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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 paper<sup>1</sup> (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,<sup>2</sup> 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 Davidson<sup>3</sup> 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  $\beta$  term of Eqs. (12) and (13) of I gives results much worse than excluding it. This might be for the following reason.  $\beta$  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  $\alpha$  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  $\beta$ , for which the dependence is direct, is the same order of magnitude as the influence of  $\alpha$ , 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  $\beta$  is negligible. In Table II are compared our theoretical and the experimental (Born Oppenheimer "deperturbed") values of Freund and Miller.<sup>4-6</sup>

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. <sup>a</sup>	$Pe$ exptl.	$\Delta P/\Delta v$ theor. <sup>b</sup>	$\Delta P/\Delta v$ theor. <sup>a</sup>	$\Delta P/\Delta v$ exptl.	$Pe$ theor. <sup>a</sup>	$Pe$ exptl.	$\Delta P/\Delta v$ theor. <sup>b</sup>	$\Delta P/\Delta v$ theor. <sup>a</sup>	$\Delta P/\Delta v$ exptl.	$Pe$ theor. <sup>a</sup>	$\Delta P/\Delta v$ theor. <sup>a</sup>
$a_F$	462	465	-4	-18	-10	458		-3	-17		463	-18
$c$	6.0	6.9	-0.13	-0.24	-0.3	2.1	2.5	-0.2	-0.1	-0.4	0.21	-0.006
$a$	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

<sup>a</sup>Without  $\beta$  term.

<sup>b</sup>With  $\beta$  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.<sup>3</sup> wavefunctions for this state. But these results are dubious: these wavefunctions include powers in  $\xi$  up to 3 only, whereas proper account of the quasihydrogenoid  $5p$  electronic state would need a  $\xi^4$  term.

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<sup>1</sup>M. Lombardi, J. Chem. Phys. **58**, 797 (1973).

<sup>2</sup>T. A. Miller and R. S. Freund, International Conference on Doppler-Free Spectroscopy of Small Molecules, Aussois (France), 1973 (to be published by Centre National de la Recherche Scientifique, Paris, 1974).

<sup>3</sup>S. Rothenberg and E. R. Davidson, J. Chem. Phys. **45**, 2560 (1966).

<sup>4</sup>T. A. Miller and R. S. Freund, J. Chem. Phys. **59**, 4093 (1973).

<sup>5</sup>T. A. Miller, J. Chem. Phys. **59**, 4078 (1973).

<sup>6</sup>T. A. Miller, R. S. Freund, and B. R. Zegarski (unpublished).