

## Wavelengths, oscillator strengths and transition probabilities of the H<sub>2</sub> molecule for Lyman and Werner systems

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**Summary.** — Wavelengths, oscillator strengths and transition probabilities are calculated for the Lyman and Werner band systems of the H<sub>2</sub> molecule. Those calculations are performed for the first 15 rotational excited levels by including rotational coupling effects between the B and C electronic states. The expected accuracy should be better than 1 reciprocal centimeter for the wavenumbers.

**Key words:** molecular spectroscopy — hydrogen molecule — transition probabilities.

### 1. Introduction.

Lyman and Werner band systems of molecular hydrogen involve the ground X<sup>1</sup>Σ<sub>g</sub><sup>+</sup> state and the two excited electronic states B<sup>1</sup>Σ<sub>u</sub><sup>+</sup> and C<sup>1</sup>Π<sub>u</sub> respectively. The corresponding potential energy curves have been accurately calculated with the inclusion of relativistic and non adiabatic corrections (Bishop and Shih, 1976; Kolos and Wolniewicz, 1975; Kolos, 1975; Kolos and Rychlewski, 1976; Ford *et al.*, 1977; Dressler and Wolniewicz, 1986). Moreover the electronic dipole moments of the B-X and C-X electronic transitions have been recently recalculated by Dressler and Wolniewicz (1985).

The two excited states are furthermore coupled through a rotational non-adiabatic coupling (which is responsible of a doubling effect in the C<sup>1</sup>Π<sub>u</sub> state) recently calculated by Ford (1975) and Wolniewicz and Dressler (1988). These theoretical new results are used here to predict accurate energies, oscillator strengths and transition probabilities of the H<sub>2</sub> Lyman and Werner band systems. Such data are indeed needed in various astrophysical contexts (interstellar

matter, planetary and stellar atmospheres) and extend the widely used results of Allison and Dalgarno (1970) which were obtained without rotational angular momentum effects ( $J'' = J' = 0$ ).

### 2. Theory.

The importance of rotational coupling has been clearly demonstrated by Abgrall *et al.* (1987) subsequently referred to as paper I when these authors compare theoretical and experimental ratios of selected line intensities belonging to the Lyman and Werner band systems obtained through high resolution photoelectric recording of the vuv emission spectrum at the National 10 m VUV spectrograph of the Meudon Observatory. The theoretical frame for obtaining the total rovibronic (i.e. electronic × vibrational × rotational) wave functions is described in paper I and is only recalled rapidly.

The total wave function  $\Phi''$  related to the ground electronic X<sup>1</sup>Σ<sub>g</sub><sup>+</sup> state is written in a straightforward way in a Hund's case (a) molecular basis

$$\Phi''_e = \left( \frac{2J'' + 1}{4\pi} \right)^{1/2} \frac{1}{R} f_{xv''J''}(R) D_M^{*J''}(\varphi, \theta, 0) \Psi_x(r, R) \quad (1)$$

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$\Psi_x$  is the Born-Oppenheimer (BO) electronic wave function dependent on the electronic  $r$  and nuclear  $R$  coordinates where  $R$  is the internuclear distance ;  $f_{xv''J''}$  is the corresponding vibrational wave function.

$v''$  and  $J''$  are respectively the vibrational and rotational quantum numbers and  $D^J$  is a rotation matrix (Rose, 1957).  $\Phi_e''$  is an e type state according to the definition of Brown *et al.* (1975) from total parity properties.

The rovibronic functions related to the excited electronic  $B^1\Sigma_u^+$  states are of e parity type whereas the  $C^1\Pi_u$  electronic state contains both e and f parity type levels which are degenerate when the rotational coupling is neglected.

Excited states of e parity type are then obtained from the mixing of the two B and C electronic states through the  $\frac{L^+}{\sqrt{2}}$  rotational coupling operator.

$$\Phi'_e = \left( \frac{2J' + 1}{4\pi} \right)^{1/2} \frac{1}{R} \left\{ f_{Bv'J'}(R) D_M^{*J'}_0(\varphi, \theta, 0) \Psi_B(r, R) + \frac{1}{\sqrt{2}} f_{C+v'J'}(R) \right. \\ \left[ D_M^{*J'}_1(\varphi, \theta, 0) \Psi_C, 1(r, R) + D_M^{*J'}_{-1}(\varphi, \theta, 0) \Psi_C, -1(r, R) \right] \right\} \quad (2)$$

The rovibronic functions related to f parity type are given by the following expression :

$$\Phi'_f = \left( \frac{2J' + 1}{4\pi} \right)^{1/2} \frac{1}{R} \frac{1}{\sqrt{2}} f_{C-v'J'}(R) \times \\ \times \left[ D_M^{*J'}_1(\varphi, \theta, 0) \Psi_C, 1(r, R) - D_M^{*J'}_{-1}(\varphi, \theta, 0) \Psi_C, -1(r, R) \right] \quad (3)$$

The normalization of  $\Phi'_e$  is such that if  $\eta_B = \int_0^\infty f^2_{Bv'J'}(R) dR$  and

$$\eta_C = \int_0^\infty f^2_{Cv'J'}(R) dR$$

$$\eta_B + \eta_C = 1$$

This has the immediate consequence that excited "e" states are not pure. Most often  $\eta_B$  and  $\eta_C$  are very close to 1 so that one state is unambiguously related to a specific electronic symmetry. However exceptions do occur where the assignment of the state (and the corresponding level) to B or C electronic state is ambiguous.

Whereas  $\Phi'_e$  and  $\Phi'_f$  are obtained from the resolution of the one dimensional Schrödinger nuclear equation,  $\Phi'_e$  (i.e.  $f_B$  and  $f_C$ ) is obtained from a coupled system of second order differential equations detailed in paper I.

One obtains at the same time the corresponding eigenvalues which give the energy levels values.

### 3. Calculations.

We have calculated the eigenfunctions and eigenvalues for all possible vibrational states and the first 15 rotational angular momenta involved in the Lyman and Werner

band systems of molecular hydrogen by using the method described in paper I. Level energies which are not perturbed (i.e. f levels belonging to  $C^-$  and  $J'' = 0$  e levels) are calculated with slightly adjusted potentials in order to agree with high resolution measurements within  $1 \text{ cm}^{-1}$  (Roncin *et al.*, 1984; Dabrowski, 1984; Launay and Roncin, 1988). The wavenumbers  $\sigma$  of the various transitions are obtained from the differences between lower and upper excited energy levels. The corresponding wavelengths in the vacuum are then calculated :  $\lambda = \frac{1}{\sigma}$ .

Molecular transitions are distributed into three branches depending on the value of  $J' - J'' = \Delta J$  where ' and '' refer respectively to the excited and ground electronic states. P and R transitions ( $\Delta J = -1$  and  $\Delta J = +1$  respectively) connect only e type states whereas Q transitions ( $\Delta J = 0$ ) connect the e type lower level to f type excited level.

According to paper I different expressions arise for the electronic dipole matrix element  $M$  involved for each branch which we define as  $M^P$ ,  $M^Q$ ,  $M^R$  for P, Q, R branches.

$$M^P = (J' + 1)^{1/2} \langle f_{Bv'J'} | M_{BX} | f_{Xv''J''} \rangle + J'^{1/2} \langle f_{C+v'J'} | M_{CX} | f_{Xv''J''} \rangle \\ M^Q = \langle f_{C-v'J'} | M_{CX} | f_{Xv''J''} \rangle \\ M^R = J'^{1/2} \langle f_{Bv'J'} | M_{BX} | f_{Xv''J''} \rangle - (J' + 1)^{1/2} \langle f_{C+v'J'} | M_{CX} | f_{Xv''J''} \rangle \quad (4)$$

where  $M_{BX}$  and  $M_{CX}$  are the electronic transition moments given by Dressler and Wolniewicz (1985).

Using  $M^\alpha$  where  $\alpha = P, Q, R$ , we can give general

$$f_{v'' J'', v' J'} = \frac{2}{3(2J'' + 1)} (E_{v' J'} - E_{v'' J''}) |M^\alpha|^2$$

$$A_{v' J', v'' J''} = \frac{4}{3\hbar^4 c^3 (2J' + 1)} (E_{v' J'} - E_{v'' J''})^3 |M^\alpha|^2$$

$$= \frac{2.14 \times 10^{10}}{(2J' + 1)} (E_{v' J'} - E_{v'' J''})^3 |M^\alpha|^2$$

where all quantities  
are in atomic units.

in  $s^{-1}$  with all quantities  
in atomic units.

#### 4. Results.

Tables I, II, III give the level energy terms  $T'_{v' J'}$  in reciprocal centimeters for the first 15 rotational angular momenta  $J'$  and all possible vibrational levels of the three excited electronic levels, B, C<sup>+</sup> and C<sup>-</sup>. The origin is taken to be the ground rovibrational term of the ground state  $X^1\Sigma_g^+ g, v'' = 0, J = 0$ . The percentage of B character of the level which is defined as % B = 100η<sub>B</sub> is also given in tables I and II relative to B and C<sup>+</sup> electronic states. As mentioned in paper I, the assignment to a specific electronic state is most often unambiguous. However, some cases arise where % B is close to 50 and it is then meaningless to specify the electronic state.

Oscillator strengths from  $v'' = 0$  and emission probabilities in  $s^{-1}$  toward  $v'' = 0$  are displayed in tables IV and V for B and C according to the labelling given in the tables I and II with the corresponding wavenumbers (in

$cm^{-1}$ ) and wavelengths (in Å). The expected accuracy is better than 1  $cm^{-1}$  for the wavenumbers. This has been verified by comparison with experimental spectra (Dabrowski, 1984; Roncin *et al.* 1984, Launay and Roncin, 1988).

These data extend in a more accurate way those compiled by Morton and Dinerstein (1976) for interstellar studies. The differences with earlier results of Allison and Dalgarno (1970) is of the order of a few percents. In unambiguous cases, results concerning transitions with excited vibrational levels belonging to the  $X^1\Sigma_g^+$  electronic ground state can be obtained under request to the authors.

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TABLE IV (*continued*).

v'	J'	$\sigma$	$\lambda$	f	A	v'	J'	$\sigma$	$\lambda$	f	A		
33	10	P R	111037.47 113167.53	900.5969 883.6457	0.12E-04 0.29E-03	0.11E+06 0.23E+07	35	3 5	P R	117109.51 117923.94	853.9016 846.0043	0.27E-04 0.61E-04	0.32E+06 0.40E+06
33	11	P R	109936.85 112206.65	909.5966 891.2126	0.50E-04 0.21E-03	0.44E+06 0.16E+07	35	4 5	P R	116553.10 117587.77	857.9780 850.4286	0.27E-04 0.51E-04	0.30E+06 0.37E+06
33	12	P R	108778.35 111170.14	919.3006 899.5222	0.11E-03 0.13E-03	0.94E+06 0.98E+06	35	5 6	P R	115895.57 117141.55	862.8457 853.6680	0.28E-04 0.39E-04	0.30E+06 0.29E+06
33	13	P R	107539.39 110041.72	929.8919 908.7463	0.15E-03 0.46E-03	0.12E+07 0.35E+07	35	6 7	P R	115140.61 116586.17	868.5018 857.7199	0.36E-04 0.21E-04	0.37E+06 0.16E+06
33	14	P R	106123.87 108723.71	942.2951 919.7626	0.11E-03 0.29E-03	0.86E+06 0.21E+07	35	7 8	P R	114283.29 115920.26	875.0186 862.6620	0.66E-04 0.19E-03	0.65E+06 0.15E+07
34	0	P	117936.19	847.9161	0.53E-04	0.15E+07	35	8 9	P R	113356.42 115170.82	882.1732 866.2755	0.37E-05 0.38E-04	0.36E+05 0.30E+06
34	1	P R	117707.36 118061.71	849.5646 847.0147	0.64E-04 0.16E-03	0.96E+06 0.49E+06	35	9 10	P R	112341.70 114320.78	890.1414 874.7316	0.00E+00 0.19E-04	0.00E+00 0.15E+06
34	2	P R	117370.11 117957.15	852.0057 847.7655	0.71E-04 0.10E-03	0.92E+06 0.56E+06	36	0 1	P R	118217.98 117983.65	845.8950 847.5750	0.64E-05 0.34E-05	0.23E+06 0.53E+05
34	3	F R	116927.64 117742.07	855.2298 849.3141	0.82E-04 0.80E-04	0.96E+06 0.53E+06	36	1 2	P R	117635.98 118223.02	850.0801 845.8590	0.50E-05 0.32E-04	0.65E+05 0.18E+06
34	4	P R	116384.01 117416.68	859.2246 851.6533	0.11E-03 0.50E-04	0.12E+07 0.36E+06	36	3 4	P R	117177.78 117992.21	853.4041 847.5136	0.59E-05 0.23E-04	0.70E+05 0.15E+06
34	5	P R	115748.61 116994.79	863.9398 854.7389	0.23E-03 0.17E-06	0.24E+07 0.13E+02	36	4 5	P R	116612.64 117647.31	857.5400 849.9982	0.65E-05 0.18E-04	0.72E+05 0.13E+06
34	6	P R	114993.71 116441.07	869.6128 858.8035	0.19E-05 0.23E-03	0.20E+05 0.18E+07	36	5 6	P R	115945.25 117191.23	862.4760 853.3062	0.71E-05 0.14E-04	0.75E+05 0.10E+06
34	7	P R	114172.04 115809.01	875.8712 863.4907	0.22E-04 0.16E-03	0.22E+06 0.12E+07	36	6 7	P R	115180.00 116627.36	866.2063 857.4318	0.00E+00 0.67E-05	0.00E+00 0.67E-05
34	8	P R	113263.70 115078.10	882.8954 888.9751	0.38E-04 0.12E-03	0.36E+06 0.91E+06	36	7 8	P R	114303.12 115940.09	874.8667 862.5144	0.19E-03 0.59E-04	0.19E+07 0.46E+06
34	9	P R	112275.95 114255.03	890.6627 875.2350	0.57E-04 0.77E-04	0.53E+06 0.60E+06	36	8 9	P R	117661.69 118248.73	849.8943 845.6750	0.59E-07 0.38E-04	0.76E+03 0.21E+06
34	10	P R	111215.78 113345.84	899.1530 882.2556	0.17E-03 0.33E-05	0.15E+07 0.25E+05	37	0 1	P R	118245.49 118011.56	845.6982 847.3746	0.27E-05 0.61E-05	0.75E+05 0.94E+05
34	11	P R	110069.85 112337.65	908.5140 890.1735	0.20E-05 0.87E-04	0.17E+05 0.67E+06	37	1 2	P R	118365.91 117661.69	844.8378 849.8943	0.27E-05 0.59E-07	0.85E+04 0.76E+03
35	0	P	118135.16	846.4880	0.28E-04	0.80E+06	37	2 3	P R	117201.40 117201.40	853.2321 847.3440	0.18E-05 0.12E-04	0.21E+05 0.77E+05
35	1	P R	117903.56 118257.91	848.1508 845.6094	0.30E-04 0.11E-03	0.46E+06 0.33E+06	37	3 4	P R	116633.52 117668.19	857.3864 849.8473	0.27E-05 0.92E-05	0.30E+05 0.66E+05
35	2	P R	117560.71 118147.75	850.6243 846.3979	0.28E-04 0.72E-04	0.37E+06 0.40E+06							





