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

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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 upset 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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