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The absorption spectrum of phosphine (PH_3) between 2.8 and 3.7 μm: Line positions, intensities, and assignments

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Abstract

Over 8000 line positions and intensities of phosphine (PH_3) at 3 μm have been measured at 0.0115 cm^{-1} resolution with the McMath-Pierce Fourier Transform spectrometer at Kitt Peak. The observed line intensities ranged from 4.13×10^{-6} to 4.69×10^{-2} cm^{-2} atm^{-1} at 296 K, for line positions between 2724.477 and 3601.652 cm^{-1}. This region spans eight interacting vibrational states: $3\nu_2$ (2940.8 cm^{-1}), $2\nu_2 + \nu_4$ (3085.6 cm^{-1}), $\nu_2 + 2\nu_4$ (3214.9 cm^{-1}), $\nu_1 + \nu_2$ (3307.6 cm^{-1}), $\nu_2 + \nu_3$ (3310.5 cm^{-1}), $3\nu_4$ (~3345 cm^{-1}), $\nu_1 + \nu_4$ (3426.9 cm^{-1}), and $\nu_3 + \nu_4$ (3432.9 cm^{-1}). Assignments have been determined for all the bands except $3\nu_4$ (a weak band in a highly congested area) for a total of 4232 transitions. The total integrated intensity for this region is 5.70 cm^{-2} atm^{-1} near 296 K, and assigned lines account for 79% of the observed absorption. The two strongest bands in the region are $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$ with band strengths at 296 K of 1.61 and 2.01 cm^{-2} atm^{-1}, respectively. An empirical database of PH_3 line parameters (positions, intensities, and assignments) is now available. Lower state energies (corresponding to assignments from this study) and line widths from the literature are included; default values are used for unassigned features.

Keywords: Phosphine; PH_3; 3 μm bands; Positions; Intensities; Near infrared; Assignments; Line parameters

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1. Introduction

Phosphine (PH_3) is a symmetric top in the C_{3v} point group and a pyramid molecule where the expected inversion doubling is too small to be seen in the infrared even at Doppler-limited resolution. It is a molecule of interest both astronomically, as it has been observed on both Jupiter and Saturn [e.g. 1,2], and spectroscopically, due to its numerous Coriolis and anharmonic interactions. The 3 μm region is a good spectral interval for advancing both of these topics. Features of PH_3 near 3425 cm^{-1} are clearly seen in ground-based spectra of Saturn [3], and line parameters for these bands are needed for the interpretation of data recorded by VIMS (Visible and Infrared Mapping Spectrometer) on the Cassini spacecraft [4]. The region is also a challenging spectroscopic problem due to the eight interacting vibrational bands (the octad) with 13 sub-components: $3\nu_2$ (A_1), $2\nu_2 + \nu_4$ (E), $\nu_2 + 2\nu_4$ (A_1, E), $\nu_1 + \nu_2$ (A_1), $\nu_2 + \nu_3$ (E), $3\nu_4$ (A_1, A_2, E), $\nu_1 + \nu_4$ (E), and $\nu_3 + \nu_4$ (A_1, A_2, E). The energy levels of each symmetry state in the region are shown in Fig. 1. Dotted lines are the A states, dashed lines are the E states, and the single solid line is the predicted energy of the state with no line assignments, $3\nu_4$. First order Coriolis-type interactions are possible when $|\Delta K| = 1$, and Fermi-type interactions when $\Delta K = 0$ and the two interacting states have the same symmetry. For C_{3v} molecules, Coriolis-type or Fermi-type resonances between different vibrational modes, or any essential resonances within the same vibrational mode, are possible whenever the difference $\Delta K - \sum_t \Delta l_t = 3p$ ($p = 0, \pm 1, \ldots$), where K is the quantum number associated

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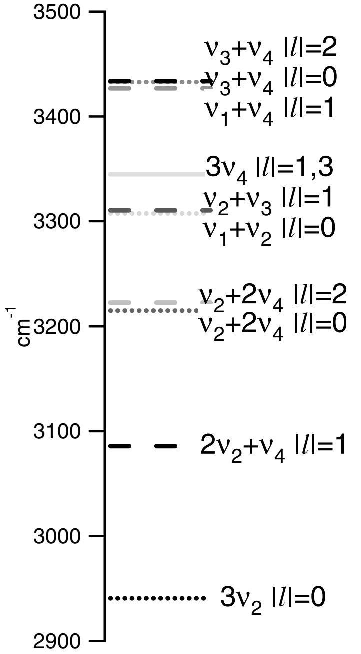

Fig. 1. The energy levels of the octad in the 3 μm region of PH_3. Dotted lines are the *A* states and dashed lines are the *E* states, while the single solid line is the predicted energy of the state with no line assignments, $3\nu_4$.

with the projection of rotational angular momentum on the symmetry axis and *l* is the quantum number associated with the vibrational angular momentum.

The ground state has been studied in both the microwave and the far-infrared [e.g., 5,6]. The line positions of the two lowest fundamentals, the dyad ν_2 ($992.13\ cm^{-1}$) and ν_4 ($1118.31\ cm^{-1}$), were assigned and fitted in several works [e.g., 7,8]. In particular, Fusina and DiLonardo [8] modeled some 2500 dyad positions. Later, some 1000 line intensities of the dyad were measured and modeled within 2% by Brown et al. [9]. Recently, self-broadening coefficients and absolute intensities for the dyad were reported by Salem et al. [10]; on average, their 25 line intensities were within 1% of Brown et al. results.

The next higher polyad of vibrational states is the pentad at 5 μm: $2\nu_2$ ($1973\ cm^{-1}$), $\nu_2+\nu_4$ ($2108\ cm^{-1}$), $2\nu_4$ ($2227\ cm^{-1}$), ν_1 ($2321\ cm^{-1}$), and ν_3 ($2326\ cm^{-1}$). This region was first successfully analyzed by Tarrago et al. [11], and later reconsidered by Ulenikov et al. [12]. Line intensities for ν_1 and ν_3 were reported by Suarez [13] and Lovejoy et al. [14] and recently by Wang et al. [15]. Available results from both the 5 and the 10 μm were collected in 2003 [16] to provide a database of phosphine line parameters [17–19] for planetary studies.

For the octad at 3 μm, $3\nu_2$ and the hot band $4\nu_2-\nu_2$ positions and identifications were first given and modeled as non-interacting states by Maki et al. [20]. Later, assignments for 572 lines for the strongest bands in the region, $\nu_1+\nu_4$ and $\nu_3+\nu_4$ were reported by Ulenikov et al. [21]. The only reported octad line intensities are from Wang et al. [15].

Concurrent with the Ulenikov et al. and Wang et al. studies, we analyzed the 2.8–3.7-μm region of PH_3 by identifying transitions to four additional bands of the octad and increasing and correcting assignments in the three previously studied states. We also measured line positions and intensities of over 8000 features and assigned 4232 transitions to seven of the octad bands. The resulting empirical line list extends the phosphine database for planetary astronomy up to $3600\ cm^{-1}$ and provides a reference linelist for the continued analysis of the octad polyad.

2. Experimental details

The spectra were recorded at a resolution of $0.0115\ cm^{-1}$ using the McMath-Pierce Fourier transform spectrometer located at the National Solar Observatory on Kitt Peak in Arizona. The optical source was a Globar, which shone through the absorption cell onto a CaF_2 beamsplitter in the FTS, and focused onto two InSb detectors. The spectral bandpass covered an interval from 1800 to $5200\ cm^{-1}$. The experimental conditions for each run are listed in Table 1. The data were obtained near room temperature (between 294 and 289 K) using a stainless steel multipass cell with a 1-m base length. The gas temperatures were measured by four thermistors imbedded in the exterior wall of the cell. Six runs were taken with a path length of 4.25 m and one at 16.4 m. The gas pressures ranged from 1.5 to 11.2 torr, measured by a capacitance manometer during the one hour required to obtain a spectrum. Pressures were selected to avoid too much self-broadening and yet maintain a stable sample pressure. The phosphine gas sample from a commercial supplier was used without purification. After the 2nd scan at 3.72 torr, the phosphine sample was incrementally added to the chamber to increase the optical densities of the next three runs up to pressures of 11.2 torr. Then the cell was evacuated overnight, and the cell refilled for the following three pressures. Thus the sample remained in the cell for a period of six hours for the 2nd, 3rd, and 4th scans in Table 1 and for five hours for the next three scans. To calibrate line positions, two low pressure PH_3 spectra were obtained with a longer (6 m) multipass absorption cell that was in tandem with a 2.4 m cell. The shorter cell contained CO so that the 2–0 band at $4260\ cm^{-1}$ [22] could be used as the standard. Calibrated PH_3 lines from these low pressure scans were then utilized for the other PH_3 spectra.

A sample run is shown in Fig. 2, with a pressure of 6.3 torr, a path length of 16.4 m, and a temperature of 289.5 K. The strong absorptions on the far right, especially beyond $3600\ cm^{-1}$, are water lines. There was residual water at low pressure inside the FTS enclosure, creating small narrow features, but atmospheric water at 600 torr in the optical paths external to the absorption cells gave rise to broad features in the PH_3 spectrum. A strong, broad water line at $3466.88\ cm^{-1}$ is visible in Fig. 3, along with several weaker water transitions. Water was present in all the runs, but the transitions were easily identified by their