et al. 1998). We had also calculated the continuum fluorescence spectrum up to $J = 10$ and compared successfully our theoretical results with experiments performed at the Jet Propulsion Laboratory (Liu et al. 1995; Abgrall et al. 1997). The kinetic energy released in the emergent hydrogen atoms is a heating mechanism in the considered environment (Stephens & Dalgarno 1973). In this paper we extend our previous results up to values of $J = 25$. We recall briefly the theoretical frame of our calculations in Sect. 2 and describe the ab-initio input data needed to solve the Schrödinger coupled equations in Sect. 3. Finally, we present and discuss our results. We give the electronic character percentage of the considered excited states, the calculated energy levels obtained from the eigenvalues of the equations together with the total transition probabilities, the total transition probability towards continuum and the mean kinetic energy released in the dissociation.

2. Theory

The spontaneous emission probability is given by the expression:

$$A(v_j, v_i; J_j, J_i) = \frac{4}{3\hbar^4 c^3 (2J_j + 1)} (E_{v_j J_j} - E_{v_i J_i})^3 |M_{S\alpha}|^2 \quad (1)$$

where E_{vJ} is the energy of the level (v, J), $M_{S\alpha}$ is the electric dipole matrix element between wavefunctions of

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excited $S(v_j, J_j)$ and ground electronic $X(v_i, J_i)$ states, and α indicates whether the spectroscopic branch label is P, Q or R. When the emission takes place into the X continuum states, the expression is modified as:

$$A(v_j, e_i; J_j, J_i) = \frac{4}{3\hbar^4 c^3 (2J_j+1)} (E_{v_j J_j} - E_{e_i J_i})^3 |M_{S\alpha}|^2 \quad (2)$$

where the kinetic energy of dissociating atoms e_i replaces the vibrational indice v_i. The total part of the emission which produces dissociation is:

$$A_c(v_j; J_j) = \sum_{J_i} \int_0^\infty A(v_j, e_i; J_j, J_i) de_i. \quad (3)$$

The mean kinetic energy of dissociating products is defined by:

$$\bar{E}_k(v_j; J_j) = \frac{\sum_{J_i} \int_0^\infty e_i A(v_j, e_i; J_j, J_i) de_i}{A_c(v_j; J_j)}. \quad (4)$$

The total emission probability is:

$$A_t(v_j; J_j) = A_c(v_j; J_j) + \sum_{v_i, J_i} A(v_j, v_i; J_j, J_i). \quad (5)$$

To go beyond the adiabatic approximation, we express the rovibronic wavefunction of excited states as an expansion over the electronic Born Oppenheimer (B.O.) wavefunctions. It is a good approximation to limit the expansion to the 4 B, C, B′ and D states and we write $\Phi_{SvJ} = \sum_T \Psi_{TJ} f_{STvJ}$ where S, T are dummy labels for B, C, B′ and D. Each Ψ is the product of the electronic B.O. wavefunction and the pure rotational nuclear wavefunction. We calculate the vibrational function f_{STvJ} and the energy level $E_{v_j J_j}$ by searching the eigenvalues of the coupled equations whose diagonal terms are adiabatic potentials and off-diagonal terms are rotational and radial electronic coupling matrix elements. The formalism is described in detail by Senn et al. (1988).

We define

$$\rho(T) = \int (f_{STvJ}(R))^2 dR \quad (6)$$

as the fraction of T in the state SvJ (the normalisation is such that $\rho(B) + \rho(C) + \rho(B') + \rho(D) = 1$). Except for very few cases, one value of T is preponderant and by convention, in our tables, the label S stands for the state of greatest weight.

As in Abgrall et al. (1999), the dipole matrix elements $M_{S\alpha}$ appearing in Eq. (2) are given by the expressions[1]

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[1] for M_{SQ} the $(2J_j + 1)^{1/2}$ factor was erroneously omitted in Abgrall et al. (1999) and in Abgrall & Roueff (1989). However the factor was taken into account in the calculations.

(7):

$$M_{SP} =$$
$$(J_j+1)^{1/2}\{\langle f_{Bv_j J_j}|M_{BX}|f_{Xv_i J_i}\rangle + \langle f_{B'v_j J_j}|M_{B'X}|f_{Xv_i J_i}\rangle\}$$
$$+J_j^{1/2}\{\langle f_{C+_{v_j J_j}}|M_{CX}|f_{Xv_i J_i}\rangle + \langle f_{D+_{v_j J_j}}|M_{DX}|f_{Xv_i J_i}\rangle\}$$

$$M_{SQ} =$$
$$(2J_j+1)^{1/2}\{\langle f_{C-_{v_j J_j}}|M_{CX}|f_{Xv_i J_i}\rangle + \langle f_{D-_{v_j J_j}}|M_{DX}|f_{Xv_i J_i}\rangle\}$$

$$M_{SR} =$$
$$J_j^{1/2}\{\langle f_{Bv_j J_j}|M_{BX}|f_{Xv_i J_i}\rangle + \langle f_{B'v_j J_j}|M_{B'X}|f_{Xv_i J_i}\rangle\}-$$
$$(J_j+1)^{1/2}\{\langle f_{C+_{v_j J_j}}|M_{CX}|f_{Xv_i J_i}\rangle + \langle f_{D+_{v_j J_j}}|M_{DX}|f_{Xv_i J_i}\rangle\}$$

were M_{BX}, M_{CX}, $M_{B'X}$ and M_{DX} are the real values of electronic transition moments calculated for each internuclear distance in the B.O. approximation.

3. Electronic matrix elements

We have used the ab-initio matrix elements calculated by Wolniewicz and Dressler (1988) as functions of the internuclear distance (B.O. Potential and adiabatic corrections for diagonal elements, radial coupling and rotational coupling for off diagonal elements) to solve the coupled equations. However we have slightly modified the diagonal matrix elements as indicated by Abgrall et al. (1994) by fitting them to experimental levels which are not affected by the rotational coupling (i.e. levels with $J = 0$ and levels with $J = 1$ belonging to C$^-$ and D$^-$). This procedure was necessary because the wavefunctions and energy levels are very sensitive to the relative position of zero order energy levels (i.e. the solutions of the uncoupled equations). With this method, almost all energy levels are obtained within 0.5 wavenumber of the experimental value up to high rotational quantum numbers, and the mixing between the electronic B.O. wavefunctions is improved. The electronic transition moment M_{BX} and M_{CX} are those of Dressler & Wolniewicz (1985), $M_{B'X}$ is taken from Ford et al. (1975) and M_{DX} from Rothenberg & Davidson (1967). In this latter case, only few points were available with poor claimed accuracy. Drira (1999) has recently recalculated M_{DX} with a precise interaction configuration method (MRCI) and a fine grid of internuclear distances. We have thus introduced her value in our calculations. Particular care was taken in the calculations that all matrix elements involve wavefunctions with coherent values of the relative phases and we have explicitly verified these properties with the MOLPRO software package (Knowles & Werner 1992).

4. Results and discussion

We have obtained energies and wavefunctions of all discrete levels under the dissociation limit H(1s)+H(2s) by solving the Schrödinger coupled equations. We have then calculated all the transition emission probabilities towards the levels of X state, and the emission profile towards the

X continuum for values of J up to 25. The amount of data is too considerable to be displayed on a paper form but can be sent on electronic file form if requested. Present data are shown up to $J = 10$.

Tables 1 - 6 display our calculated rovibrational energy level positions measured from the X rovibrational ground state, the total emission probabilities towards X rovibrational states, the total dissociating emission and the mean kinetic enegy $\bar{E}_k$ of the emergent H atoms. These quantities are obtained by summation of individual lines and profiles as indicated in Eqs. (3)-(5). In order to compare easily with the calculations without rotation and coupling of Stephens & Dalgarno (1973), $\bar{E}_k$ is in unit of electronvolt.

As the wavefunctions result from a superposition of B.O. states, we have indicated the fractions $\rho(B)$, $\rho(C)$, $\rho(B')$, $\rho(D)$ of the B.O. states for each rovibrational level, as defined in Sect. 2. These fractions are significantly linked to the physical properties of the included B.O. states. In most cases one ρ is dominant and it is justified to keep the classification B, C, B' D, and to label with the B.O. state of greatest weight. However for some very few rovibrational states the fraction is close to 0.5 and this classification is arbitrary, (see for example B($v = 21$, $J = 4$) in Table 1).

The C and D states have Π symmetry, and the energy degeneracy is removed by rotational coupling. We give the results for Π^+ and Π^- into separate tables.

For the + manifold with $J > 0$, B, C$^+$, B' and D$^+$ states are coupled through rotational coupling and results are obtained by solving a system of 4 equations coupled by a strong rotational coupling (B with C$^+$, D$^+$ and B' with C$^+$, D$^+$) and a weak radial coupling (B with B' and C$^+$ with D$^+$). In the case of $J = 0$, only the radial coupling (B with B') remains, and the system involves 2 equations.

A weak radial coupling (C$^-$ with D$^-$) is involved in the - manifold and the system involves then 2 coupled equations. We included the different values of $\rho(C)$ and $\rho(D)$ in the corresponding table. Stephens & Dalgarno (1972, 1973) calculated the total dissociation probabilities and the kinetic energy released in the dissociation for B and C but neglected all rotational effects and radial couplings. Significant differences are obtained for the lower vibrational levels with $J = 1$ of the C$^+$ state, due to the fact that the dissociating branch of the C B.O. state is negligible and the contamination with B is large enough to increase the dissociating branch, giving about the same energy profile as the closer B level. Interference effects which are important for individual spectral lines do not appear in the summed quantities of our tables.

4.1. The case of D state

The D B.O. state dissociates into H(1s)+H(3s). Then all the rovibrational states above the H(1s) + H(2s) limit are predissociated by the B, C and B' continua and cannot be

calculated by our method. D$^+$ is significantly predissociated by rotational coupling with B' and the corresponding levels are not observed in emission.

D$^-$ undergoes only a weak radial coupling with C$^-$ and the predissociation lifetime is sufficiently large to allow an emission line towards the ground state. It is a good approximation to neglect this coupling. Therefore we have solved the Schrödinger equation with the diagonal term only i.e. the D$^-$ potential as in Abgrall et al. (1994). The effect of the different values of the M_{DX} transition moment is shown in Table 7 for the line emitted from the D$^-$ ($v' = 3$, $J' = 1$) level. Apart from the very small values of the emission probabilities towards upper v'' X vibrational levels, the results stay within 10%. The weak values are obtained by destructive integration of oscillating functions and any small difference in the shapes or inaccuracy become significantly amplified. When the wavefunctions overlap constructively, the accuracy is expected to be better than 1%. Branchett & Tennyson (1992) have calculated the electronic transition moment with the R-Matrix method but used less configurations than Drira (1999). Glass-Maujean (1984) has used a dipole moment taken from Rothenberg & Davidson (1967), with an estimated uncertainty of 10%, and an adiabatic potential built from Kolos & Rychlewski (1981) and Lewis-Ford et al. (1977). The comparison with the measured lifetime of the D$^-$ levels for $J' = 1$ by Glass-Maujean et al. (1984) is however very satisfactory.

We compare in Table 8 the total emission probabilities, the total dissociating emission probabilities and the mean kinetic energy $\bar{E}_k$ released in the dissociated products obtained with the recent accurate values of Drira (1999) and those of Rothenberg & Davidson (1967). The two sets of results differ by about 10%. Nevertheless when the dissociative branch is very weak, the two calculations display important differences for the same reason as explained above. However we must note that it is not very important to know $\bar{E}_k$ when the dissociative branch is insignificant. In Table 8 we have also displayed the energy levels, they differ from Table 6 by a weak shift due to the small radial coupling.

5. Explanations of tables

The tables display the total emission probabilities, the total dissociation probabilities and the mean kinetic energies released in the dissociation for the rovibronic levels of B, C, B' and D states. As these states are mixed together, we have labeleled and ordered them according to the B.O. state of greatest weight.

Tables 1, 2, 4, 5:

They concern the states mixed by rotational and radial coupling, i.e. B $^1\Sigma_u^+$, C $^1\Pi_u^+$, B' $^1\Sigma_u^+$ and D $^1\Pi_u^+$.

Columns 1 and 2 give the rotational and vibrational numbers.

Columns 3-6 give the fractions of B.O. state as defined in

Sect. 2, Eq. (6). There is no mixing with C and D when $J = 0$.

Column 7 gives the term values.

Column 8 gives the total emission probability towards X ground electronic state in s^{-1}.

Column 9 gives the total dissociation probability towards X continuum in s^{-1}.

Column 10 gives the mean kinetic energy released in the dissociation in unit of eV.

Tables 3, 6:

They concern the states mixed by radial coupling only i.e. C $^1\Pi_u^-$ and D $^1\Pi_u^-$. (they don't display the predissociated levels of D above the dissociation limit H1s, H2s).

Columns 1 and 2 give the rotational and vibrational numbers.

Columns 3, 4 give the fractions of B.O. state as defined in Sect. 2, Eq. (6).

Column 5 gives the term values.

Column 6 gives the total emission probability towards X ground electronic state in s^{-1}.

Column 7 gives the total dissociation probability towards X continuum in s^{-1}.

Column 8 gives the mean kinetic energy released in the dissociation in eV.

Table 7:

We show typical changes in the emission probabilities from D when we use different published electronic transition moments $M_{DX}(R)$. Calculations displayed in this table have been made without coupling. The levels above the limit H1s, H2s are not predissociated, and are bound in this approximation. Indeed the coupling is very weak for D^- and levels above the dissociation limit are observed. We display the Q lines emitted from D $^1\Pi_u^-$, $v = 3$, $J = 1$. As for this level the emission towards continuum is negligible, the sums displayed in the last line are the total emission towards X ground state

Table 8:

We show the total emission probabilities, the total dissociation probababilities and the mean kinetic energy released in the dissociation in case of rovibronic levels of the D state without coupling under and above the dissociation limit H1s, H2s. We compare the effect of using the calculated moment of one of us (Drira 1999) in place of the moment of Rothenberg & Davidson (1967). The coupled states (B, C$^+$, C$^-$, B', D$^+$, D$^-$) should be modified proportionally to the mixing fraction $\rho(D)$ due to the coupling and Tables 1-5 show that the modification is negligible.

Columns 1 and 2 indicate the rotational and vibrational numbers.

Column 3 displays the levels'energies in unit of cm^{-1}.

Column 4 displays the total emission probability calculated with the moment of Drira (1999) in s^{-1}.

Column 5 displays the total emission probability calculated with the moment of Rothenberg & Davidson (1967) in s^{-1}.

Column 6 displays the total dissociative emission calculated with the moment of Drira (1999) in s^{-1}.

Column 7 displays the total dissociative emission calculated with the moment of Rothenberg & Davidson (1967) in s^{-1}.

Column 8 displays the mean kinetic energy for dissociation calculated with the moment of Drira (1999) in eV.

Column 9 displays the mean kinetic energy for dissociation calculated with the moment of Rothenberg & Davidson (1967) in eV.

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