Infrared Fourier Transform Spectroscopy of PH

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The infrared vibration–rotation spectrum of the PH radical was observed in emission using a high-resolution Fourier transform spectrometer. The observation of five bands (1–0, 2–1, 3–2, 4–3, and 5–4) allowed the first six vibrational energy levels of the ground $X^3\Sigma^-$ state to be characterized. An RKR potential curve for the ground state was computed. © 1987 Academic Press, Inc.

INTRODUCTION

The spectrum of the free radical PH has been studied extensively from the far-infrared to the vacuum-ultraviolet spectral regions. The $A^3\Pi-X^3\Sigma^-$ electronic spectrum of PH was first observed and assigned by Pearse (*1*) in 1930 from a continuous discharge through a mixture of hydrogen and phosphorus vapor.

Since then the $A^3\Pi-X^3\Sigma^-$ transition of PH and PD has been analyzed many times (*2–6*), most recently by Rostas *et al.* (*7*). The vacuum-ultraviolet absorption spectrum of PH was observed by Balfour and Douglas (*8*). Droege and Engelking (*9*) observed the weak $b^1\Sigma^+-X^3\Sigma^-$ intercombination transition of PH.

Far-infrared laser magnetic resonance spectra of the $X^3\Sigma^-$ and $a^1\Delta$ states of PH were detected by two groups (*10–12*). Uehara and Hakuta established accurate constants for the fundamental vibration–rotation band of PD from a midinfrared laser magnetic resonance experiment (*13*). The corresponding 1–0 vibration–rotation spectrum of PH ($X^3\Sigma^-$) was analyzed by Anacona *et al.* (*14*) from a diode laser absorption spectrum. Our Fourier transform observations of the vibration–rotation spectrum are much more extensive, but are in excellent agreement with the work of Anacona *et al.* (*14*).

The photoelectron spectrum of PH⁻ (*15*) and the emission of spectrum of PH⁺ (*16*) are known. The PH molecule can be made by photochemical decomposition of PH_3 (*17–23*). Theoretical calculations are available for PH (*24–27*). Finally, PH may occur in the sun (*28*) and cool stellar atmospheres (*29*).

EXPERIMENTAL DETAILS

The spectrum of PH was excited in an electrodeless quartz discharge tube with a 2450-MHz microwave oscillator. A mixture of 0.45 Torr of hydrogen and 0.04 Torr of white phosphorus vapor flowed through the cell. The emission from the discharge was observed with the Fourier transform spectrometer associated with the National Solar Observatory[1] at Kitt Peak. Nine scans were coadded in 1 hr of integration. The unapodized resolution was set to 0.02 cm⁻¹. InSb detectors and a silicon filter restricted the spectrum to the 1800- to 8800-cm⁻¹ region.

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[1] The National Solar Observatory is operated by the Association of Universities for Research in Astronomy, Inc., under contract with the National Science Foundation.

TABLE I

The Observed Line Positions for the Vibration–Rotation Spectrum of PH (in cm^{-1})

1–0 band

J	R_1	R_2	R_3	P_1	P_2	P_3
0	–	–	2 309.9615(5)	–	–	–
1	2 292.1891(-16)	2 308.3277(-10)	2 323.9373(5)	–	–	2 240.4245[a]
2	2 308.1498(-6)	2 323.6085(12)	2 338.5246(7)	2 259.7221[a]	2 242.0659[a]	2 223.9221(-5)
3	2 323.4826(0)	2 338.3497(-6)	2 352.6670(-4)	2 242.2270[a]	2 224.2656(-5)	2 205.7962(-17)
4	2 338.2523(4)	2 352.5484(9)	2 366.2855(32)	2 224.4127(-3)	2 205.9867(-72)	2 187.1107(4)
5	2 352.4659(7)	2 366.1885(-4)	2 379.3412(-6)	2 206.1219(-2)	2 187.2606(3)	2 167.9451(-2)
6	2 366.1183(5)	2 379.2648(4)	2 391.8312(8)	2 187.3800(1)	2 168.0769(6)	2 148.3296(-9)
7	2 379.2026(5)	2 391.7651(7)	2 403.7362(0)	2 168.1918(-2)	2 148.4534(7)	2 128.2791(-35)
8	2 391.7093(-1)	2 403.6796(7)	2 415.0490(5)	2 148.5661(-8)	2 128.4017(12)	2 107.8160(13)
9	2 403.6304(-1)	2 414.9982(-4)	2 425.7593(19)	2 128.5154(8)	2 107.9321(13)	2 086.9408(19)
10	2 414.9542(-19)	2 425.7114(-26)	2 435.8522(-11)	2 108.0445(-11)	2 087.0552(7)	2 065.6678(11)
11	2 425.6750(-21)	2 435.8123(-35)	2 445.3268(0)	2 087.1711(6)	2 065.7804(-21)	2 044.0113(21)
12	2 435.7831(-12)	2 445.2934(-14)	2 454.1677(-13)	2 065.9015(14)	2 044.1254(-5)	2 021.9782(5)
13	2 445.2709(23)	2 454.1438(15)	2 462.3746(37)	2 044.2442(-10)	2 022.0969(15)	1 999.5869(42)
14	2 454.1220(8)	2 462.3552(58)	2 469.9179(-62)	2 022.2148(-17)	1 999.6972(-44)	1 976.8308(-42)
15	2 462.3367(34)	2 469.9114(39)	2 476.8152(-50)	1 999.8276(30)	1 976.9575(22)	1 953.7460(9)
16	2 469.8998(33)	2 476.8083(-3)	2 483.0468(-44)	1 977.0785(-17)	1 953.8670(3)	1 930.3240(8)
17	2 476.8083(57)	2 483.0468(23)	2 488.6096(1)	1 953.9987(53)	1 930.4442(-19)	1 906.5798(6)
18	2 483.0468(33)	2 488.6096(21)	–	1 930.5765(19)	1 906.7108(75)	1 882.5218(-11)
19	2 488.6096(-19)	–	2 497.6823(37)	1 906.8318(-19)	1 882.6491(8)	
20	–	2 497.6823(-38)		1 882.7814(10)		
21	2 497.6823(-179)					

2–1 band

J	R_1	R_2	R_3	P_1	P_2	P_3
0	–	–	–	–	–	–
1	–	2 219.9196(-9)	2 235.0224(11)	–	–	2 154.0349(-19)
2	2 219.7470(5)	2 234.6943(-2)	2 249.1052(8)	2 172.8223(-14)	2 155.6753(0)	2 138.0416(-4)
3	2 234.5748(9)	2 248.9334(5)	2 262.7438(1)	2 155.8650(8)	2 138.3785(-7)	2 120.4194(-6)
4	2 248.8393(8)	2 262.6263(7)	2 275.8566(24)	2 138.5227(1)	2 120.6100(-3)	2 102.2336(-15)
5	2 262.5483(12)	2 275.7601(-23)	2 288.4107(17)	2 120.7353(4)	2 102.3790(-4)	2 083.5707(-9)
6	2 275.6973(23)	2 288.3334(2)	2 300.3896(-33)	2 102.4956(2)	2 083.6954(-17)	2 064.4546(-30)
7	2 288.2755(9)	2 300.3283(0)	2 311.7937(2)	2 083.8097(5)	2 064.5786(44)	2 044.9097(5)
8	2 300.2781(11)	2 311.7380(3)	2 322.6049(47)	2 064.6832(-17)	2 045.0248(33)	2 024.9402(10)
9	2 311.6936(6)	2 322.5547(30)	2 332.8063(35)	2 045.1321(0)	2 025.0529(31)	2 004.5615(19)
10	2 322.5067(-64)	2 332.7610(1)	–	2 025.1571(-41)	2 004.6685(-13)	1 983.7805(-11)
11	–	–		2 004.7831(6)	1 983.8918(-4)	1 962.6171(9)
12	2 342.3318(33)	–	2 359.6866(-31)	1 984.0058(-8)	1 962.7270(-7)	1 941.0744(4)
13	–	2 359.6638(-14)	2 367.3720(-87)	1 962.8438(-2)	1 941.1844(-24)	1 919.1634(-22)
14	2 359.6501(11)	2 367.3552(-64)	2 374.4163(-48)	1 941.3041(-11)	1 919.2788(-11)	1 896.9008(-7)
15	2 367.3552(42)	2 374.4089(14)	2 380.8096(74)	1 919.3999(-6)	1 897.0191(17)	
16	2 374.4089(65)	2 380.8107(167)	2 386.5164(8)			
17	2 380.8107(161)	2 386.5164(36)				
18	2 386.5164(-27)					

3–2 band

J	R_1	R_2	R_3	P_1	P_2	P_3
0	–	–	–	–	–	–
1	–	2 131.2324(3)	2 145.8208(-2)	–	–	2 067.3792(32)
2	2 131.0661(13)	2 145.4964(4)	2 159.3944(18)	2 085.6489(-28)	2 069.0122(36)	2 051.8808(-27)
3	2 145.3821(1)	2 159.2234(9)	2 172.5180(0)	2 069.1949(-10)	2 052.2141(11)	2 034.7567(-20)
4	2 159.1343(-4)	2 172.4009(-3)	2 185.1131(6)	2 052.3553(1)	2 034.9411(-12)	2 017.0685(-4)
5	2 172.3293(-2)	2 185.0221(1)	2 197.1499(6)	2 035.0651(-10)	2 017.2107(35)	1 998.8947(-40)
6	2 184.9611(-5)	2 197.0739(-8)	2 208.6120(-6)	2 017.3205(-21)	1 999.0172(-10)	1 980.2734(-17)
7	2 197.0253(21)	2 208.5503(10)	2 219.4891(-11)	1 999.1246(-53)	1 980.3845(-14)	1 961.2171(31)
8	2 208.5045(-8)	2 219.4353(-4)	2 229.7721(9)	1 980.4943(-19)	1 961.3227(20)	1 941.7293(10)
9	2 219.3963(-20)	2 229.7211(-28)	2 239.4441(-9)	1 961.4311(1)	1 941.8320(-12)	1 921.8321(28)
10	2 229.6918(-10)	2 239.3982(-61)	2 248.5054(37)	1 941.9447(3)	1 921.9344(7)	1 901.5288(8)
11	2 239.3793(3)	2 248.4631(-38)	2 256.9333(19)	1 922.0451(-12)	1 901.6330(2)	1 880.8366(15)
12	2 248.4502(29)	2 256.8990(-32)	2 264.7195(-48)			
13	2 256.8896(14)	2 264.7005(0)	2 271.8612(-99)			
14	2 264.6929(8)	2 271.8427(-98)	2 278.3547(-77)			
15	2 271.8427(-70)	2 278.3547(58)	2 284.1877(-12)			
16	2 278.3547(30)	2 284.1877(71)	2 289.3440(22)			
17	2 284.1877(-13)	2 289.3440(55)	2 293.8273(151)			
18	2 289.3440(-86)	2 293.8273(133)				
19	2 293.8273(-65)					

TABLE I—*Continued*

4-3 band

J	R_1	R_2	R_3	P_1	P_2	P_3
0	–		–			
1	2 027.2603(1)	2 041.8500(-10)	2 055.9207(-11)			
2	2 041.6837(-72)	2 055.5923(-41)	2 068.9743(30)	–	1981.6618(8)	1965.0434(-15)
3	2 055.4914(22)	–	2 081.5677(-20)	1981.8470(-1)	1965.3647(11)	1948.4162(34)
4	2 068.7136(-54)	2 081.4480(-36)	2 093.6318(-5)	1965.5039(-9)	1948.5860(-8)	1931.2053(-67)
5	2 081.3874(11)	2 093.5426(22)	–	1948.7192(95)	1931.3434(23)	1913.5260(-1)
6	2 093.4859(-5)	2 105.0627(64)	2 116.0511(-18)	1931.4560(5)	1913.6358(-10)	1895.3895(78)
7	2 105.0098(-13)	2 115.9902(15)	2 126.3848(22)	1913.7468(-5)	1895.4861(22)	1876.7936(-9)
8	2 115.9498(-13)	2 126.3198(-77)	–	1895.5918(-13)	1876.8950(21)	1857.7760(8)
9	2 126.2936(-30)	2 136.0604(-20)	2 145.2285(50)	1877.0034(14)	1857.8758(21)	
10	2 136.0367(-12)	2 145.1799(-35)	2 153.7120(-20)	1857.9836(-2)	–	
11	2 145.1659(8)	2 153.6762(-44)	2 161.5750(38)			
12	2 153.6762(77)	2 161.5429(-15)				
13	2 161.5429(45)	2 168.7669(15)				
14	2 168.7669(13)	2 175.3368(23)				
15	2 175.3368(-43)					

5-4 band

J	R_1	R_2	R_3	P_1	P_2	P_3
0	–	–	–	–	–	–
1	–	–	1 964.8089(-2)	–	–	–
2	–	1 964.4863(21)	1 977.3226(28)	1 908.7723(17)	1 893.1355(-17)	
3	1 964.3855(-5)	1 977.1462(-22)	1 989.3697(-17)	1 893.3233(0)	1 877.3346(-11)	
4	1 977.0756(-5)	1 989.2557(29)	2 000.8809(14)	1 877.4763(-16)	1 861.0505(27)	
5	1 989.1937(-27)	2 000.7907(37)	2 011.8172(1)	1 861.1713(-6)		
6	2 000.7386(-30)	2 011.7412(9)	2 022.1650(-30)			
7	2 011.7018(-16)	2 022.0999(-23)	2 031.9185(-9)			
8	2 022.0774(52)	2 031.8564(-56)	–			
9	2 031.8406(26)	2 041.0076(-14)	–			
10	2 040.9955(51)	2 049.5233(-94)	2 057.4614(-2)			
11	2 049.5233(44)	2 057.4182(-40)	–			
12	2 057.4182(52)	–	2 071.2900(31)			
13	–	2 071.2546(-19)				
14	2 071.2546(-7)					

Note. The numbers in parentheses are observed − calculated line positions using the constants of Table II (in 10^{-4} cm^{-1}).

[a] Blended lines.

RESULTS AND DISCUSSION

The interferograms were transformed by standard methods to provide the spectrum. Some ringing was present, particularly near strong atomic lines, so the spectrum was slightly apodized. The final linewidth of the PH emission features was about 0.045 cm^{-1} (FWHM).

The line positions were extracted with the aid of a data reduction program called DECOMP developed at Kitt Peak. To find the peak positions, a Voigt lineshape function was fitted to the PH lines by a nonlinear least-squares procedure.

The signal-to-noise ratio was greater than 100 for strong, unblended lines, so the peak positions have a precision of about 0.0005 cm^{-1}. The absolute calibration was made with impurity CO lines (*30*) and the previous diode laser observations of PH (*14*). The absolute accuracy of the line positions is estimated to be ±0.001 cm^{-1}.

The spectral region from 1800–8800 cm^{-1} contained emission features from many molecules including PH, CO, C_2, P_2, CP, and H_2. The results of our analysis of the $A^2\Pi$–$X^2\Sigma^+$ transition of CP will be published separately (*31*). The vibration–rotation
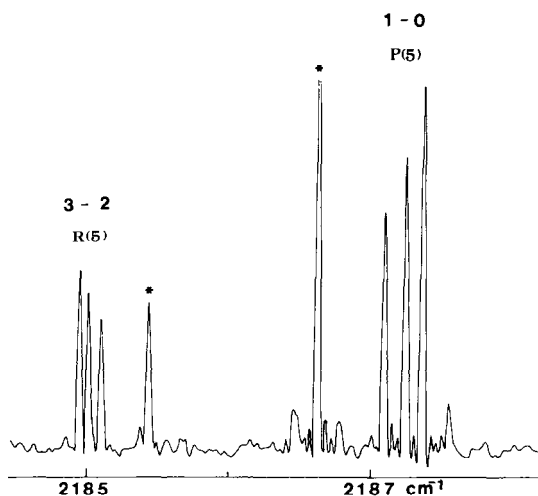
FIG. 1. Part of the rotational structure of the 1–0 and 3–2 vibration–rotation bands of PH ($X^3\Sigma$). The lines marked with asterisks are from the impurity CO. The R ($N'' = 5$) and P ($N'' = 5$) triplets of lines of the 3–2 and 1–0 bands, respectively, are labeled.

bands of PH were easily identified because of the characteristic triplet pattern of a $^3\Sigma$–$^3\Sigma$ transition.

Once the lines of the fundamental 1–0 band were identified and fitted, the lines of the 2–1, 3–2, 4–3, and 5–4 bands were predicted (with the help of the vibrational constants of Rostas *et al.* (*7*)) and found. The observed line positions are listed in Table I. The number of P-branch lines that could be detected was limited by the red cutoff of the InSb detectors near 1800 cm^{-1}.

The structure of each band consists of six branches: P_1, P_2, P_3, R_1, R_2, and R_3. The triplet structure is shown in Fig. 1 where P ($N'' = 5$) of the 1–0 band is split into P_1 ($J'' = 6$), P_2 ($J'' = 5$), and P_3 ($J'' = 4$) lines, and R ($N'' = 5$) of the 3–2 band is split

TABLE II

Molecular Constants for the Ground ($X^3\Sigma^-$) State of PH (in cm^{-1}; 1 SD in Parentheses)

Constants	v = 0	v = 1	v = 2	v = 3	v = 4	v = 5
T_v	0.0	2 276.2094(6)	4 465.0201(8)	6 566.1589(9)	8 578.9440(11)	10 502.1950(13)
B_v	8.412445(30)	8.160260(22)	7.908014(23)	7.654823(25)	7.399633(36)	7.140828(48)
$10^4\times D_v$	4.4228(28)	4.3822(13)	4.3524(17)	4.3362(19)	4.3468(35)	4.3627(56)
$10^8\times H_v$	1.02(11)	0.844(20)	0.742(33)	0.654(38)	0.912(98)	0.73(18)
$10^{11}\times L_v$	0.50(14)	–	–	–	–	–
λ_v	2.2089(17)	2.2092(17)	2.2085(16)	2.2053(16)	2.1978(17)	2.1857(18)
γ_v	-0.07668(22)	-0.07312(21)	-0.06972(21)	-0.06620(22)	-0.06290(23)	-0.05932(23)
$10^5\times \lambda_D$	2.09(91)	1.60(88)	0.99(72)	–	–	–
$10^5\times \gamma_D$	1.287(60)	1.249(61)	1.300(59)	1.312(65)	1.511(88)	1.25(10)

TABLE III

Equilibrium Molecular Constants for the $X^3\Sigma^-$ State of PH

ω_e	2 363.779(36)	B_e	8.53899(19)
$\omega_e x_e$	43.911(27)	α_e	0.25343(27)
$\omega_e y_e$	0.1068(71)	γ_e	0.00089(11)
$\omega_e z_e$	−0.01871(61)	δ_e	−0.000187(12)

into R_1 ($J'' = 6$), R_2 ($J'' = 5$), and R_3 ($J'' = 4$). Note that in Table I, J'' rather than N'' is used to label the transitions.

Initially each vibrational band observed was fitted separately using the customary $^3\Sigma^-$ Hamiltonian (32). An explicit listing of the Hamiltonian matrix elements employed can be found in our paper on NH (33). For the final fit all lines of Table I were simultaneously fitted to obtain the spectroscopic constants of Table II. Only one L value was required so L_0 was chosen in the final fit. The data were also not extensive enough to determine λ_D for $v = 3, 4,$ and 5, so these parameters were constrained to zero.

The constants of Table II are in good agreement with the less accurate values of Rostas et al. (7) and the less extensive set of constants derived by Anacona et al. (14). There is also reasonable agreement with the constants of Ohashi et al. (12), which were determined by far-infrared laser magnetic resonance.

The determination of molecular constants for the first six vibrational levels in the $X^3\Sigma^-$ state enables us to compute equilibrium constants and an RKR potential curve. The conventional equilibrium vibrational and rotational constants (34) of Table III were derived by polynomial least-squares fits to the data of Table II.

The values of ω_e and $\omega_e x_e$ are well outside the statistical error estimates of the previous determinations (7, 12). However, the previous values were indirectly determined by application of isotopic relationships to the $\Delta G''_{1/2}$ values of PH and PD. The B_e value of Table III results in $r_e = 1.42218$ Å, where no attempt was made to compute r_e^{BO} (35).

The equilibrium constants of Table III were used as input for an RKR program[2] in order to calculate the ground state $X^3\Sigma^-$ potential curve. The classical turning points are given in Table IV and the potential curve is plotted in Fig. 2. Since the

[2] This program was kindly provided by Professor R. J. LeRoy, University of Waterloo.

TABLE IV

Turning Points of the Potential Energy Curve of the $X^3\Sigma^-$ State of PH

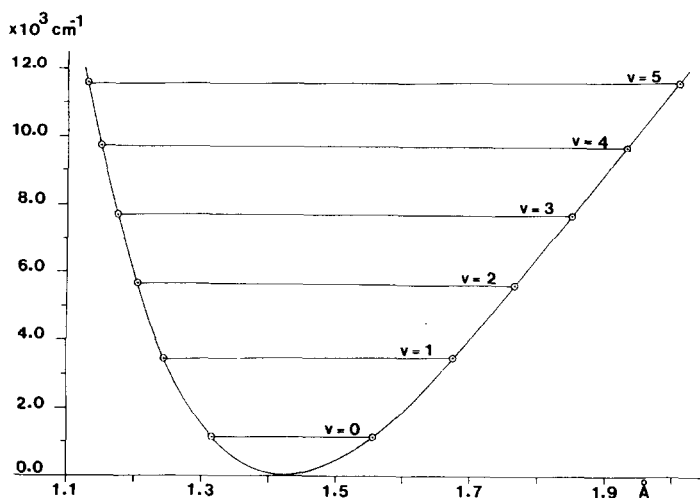| v	E_v (cm^{-1})	R_{min} (Å)	R_{max} (Å)
0	1 171.9287	1.31257	1.55633
1	3 448.1410	1.24514	1.67401
2	5 636.9519	1.20417	1.76701
3	7 738.1060	1.17388	1.85134
4	9 750.8987	1.14976	1.93181
5	11 674.1770	1.12978	2.01082

FIG. 2. The potential energy curve of the ground $X^3\Sigma$ state of PH. The equilibrium molecular constants, derived from data covering $v = 0$–5, were used to calculate this RKR potential curve.

calculated dissociation energy of PH is 24 400 cm^{-1} (27), the RKR curve (Fig. 2) covers nearly one-half of the ground state potential well.

CONCLUSION

Five vibration–rotation bands of PH have been observed in emission with a high-resolution Fourier transform spectrometer. Molecular constants were determined for $v = 0$ to 5 and an RKR potential curve computed for the lower half of the ground state potential well.

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