Analysis of PH_3 spectra in the Octad range 2733–3660 cm^{-1}

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ABSTRACT

Improved analysis of positions and intensities of phosphine spectral lines in the Octad region 2733–3660 cm^{-1} is reported. Some 5768 positions and 1752 intensities were modelled with RMS deviations of 0.00185 cm^{-1} and 10.9%, respectively. Based on an *ab initio* potential energy surface, the full Hamiltonian of phosphine nuclear motion was reduced to an effective Hamiltonian using high-order Contact Transformations method adapted to polyads of symmetric top AB_3-type molecules with a subsequent empirical optimization of parameters. More than 2000 new ro-vibrational lines were assigned that include transitions for all 13 vibrational Octad sublevels. This new fitting of measured positions and intensities considerably improved the accuracy of line parameters in the calculated database. A comparison of our results with experimental spectra of PNNL showed that the new set of line parameters from this work permits better simulation of observed cross-sections than the HITRAN2012 linelist. In the 2733–3660 cm^{-1} range, our integrated intensities show a good consistency with recent *ab initio* variational calculations.

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1. Introduction

Phosphine (PH_3) is a semi-rigid symmetric top molecule. Small concentrations of phosphine occur in the atmospheres of Jupiter and Saturn [1–4]. The 3 μm range of PH_3 infrared (IR) spectrum is especially interesting due to a strong absorption near 3425 cm^{-1} observed in ground-based spectra of Saturn [5]. The HITRAN 2012 database [6] contains a set of 22,189 lines in the 0–3601.652 cm^{-1} range; of these, 8309 measured features [7] are listed for the Octad range (2570–3630 cm^{-1}), but only half (4218) have quantum identifications. Several bands in the PH_3 Octad were previously assigned [7–9] and modelled using an effective Hamiltonian and effective transition moments. Recently, line positions and intensities in the Pentad range have also been revised [10]. In addition, theoretical studies [11–13] have provided variational predictions of transitions obtained from *ab initio* potential energy surfaces (PES) and dipole moment surfaces (DMS) [12–15]. Sousa-Silva et al. [16] applied the DMS of Ref. [15] to rotation-vibrational calculations of PH_3 spectra at $T = 296$ K [16] and at 1500 K [17] using the TROVE program [18]. Rey et al. [19] have calculated a theoretical list of lines at room temperature using the *ab initio* PES and DMS of Nikitin et al. [12,13].

However, reliable line assignments are still absent in a number of spectral ranges, for example, in the upper part of the PH_3 Octad where resonance perturbations are quite large. This present study is a part of a project aimed to improve and extend the analysis of high-resolution spectroscopic data of phosphine in the IR range [9,12] (see also references therein). The goal of this work is to obtain an accurate modeling of positions and intensities of PH_3 in the Octad range. This paper is a continuation of the earlier work [9], but in the present study we use the contact transformation (CT) method that permits deriving initial effective Hamiltonians from an *ab initio* PES as described in [20]. We have built a CT effective Hamiltonian from the PES of Ref. [12] using a multi-step procedure. Firstly, we applied empirical corrections to harmonic frequencies and to the equilibrium geometry. The full nuclear motion Hamiltonian of phosphine was reduced to an effective Hamiltonian using high-order CT method [20] that included resonance coupling intra-polyad terms. After that, we have expressed this in the irreducible tensor operator (ITO) [21,22] formalism for a full account of symmetry properties for AB_3-type molecules following the procedure described in [23]. At this step the technique of transformation is similar to that of methane previously considered in [24]. The new CT-based effective Hamiltonian contains less than half number of adjustable parameters and has better predictive properties, in comparison to purely empirical models [9].

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Table 1
Energy levels, line positions and intensity fit statistics.

Band	Bands centers This Work	Band centers Previous works	#Positions	RMS	STD	J min	J max	#Intens	RMS
$\nu_1+\nu_2$	3307.560*	3307.6 [7]	274	1.81	0.76	0	18	100	0.095
$\nu_1+\nu_4$	3424.630*	3424.50 [8]	932	1.80	0.76	0	20	253	11.4
$3\nu_2$	2940.766*	2940.8 [7]	600	1.45	0.58	0	19	249	9.2
$2\nu_2+\nu_4$	3085.652*	3085.6 [7]	800	1.84	0.78	0	17	350	10.3
$\nu_2+\nu_3$	3311.925	3310.5 [7]	295	1.79	0.74	1	16	84	10.3
$\nu_2+2\nu_4(E)$	3222.506	3221.87 [12]	408	1.92	0.80	1	14	102	11.8
$\nu_2+2\nu_4(A_1)$	3214.930*	3214.9 [7]	274	1.61	0.69	0	16	132	10.9
$\nu_3+\nu_4(A_1)$	3440.258*	3440.26 [8]	572	2.17	0.94	0	17	106	10.1
$\nu_3+\nu_4(A_2)$	3424.440	3423.79 [12]	359	1.73	0.74	1	18	91	10.4
$\nu_3+\nu_4(E)$	3435.624	3435.27 [8]	1059	1.86	0.76	1	19	228	11.3
$3\nu_4 (A_1)$	3349.69	3348.48 [12]	58	1.95	0.87	6	15	22	12.2
$3\nu_4 (A_2)$	3349.21	3348.03 [12]	73	2.88	1.15	6	15	14	12.3
$3\nu_4 (E)$	3333.55	3332.54 [12]	64	3.08	1.32	4	18	21	12.6
All			5768	1.86	0.78			1752	10.9

Note: * Directly observed band center: E_{upper} (cm^{-1}) = E_{lower} (cm^{-1}) + (transition wavenumber); RMS for line positions is given in units [0.001 cm^{-1}]; STD is dimensionless weighted standard deviation; RMS for line intensities is in %.

2. Positions and intensities analysis in the Octad range

The Kitt Peak spectra recorded specifically for the Octad study were given in Table 1 of Ref. [7]. An overview of experimental data (including several low temperature scans at 210 K) for global modeling of PH$_3$ polyads was given also in Table 1 of Ref. [9]. In [9], we attempted to perform a simultaneous modeling of three lower polyads of PH$_3$. One of the weak points of [9] was poor simulation of the spectra above 3100 cm^{-1}. For example, they could not assign some weak bands. In particular, the discrepancy in the $\nu_2 + \nu_3$ band (origin near 3310 cm^{-1}) was believed to arise essentially from inaccuracies in the intensity modeling. In [9], a simulation of strong bands was not sufficiently accurate even for strong transitions, and the RMS for intensity fitting exceeded 18%. Thus, the program for absorption line identification could not identify weak spectral lines because of poor accuracy in the modeling of intensities. In fact, the model for the PH$_3$ Octad had lower accuracy than simulated spectra in the methane Octad. This seemed rather strange because the methane molecule has more vibrational degrees of freedom. Probably, the PH$_3$ molecule is less rigid in comparison with CH$_4$, but this should not complicate the spectral modeling because these differences are relatively small. The umbrella bending effects occur only in spectral ranges that are considerably higher than the Octad range [25]. In addition, phosphorus has only one stable isotope ^{31}P, while natural methane contains $\sim$ 1% of ^{13}CH$_4$. This should simplify assignment of PH$_3$ spectra. The past studies of the PH$_3$ Octad [8,7] considered only part of 13 vibration sub-levels. The work [8] reported four sub-levels: $\nu_1 + \nu_4$(E), $\nu_3 + \nu_4$(E), $\nu_3 + \nu_4$(A$_1$), and $\nu_3 + \nu_4$(A$_2$). But the $\nu_3 + \nu_4$ (A$_2$) level shown in Fig. 4 of [8] is invalid: its correct value (see Table 1) is 3424.440 cm^{-1} (16 cm^{-1} lower). Note that independent variational predictions from PPES's [12,11] reported vibration levels in the Octad range that are consistent with results from ref [9].

The work [7] included a more complete set of vibration sub-levels. In [7], the authors assigned four times more lines than in [8], but they could not assign ro-vibrational transitions belonging to five of thirteen sub-levels. HITRAN-2012 database contains essentially experimental line list in this range including 8309 transitions from Ref [7]: 4091 unassigned and 4107 assigned lines for Octad cold bands and 111 hot band transitions. Maki et al. [26] reported 84 transitions for the $4\nu_2$-ν_2 hot band. Butler et al. [7] extended the number of assignments of the $4\nu_2$-ν_2 band to 125. We began new analysis using empirically based line list of HITRAN-2012 with complementary measured lines extracted from two 6.3 Torr Kitt Peak spectra (see Table 1 of Ref. [7]).

Note that in a lot of cases, our assignments considerably differ from those in [7] where several different assignments were often suggested for the same line position. In our work, we found that the positions of the corresponding nearly overlapping transitions could be shifted by 0.001–0.005 cm^{-1}. If the multiplets were not possible to be resolved we kept only dominant intensity assignments. For example, if our calculations for a couple of coinciding lines from [7] showed that the intensity of one of them is considerably higher (by 10–20 times), we kept only one stronger line. If an upper level for one of several assignments was available from an analysis of other transitions, we simply shifted a transition frequency using combination differences. Otherwise, we removed an ambiguous assignment, because such transitions could not be used for positions and intensities fitting. Note, that in the work [7], the assignments of isolated lines were quite accurate, and we made changes only to assignments of a few isolated lines. For extended spectra assignments, we applied the same algorithm based on an iterative fit of line intensities and positions as discussed in [9]. Only the number of transitions from the ground state to the Octad, and from the Dyad to the Octad, have been changed. Table 1 shows that we have assigned all transitions to the levels with J=0 and

Table 2
Integrated absorbance (in PNNL units) of natural isotopic composition of PH$_3$ at various spectral ranges. Weak bands are marked with grey background.

Range/cm^{-1}	The integrated absorbance (in PNNL units)				Ratio	
	PNNL [28]*	This work**	ab initio [19]	HITRAN [6]	PNNL/TW	HITRAN/TW
2800–2900	–	2.10E−5	2.25E−5	2.18E−5	–	1.04
2920–2950	–	4.74E−5	4.70E−5	4.39E−5	–	0.93
2950–3200	–	1.26E−4	1.19E−4	1.12E−4	–	0.88
3200–3400	1.61E−3	1.46E−3	1.46E−3	1.30E−3	1.10	0.89
3400–3440	1.05E−3	0.98E−3	1.00E−3	0.87E−3	1.08	0.88
3440–3630	2.03E−3	1.92E−3	1.96E−3	1.66E−3	1.05	0.86

Note:
* In the ranges 2800–3200 cm^{-1} the integrated absorbance could not be reliably determined from the observed spectra due to the weakness of the bands and low signal-to-noise ratio. Grey fields correspond to the weakest bands in the PNNL spectra. TW = This Work.
** Hot bands are not included in our list.