

High-Resolution Infrared Study of PHD₂: The P–H Stretching Bands ν_1 and $2\nu_1$

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For the first time the infrared spectrum of PHD₂ was recorded in the region of the PH stretching fundamental ν_1 at 2324.005 cm⁻¹ and the overtone $2\nu_1$ at 4563.634 cm⁻¹ with a resolution of 4.2×10^{-3} cm⁻¹ and 8.8×10^{-3} cm⁻¹, respectively. In the analyses about 1340 and 1020 transitions were assigned to the corresponding ν_1 and $2\nu_1$ bands, which provided 316 and 248 upper energies, respectively. Since both the bands are sufficiently isolated, a standard Watson-type Hamiltonian (*A*-reduction, *I'*-representation) was employed. The obtained sets of spectroscopic parameters correlate very well both with each other, and with the corresponding parameters of the ground vibrational state. © 2002 Elsevier Science (USA)

Key Words: vibration–rotation spectra; PHD₂ molecule; spectroscopic parameters.

1. INTRODUCTION

In former contributions (1–3) we have reported on the ground and the low-lying bending states of the phosphine species PHD₂ and PH₂D. This systematic study will now be extended to the stretching bands. In the present contribution our targets are the P–H stretching fundamental and the first overtone bands, ν_1 and $2\nu_1$, respectively, of the PHD₂ species.

Formerly, PHD₂ has been studied only in the microwave region (4–7) and in the infrared region at low resolution (8). Recently, the infrared spectrum has been investigated for the first time with high resolution (1, 3). The pure rotational spectrum was reanalyzed in (1), while Ref. (3) deals with the high-resolution analysis of the three lowest vibrational bands ν_3 , ν_4 , and ν_6 . The P–H stretching bands ν_1 and $2\nu_1$ have not yet been investigated in any detail.

Here we present the results of the first high-resolution vibration–rotation study of the ν_1 and $2\nu_1$ bands, whose band centers are located at 2324.005 and 4563.634 cm⁻¹. Spectra were recorded with a Bruker IFS 120HR interferometer at Wuppertal using an optical resolution of 0.0042 and 0.0088 cm⁻¹ in the regions 2170–2460 and 4350–4720 cm⁻¹, respectively. Experimental details are reported in Section 2. Assignments of the recorded transitions, and the further theoretical analysis of the obtained experimental data, are given in Section 3. A conclusion is drawn in Section 4.

2. EXPERIMENTAL DETAILS

The synthesis of a sample enriched to 60% PHD₂, 25% PH₂D, 10% PD₃, and 5% PH₃ has been described (1). Moreover, a

sample composed of 5% PH₂D, 10% PHD₂, and 85% PD₃ was available for comparison and identification of lines belonging to other isotopomers of phosphine than PHD₂ by means of relative intensities of lines. The resolution (1/maximum optical path difference) was 4.2 and 8.8×10^{-3} cm⁻¹, respectively, for the ν_1 and $2\nu_1$ bands, which may be compared to the Doppler width at room temperature, 4.8 and 9.4×10^{-3} cm⁻¹ (full width half-maximum). The raw spectrum was zero-filled by a factor of 4. For the ν_1 band a path length of 280 mm and a pressure of 70 Pa were chosen, and the interferometer was equipped with a KBr beam splitter, an InSb detector, and a 2000–3000 cm⁻¹ band-pass filter. In total 254 scans were coadded, and calibration done using CO₂ lines near 2350 cm⁻¹ (9, 10). We used also the Giessen peak-picking software package written by P. Jensen. Precision of line positions is ca. 0.2×10^{-3} cm⁻¹.

For the $2\nu_1$ band a White-type multipass cell operated at a path length of 12.8 m was used, a pressure of 1000 Pa adjusted, and the interferometer was equipped with a NIR-quartz beam splitter, an InSb detector, and a 3700–5200 cm⁻¹ band-pass filter. In total 1050 scans were coadded, and calibration was done with H₂O lines in the 3800–3900 cm⁻¹ region (11). Wavenumber precision is ca. 0.5×10^{-3} cm⁻¹.

For illustration, two parts of the recorded spectra are presented in Figs. 1 and 2.

3. ANALYSIS AND DISCUSSION

The PHD₂ molecule is an asymmetric top with the value of the parameter of asymmetry $\kappa \simeq 0.174$. Its six fundamental bands, ν_1 , ν_2 , ν_3 , ν_4 , ν_5 , and ν_6 , are located at 2324.005, 1686.085,

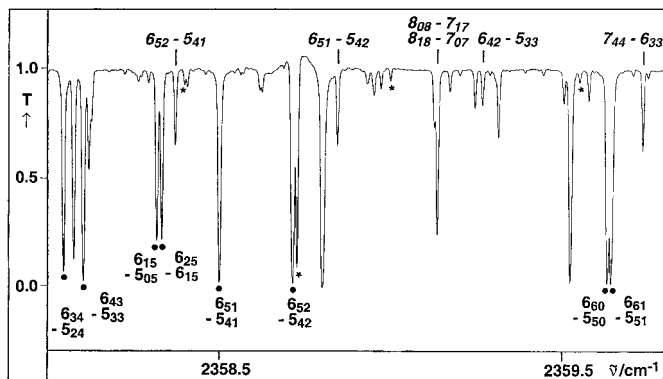


FIG. 1. Detail of the ν_1 band of PHD₂ in the *R* branch. Transitions of type *b* are denoted by ticks on top of the trace and assignments are given in italics. Transitions of type *c* are denoted by full dots. Lines belonging to CO₂ are indicated by asterisks.

911.652, 766.887, 1692.765, and 978.559 cm^{-1} , respectively (data from Refs. (3, 12) and the present contribution). As a consequence, both the ν_1 , and $2\nu_1$ bands are located away from other vibrational bands, the levels $\nu_2 + \nu_4$ and $\nu_4 + \nu_5$ near 2453

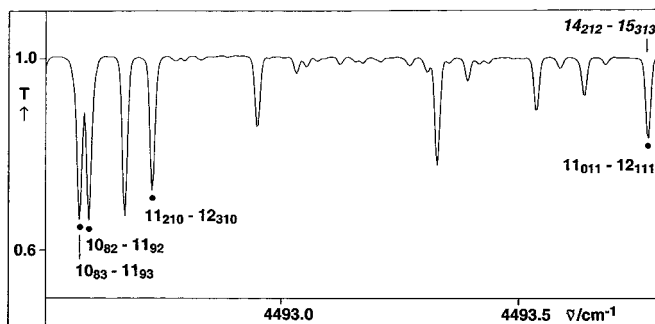


FIG. 2. Detail of the $2\nu_1$ band of PHD₂ in the *P* branch. Transitions of type *b* are denoted by ticks on top of the trace and assignments are given in italics. Transitions of type *c* are denoted by full dots.

and 2450 cm^{-1} , which are the nearest binary combination, being fairly far apart from ν_1 . So, the usual Watson-type Hamiltonian of an isolated vibrational state is suitable for the theoretical analysis of the rotational structures of both the (100000) and (200000) vibrational states,

TABLE 1
Rotational and Centrifugal Distortion Parameters for Some Vibrational States of the PHD₂ Molecule (in cm^{-1})^a

Parameter	(000000)	(100000)	(200000)	(200000)
1	2	3	4	5
ν		2324.004833(13)		4563.634195(26)
<i>A</i>	3.132704198	3.099412975(929)	3.066122	3.06554577(123)
<i>B</i>	2.732228719	2.711396222(589)	2.690564	2.689981877(766)
<i>C</i>	2.162945246	2.163456412(326)	2.163968	2.164060821(491)
$\Delta_K \times 10^4$	0.9863227	0.916355(117)	0.846387	0.848097(104)
$\Delta_{JK} \times 10^4$	-0.4549697	-0.410551(129)	-0.366132	-0.3658462(957)
$\Delta_J \times 10^4$	0.3728591	0.3669201(252)	0.360981	0.3612162(159)
$\delta_K \times 10^4$	-0.3401298	-0.3463185(486)	-0.352507	-0.3515833(340)
$\delta_J \times 10^4$	0.10895370	0.1051544(136)	0.101355	0.10140787(894)
<i>H_K</i> × 10 ⁸	0.27827	0.32346(681)	0.36865	0.36966(399)
<i>H_{KJ}</i> × 10 ⁸	0.97303	0.81828(820)	0.66353	0.68519(376)
<i>H_{JK}</i> × 10 ⁸	-0.64788	-0.57423(310)	-0.50058	-0.50058
<i>H_J</i> × 10 ⁸	0.189953	0.182686(523)	0.175419	0.175419
<i>h_K</i> × 10 ⁸	-0.09708	-0.10051(278)	-0.10394	-0.10394
<i>h_{JK}</i> × 10 ⁸	-0.247351	-0.23940(122)	-0.23140	-0.23140
<i>h_J</i> × 10 ⁸	0.088304	0.085355(265)	0.082406	0.082406
<i>L_K</i> × 10 ¹²	-2.070	-2.554(178)	-3.038	-3.038
<i>L_{KKJ}</i> × 10 ¹²	2.737	3.174(192)	3.611	3.611
<i>L_{JK}</i> × 10 ¹²	-2.211	-2.211	-2.211	-2.211
<i>L_{KJJ}</i> × 10 ¹²	0.8163	0.8163	0.8163	0.8163
<i>L_J</i> × 10 ¹²	-0.19426	-0.19426	-0.19426	-0.19426
<i>l_K</i> × 10 ¹²	-0.2961	-0.2961	-0.2961	-0.2961
<i>l_{KJ}</i> × 10 ¹²	0.0	0.0	0.0	0.0
<i>l_{JK}</i> × 10 ¹²	0.0	0.0	0.0	0.0
<i>l_J</i> × 10 ¹²	-0.07629	-0.07629	-0.07629	-0.07629

^a Column 2 presents the values of spectroscopic parameters of the ground vibrational state which are reproduced from Ref. (1). Parameters of the states (100000) and (200000) as obtained from the fits are shown in columns 3 and 5, respectively. Here, values in parentheses are the 1σ statistical confidence intervals. Parameters presented without confidence intervals were fixed to the values of corresponding parameters of the ground vibrational state. Column 4 gives “predicted” values of parameters of the (200000) state derived from a linear extrapolation of the values of corresponding parameters of the ground and the (100000) vibrational states.

TABLE 2
 Experimental Rovibrational Term Values for the (100000) and (200000) Vibrational States of the PHD₂ Molecule (in cm^{-1})^a

J	K_a	K_c	(100000)			(200000)			J	K_a	K_c	(100000)			(200000)		
			E	Δ	δ	E	Δ	δ				E	Δ	δ	E	Δ	δ
		1	2	3	4	5	6	7			1	2	3	4	5	6	7
0	0	0	2324.00483			4563.63377		-43	7	3	5	2466.99247	3	0	4705.80786	8	2
1	0	1	2328.87950		-4	4568.48819		10	7	3	4	2472.47079	3	-4	4711.06123	13	14
1	1	1	2329.26756		4	4568.86366		5	7	4	4	2473.35173	4	-1	4711.92454	4	0
1	1	0	2329.81559	8	8	4569.38949	26	-11	7	4	3	2475.99824	22	-23	4714.44985	3	9
2	0	2	2338.32305	1	7	4577.90340		5	7	5	3	2479.16533	5	0	4717.52782	3	-4
2	1	2	2338.46844	3	-3	4578.04499	4	4	7	5	2	2479.76026	5	-1	4718.09029	2	4
2	1	1	2340.11196	4	0	4579.62236	8	-5	7	6	2	2485.56562	10	5	4723.70760	5	-5
2	2	1	2341.27559	6	5	4580.74859		-5	7	6	1	2485.61053	5	0	4723.74965	4	-13
2	2	0	2341.58061		-2	4581.04027	16	-5	7	7	1	2493.17461		31	4731.05674		0
3	0	3	2352.07230		9	4591.62703		9	7	7	0	2493.17495		-34			
3	1	3	2352.10957	9	5	4591.66329	24	-21	8	0	8	2485.37771	9	-1	4724.82916	17	1
3	1	2	2355.26752	2	-1	4594.69584	2	7	8	1	8	2485.37771	9	-2	4724.82916	17	0
3	2	2	2355.89712	1	0	4595.30773	8	-2	8	1	7	2496.00720	65	43	4735.04682		40
3	2	1	2357.07354	1	-3	4596.43410	3	6	8	2	7	2496.00720	65	-30	4735.04682		-33
3	3	1	2359.36242	7	4	4598.64918	19	21	8	2	6	2505.09209	6	-1	4743.77878	4	1
3	3	0	2359.48978	1	-3	4598.77013	1	-1	8	3	6	2505.11513	5	1	4743.80163	30	-5
4	0	4	2370.10669	12	10	4609.63765		-50	8	3	5	2512.38833	1	2	4750.78517	6	5
4	1	4	2370.11447	4	-4	4609.64606		10	8	4	5	2512.72284	8	-6	4751.11545	4	-3
4	1	3	2374.89452	4	0	4614.23851	6	3	8	4	4	2517.31363	5	-2	4755.50648	10	5
4	2	3	2375.13129	3	-1	4614.47013	3	3	8	5	4	2519.25820	6	0	4757.40633	9	-7
4	2	2	2377.71947	5	1	4616.95065	2	6	8	5	3	2520.96383	5	0	4759.02578	3	-4
4	3	2	2379.24724	5	0	4618.43371	7	-5	8	6	3	2525.77090	5	-1	4763.68997	7	-5
4	3	1	2379.93970	13	9	4619.09397	25	22	8	6	2	2526.02751	6	-3	4763.93118	4	2
4	4	1	2383.57734	5	0	4622.61229	15	-5	8	7	2	2533.24778	12	-9	4770.91189		-13
4	4	0	2383.62126	2	-2	4622.65388	11	-1	8	7	1	2533.26246	1	5	4770.92603		46
5	0	5	2392.45024		1	4631.96027		22	8	8	1	2542.01340	21	-12			
5	1	5	2392.45178		2	4631.96187		30	8	8	0	2542.01340	21	-42			
5	1	4	2398.76312	5	3	4638.02771		5	9	0	9	2524.97913	10	-8	4764.41315	10	-12
5	2	4	2398.82995	5	2	4638.09349	10	1	9	1	9	2524.97913	10	-8	4764.41315	10	-12
5	2	3	2403.14746	2	0	4642.23585	10	-9	9	1	8	2537.02467		4	4775.99167	8	9
5	3	3	2403.93100	15	11	4643.00074	2	4	9	2	8	2537.02467		-10	4775.99167	8	-6
5	3	2	2405.80818	12	-8	4644.79455	3	3	9	2	7	2547.54913	2	-5	4786.10792	32	16
5	4	2	2408.59878	6	0	4647.50060	5	-2	9	3	7	2547.55465	2	-4	4786.11268		-60
5	4	1	2408.92576	13	8	4647.81044		-4	9	3	6	2556.43037	6	0	4794.64109	4	4
5	5	1	2413.94792	18	-13	4652.66509		-28	9	4	6	2556.53474	8	0	4794.74478	7	0
5	5	0	2413.96172	9	8	4652.67822		6	9	4	5	2563.17470	12	4	4801.10937	10	9
6	0	6	2419.11057		11	4658.59985	14	11	9	5	5	2564.11636	6	0	4802.03614		9
6	1	6	2419.11057		-18	4658.59985	14	-17	9	5	4	2567.59180	6	-2	4805.34838	12	15
6	1	5	2426.88306	5	0	4666.07130	5	6	9	6	4	2571.04176	18	10	4808.70939		-12
6	2	5	2426.89901	14	-8	4666.08725	16	12	9	6	3	2571.97094	7	-3	4809.58638	3	2
6	2	4	2432.93577	6	1	4671.88495	6	5	9	7	3	2578.45692	10	2	4815.86933	10	-7
6	3	4	2433.23176	2	-2	4672.17590	3	2	9	7	2	2578.55463	7	0	4815.96062	7	-9
6	3	3	2436.80339	3	-4	4675.59506	6	6	9	8	2	2587.07065		17	4824.19154		15
6	4	3	2438.57962	5	-3	4677.32475	17	-9	9	8	1	2587.07483		-11	4824.19470		-10
6	4	2	2439.74070	1	-4	4678.42915	3	0	9	9	1	2596.98535		9	4833.76845		-23
6	5	2	2444.02262	5	0	4682.57686	5	-6	9	9	0	2596.98535		2	4833.76845		-30
6	5	1	2444.15133	0	0	4682.69815	4	-6	10	0	10	2568.88801	8	3	4808.30564		0
6	6	1	2450.48216		20	4688.81541		29	10	1	10	2568.88801	8	3	4808.30564		0
6	6	0	2450.48561		-29	4688.81896		15	10	1	9	2582.34408	18	9	4821.23914	13	-5
7	0	7	2450.08702		-7	4689.55717	19	26	10	2	9	2582.34408	18	6	4821.23914	13	-8
7	1	7	2450.08702		-12	4689.55717	19	21	10	2	8	2594.29243		9	4832.72458	68	66
7	1	6	2459.29322	2	-3	4698.40668		9	10	3	8	2594.29357		-2	4832.72458	68	-59
7	2	6	2459.29686	14	10	4698.41013		4	10	3	7	2604.66202	8	0	4842.68971	13	-2
7	2	5	2466.90397	6	2	4705.72029	11	3	10	4	7	2604.69088	8	0	4842.71859	5	0

^a In Table 2, Δ is the experimental uncertainty of the energy value, equal to one standard deviation in units of 10^{-5} cm^{-1} ; δ is the difference $E^{\text{exp.}} - E^{\text{calc.}}$, also in units of 10^{-5} cm^{-1} ; Δ is not quoted when the energy value was obtained from only one transition.

TABLE 2—Continued

<i>J</i>	<i>K_a</i>	<i>K_c</i>	(100000)			(200000)			<i>J</i>	<i>K_a</i>	<i>K_c</i>	(100000)			(200000)		
			<i>E</i>	Δ	δ	<i>E</i>	Δ	δ				<i>E</i>	Δ	δ	<i>E</i>	Δ	δ
		1	2	3	4	5	6	7			1	2	3	4	5	6	7
10	4	6	2613.18284	7	-2	4850.87068	10	6	12	11	2	2785.25537	21	3	5020.35024	20	16
10	5	6	2613.54301	8	-1	4851.22772	2	0	12	11	1	2785.25537	21	-8	5020.35024	20	6
10	5	5	2619.17969	8	0	4856.61601	14	24	12	12	1	2798.51432	17	2	5033.16241	18	3
10	6	5	2621.23717	7	2	4858.63275	17	6	12	12	0	2798.51432	17	2	5033.16241	18	3
10	6	4	2623.55476	8	0	4860.83019	7	-7	13	0	13	2726.41612	3	0	4965.79005	12	14
10	7	4	2628.79306	8	0	4865.92181	8	-3	13	1	13	2726.41612	3	0	4965.79005	12	14
10	7	3	2629.22264	9	-2	4866.32451	12	-4	13	1	12	2744.06739	11	2	4982.75227	9	3
10	8	3	2637.25474	18	7	4874.09559	9	-15	13	2	12	2744.06739	11	2	4982.75227	9	3
10	8	2	2637.28903	19	11	4874.12743		-14	13	2	11	2760.23705		11	4998.29215		-39
10	9	2	2647.02410	120	64	4883.53467		89	13	3	11	2760.23705		10	4998.29215		-40
10	9	1	2647.02410	120	-68	4883.53467		-33	13	3	10	2774.89160		32	5012.37759	31	19
10	10	1	2658.07232	12	0	4894.20775	37	-48	13	4	10	2774.89160		-11	5012.37759	31	-25
10	10	0	2658.07232	12	-2	4894.20775	37	-50	13	4	9	2787.97140	22	-8	5024.94831	11	-29
11	0	11	2617.10002	2	0	4856.50215	17	-6	13	5	9	2787.98065	9	-6	5024.95783	7	-7
11	1	11	2617.10002	2	0	4856.50215	17	-6	13	5	8	2799.32278	13	2	5035.85310	12	-2
11	1	10	2631.96082	6	3	4870.78514	13	5	13	6	8	2799.44898	9	3	5035.97926		-23
11	2	10	2631.96082	6	3	4870.78514	13	4	13	6	7	2808.39631	1	8	5044.55208	17	15
11	2	9	2645.32382	18	14	4883.62920	24	5	13	7	7	2809.40161	20	1	5045.54864	12	3
11	3	9	2645.32382	18	-13	4883.62920	24	-23	13	7	6	2814.66327	15	3	5050.55615	15	13
11	3	8	2657.13889	14	-4	4894.98519		0	13	8	6	2818.49361	16	-4	5054.30677	17	8
11	4	8	2657.14637	12	3	4894.99256		-7	13	8	5	2820.26982	12	-3	5055.97830	11	18
11	4	7	2667.26649	10	0	4904.71490	9	-1	13	9	5	2827.87999	11	0	5063.36901	17	3
11	5	7	2667.38287	10	0	4904.83105	25	0	13	9	4	2828.15810	9	1	5063.62778		19
11	5	6	2675.18086	11	3	4912.30363	12	9	13	10	4	2838.42113	17	5	5073.55515	22	0
11	6	6	2676.16060	10	-1	4913.27145	8	0	13	10	3	2838.44375		-19	5073.57645	14	22
11	6	5	2680.51221	12	1	4917.41544		26	13	11	3	2850.32255		54	5085.05643	43	81
11	7	5	2684.17629	10	-1	4920.99433	30	20	13	11	2	2850.32255		-56	5085.05643	43	-21
11	7	4	2685.50176	6	-4	4922.24290	17	3	13	12	2	2863.49482	23	5	5097.78507	19	9
11	8	4	2692.58372	11	-3	4929.11185		4	13	12	1	2863.49482	23	2	5097.78507	19	6
11	8	3	2692.75871	4	8	4929.27482	20	4	13	13	1	2877.82556	19	-2	5111.63480	17	3
11	9	3	2702.17137	15	-5	4938.37554		2	13	13	0	2877.82556	19	-2	5111.63480	17	3
11	9	2	2702.18279	10	4	4938.38598		-1	14	0	14	2787.51037	8	4	5026.87139		32
11	10	2	2713.09149	32	19	4948.92635	33	6	14	1	14	2787.51037	8	4	5026.87139		32
11	10	1	2713.09149	32	-19	4948.92635	33	-29	14	1	13	2806.54652	12	7	5045.16257	4	-6
11	11	1	2725.25564	14	0	4960.67952		-2	14	2	13	2806.54652	12	7	5045.16257	4	-6
11	11	0	2725.25564	14	-1	4960.67952		-3	14	2	12	2824.10836	15	-1	5062.03998	14	-3
12	0	12	2669.61094	1	-5	4908.99864	3	7	14	3	12	2824.10836	15	-1	5062.03998	14	-4
12	1	12	2669.61094	1	-5	4908.99864	3	7	14	3	11	2840.16671		15	5077.47359	14	-10
12	1	11	2685.87031	7	1	4924.62448	3	-4	14	4	11	2840.16671		5	5077.47359	14	-20
12	2	11	2685.87031	7	1	4924.62448	3	-4	14	4	10	2854.67432		-11	5091.41850	67	100
12	2	10	2700.64018	12	2	4938.82028	12	-5	14	5	10				5091.41850	67	-144
12	3	10	2700.64018	12	-4	4938.82028	12	-12	14	5	9	2867.53748	4	11			
12	3	9	2713.88103		0				14	6	9	2867.57579	16	-1	5103.81717		54
12	4	9	2713.88284		0				14	6	8	2878.45108	14	-1	5114.25435	18	12
12	4	8	2725.50941	14	0	4962.72141	13	-7	14	7	8	2878.84387	16	2	5114.64656	12	11
12	5	8	2725.54322	4	-7	4962.75549		2	14	7	7	2886.60968	13	3	5122.06499	10	18
12	5	7	2735.23637	9	4	4972.05943		23	14	8	7	2888.79946	17	-2	5124.22504	13	10
12	6	7	2735.61448	5	-3	4972.43564	24	0	14	8	6	2892.49772	21	9	5127.72583		17
12	6	6	2742.31324	11	2	4978.83625	4	3	14	9	6	2898.40041	15	-4	5133.48468		53
12	7	6	2744.44732	12	-1	4980.93506	10	5	14	9	5	2899.30826	6	6	5134.33253	33	20
12	7	5	2747.43344	11	1	4983.76365		-2	14	10	5	2908.77580	15	-3			
12	8	5	2753.03058	11	14	4989.21394		10	14	10	4	2908.88480	34	-1			
12	8	4	2753.67795	11	-3	4989.81966		-8	14	11	4	2920.47620	1	15	5154.81554		24
12	9	4	2762.45506	3	-12	4998.31867	8	-7	14	11	3	2920.48391	13	20	5154.82322		19
12	9	3	2762.52039	13	0	4998.37915	10	-3	14	12	3	2933.51980	27	11			
12	10	3	2773.19958		38				14	12	2	2933.51980	27	-22			
12	10	2	2773.20269		-10				14	13	2	2947.78691	19	-2			

TABLE 2—Continued

J	K _a	K _c	(100000)			(200000)			J	K _a	K _c	(100000)			(200000)		
			E	Δ	δ	E	Δ	δ				E	Δ	δ	E	Δ	δ
		1	2	3	4	5	6	7			1	2	3	4	5	6	7
14	13	1	2947.78691	19	-3				16	12	4	3088.77950	34	17	5321.80254		32
14	14	1	2963.16501	23	-3	5196.07320	22	12	16	13	4	3102.78369		36	5335.33850		32
14	14	0	2963.16501	23	-3	5196.07320	22	12	16	13	3	3102.78369		-42	5335.33850		-40
15	0	15				5092.23663	30	12	16	14	3	3118.04727	25	2	5350.09151		1
15	1	15				5092.23663	30	12	16	14	2	3118.04727	25	-1	5350.09151		-2
15	1	14	2873.30161	12	0	5111.84963	8	-6	16	15	2	3134.43026	25	-7	5365.92782		-83
15	2	14	2873.30161	12	0	5111.84963	8	-6	16	15	1	3134.43026	25	-7	5365.92782		-83
15	2	13	2892.24819	14	-5	5130.05648	19	2	16	16	1	3151.82231	29	-18	5382.74495		-2
15	3	13	2892.24819	14	-5	5130.05648	19	2	16	16	0	3151.82231	29	-18	5382.74495		-2
15	3	12	2909.70148	28	4	5146.82998	20	-16	17	0	17	2996.47078	11	-3	5235.79631	9	12
15	4	12	2909.70148	28	1	5146.82998	20	-18	17	1	17	2996.47078	11	-3	5235.79631	9	12
15	4	11	2925.62242		46	5162.13198	27	31	17	1	16	3019.61451	14	-7	5258.02782	9	-5
15	5	11	2925.62242		-15	5162.13198	27	-31	17	2	16	3019.61451	14	-7	5258.02782	9	-5
15	5	10	2939.94282		36	5175.89433	10	-19	17	2	15	3041.30623	16	-9	5278.86885	17	-8
15	6	10	2939.95327		-21	5175.90542	14	-25	17	3	15	3041.30623	16	-9			
15	6	9	2952.49540	10	19	5187.95269	25	1	17	3	14	3061.52354	21	13	5298.29625	25	-19
15	7	9	2952.63035	16	5	5188.08856		19	17	4	14	3061.52354	21	13	5298.29625	25	-19
15	7	8	2962.71301	17	0				17	4	13	3080.23687		-14	5316.27976	10	10
15	8	8	2963.73929		13	5198.76826	30	-7	17	5	13	3080.23687		-18	5316.27976	10	6
15	8	7	2969.93054	7	-5	5204.65829		-4	17	5	12	3097.39736	40	34	5332.77470	35	49
15	9	7	2973.89746	11	0	5208.55196		3	17	6	12	3097.39736	40	-47	5332.77470	35	-35
15	9	6	2976.16888	12	-1	5210.68770		-25	17	6	11	3112.93367	3	4	5347.70634		62
15	10	6	2984.25603	17	-4	5218.55202	10	-11	17	7	11	3112.94649	22	-4	5347.71874	5	-6
15	10	5	2984.66341	15	-5	5218.93036	19	0	17	7	10	3126.66550		14	5360.89648	20	30
15	11	5	2995.73815	13	-23	5229.64899	4	14	17	8	10	3126.80949		3	5361.04188		57
15	11	4	2995.77837	17	-4	5229.68580	17	10	17	8	9	3138.00905	19	23	5371.77078	22	54
15	12	4				5242.08387		54	17	9	9	3139.05668	18	-5	5372.81545	10	24
15	12	3				5242.08520		-40	17	9	8	3146.18346	34	24	5379.59336	20	-20
15	13	3	3022.76977	28	17	5255.77410	42	21	17	10	8	3150.27335		31			
15	13	2	3022.76977	28	7	5255.77410	42	12	17	10	7	3153.07193	23	-13			
15	14	2	3038.10739	23	-5	5270.59885	34	21	17	11	7	3161.60183	4	0	5394.55223	5	-6
15	14	1	3038.10739	23	-6	5270.59885	34	21	17	11	6	3162.16263	22	-2	5395.07256	10	0
15	15	1	3054.50655	24	-3	5286.45226	21	17	17	12	6	3174.02003	13	0	5406.55432	4	7
15	15	0	3054.50655	24	-3	5286.45226	21	17	17	12	5	3174.08365	16		5406.61291		34
16	0	16	2922.54370		0	5161.88030	8	-1	17	13	5	3187.84106		26			
16	1	16	2922.54370		0	5161.88030	8	-1	17	13	4	3187.84552		-2	5419.91774	14	-15
16	1	15	2944.32653	11	0	5182.80699	16	-3	17	14	4	3202.98958	20	2	5434.55620	7	15
16	2	15	2944.32653	11	0	5182.80699	16	-3	17	14	3	3202.98958	20	-22	5434.55620	7	-7
16	2	14	2964.64990	13	-1	5202.33512	8	-3	17	15	3	3219.32653	21	-2	5450.34803		-20
16	3	14	2964.64990	13	-1	5202.33512	8	-3	17	15	2	3219.32653	21	-3	5450.34803		-20
16	3	13	2983.48938	21	-6	5220.44004	7	-9	17	16	2	3236.72795	23	-8	5467.17255	28	17
16	4	13	2983.48938	21	-7	5220.44004	7	-10	17	16	1	3236.72795	23	-8	5467.17255	28	17
16	4	12	3000.81107		22	5237.08771	16	-3	17	17	1	3255.08361	11		5484.92345	17	1
16	5	12	3000.81107		7	5237.08771	16	-19	17	17	0	3255.08361	11		5484.92345	17	1
16	5	11	3016.56091	18	-1				18	0	18	3074.66285		-5	5313.97750	25	1
16	6	11	3016.56384	16	-12				18	1	18	3074.66285		-5	5313.97750	25	1
16	6	10	3030.63474	18	-14	5265.74925		15	18	1	17	3099.15883	14	14	5337.50459		-54
16	7	10	3030.67774	18	0	5265.79232	15	-5	18	2	17	3099.15883	14	14	5337.50459		-54
16	7	9	3042.71483	16	0	5277.34464	20	14	18	2	16	3122.21007	18	2	5359.65015	14	-13
16	8	9	3043.12156	12	0	5277.75183	8	-6	18	3	16	3122.21007	18	2	5359.65015	14	-13
16	8	8	3051.94915	10	-8	5286.18330		-13	18	3	15	3143.79576		4	5380.39132	10	3
16	9	8	3054.18601		-23	5288.39576		-49	18	4	15	3143.79576		4	5380.39132	10	3
16	9	7	3058.62587	29	22				18	4	14	3163.88775	20	-8	5399.70034	16	10
16	10	7	3064.79974	11	-5	5298.63039	17	-16	18	5	14	3163.88775	20	-9	5399.70034	16	9
16	10	6	3066.00454	12	0	5299.75501	26	-10	18	5	13				5417.53815	21	22
16	11	6	3076.12018	12	-1	5309.56691	19	-23	18	6	13				5417.53815	21	0
16	11	5	3076.28645	17	-3	5309.72083	14	15	18	6	12	3199.41521	15	-2	5433.84629		41
16	12	5	3088.76527	21	-4	5321.78953		16	18	7	12	3199.41895	16	-3			

TABLE 2—Continued

J	K _a	K _c	(100000)			(200000)			J	K _a	K _c	(100000)			(200000)		
			E	Δ	δ	E	Δ	δ				E	Δ	δ	E	Δ	δ
		1	2	3	4	5	6	7		1		2	3	4	5	6	7
18	7	11	3214.67662	7	-3	5448.51163		87	19	18	2	3459.13020		7			
18	8	11	3214.72415	22	-3	5448.55891		7	19	18	1	3459.13020		7			
18	8	10	3227.90065	18	0	5461.20456		21	19	19	1	3479.31615	22	-22	5706.81704	28	27
18	9	10	3228.32289		-17				19	19	0	3479.31615	22	-22	5706.81704	28	27
18	9	9	3238.19785	7	8				20	0	20	3243.81392		0			
18	10	9	3240.48375		19	5473.32699		75	20	1	20	3243.81392		0			
18	10	8	3245.67826	11	-3	5478.24023		33	20	1	19	3270.98501		-27			
18	11	8	3252.10638		-21				20	2	19	3270.98501		-27			
18	11	7	3253.63714	18	0	5485.96053	22	24	20	2	18	3296.72812		18			
18	12	7	3264.37134		-18				20	3	18	3296.72812		18			
18	12	6	3264.60824	14	-4				20	3	17	3321.02255	4	-9			
18	13	6	3277.95672		-3				20	4	17	3321.02255	4	-9			
18	13	5	3277.97985	11	5	5509.53465		-12	20	4	16	3343.84507	6	-32			
18	14	5	3292.94236		32	5523.99980	68	70	20	5	16	3343.84507	6	-32			
18	14	4				5523.99980	68	-71	20	5	15	3365.16477	17	-9			
18	15	4	3309.19612	55	-16	5539.71152	30	22	20	6	15	3365.16477	17	-10			
18	15	3	3309.19612	55	-23	5539.71152	30	15	20	6	14	3384.93780		4			
18	16	3	3326.58005	36	16	5556.51716		-16	20	7	14	3384.93780		-26			
18	16	2	3326.58005	36	16	5556.51716		-16	20	7	13	3403.09864		13			
18	17	2	3344.97139	15	-8	5574.30167	1	-3	20	8	12	3419.52375		38			
18	17	1	3344.97139	15	-8	5574.30167	1	-3	20	9	12	3419.57636		25			
18	18	1	3364.25884		-2	5592.95736		-39	20	9	11	3433.86761		23			
18	18	0	3364.25884		-2	5592.95736		-39	20	10	11	3434.30895		-10			
19	0	19	3157.11303		0				20	10	10	3445.20740		17			
19	1	19	3157.11303		0				20	11	10	3447.55197		17			
19	1	18	3182.95150	17	0				20	11	9	3453.50041		-6			
19	2	18	3182.95150	17	0				20	12	9	3460.18200		-12			
19	2	17	3207.35321	21	-10				20	13	7	3473.71364		8			
19	3	17	3207.35321	21	-10				20	14	7	3487.92035		-39	5717.86072		73
19	3	16	3230.29843	21	14	5466.71630		-20	20	14	6	3487.95575		12	5717.89206		17
19	4	16	3230.29843	21	14	5466.71630		-20	20	16	5	3521.11437	9	12			
19	4	15	3251.76090	53	17	5487.34107	10	16	20	16	4	3521.11437	9	-4			
19	5	15	3251.76090	53	16	5487.34107	10	15	20	17	4	3539.49814		5	5767.72422		-12
19	5	14	3271.70605	8	-1	5506.51039	30	46	20	17	3	3539.49814		5	5767.72422		-12
19	6	14	3271.70605	8	-6	5506.51039	30	41	20	18	3	3558.89093		-4			
19	6	13	3290.08470		34				20	18	2	3558.89093		-4			
19	7	13	3290.08470		-72				20	19	2	3579.17216	16	7	5806.09773	11	12
19	7	12	3306.81312		22	5540.25135		10	20	19	1	3579.17216	16	7	5806.09773	11	12
19	8	12	3306.82786	14	1				20	20	1	3600.22232		-17			
19	8	11				5554.55221		22	20	20	0	3600.22232		-17			
19	9	11	3321.85464		22				21	1	20	3363.25212		20			
19	9	10	3334.14727		21	5566.48414	14	18	21	2	20	3363.25212		20			
19	10	10	3335.22222	11	-3	5567.55809		-48	21	2	19	3390.32545	12	0			
19	10	9	3343.27658	19	11				21	3	19	3390.32545	12	0			
19	11	9							21	3	18	3415.96020		27			
19	11	8	3350.83412		9				21	4	18	3415.96020		27			
19	12	8	3359.78866		6				21	4	17	3440.13278		2			
19	12	7	3360.52287		-13				21	5	17	3440.13278		2			
19	13	7							21	5	16	3462.81522		4			
19	13	6	3373.23623		16				21	7	15	3483.96893		8			
19	14	6	3387.91542		23	5618.42988		-28	21	9	13	3521.45184		11			
19	14	5							21	11	10	3561.04952		-5			
19	15	5	3404.04286	36	21	5634.02065	60	33	21	13	9	3578.67102		9			
19	15	4	3404.04286	36	-29	5634.02065	60	-13	21	14	8	3592.96539		-20			
19	16	4	3421.37549	38	-7	5650.77660		-27	21	17	5	3644.12727		28			
19	16	3	3421.37549	38	-9	5650.77660		-29	21	17	4	3644.12727		24			
19	17	3	3439.77816	9	-2	5668.57013		-49	21	18	4	3663.53339		18			
19	17	2	3439.77816	9	-2	5668.57013		-49	21	18	3	3663.53339		18			

TABLE 2—Continued

<i>J</i>	<i>K_a</i>	<i>K_c</i>	(100000)			(200000)			<i>J</i>	<i>K_a</i>	<i>K_c</i>	(100000)			(200000)		
			<i>E</i>	Δ	δ	<i>E</i>	Δ	δ				<i>E</i>	Δ	δ	<i>E</i>	Δ	δ
	1		2	3	4	5	6	7		1		2	3	4	5	6	7
21	19	3	3683.88621		−22				22	19	4	3793.44896		−3			
21	19	2	3683.88621		−22				22	19	3	3793.44896		−3			
21	20	2	3705.06394	14	−17				22	22	1	3859.43996		14			
21	20	1	3705.06394	14	−17				22	22	0	3859.43996		14			
21	21	1	3726.94228		−6				23	0	23	3529.34240		−20			
21	21	0	3726.94228		−6				23	1	23	3529.34240		−20			
22	0	22	3429.93680		−11				23	1	22	3560.44975		10			
22	1	22	3429.93680		−11				23	2	22	3560.44975		10			
22	4	18	3540.61351		10				23	2	21	3590.15377		45			
22	5	18	3540.61351		10				23	3	21	3590.15377		45			
22	5	17	3564.64765		0				23	4	19	3645.27741		−9			
22	6	17	3564.64765		0				23	5	19	3645.27741		−9			
22	6	16	3587.16905		5				24	1	23	3665.36280		0			
22	7	16	3587.16905		3				24	2	23	3665.36280		0			
22	7	15	3608.12997		17				24	4	20	3754.11504		21			
22	8	15	3608.13005		−15				24	5	20	3754.11504		21			

$$\begin{aligned}
H^{ii} = & E^i + \left[A^i - \frac{1}{2}(B^i + C^i) \right] J_z^2 + \frac{1}{2}(B^i + C^i) J^2 \\
& + \frac{1}{2}(B^i - C^i) J_{xy}^2 - \Delta_K^i J_z^4 - \Delta_{JK}^i J_z^2 J^2 - \Delta_J^i J^4 \\
& - \delta_K^i [J_z^2, J_{xy}^2]_+ - 2\delta_J^i J^2 J_{xy}^2 + H_K^i J_z^6 + H_{KJ}^i J_z^4 J^2 \\
& + H_{JK}^i J_z^2 J^4 + H_J^i J^6 + [J_{xy}^2, h_K^i J_z^4 + h_{JK}^i J^2 J_z^2 \\
& + h_J^i J^4]_+ + L_K^i J_z^8 + L_{KKJ}^i J_z^6 J^2 + L_{KJ}^i J_z^4 J^4 \\
& + L_{KJJ}^i J_z^2 J^6 + L_J^i J^8 + [J_{xy}^2, l_K^i J_z^6 + l_{KJ}^i J^4 J_z^2 \\
& + l_{JK}^i J^2 J_z^4 + l_J^i J^6]_+ + \dots, \quad [1]
\end{aligned}$$

where $i = 1$, or 2 , and $|1\rangle = (100000)$, $|2\rangle = (200000)$; $J_{xy}^2 = J_x^2 - J_y^2$ and $J^2 = J_x^2 + J_y^2 + J_z^2$. In this case, both the states (100000) and (200000) are the symmetric ones, and hence both bands ν_1 and $2\nu_1$ are of hybrid type allowing the observation of b - and c -type transitions.

Assignments of transitions were made with the Ground State Combination Differences method. In the present case, the ground state parameters were taken from Ref. (1) (for the convenience of the reader, they are reproduced in column 2 of Table 1). Transitions of both types, b and c , were assigned in both, ν_1 and $2\nu_1$, bands. However, we found that the b -type transitions are much weaker in comparison to those of c -type both in the ν_1 and in the $2\nu_1$ bands (the relative linestrengths of comparable c - and b -type transitions were estimated as 200–250/1 for both the ν_1 and $2\nu_1$ bands). For this reason, only c -type transitions were used for the determination of upper rovibrational energies. The latter were obtained as the mean values of energies calculated from several transitions reaching the same upper level.

As the result of the analysis, 899 transitions ($J^{max.} = 24$, $K_a^{max.} = 22$) of c -type and 441 very weak transitions ($J^{max.} =$

20, $K_a^{max.} = 18$) of b -type were assigned to the ν_1 band. Analogously, 695 c -type transitions ($J^{max.} = 20$, $K_a^{max.} = 19$) and 325 weak b -type transitions ($J^{max.} = 18$, $K_a^{max.} = 16$) were assigned to the $2\nu_1$ band. They provided 316 and 248 upper energies for the (100000) and (200000) vibrational states, respectively. These energies are presented in columns 2 and 5 of Table 2 together with their experimental uncertainties Δ in units of 10^{-5} cm^{-1} .

The energies gathered in Table 2 were fitted with the Hamiltonian, Eq. [1]. They lead to the sets of rotational parameters presented in Columns 3 and 5 of Table 1, together with their 1σ statistical confidence intervals. The parameters of the (100000) vibrational state which are given in column 3 of Table 1 without confidence intervals were fixed to the respective values of the corresponding ground vibrational state parameters.

The starting values of the parameters of the (200000) state were obtained by simple linear extrapolation of corresponding parameters of the ground and the (100000) vibrational states. It is interesting to realize that such extrapolation leads to excellent predictions of the values of the rotational and centrifugal distortion parameters of the (200000) state (see, for illustration, column 4 of Table 1). This point, together with the substantial separation of higher overtones of ν_1 from possible perturbers of the rotational structure of the $n\nu_1$ levels, should enable one to provide excellent predictions by simple extrapolation of rotational and centrifugal distortion parameters for the higher vibrational states.

The 18 fitted spectroscopic parameters of the ν_1 band and the 11 of the $2\nu_1$ band reproduce the 316 and 248 values for the upper energies, respectively, with accuracies close to experimental uncertainties (compare the Δ and δ values for concrete upper energies as given in Table 2). The final statistical information on the analyzed bands is gathered in Table 3. The last column of Table 3 gives the *rms* deviations of the fit of upper energies for both vibrational states studied in the present contribution.

TABLE 3
Statistical Information Concerning the ν_1 and $2\nu_1$ Bands of PHD₂

Band	Center/cm ⁻¹	J^{max}	K_a^{max}	n_{tr}^c/n_{tr}^b ^a	N_l ^b	m_1 ^c	m_2 ^c	m_3 ^c	$rms/10^{-4}$ cm ⁻¹
1	2	3	4	5	6	7	8	9	10
ν_1	2324.00483	24	22	899/441	316	77.2	20.3	2.5	1.99
$2\nu_1$	4563.63420	20	19	695/325	248	72.2	23.0	4.8	3.50

^a n_{tr}^c and n_{tr}^b are the numbers of assigned *c*- and *b*-type transitions, respectively.

^b N_l is the number of experimental upper energies.

^c Here $m_i = n_i/N_l \times 100\%$ ($i = 1, 2, 3$); n_1 , n_2 , and n_3 are the numbers of upper energies for which differences $\delta = E^{exp} - E^{calc}$ satisfy the conditions $\delta \leq 20 \times 10^{-5}$ cm⁻¹, 20×10^{-5} cm⁻¹ $< \delta \leq 40 \times 10^{-5}$ cm⁻¹, and $\delta > 40 \times 10^{-5}$ cm⁻¹, respectively.

4. CONCLUSION

High-resolution, essentially Doppler-limited infrared spectra of phosphine containing ca. 60% PHD₂ have been recorded for the first time in the regions of the P–H stretching band ν_1 and the overtone band $2\nu_1$. A theoretical analysis of the experimental data with a Watson-type Hamiltonian for an isolated vibrational state allowed us to derive sets of 18 and 11 fitted rotational and centrifugal distortion parameters, respectively. These reproduce the 316 and 248 “experimental” upper rovibrational energies with *rms* deviations of 1.99×10^{-4} cm⁻¹ and 3.50×10^{-4} cm⁻¹ for the states (100000) and (200000), respectively.

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