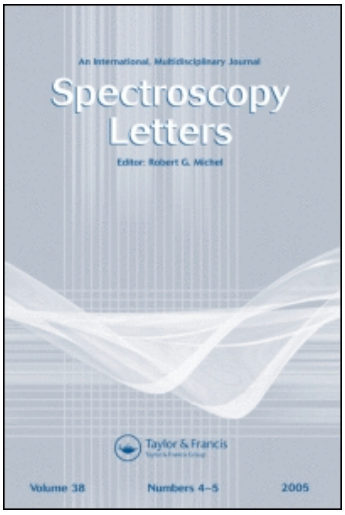

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

LINE INTENSITY MEASUREMENT FOR THE ν_1 AND ν_3 BANDS OF PHOSPHINE

Carlos B. Suárez[a]
[a] Centro de Química Inorgánica, Universidad Nacional de La Plata y Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina, La Plata, Argentina

Online publication date: 14 November 2002

To cite this Article Suárez, Carlos B.(2002) 'LINE INTENSITY MEASUREMENT FOR THE ν_1 AND ν_3 BANDS OF PHOSPHINE', Spectroscopy Letters, 35: 6, 757 — 767
To link to this Article: DOI: 10.1081/SL-120016278
URL: http://dx.doi.org/10.1081/SL-120016278

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SPECTROSCOPY LETTERS
Vol. 35, No. 6, pp. 757–767, 2002

LINE INTENSITY MEASUREMENT FOR THE ν_1 AND ν_3 BANDS OF PHOSPHINE

Carlos B. Suárez*

Centro de Química Inorgánica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata y Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina, C.C. 962, 1900, La Plata, Argentina

ABSTRACT

We have obtained laboratory spectrum of PH_3 in the important 5 μm observational window of Jupiter, between 2200 and 2400 cm^{-1} and measured the intensity coefficients at 294 K for 138 individual lines of the ν_1 and ν_3 bands, for which the band strength are reported. As PH_3 is known to be present in Jupiter, as well as in Saturn, as a minority component appears indeed as a good tracer and the investigation of line parameters in the laboratory is hence of importance for astrophysical applications.

Key Words: ν_1 and ν_3 bands; Phosphine; Astrophysical measurements

*E-mail: suarez@nahuel.biol.unlp.edu.ar

DOI: 10.1081/SL-120016278
0038-7010 (Print); 1532-2289 (Online)

www.dekker.com

INTRODUCTION

The investigation of phosphine in the 4–5 μm range of the spectra of Jupiter and Saturn has produced over the last years important information on this minor constituent in the deep atmosphere layers of both planets. Mean vertical profile and elemental ratio P/H were attained from ground-based, airborne, and from space probe spectra. In view of planetary spectra expected in the future, spatial and temporal PH_3 variations should be more extensively investigated. PH_3 appears indeed as a good tracer of convective circulation and nonequilibrium chemistry on outer planets, and to determine chemical composition and physical state of their atmosphere. In the 4–5 μm range no fewer than five vibrational bands contribute to absorption (or emission): the two strong fundamentals ν_1 and ν_3 at 2321 and 2326 cm^{-1}, and the three overtone and combination bands $2\nu_2$, $\nu_2 + \nu_4$, and $2\nu_4$ at 1972, 2108, and 2226 cm^{-1}, respectively. These bands overlap, and together with strong Coriolis interactions and Fermi resonance make any analysis more difficult to perform. At 5 μm the PH_3 and CH_3D spectra coincide, and in order to obtain accurate column densities for both, absolute intensities and line broadening parameters need to be determined for both species. In this area supporting laboratory studies are required to obtain meaningful interpretation from both spacecraft and ground-based measurements. Thus, accurate quantification of PH_3 is of prime importance from the point of view of both tropospheric modeling and stratospheric chemistry. Consequently, IR line profile measurements appear then as a basic necessity in order to provide pertinent data usable by atmospheric chemist and modelers and the 5 μm region is of particular interest in being a window almost completely free of strong molecular absorptions. Also, in view of the increased level of accuracy required for the remote sensing of temperature it is of interest to perform detailed investigation of these parameters. In an attempt to unravel the PH_3 spectrum and to separate the CH_3D and PH_3 lines in Jupiter's spectrum, high resolution spectra of PH_3 at various temperatures and pressures have been obtained using a Fourier Transform Spectrometer. The low temperature eliminates high J lines from the spectra, thus simplifying them, as well as providing spectra which imitate actual planetary conditions. The high resolution available will aid in a more complete assignment. This paper will deal with room temperature conditions only. A nonlinear least-squares technique is applied to the bands to obtain lineshape parameters (position, intensity and broadening).

EXPERIMENTAL CONDITIONS

Several sets of PH_3 spectra were recorded under different conditions related with the PH_3 pressures and abundances, for further use in a fitting series of our spectral lines model. The spectra analyzed here were recorded with a Bomem DA 3.002 FTS instrument with actual resolution of $0.006\,cm^{-1}$, in the spectral range of $2000–2400\,cm^{-1}$, using an InSb detector cooled at liquid-nitrogen temperatures. Each spectrum comprised 30 co-added scans averaged to improve the signal to noise ratio. In addition, the empty cell spectrograms were obtained for further appropiate ratioing. We used absorption cells of 2 and 5 mm in length, i.e., relatively short in view of the strong absorption of PH_3 in this region, made out of stainless steel, as this is a very corrosive substance, with sapphire windows and indium gaskets at room temperature measure by means of a calibrated thermocouple that was simultaneous and continuously monitored on a strip chart recorder to ensure that a uniform temperature was being obtained. Those runs showing a deviation of more than one degree were discarded. The pressure was measure with a MKS made absolute Baratron pressured transducers. Phosphine is a very dangerous species, so special care has to be taken to handle it.

The spectral intensities, half-widths and wavenumbers were obtained by means of non-linear least-squared fitting techniques of each individual lines or multiplets, as appropriate. In short, each fitting was started by introducing an initial guess of these parameters from which a calculated spectrum was derived on the assumption of purely additive Voigt-shaped lines. The absorption profile so obtained was then convolved with the instrument function thus yielding a theoretical spectrum to be compared to the experimental one. The quality of the fit can be estimated by calculating the standard deviations of the ''observed-line minus calculated-line'' values, point by point, for the set of about 150 points that each line, or spectral segment under consideration, spanned. This deviation was only a fraction of 1%. By inspecting the plots of the fits and of the points-by-point differences we have found that the absolute magnitude of discrepancies never exceeded 1% for each digital point. The higher ones usually corresponded to the cases of very strong lines which probably can be adscribed to severe blending that could not be resolved by our instrument. These cases were not included in our report. We took special care to simultaneously fit all component of detected multiplets or ''individual'' lines together with neighboring lines contributing to the line profile. Our program is capable of doing fitting of ten lines at the same time when necessary. However, computer time is very long for these cases, and that is a reason for us to have concentrated more on fewer lines than actually observed, taking into account those relatively

isolated from contribution of far wings from neighbor lines. To date 138 out of 212 line intensities recorded at room temperature have been reported here.

RESULTS AND DISCUSSION

The measured intensities belonging to the strongest ν_1 and ν_3 were analyzed and 138 lines, single or only apparently slightly blended, were retained. The line assignments was taken from Ref. [1]. The results are as follows:

The band strenght of ν_1 and ν_3 were calculated from

$$S_V^0\,(\text{in cm}^{-2}\,\text{atm}^{-1}\,\text{at T}) = \frac{8\pi^3\nu_V}{3hc} Z_V L \mu_V \frac{T_0}{T}$$

with $L = 2.6875 \times 10^{19}\,\text{cm}^{-3}\,\text{atm}^{-1}$ at $T_0 = 273.15\,\text{K}$ and $Z_V = 1.018217$ at 300 K is the partition function.

For the ν_1 band at $2321.118\,\text{cm}^{-1}$ $\mu_1 = 0.0606$ (20) Debye and $S_1^0 = (85 \pm 4)\,\text{cm}^{-2}\,\text{atm}^{-1}$ at 300 K.

For the ν_3 band at $2326.858\,\text{cm}^{-1}$ $\mu_3 = 0.1150$ (12) Debye and $S_3^0 = (306 \pm 6)\,\text{cm}^{-2}\,\text{atm}^{-1}$ at 300 K.

The quoted errors for μ_V represent three standard deviations. Ref. [2] provide tools to calculate vibration-rotation intensities in the case of strongly interacting vibrational polyads. Fortunately, G.Tarrago[3] calculated the values of μ_V for us.

With the experimental setup described we recorded the whole region specified at 294 K processing the data of five sets, with pressures from 3 to 10 torr of PH_3. We report our study for 138 individual lines of the ν_1 and ν_3 bands in Table 1. At these pressures dominated by Doppler broadening we did not obtain significant half-width broadening coefficient, and so only report the average of the five set for absolute intensities, as shown in Table 1. With our model we can reproduce experimental digital point for individual lines with a goodness of fit better than 1%. However, that shows the statistic involved to reproduced the line profile, point by point. But from the average and the dispersion of the five set of measurements it is found an absolute error of about 5% for each intensity coefficient. Values, derived for the band strength S_1^0 and S_3^0 confirm the ratio of 0.28 previously determined for S_1^0/S_3^0,[1] but lead to an overall strength $S_1^0 + S_3^0$ about 15% lower than the value measured by Van Straten.[4]

Table 1. Experimental Line Intensity Measurement for Phosphine

		Assignment			Upper Level						
Order	Branch	J	K	Symmetry	J′	|K|′	l′	Symmetry	Band	Wavenumber cm^{-1}	Intensity $cm^{-1}atm^{-1}$
1	(P)P	3	1	E	2	0	1	E	NU3	2300.439	0.5989
2	(P)P	3	2	E	2	1	−1	E	NU3	2301.674	1.1200
3	(P)P	3	3	A+	2	2	−1	A+	NU3	2302.976	1.5630
4	(P)P	3	3	A−	2	2	−1	A−	NU3	2302.976	1.5630
5	(Q)P	2	0	A+	1	0	0	A+	NU1	2303.224	0.3910
6	(Q)P	2	1	E	1	1	0	E	NU1	2303.234	0.2831
7	(R)P	2	0	A+	1	1	1	A+	NU3	2308.325	0.3583
8	(P)P	2	1	E	1	0	1	E	NU3	2309.507	0.5360
9	(P)P	2	2	E	1	1	−1	E	NU3	2310.745	1.0770
10	(Q)Q	11	7	E	11	7	0	E	NU1	2316.585	0.2723
11	(Q)Q	10	7	E	10	7	0	E	NU1	2317.265	0.3286
12	(Q)Q	10	6	A	10	6	0	A	NU1	2317.475	0.6125
13	(R)Q	10	5	E	10	6	1	E	NU3	2317.836	0.2973
14	(Q)Q	9	7	E	9	7	0	E	NU1	2317.914	0.4802
15	(Q)Q	9	6	A	9	6	0	A	NU1	2318.081	0.9148
16	(R)Q	9	5	E	9	6	1	E	NU3	2318.426	0.4594
17	(P)P	1	1	E	0	0	1	E	NU3	2318.495	0.4610
18	(Q)Q	8	6	A	8	6	0	A	NU1	2318.640	1.3450
19	(R)Q	8	5	E	8	6	1	E	NU3	2318.961	0.6902
20	(R)Q	9	4	E	9	5	1	E	NU3	2318.979	0.4940
21	(R)Q	7	5	E	7	6	1	E	NU3	2319.430	0.7906
22	(R)Q	8	4	E	8	5	1	E	NU3	2319.544	0.5575

(*continued*)

Table 1. Continued

		Assignment			Upper Level						
Order	Branch	J	K	Symmetry	J′	|K|′	l′	Symmetry	Band	Wavenumber cm^{-1}	Intensity $cm^{-1}atm^{-1}$
23	(R)Q	10	2	E	10	3	1	E	NU3	2319.855	0.3586
24	(Q)Q	5	5	E	5	5	0	E	NU1	2320.019	1.0590
25	(R)Q	7	4	E	7	5	1	E	NU3	2320.053	0.7581
26	(Q)Q	4	3	A	4	3	0	A	NU1	2320.281	0.8940
27	(R)Q	8	3	A−	8	4	1	A+	NU3	2320.320	0.5715
28	(R)Q	8	3	A+	8	4	1	A−	NU3	2320.320	0.5715
29	(Q)Q	4	4	E	4	4	0	E	NU1	2320.379	1.0090
30	(R)Q	6	4	E	6	5	1	E	NU3	2320.502	0.7882
31	(Q)Q	3	2	E	3	2	0	E	NU1	2320.611	0.3585
32	(Q)Q	1	1	E	1	1	0	E	NU1	2321.040	0.3175
33	(R)Q	8	2	E	8	3	1	E	NU3	2321.214	0.6139
34	(R)Q	11	0	A+	11	1	1	A−	NU3	2321.356	0.4847
35	(R)Q	9	1	E	9	2	1	E	NU3	2321.497	0.3689
36	(R)Q	10	0	A+	10	1	1	A−	NU3	2322.111	0.6927
37	(R)Q	4	3	A	4	4	1	A	NU3	2322.199	1.3160
38	(R)Q	6	2	E	6	3	1	E	NU3	2322.347	0.8613
39	(P)Q	12	2	E	12	1	−1	E	NU3	2322.634	0.1152
40	(P)Q	10	1	E	10	0	1	E	NU3	2322.984	0.4156
41	(R)Q	4	2	E	4	3	1	E	NU3	2323.211	0.8211
42	(R)Q	6	1	E	6	2	1	E	NU3	2323.370	0.8701
43	(P)Q	11	2	E	11	1	−1	E	NU3	2323.423	0.2047
44	(R)Q	8	0	A+	8	1	1	A−	NU3	2323.467	1.3150
45	(R)Q	3	2	E	3	3	1	E	NU3	2323.533	0.5771
46	(P)Q	9	1	E	9	0	1	E	NU3	2323.731	0.6628

47	(R)Q	5	1	E	5	2	1	E	NU3	2323.856	0.9722
48	(P)Q	10	2	E	10	1	−1	E	NU3	2324.200	0.3639
49	(R)Q	4	1	E	4	2	1	E	NU3	2324.265	1.0370
50	(P)Q	8	1	E	8	0	1	E	NU3	2324.425	0.7995
51	(R)Q	6	0	A+	6	1	1	A−	NU3	2324.585	0.2134
52	(R)Q	3	1	E	3	2	1	E	NU3	2324.596	8.4760
53	(R)Q	2	1	E	2	2	1	E	NU3	2324.847	0.5955
54	(P)Q	9	2	E	9	1	−1	E	NU3	2324.943	0.5066
55	(P)Q	12	4	E	12	3	−1	E	NU3	2325.006	0.8593
56	(R)Q	5	0	A+	5	1	1	A−	NU3	2325.043	0.0223
57	(R)Q	4	0	A+	4	1	1	A−	NU3	2325.431	2.3290
58	(R)Q	3	0	A+	3	1	1	A−	NU3	2325.745	2.1730
59	(R)Q	2	0	A+	2	1	1	A−	NU3	2325.982	1.8030
60	(P)Q	7	2	E	7	1	−1	E	NU3	2326.278	8.5200
61	(P)Q	9	3	A−	9	2	−1	A+	NU3	2326.428	0.3280
62	(P)Q	4	1	E	4	0	1	E	NU3	2326.543	1.1890
63	(P)Q	8	3	A+	8	2	−1	A−	NU3	2326.745	0.7279
64	(P)Q	10	4	E	10	3	−1	E	NU3	2326.821	0.3248
65	(P)Q	6	2	E	6	1	−1	E	NU3	2326.850	1.0730
66	(P)Q	3	1	E	3	0	1	E	NU3	2326.883	1.1510
67	(P)Q	8	3	A−	8	2	−1	A+	NU3	2327.093	0.6225
68	(P)Q	2	1	E	2	0	1	E	NU3	2327.140	0.9538
69	(P)Q	1	1	E	1	0	1	E	NU3	2327.313	0.6334
70	(P)Q	5	2	E	5	1	−1	E	NU3	2327.351	1.1360
71	(P)Q	7	3	A+	7	2	−1	A−	NU3	2327.458	0.8375
72	(P)Q	7	3	A−	7	2	−1	A+	NU3	2327.685	0.7718
73	(P)Q	4	2	E	4	1	−1	E	NU3	2327.775	1.0590
74	(P)Q	6	3	A+	6	2	−1	A−	NU3	2328.082	0.9177

(*continued*)

Table 1. Continued

Order	Branch	Assignment J	K	Symmetry	Upper Level J′	|K|′	l′	Symmetry	Band	Wavenumber cm^{-1}	Intensity $cm^{-1}atm^{-1}$
75	(P)Q	3	2	E	3	1	−1	E	NU3	2328.118	0.9797
76	(P)Q	6	3	A−	6	2	−1	A+	NU3	2328.216	0.9515
77	(P)Q	8	4	E	8	3	−1	E	NU3	2328.332	0.6188
78	(P)Q	2	2	E	2	1	−1	E	NU3	2328.378	0.6584
79	(P)Q	5	3	A+	5	2	−1	A−	NU3	2328.617	1.0320
80	(P)Q	7	4	E	7	3	−1	E	NU3	2328.972	0.6623
81	(P)Q	4	3	A+	4	2	−1	A−	NU3	2329.062	0.8487
82	(P)Q	4	3	A−	4	2	−1	A+	NU3	2329.093	0.9028
83	(P)Q	9	5	E	9	4	−1	E	NU3	2329.257	0.3084
84	(P)Q	3	3	A+	3	2	−1	A−	NU3	2329.418	0.5923
85	(P)Q	3	3	A−	3	2	−1	A+	NU3	2329.428	0.5846
86	(P)Q	6	4	E	6	3	−1	E	NU3	2329.540	0.8201
87	(P)Q	9	6	A	9	5	−1	A	NU3	2329.830	0.6917
88	(P)Q	5	4	E	5	3	−1	E	NU3	2330.035	0.8376
89	(P)Q	4	4	E	4	3	−1	E	NU3	2330.457	0.5374
90	(P)Q	7	5	E	7	4	−1	E	NU3	2330.561	0.4932
91	(P)Q	6	5	E	6	4	−1	E	NU3	2331.091	0.5731
92	(P)Q	5	5	E	5	4	−1	E	NU3	2331.545	0.4290
93	(P)Q	7	6	A	7	5	−1	A	NU3	2331.684	0.9187
94	(P)Q	9	7	E	9	6	−1	E	NU3	2331.831	0.3510
95	(P)Q	6	6	A	6	5	−1	A	NU3	2332.400	0.7482
96	(P)Q	8	7	E	8	6	−1	E	NU3	2332.696	0.3801
97	(P)Q	7	7	E	7	6	−1	E	NU3	2333.450	0.3017
98	(P)Q	9	8	E	9	7	−1	E	NU3	2333.711	0.2792

99	(R)R	0	0	A+	1	1	1	A+	NU3	2335.034	0.8209
100	(P)Q	9	9	A	9	8	−1	A	NU3	2335.644	0.3376
101	(Q)R	1	0	A+	2	0	0	A+	NU1	2338.653	0.4070
102	(Q)R	1	1	E	2	1	0	E	NU1	2338.664	0.2888
103	(R)R	1	1	E	2	2	1	E	NU3	2342.653	1.1410
104	(R)R	1	0	A+	2	1	1	A+	NU3	2343.754	1.1490
105	(R)R	2	2	E	3	3	1	E	NU3	2350.237	1.7460
106	(R)R	2	1	E	3	2	1	E	NU3	2351.298	1.1620
107	(R)R	2	0	A+	3	1	1	A+	NU3	2352.377	1.4134
108	(P)R	2	1	E	3	0	1	E	NU3	2353.584	0.3331
109	(Q)R	3	3	A	4	3	0	A	NU1	2355.879	0.9009
110	(R)R	3	2	E	4	3	1	E	NU3	2358.802	1.5620
111	(R)R	3	1	E	4	2	1	E	NU3	2359.852	1.1140
112	(R)R	3	0	A+	4	1	1	A+	NU3	2360.904	1.5290
113	(P)R	3	1	E	4	0	1	E	NU3	2362.130	0.4318
114	(Q)R	4	2	E	5	2	0	E	NU1	2364.134	0.5425
115	(Q)R	4	3	A	5	3	0	A	NU1	2364.281	1.4990
116	(Q)R	4	4	E	5	4	0	E	NU1	2364.315	0.8792
117	(R)R	4	4	E	5	5	1	E	NU3	2365.370	1.8280
118	(R)R	4	3	A	5	4	1	A	NU3	2366.299	3.1770
119	(R)R	4	2	E	5	3	1	E	NU3	2367.280	1.2800
120	(R)R	4	0	A+	5	1	1	A+	NU3	2369.333	1.5390
121	(P)R	4	2	E	5	1	−1	E	NU3	2371.816	0.3051
122	(Q)R	5	2	E	6	2	0	E	NU1	2372.333	0.3916
123	(R)R	5	5	E	6	6	1	E	NU3	2372.390	2.1270
124	(Q)R	5	4	E	6	4	0	E	NU1	2372.538	1.0980
125	(Q)R	5	3	A	6	3	0	A	NU1	2372.592	1.7840

(*continued*)

Table 1. Continued

		Assignment			Upper Level						
Order	Branch	J	K	Symmetry	J′	|K|′	l′	Symmetry	Band	Wavenumber cm^{-1}	Intensity $cm^{-1}atm^{-1}$
126	(Q)R	5	5	E	6	5	0	E	NU1	2373.183	0.5252
127	(S)R	5	2	E	6	4	−1	E	NU3	2373.279	0.3077
128	(R)R	5	4	E	6	5	1	E	NU3	2373.850	1.1690
129	(R)R	5	3	A	6	4	1	A	NU3	2374.718	2.4490
130	(R)R	5	2	E	6	3	1	E	NU3	2375.671	1.0380
131	(R)R	5	1	E	6	2	1	E	NU3	2376.688	0.9674
132	(R)R	5	0	A+	6	1	1	A+	NU3	2377.665	1.2790
133	(Q)R	6	2	E	7	2	0	E	NU1	2380.393	0.3950
134	(Q)R	6	5	E	7	5	0	E	NU1	2380.436	1.7970
135	(Q)R	6	1	E	7	1	0	E	NU1	2380.512	0.5514
136	(Q)R	6	0	A+	7	0	0	A+	NU1	2380.530	0.5011
137	(Q)R	6	4	E	7	4	0	E	NU1	2380.655	1.1110
138	(Q)R	6	3	A	7	3	0	A	NU1	2380.818	1.6990

CONCLUSIONS

Summarizing, we have obtained the spectrum of PH_3 in the important 5 μm observational window of Jupiter, between 2200 and 2400 cm^{-1} and measured the intensity coefficients at 294 K for individual lines. The number of 138 lines reported is only limited by the rather time consuming computer processing involved. Our fitting procedure allowed us to accurate reproducing individual lines or set of lines within limited segments. From five relevant sets of spectra involving different experimental conditions we estimate the absolute error for any of our retrieved intensity coefficients to be about 5%. As PH_3 is known to be present in Jupiter, as well as in Saturn, the investigation of line parameters in the laboratory is hence of importance for astrophysical applications.

REFERENCES

1. Baldacci, A.; Malathy Devi, V.; Narahari Rao, K; Tarrago, G. J. Mol. Spectrosc. **1980**, *88*, 311–322.
2. Tarrago, G.; Ulenikov, O.N.; Poussigue, G. J. Physique. **1984**, *45*, 1429–1447.
3. Tarrago, G. Private communication.
4. Van Straten, A.J. J. Molec. Spectrosc. **1977**, *65*, 202.

Received December 11, 2001
Accepted June 15, 2002