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Line positions and intensities of the phosphine (PH_3) Pentad near 4.5 µm

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ABSTRACT

In order to improve the spectroscopic database for remote sensing of the giant planets, line positions and intensities are determined for the five bands ($2\nu_2$, $\nu_2+\nu_4$, $2\nu_4$, ν_1 and ν_3) that comprise the Pentad of PH_3 between 1950 and 2450 cm^{-1}. Knowledge of PH_3 spectral line parameters in this region is important for the exploration of dynamics and chemistry on Saturn, (using existing Cassini/VIMS observations) and future near-IR data of Jupiter from Juno and ESA's Jupiter Icy Moons Explorer (JUICE). For this study, spectra of pure PH_3 from two Fourier transform spectrometers were obtained: (a) five high-resolution (0.00223 cm^{-1}), high signal-to-noise (~1800) spectra recorded at room temperature (298.2 K) with the Bruker IFS 125HR Fourier transform spectrometer (FTS) at the Pacific Northwest National Laboratory (PNNL), Richland, Washington and (b) four high-resolution (at 0.0115 cm^{-1} resolution), high signal-to-noise (~700) spectra recorded at room temperature in the region 1800–5200 cm^{-1} using the McMath-Pierce Fourier transform spectrometer located at the National Solar Observatory (NSO) on Kitt Peak. Individual line parameters above 2150 cm^{-1} were retrieved by simultaneous multispectrum fittings of all five Bruker spectra, while retrievals with the four Kitt Peak spectra were done in the 1938–2168 cm^{-1} range spectrum by spectrum and averaged. In all, positions and intensities were obtained for more than 4400 lines. These included 53 A+A– split pairs of transitions (arising due to vibration–rotation interactions (Coriolis-type interaction) between the ν_3 and ν_1 fundamental bands) for $K''=3$, 6, and 9. Over 3400 positions and 1750 intensities of these lines were ultimately identified as relatively unblended and modeled up to $J=14$ and $K=12$ with rms values of 0.00133 cm^{-1} and 7.7%, respectively. The PH_3 line parameters (observed positions and measured intensities with known quantum assignments) and Hamiltonian constants are reported. Comparisons with other recent studies are discussed.

1. Introduction

Phosphine features have long been identified in the spectra of Jupiter and Saturn [1–9] and even searched for in Titan data [10]. Accurate knowledge of line parameters for PH_3 is particularly crucial to interpret Cassini/VIMS in the 1–5 µm range and Cassini/CIRS observations in the 7–1000 µm range [8–10]. However, a startling inconsistency in the derived PH_3 mixing ratios with altitude was noticed by Cassini astronomers who suspected inaccuracies in the 4.5 µm line intensities in the PH_3 database [11–14]. Line positions and intensities of PH_3 had been extensively studied for its ground state, the four fundamental bands, and most of its overtone and combination bands up to 2.7 µm [14–31]. It was therefore unexpected when the planetary mixing ratios retrieved for PH_3 using the Pentad bands at 4.5 µm [9] were nearly half those obtained using the fundamentals near 10 µm [15]. The Pentad bands are expected to probe deeper into Saturn's convective troposphere than the Dyad bands near 10 µm. As phosphine is a disequilibrium species at the cold temperatures of Saturn's upper troposphere, being dredged from the deeper interior by vertical mixing, there was no explanation for a depletion of phosphine with depth (from the 4.5-µm analysis). Furthermore, there are no phosphine sources to explain the higher values derived in the upper troposphere from the 10-µm analysis. This inconsistency between the two values could be due to a poor understanding of aerosol opacity in the VIMS observations (aerosols affect the 4.5-µm analysis more strongly than in the 10-µm analysis). However, it was important

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first to check the underlying spectral line parameter database to eliminate potential inconsistencies between the Pentad and the Dyad. The present study was undertaken to investigate this problem by obtaining new intensity measurements of PH_3 in the Pentad.

From past studies, a great deal of information is known about the absorption spectrum of the PH_3 Pentad between 1900 and 2500 cm^{-1}. Observed spectra used in the present study are shown in Figs. 1 and 2. The most prominent features of PH_3 absorptions in the Pentad region arise from the two strong overlapping fundamentals ν_1 and ν_3 centered at 2321.1 and 2326.5 cm^{-1}, respectively, which are in strong Coriolis-type interaction. The 1930–2150 cm^{-1} interval is dominated by the two weaker bands: $2\nu_2$ (at 1972.6 cm^{-1}) and $\nu_2 + \nu_4$ (at 2108.2 cm^{-1}). The rotational levels of the middle band $2\nu_4^0$ (at 2226.8 cm^{-1}) and $2\nu_4^2$ (at 2235.3 cm^{-1}) perturb those of the four other bands. Hence, the theoretical models for the Pentad must consider several types of interactions (such as Coriolis, Fermi, K-type and ℓ-type). As a result, the rovibrational and intensity analyses are quite challenging.

Various theoretical models have been applied to describe the infrared spectrum of PH_3. Spectroscopic parameters for the ground vibrational state of PH_3 have been reported by Fusina and Carlotti [25] and more recently by Müller [32] (who performed a reanalysis of the ground state rotational spectrum of PH_3 by combining data from sub-Doppler, conventional absorption spectroscopy and radio-frequency measurements in the far-infrared regions). In the present analysis, however, an effective Hamiltonian similar to the one applied to model the ν_2/ν_4 Dyad at 10 µm [15] was used, along with the earlier ground state parameters [25]. The Pentad $2\nu_2$, $\nu_2 + \nu_4$, $2\nu_4$, ν_1 and the ν_3 at 4.5 µm [14] was studied by Tarrago who developed the initial theoretical model for C_{3v} molecules [16]. That analysis of FTIR spectra recorded in France at 0.0054 cm^{-1} resolution permitted assignments for over 4400 lines of which 3766 line positions were modeled with a root-mean-square (rms) deviation of 0.009 cm^{-1}; line intensities were also measured, and 810 of these were reproduced by theory with a standard deviation of ~11–13%. However, this study used an absorption path of 12 m to measure the weak overtone and combination bands. As a result, the strong transitions were saturated, and only a limited number of measured intensities were used for the fundamentals: 20 for ν_1 and 50 for ν_3 [see also Ref. 20]. The Tarrago et al. prediction [14] appeared in the public databases [12,13] beginning in 2003 [17].

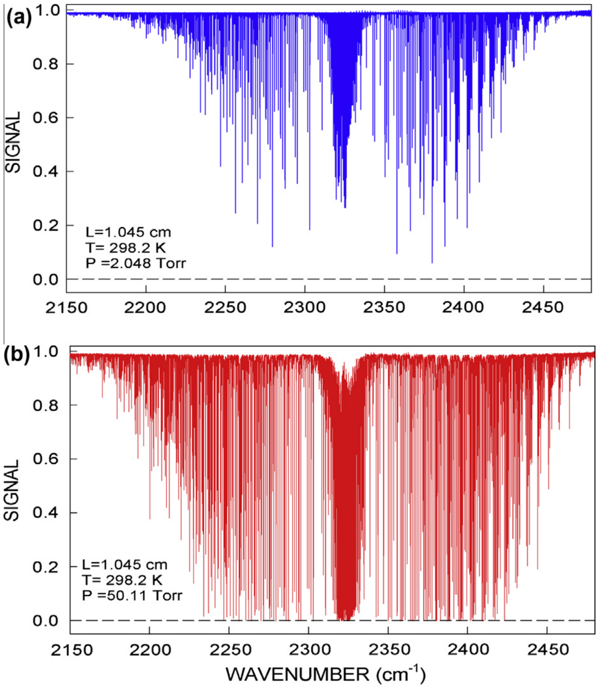

Fig. 1. Laboratory absorption spectra of PH_3 between 2150 and 2455 cm^{-1} recorded at 0.00223 cm^{-1} resolution with the Bruker FTS at PNNL. Two spectra obtained with using a 1.045 cm (2) optical path at 298.2 K are shown: (a) 2.05 Torr (b) 50.11 Torr. The strong features correspond to the fundamental bands ν_1 at 2321.11 cm^{-1} and ν_3 at 2326.37 cm^{-1}. At the higher optical densities, the other three bands appear: $2\nu_2$ (at 1972.6 cm^{-1}), $\nu_2 + \nu_4$ (at 2108.2 cm^{-1}) and $2\nu_4$ (at 2226.8 cm^{-1}).

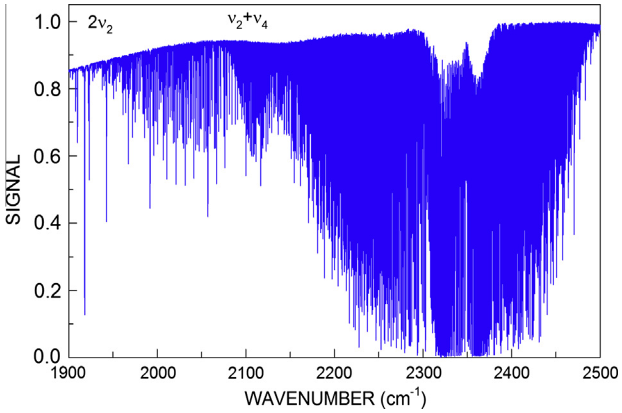

Fig. 2. An observed spectrum of PH_3 recorded with the McMath-Pierce FTS at 0.0115 cm^{-1} resolution. Absorptions of two weaker bands are evident, but $2\nu_4$ (at 2226.8 cm^{-1}) is masked by the two fundamentals. The absorption path length is 425 cm; the PH_3 gas pressure is the lowest of the four (0.95 Torr at 294 K). Measurements below 2168 cm^{-1} from the Kitt Peak spectra were combined with those from the PNNL data. The stronger transitions below 2000 cm^{-1} arise from residual water vapor outside the absorption cell. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A later study of the PH_3 Octad near 2.7 µm by Butler et al. 2006 [18] called into question the reliability of the intensity prediction for the Pentad, however. These authors wanted to confirm the effective pressures of the spectral data obtained using the longer path lengths recorded with the Kitt Peak FTS and attempted to achieve this by measuring some intensities of the $2\nu_2$ Q branch lines appearing in the same spectra. However, as seen in Table 2 and Fig. 5 of that paper [18], large systematic differences between the predicted and observed $2\nu_2$ intensities were seen *as a function of the quantum numbers J and K*. Butler et al. also compared individual line intensities of mostly ν_1 and ν_3 lines reported in earlier measurements [19,20,22] against the Tarrago et al. prediction [14,17]. The average ratios varied from 0.69 to 1.06 with rms around 6–8% (see Table 5 of [18]). In the end, there was too little information to decide if the problem arose from experimental inaccuracies or the relative intensities computed with theoretical model.

More recently, a 'global analysis' of PH_3 measurements was performed by Nikitin et al. [23] for the Dyad, Pentad and the Octad systems simultaneously. For this, measured line positions of more than 6000 transitions up to $J = 14$ arising from 34 cold bands and a few hot bands were fitted using available high resolution data, including the Kitt Peak spectra of Butler et al. [18]. That study substantially improved the rms deviations of the Pentad positions compared to the previous work [14]. Unfortunately, the extensive (1600) intensities measured by Tarrago et al. [14] were lost and hence no longer available for reanalysis in the global approach [23], and the Butler et al. spectra [18] were too saturated to retrieve accurate intensities for the stronger Pentad bands. Finally, we note that there is an ongoing effort to characterize the PH_3 spectrum up to 10,000 cm^{-1} using *ab initio* predictions [24 and the references therein].

As summarized in Table 1, a few other studies [26–31] had reported intensities for the Pentad, but only for relatively few transi-