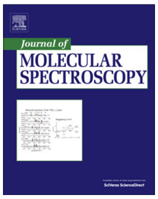
Journal of Molecular Spectroscopy 288 (2013) 28–37

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms



A computed room temperature line list for phosphine

Clara Sousa-Silva *, Sergei N. Yurchenko, Jonathan Tennyson

Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

ARTICLE INFO

Article history:
Received 7 February 2013
In revised form 4 April 2013
Available online 16 April 2013

Keywords:
Infrared
Microwave
Line lists
Phosphine
Variational calculation

ABSTRACT

An accurate and comprehensive room temperature rotation-vibration transition line list for phosphine ($^{31}PH_3$) is computed using a newly refined potential energy surface and a previously constructed *ab initio* electric dipole moment surface. Energy levels, Einstein A coefficients and transition intensities are computed using these surfaces and a variational approach to the nuclear motion problem as implemented in the program TROVE. A ro-vibrational spectrum is computed, covering the wavenumber range 0–8000 cm^{-1}. The resulting line list, which is appropriate for temperatures up to 300 K, consists of a total of 137 million transitions between 5.6 million energy levels. Several of the band centres are shifted to better match experimental transition frequencies. The line list is compared to the most recent HITRAN database and other laboratorial sources. Transition wavelengths and intensities are generally found to be in good agreement with the existing experimental data, with particularly close agreement for the rotational spectrum. An analysis of the comparison between the theoretical data created and the existing experimental data is performed, and suggestions for future improvements and assignments to the HITRAN database are made.

1. Introduction

Phosphine (PH_3) is an extremely toxic, rigid molecule found in the lower troposphere of the Earth and is expected to be of great importance for the spectroscopic studies of giant-planets, particularly for probing the deeper layers of the atmospheres [1], and cool stars. Phosphine has for a long time known to be abundant in Jupiter [2–4], where it is partially responsible for the continuum opacity in the 5 μm region of the atmosphere [5] and where it is a marker for vertical convection zones. It has also been found on Saturn [1,2], and is expected to be present in extrasolar gas giants.

Further spectroscopic investigations of phosphine in the atmospheres of astrophysical bodies requires an extrapolation of the spectra over a wide range of temperatures, pressures and path lengths. The ability to accurately identify and interpret phosphine features in astrophysical spectra is dependent on the existence of a complete description of the phosphine spectra, for all relevant temperatures.

The current CDMS [53] and HITRAN [7] databases encapsulate decades of accurate laboratorial measurements of phosphine spectra at room temperature. However, between the two databases, only a total of 22230 lines are described, all within the 0–3600 cm^{-1} region. CDMS contains transitions between 0 and 300 cm^{-1} with J values of up to 34, sensitive to 10^{-36} cm/molecule, while HITRAN has transitions between 770 and 3600 cm^{-1} stronger than 10^{-28} cm/molecule with $J \leqslant 23$. These databases are designed to be valid for temperatures below 300 K. Other sources (see Table 1 below) mostly overlap with the HITRAN and CDMS databases, and only add little more to these compilations.

The quantity and variety of spectral information required to correctly characterise hot astrophysical bodies is often beyond what can be expected to be delivered experimentally. The ExoMol project [8] (see www.exomol.com) aims to provide a solution to this problem by performing accurate quantum mechanical calculations, with the aim of providing appropriate spectroscopic data on all relevant molecules for the analysis and characterisation of cool stellar and exoplanet atmospheres. This is, however, a challenging alternative to measuring spectra, requiring highly accurate potential energy surfaces (PESs), dipole moment surfaces (DMSs) and an ability to generate precise wave functions and eigenvalues for the nuclear Schrödinger equation and the associated transition intensities. In practice, at least for the PESs, it is also necessary to incorporate a certain amount of experimental refinement.

Our aim is to develop complete line lists which could be used to accurately model the atmospheres of stars and Jupiter-like planets, for which a high temperature ($\geqslant$1500 K) line list for PH_3 is of special importance. In order to establish and test the production of such a line list, which will consist of approximately 1 billion transitions, it is first pertinent to perform a simulation of the room-temperature intensities for this molecule, which can be tested against existing reliable experimental sources. In the present paper a cool (300 K) line list is presented.

---

* Corresponding author.
E-mail address: clara_ss@star.ucl.ac.uk (C. Sousa-Silva).

0022-2852/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jms.2013.04.002

Table 1
Experimental sources of phosphine spectra.

Source	No of lines	Range (cm^{-1})	Uncertainties (cm^{-1})	Intensities
71DaNeWoKl [26][a,c]	53	0.0–4.8	Yes	No
77HeGo [27][a,c]	27	0.0–17.8	No	Calculated
81BeBuPoSh [22][a,c]	68	0.0–35.6	No	No
51LoSt [28]	1	0.94	10^{-6}	No
81PiPoCo [29][c]	1	8.9	3.3×10^{-7}	No
69HeGo [30]	3	8.9–17.8	8.3×10^{-6}	No
06CaPu [56][a]	25	8.9–35.6	*Yes*	No
81BeBuGeKr [58][a]	52	10–35.7	No	No
74ChOk [25][a,c]	12	14.6–15.8	$2.\ 7 \times 10^{-5}$	Calculated
79KrMeSk [31][c]	4	17.1–17.8	$1.7 \times 10^{-\ 6}$	No
00FuLo [32]	155(+2500)	36–125(+750–1400)	0.004	No
88FuCa [57][a]	118	44.5–166.6	10^{-4}	No
02BrSaKlCo [33][b]	>1060	770–1335	0.0002	Some
81TaDaGo [21][b]	1318	818–1340	0.05	Calculated
97AiHaSpKr [34]	62(+250[d])	924–1085	6×10^{-6}	No
01HeZhHuLi [10]	28	992–9040	<0.01	Yes
04SaArBoWa [35]	26	995–1093	No	Yes
02UlBeKoZh [36]	⩾4500	1750–9200	⩽0.0005	No
92TaLaLeGu [1][b]	6605	1885–2445	0.0054	Yes
05WaChChDi [37]	1760	1950–2480	<6%	Yes
		3280–3580		
80BaMaNaTa [38]	1244	2184–2446	0.005	Approximate
02Suarez [39]	138	2300–2381	0.006	Yes
06BuSaKlBr [40][b]	8075	2721–3601	9.2×10^{-4}	Yes
07Kshiraga [41]	400	2730–3100	3.9×10^{-4}	No
73MaSaOl [42]	414	2760–3050	No	No
04UlBeKoZh [43]	>700	3280–3580	0.005	Transmittance

[a] Used in CDMS [53].
[b] Used in HITRAN 08 [7].
[c] Used in JPL [6].
[d] Compiled from other sources.

There have been several previous attempts at *ab initio* studies of the behaviour and characteristics of phosphine spectra. Wang et al. [9] computed a PES using coupled cluster CCSD(T) theory and Dunning's correlation consistent cc-pVTZ basis sets, followed by a vibrational analysis based on second-order perturbation theory. They determined several spectroscopic constants and fundamentals largely within 4 cm^{-1} of the observed results. Zheng et al. [10] calculated an *ab initio* three-dimensional P–H stretching DMS using density functional theory and found absolute band intensities agreed with observed ones within a factor of 2. Yurchenko et al. [11] presented a calculated, albeit empirically refined, PES and, using a variational method, calculated the rotational energy levels in the vibrational ground state of PH_3 for $J \leqslant 80$ [12], thus establishing for the first time the existence of sixfold near-degenerate ro-vibrational energy clusters for this molecule. Subsequently, Yurchenko et al. [13] computed an entirely *ab initio* six-dimensional dipole moment surface (DMS) at the CCSD(T)/aug-cc-pVTZ level of theory for the electronic ground state of PH_3. This is the DMS that is used in the present work, and is described in detail below. It gives calculated transition moments within an average of 22.5% of the experimental data. The same paper also presented a PES determined by empirically refining an existing *ab initio* surface. Ovsyannikov et al. [14] complemented the variationally calculated PES and DMS of Yurchenko et al. [13] by calculating a PES at the CCSD(T) level using aug-cc-pV(Q + d)Z and aug-cc-pVQZ basis sets for P and H, respectively, and then presenting a list of computed vibrational transition moments for the electronic ground state of PH_3[15]. The PES used here is a refined version of the PES presented by Ovsyannikov et al. [14], and is discussed further below. Recently, Nikitin et al. produced a new PES [16] and used it to calculate several vibrational energy levels with only a marginal deviation from experiment. Nikitin et al. then successfully modelled the lower three polyads of phosphine using a variational approach [17]. The resulting line list is discussed and compared to the present work in Section 4 4.6. The phosphine line list presented here can be considered the analogue of the ammonia line lists computed by Yurchenko et al. [18], using TROVE.

2. Background

Phosphine is a well behaved symmetric top molecule belonging to the group-15 hydrides. The phosphorous atom is positioned on the axis of symmetry, perpendicular to the plane containing the equidistant three hydrogen atoms. As is common with molecules having $C_{3v}(M)$ symmetry [19], there is a splitting of rotational levels with $K = 3n$ (where $n \geqslant 1$) in nondegenerate vibrational states [20]. Phosphorous has only one non-synthetic, stable isotope, ^{31}P, so only $^{31}PH_3$ is considered in the present work.

Phosphine has near degenerate ν_1 symmetric and ν_3 antisymmetric stretching modes [9] with frequencies of about twice that of the asymmetric bending mode, ν_4. It is therefore natural to consider its spectrum in terms of polyads, which will be described in Section 3.1. There is also a strong Coriolis interaction between the ν_2 and ν_4 bending bands which causes large distortion effects in observations [21]. Recorded phosphine spectra show no inversion splitting. The tunnelling effect found in ammonia is expected to occur in phosphine but so far attempts to detect it have failed due to its considerably higher potential energy barrier (12 300 cm^{-1}) between the two symmetry-related minima [22,23].

In the absence of the inversion splitting, phosphine is characterised by the $C_{3v}(M)$ molecular group symmetry, i.e. each eigenfunction transforms according to one of the irreducible representations A_1, A_2 and E, the latter of which is twofold degenerate.

To fully describe the internal rovibrational motion of phosphine one needs the following minimal set of quantum numbers [24]:

$$n_1, n_2, n_3, n_4, L_3, L_4, L, \Gamma_{\rm vib}, J, K, \Gamma_{\rm rot}, \Gamma_{\rm tot}, \qquad (1)$$