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Fine and hyperfine structure of the $4p$ and $5p$ $^3\Pi_u$ states of H_2

M. Lombardi

Laboratoire de Spectrométrie Physique, Domaine Universitaire, B.P. 53, Centre de tri-38041 Grenoble-Cedex-France

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In a previous paper¹ (hereafter referred to as I), fine structure (fs) and hyperfine structure (hfs) constants of the $2p$ and $3p$ $^3\Pi_u$ states of H_2 have been calculated. In a recent congress,² measurements by Freund and Miller upon the $4p$ $^3\Pi_u$ state have been reported. The programs described in I have therefore been used to calculate fs and hfs constants of the next two higher $4p$ and $5p$ $^3\Pi_u$ states. The results for the five interatomic distances for which Rothenberg and Davidson³ have calculated wavefunctions are given in Table I.

In Table II, the equilibrium values ($v = -\frac{1}{2}$) and the variations per vibrational quantum are displayed for the various fs and hfs constants of the 3, 4, and $5p$ $^3\Pi_u$ states. The vibrational averaging, made with the method described in I caused us some trouble. Table II shows that taking into account the quadratic β term of Eqs. (12) and (13) of I gives results much worse than excluding it. This might be for the following reason. β is very small for most of the properties, causing typically a variation of 0.1% over the range of R used, whereas the linear term α causes a variation of 10%

over the same range. This little curvature can be completely upsetted by a curvature due to some systematic defect of the wavefunction used, e.g., lack of exponent optimization at each value of R . Unfortunately for the vibrational variation the influence of β , for which the dependence is direct, is the same order of magnitude as the influence of α , for which the dependence is only upon its product with the little coefficient of anharmonicity k_1 of the potential curve.

For the accuracy of the equilibrium values, the influence of β is negligible. In Table II are compared our theoretical and the experimental (Born Oppenheimer "deperturbed") values of Freund and Miller.⁴⁻⁶

Very similar conclusions can be given for this $4p$ level as for the $2p$ and $3p$ ones, i.e., 1% for one electron coefficients, 2%-4% for two electrons coefficients except for A . The reason for this bad result is probably that the A coefficient is the difference between two larger coefficients A_1 and A_2 . If it is supposed that the whole error comes from the two electrons A_2 coefficient, it

TABLE I. fs and hfs constants as a function of internuclear distance.

| R (a. u.) | B_0 (MHz) | B_2 (MHz) | A_2 (MHz) | A_1 (MHz) | a (MHz) | a_F (MHz) | c (MHz) | d (MHz) |
|----------------|-------------|-------------|-------------|-------------|-----------|-------------|-----------|-----------|
| $4p$ $^3\Pi_u$ | | | | | | | | |
| 1.90 | -165.44 | -445.00 | -1179.0 | 729.38 | 2.218 | 483.91 | 70.750 | -1.3980 |
| 1.95 | -160.89 | -433.79 | -1150.8 | 709.57 | 2.158 | 472.02 | 67.635 | -1.3566 |
| 2.00 | -156.28 | -422.32 | -1121.1 | 688.81 | 2.095 | 460.88 | 64.701 | -1.3137 |
| 2.05 | -151.31 | -409.77 | -1087.9 | 665.95 | 2.026 | 450.41 | 61.395 | -1.2672 |
| 2.10 | -145.78 | -395.64 | -1049.9 | 640.32 | 1.948 | 440.57 | 59.325 | -1.2157 |
| $5p$ $^3\Pi_u$ | | | | | | | | |
| 1.90 | 27.61 | -47.44 | -107.70 | 73.21 | 0.223 | 485.28 | 71.68 | -0.0902 |
| 1.95 | 26.91 | -46.01 | -104.50 | 71.15 | 0.216 | 473.38 | 68.54 | -0.0876 |
| 2.00 | 26.34 | -44.94 | -102.12 | 69.62 | 0.212 | 462.23 | 65.58 | -0.0857 |
| 2.05 | 25.89 | -44.26 | -100.62 | 68.60 | 0.209 | 451.74 | 62.79 | -0.0845 |
| 2.10 | 25.03 | -44.00 | -100.08 | 68.18 | 0.207 | 441.87 | 60.15 | -0.0842 |

TABLE II. fs and hfs constants. Comparison with experiment.

| Constant | $3p$ $^3\Pi_u$ | | | | | | $4p$ $^3\Pi_u$ | | | | | $5p$ $^3\Pi_u$ | |
|----------------------|------------------------|-----------|---|---|----------------------------|--|------------------------|-----------|---|---|----------------------------|------------------------|---|
| | Pe theor. ^a | Pe exptl. | $\Delta P/\Delta v$ theor. ^b | $\Delta P/\Delta v$ theor. ^a | $\Delta P/\Delta v$ exptl. | | Pe theor. ^a | Pe exptl. | $\Delta P/\Delta v$ theor. ^b | $\Delta P/\Delta v$ theor. ^a | $\Delta P/\Delta v$ exptl. | Pe theor. ^a | $\Delta P/\Delta v$ theor. ^a |
| a_F | 462 | 465 | -4 | -18 | -10 | | 458 | | -3 | -17 | | 463 | -18 |
| a | 6.0 | 6.9 | -0.13 | -0.24 | -0.3 | | 2.1 | 2.5 | -0.2 | -0.1 | -0.4 | 0.21 | -0.006 |
| c | 64.3 | | -1.37 | -4.7 | | | 64.0 | | -1 | -4.5 | | 65.9 | -4.7 |
| d | -3.7 | | 0.08 | 0.14 | | | -1.29 | | 0.14 | 0.07 | | -0.08 | 0.002 |
| $c-3d$ | 75.4 | 72 | -1.61 | -5.1 | -2.7 | | 67.9 | 67 | -1.4 | -4.7 | -4.3 | 66.1 | -4.7 |
| B_0 | -398 | -377 | 12 | 18 | | | -154 | -160 | 15 | 8 | | -26.4 | -1 |
| B_2 | -1116 | -1089 | 28 | 41 | | | -417 | -433 | 40 | 19 | | -45.4 | 1.4 |
| $-6^{1/2} B_2 + B_0$ | 2336 | 2289 | -56 | -83 | -96 | | 867 | 900 | -84 | -39 | -41 | 138 | -4.5 |
| $-6^{1/2} B_2 + B_0$ | -3132 | -3044 | 80 | 119 | 148 | | -1175 | -1220 | 113 | 54 | 55 | -85 | 2.5 |
| A_1 | 1980 | | -41 | -79 | | | 680 | | -76 | -35 | | 70 | -2 |
| A_2 | -3033 | | 74 | 114 | | | -1107 | | 120 | 51 | | -103 | 3 |
| A | -1053 | -842 | 32 | 35 | 55 | | -427 | -314 | 44 | 16 | 15 | -33 | 1 |

^aWithout β term.

^bWith β term.

can be concluded that A_2 is 6% too great, which is consistent with the accuracy of B_0 and B_2 . The accuracy of A_2 is somewhat worse because A_2 itself is the sum of four terms of various signs as shown in Eq. (2) of I.

The $5p\ ^3\Pi_u$ results have been included for the sake of completeness since we had R. D.³ wavefunctions for this state. But these results are dubious: these wavefunctions include powers in ξ up to 3 only, whereas proper account of the quasihydrogenoid $5p$ electronic state would need a ξ^4 term.

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⁶T. A. Miller, R. S. Freund, and B. R. Zegarski (unpublished).