Spectroscopic parameters of phosphine, PH$_3$, in its ground vibrational state

Holger S.P. Müller$^{a,*}$

$^a$I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany

Abstract

The ground state rotational spectrum of PH$_3$ has been reanalyzed taking into account recently published very accurate data from sub-Doppler and conventional absorption spectroscopy measurements as well as previous data from the radio-frequency to the far-infrared regions. These data include $\Delta J = \Delta K = 0$ transitions between $A_1$ and $A_2$ levels, $\Delta J = 0, \Delta K = 3$ transitions as well as regular $\Delta J = 1, \Delta K = 0$ rotational transitions. Hyperfine splitting caused by the $^{31}$P and $^1$H nuclei has been considered, and the treatment of the $A_1/A_2$ splitting has been discussed briefly. Improved spectroscopic parameters have been obtained. Interestingly, the most pronounced effects occured for the hyperfine parameters.

Keywords: phosphine, rotational spectroscopy, planetary molecule, centrifugal distortion, near spherical rotor, hyperfine structure

1. Introduction

Phosphine, PH$_3$, was detected as a trace constituent of the atmospheres of the giant planets Jupiter [1] and Saturn [2], respectively by infrared spectroscopy. Observations of the lowest $J = 1 - 0$ rotational transition near 267 GHz toward Jupiter [3] and Saturn [4] were also reported. Using a far- and mid-infrared (FIR and MIR) spectrometer on board of the Cassini satellite, it was even possible to study the meridional PH$_3$ distribution in Saturn’s upper troposphere [5]. Higher resolution FIR observations of Saturn’s atmosphere were carried out very recently with the Herschel satellite, and the vertical distribution of PH$_3$ was derived [6]. Phosphine is also a likely species to occur in the atmospheres of giant extrasolar planets or of brown dwarfs [7]. Moreover, it has been tentatively detected in the circumstellar shells of carbon-rich late-type stars CW Leo [8,9], also known as IRC +10216, and V1610 Cygni, also known as CRL 2688, by radio-astronomical observations of the $J = 1 - 0$ transition.

Small molecules, and even more so light hydride species, such as PH$_3$, are of great interest for basic science. In the early years, an important questions was if PH$_3$ would display measurable inversion splitting as its lighter homolog ammonia, NH$_3$, does [10,11].

Early reports on the ground state rotational spectrum of PH$_3$ were published by the Gordy group [12,13]. Burrus [14] determined the dipole moment from Stark measurements. Davies et al. [15] studied transitions between $A_1$ and $A_2$ levels with $\Delta J = \Delta K = 0$ at radio-frequencies (RF). They were unable to resolve any tunneling splitting, but obtained hyperfine structure parameters caused by the $^{31}$P and $^1$H nuclei and an improved value for the dipole moment. Chu and Oka recorded $\Delta K = 3$ transitions with $\Delta J = 0$ and $K = \pm1 - \pm2$ and estimated an effective value for the centrifugal distortion induced dipole moment from intensity measurements [16]. Later, corresponding transitions were reported for $K = 0 - 3$ [17], $K = 2 - 5$ [18], and $K = 3 - 6$ [19]. Regular rotational transitions with $\Delta J = 1$ and $\Delta K = 0$ in the millimeter and submillimeter regions [18,19] and in the far-infrared (FIR) region [20] were also studied.

Recently, Cazzoli and Puzzarini [21] obtained very accurate transition frequencies for the $J = 1 - 0$ and 2 - 1 transitions employing sub-Doppler (Lamb-dip) spectroscopy, which resolved $^{31}$P and $^1$H hyperfine structure, and for the $J = 3 - 2$ transitions using conventional absorption spectroscopy. As this study employed in their fit very limited data beyond their own, a combined fit of these data together with previous results has been carried out here to obtain an improved set of spectroscopic parameters which should be useful not only for spectroscopic observations of phosphine in planetary atmospheres, brown dwarfs, or other regions in space, but also for future analyses of rovibrational spectra or as benchmarks for quantum-chemical calculations.

2. Spectral analysis and discussion

Phosphine is an oblate rotor with a permanent dipole moment of 0.57395 (3) D [15]. It is moderately close to the spherical rotor limit with $\gamma = (C_0 - B_0)/A_0 = -0.1361$ being small in magnitude, but not particularly so.

The rotational energies and transitions of a strongly oblate rotor in its ground vibrational state and without $A_1/A_2$ splitting require for their modeling only $C - B$ and $B$ along with distortion parameters, $D_J$, $D_{JK}$, and $D_K$ to lowest order. In a strongly prolate rotor, $C$ is replaced with $A$. The purely axial parameters $C - B$, $D_K$, etc. can usually not be determined by rotational spectroscopy. Their determination requires, e.g., the observation of centrifugal distortion induced $\Delta K = 3$ transitions. The
Table 1: Spectroscopic parameters (MHz) of phosphine, PH$_3$, from the present fits in comparison to selected previous fits.

| Parameter | Present, preferred | Present, alternative | Fusina and Carlotti | Cazzoli and Puzzarini | Davies et al. |
|-----------|-------------------|---------------------|-------------------|---------------------|--------------|
| $B$       | 133 480.128 21     | 133 480.127 94      | 133 480.122 80    | 133 480.128 989    | –            |
| $C$       | 117 489.430 4 (73)$^c$ | 117 489.427 0 (73)$^c$ | 117 489.425 6 (73) | 117 489.436 $^{c,d}$ | –            |
| $D_1$     | 3.936 391 (22)     | 3.936 210 (22)      | 3.936 059 (105)   | 3.936 901 (36)     | –            |
| $D_2$     | $-5.168 535 (78)$  | $-5.167 110 (78)$  | $-5.167 280 (86)$ | $-5.171 02 (44)$  | –            |
| $D_3$     | 4.234 45 (54)      | 4.232 60 (54)       | 4.233 82 (51)     | –                   | –            |
| $H_1 \times 10^6$ | 348.906 (142)   | 326.315 (142)      | 325.74 (39)       | 415.7 (39)         | –            |
| $H_2 \times 10^6$ | $-868.02 (50)$      | $-664.97 (50)$     | $-665.33 (73)$    | $-1 237. (85)$    | –            |
| $H_{JK} \times 10^6$ | 801.49 (148)       | 463.43 (149)       | 464.10 (276)      | 1 340. (270)       | –            |
| $h_3 \times 10^6$ | 11.3$^b$           | –                   | –                 | –                   | –            |
| $L_{1J}$ $\times 10^9$ | $-37.667 (218)$     | $-37.672 (218)$    | $-36.96 (43)$     | –                   | –            |
| $L_{1JK} \times 10^9$ | 113.71 (105)       | 149.91 (106)       | –                 | –                   | –            |
| $L_{JK} \times 10^9$ | $-222.0 (33)$      | $-408.7 (33)$      | 349.0 (39)        | –                   | –            |
| $\epsilon \times 10^3$ | 247.9 (50)         | 519.5 (50)         | $-547.7 (93)$     | –                   | –            |
| $\epsilon_1 \times 10^6$ | 714.508 2 (42)$^c$ | 831.652 2 (36)$^c$ | 829.254 (56)      | –                   | –            |
| $\epsilon_2 \times 10^6$ | $-168.896 (72)$    | $-180.210 (62)$    | $-179.611 (204)$  | –                   | –            |
| $\epsilon_3 \times 10^6$ | –                  | –                   | 265.9 (61)        | –                   | –            |
| $\epsilon_{1J} \times 10^6$ | 37.25 (29)$^j$     | 34.60 (24)$^j$     | 34.97 (199)       | –                   | –            |
| $\epsilon_{1K} \times 10^6$ | –                  | –                   | –                 | –                   | –            |
| $\epsilon_{JK} \times 10^9$ | –                  | –                   | –                 | –                   | –            |
| $C_N(P) \times 10^3$ | 114.897 (15)       | 114.897 (15)       | –                 | 115.35 (12)        | 114.90 (13) |
| $C_K(P) \times 10^3$ | 116.396 (35)$^g$  | 116.396 (35)$^g$  | –                 | 115.0 (14)$^g$    | 116.38 (32) |
| $C_N(H) \times 10^3$ | $-7.998 (9)$       | $-7.998 (9)$       | –                 | $-7.57 (13)$       | $-8.01 (8)$ |
| $C_K(H) \times 10^3$ | $-7.704 (22)$     | $-7.704 (22)$     | –                 | $-7.69$ ($^{j,k}$) | $-7.69 (19)$ |
| $-3D_1(P-H) \times 10^3$ | 3.01 (35)          | 3.01 (35)          | –                 | 3.05 (62)          | $k$         |
| $-0.5D_2(P-H) \times 10^3$ | $-9.15^j$         | $-9.15^k$         | –                 | $-9.15^j$         | $k$         |
| $1.5D_2(H-H) \times 10^3$ | 20.62 (13)         | 20.62 (13)         | –                 | 25.3 (19)          | $k$         |

$^a$Numbers in parentheses are one standard deviation in units of the least significant figures.
$^b$The parameter $h_3$ was kept fixed to the value calculated in Ref. [22].
$^c$The parameter $h_3$ was constrained to zero.
$^d$Ref. [20], preferred fit with $h_3$ etc. kept fixed to zero.
$^e$Ref. [21].

$^f$Ref. [15].
$^g$The parameter $C$ was kept fixed to the value in Ref. [22].
$^{h}$The parameter $C$ was determined from $C - B$ and $B$, taking correlation into account. Analogously, $C_K$ was calculated from $C_K - C_N$ and $C_N$.

$^i$The parameters determined in the fit are $\sqrt{2} \epsilon$ etc.
$^j$Ref. [15].
$^k$The tensorial spin-spin coupling parameters were kept fixed to values calculated from structural parameters, but were not given specifically.
$^l$Ref. [15].

$^m$The parameter $D_2$ was kept fixed to the value calculated in Ref. [21].
The $A_1/A_2$ splitting is modeled to lowest order by $h_3(J_x^2 + J_y^2)$ with $J_x = J_y = J$, and $K$ distortion corrections and possibly even higher order terms may be required in the fit. Early treatments of the rotational spectrum of PH$_3$ used parameters as described above to fit the rotational transitions. However, it was recognized early on that the parameter derived for $h_3$ was too large by about a factor of 4 [15]. Moreover, it was found later, that the Hamiltonian converged rather slowly [19].

Tarrago and Dang Nhu [22] discussed the formulation of the Hamiltonian for symmetric top molecules approaching the spheric rotor limit employing the examples OPF$_3$ and PH$_3$. They pointed out that for such molecules not only the $\Delta K = 6$ terms derived from $h_3$, also called $f_\text{pb}$ in their work, affect the $A_1/A_2$ splitting, but also terms with $\Delta K = 3$, whose lowest order term is $\epsilon$, which is also called $q_3$. The parameter $\epsilon$ is the coefficient of $[J_x^2 + J_y^2, J_z]$, so that $[A, B, C] = AB + BA$ is the anti-commutator of $A$ and $B$. They presented one fit with parameters derived from $h_3$, and one fit with parameters derived from $\epsilon$ and $h_3$. The latter fit was slightly better, but yielded a value for $h_3$ only slightly smaller than in the fit without $\epsilon$, meaning that their value was still too lage by almost a factor of 4. Moreover, their value for $\epsilon$ was too small by about a factor of 3. Interestingly, they did not attempt any fits without parameters derived from $h_3$.

Fusina and Carlotti recorded the FIR spectrum of PH$_3$ and made assignments for the ground vibrational state between 44 and 202 cm$^{-1}$ with $J''$ between 4 and 22 and $K$ between 19 and 0 [20]. They used in their fits their own data together with previous data from Refs. [13, 15, 16, 17, 18, 19]. Three different fits were presented which included parameters derived from both $h_3$ and $\epsilon$ as well as parameters derived either from $\epsilon$ or $h_3$. The parameters $\epsilon$ and $h_3$ were completely correlated if both were used. The parameters $h_3$ and $h_{3K}$ were completely correlated in the fit without parameters derived from $\epsilon$. In contrast, the fit with only parameters derived from $\epsilon$ did not produce severe correlations, yielded the best standard deviation, but employed two more parameters than the other two fits. This fit was their preferred one.

The fits carried out in the course of the present investigation employed Herb Pickett’s SPFIT and SPACAT programs [23]. They started from the preferred parameters from Fusina and Carlotti [20] and the hyperfine parameters employed by Cazzolli and Puzzarini [21] using transition frequencies from Refs. [15, 16, 17, 18, 19, 20, 21] with uncertainties as reported. The RF transitions [15] were reported accurately to between 0.1 and 0.2 kHz. Initially, 0.2 kHz were used in the fits because the published deviations from the measured frequencies exceeded 0.6 kHz in two cases. However, the transitions were reproduced in the present fits to well within 0.1 kHz on average with no severe outliers. Therefore, 0.1 kHz uncertainties were employed to make the parameters used in this data for the final fits. The uncertainties of Ref. [18] were used as reported in Ref. [19]. Including $L_{3JK}$ in the fit, which was contrained to zero in Ref. [20], yielded a reasonable value, and suggested the parameters $\epsilon_{3K}$, $\epsilon_{JK}$, and $\epsilon_{KK}$ to be indeterminate. The latter three parameters could be omitted from the fit without significant deterioration of the fit. The resulting parameters, including those for the hyperfine structure, are given in Table I under heading ”Present, alternative”.

Hyperfine structure caused by the $^{31}$P and $^1$H nuclei was resolved in the RF spectra [18] and in the Lamb-dip measurements from Ref. [21]. The hyperfine Hamiltonian was described in sufficient detail e.g. in the latter work. As mentioned in that work, the Lamb-dip measurements were rather sensitive to the perpendicular components $C_K$ of the P and H nuclear spin-rotation tensors, which are also known as $C_{\perp}$, and to the axial components $D_L(P-H)$ and $D_J(H-H)$ of the spin-spin coupling tensors, which are also known as $d_L(P-H)$ and $d_J(B-H)$, respectively. They were not as sensitive to the axial components $C_K$ of the nuclear spin-rotation tensor, which are also known as $C_{\parallel}$, and to the perpendicular component $D_L(P-H)$ of the P–H spin-spin coupling tensor, also known as $d_L(P-H)$. In contrast, the RF data were sensitive to $C_K$ and $C_L$ of both nuclei, but not as sensitive to the spin-spin coupling tensors. In the present fit, $D_3$ could still not be determined significantly and with confidence. However, its omission increased the standard deviation of the fit somewhat. Therefore, it was retained in the fit kept fixed to the calculated value from Ref. [21]. Other parameters, such as $C_{\perp}(H)$, the off-diagonal H spin-rotation parameter, the scalar spin-spin coupling parameters, or distortion corrections to the P or H nuclear spin-rotation parameters were not determined with significance, and their inclusion had a negligible effect on the quality of the fit. Therefore, they were omitted from the final fits.

As can be seen in Table I the present hyperfine parameters are in good to very good agreement with previously determined ones [15, 21], but have much smaller uncertainties in the present fits. The values of the spin-spin coupling parameters $-3D_3$ and $1.5D_3$ agree very well with the calculated ones of 3.18 kHz and 20.7 kHz, respectively. In fact, keeping the spin-spin coupling parameters fixed to the calculated values, does not deteriorate the quality of the fit significantly. In addition, the values of the other parameters and, somewhat surprisingly, even their uncertainties are affected negligibly.

The remaining spectroscopic parameters agree for the most part well with the preferred ones from Fusina and Carlotti [20] as far as they were determined in both fits. Exceptions are the two octic distortion parameters $L_{3JK}$ and $L_{KKK}$, which is a result of the omission of $L_{3JK}$ by Fusina and Carlotti and of the omission of some higher order distortion corrections to $\epsilon$ in the present fits. Notably, the values of $\epsilon$ agree quite well, about 832 kHz versus 829 kHz. Both values, however, are slightly larger than 723 kHz calculated by Tarrago and Dang Nhu [22] and 773 kHz calculated by Fusina and Carlotti [20]. The parameter $\epsilon$ and its distortion corrections cause $\Delta K = 3$ transitions, among others, to have non-zero intensities very similar to those calculated without these parameters, but with the effective centrifugal distortion correction to the permanent dipole moment mentioned in Ref. [18]. Therefore, another fit has been carried out with $h_3$ kept fixed at the value of 11.3 Hz calculated in Ref. [22]. The $\epsilon$ value of 714.5 kHz resulting from this fit is very close to the one calculated by Tarrago and Dang Nhu [22], but somewhat smaller than the one from Fusina and Carlotti [20]. All other parameters are also affected in their magnitudes. This fit is considered to be the preferred one. The
effects on the intensities of the $\Delta K = 3$ transitions correspond closely to the square of the ratios of the $\epsilon$ values, the intensities of all other transitions change only marginally between the two data sets.

The quality of the preferred fit and of the alternative fit are identical. The experimental transition frequencies have been reproduced within the reported uncertainties on average, the rms error is 0.93, slightly better than the ideal 1.0. There is some scatter among the rms errors of individual data sets: it is 0.77 for the RF data [15] and 0.64 [16], 0.87 [17], and 0.94 [18,19] for the older millimeter and submillimeter data. The FIR data from Fusina and Carlotti [20] were given uncertainties of 0.0001 cm$^{-1}$ throughout, as suggested by the authors, even though the residuals increased somewhat for the transitions with the highest two $J$ values. Two transitions omitted already by Fusina and Carlotti were also omitted here. In addition, the frequency of the transition with $J'' = 16$ and $K = 9$ was omitted as its residual exceeded 4$\sigma$. The rms error of the FIR transitions was 0.94; the frequencies of 4 transitions, all of which are omissions, had residuals larger than 3$\sigma$, which is reasonably close to the statistical expectations in the case of 230 different transition frequencies. An rms error of 1.37 was obtained for the data from Ref. [21]. Even though this suggests slightly optimistic uncertainty estimates, no adjustments were made, as one frequency, 53381.1525 (10) MHz, contributed particularly to the rms error. Omission of this line reduced the rms error of this data set to slightly below 1.1. In addition, the omission of this line from the overall line list affected all parameters within experimental uncertainties. Therefore, this line was retained in the final fit.

The $J$-dependent parameters, in particular the ones dependent purely on $J$ have much smaller uncertainties in the present fits compared to the preferred fit of Fusina and Carlotti [20]. This is hardly surprising given the nature of the new data from Ref. [21]. The uncertainties of $D_K$ and $H_K$ here are actually slightly larger than from the FIR fit. This may be caused by differences in the correlation of the parameters or by differences in the weighting scheme.

Predictions of the rotational spectrum were made for the Cologne Database for Molecular Spectroscopy, CDMS [24,25], using the parameters of the preferred fit. The upper quantum numbers were $J = 40$ and $K = 38$, ensuring convergence of the rotational part of the partition function to $10^{-4}$ up to 500 K. The intensity cut-offs were chosen to include all experimental $\Delta J = \Delta K = 0$ transitions between $A_1$ and $A_2$ levels on one hand and to limit the number of transitions with uncertainties equal to or larger than 1 GHz, as SPCAT displays such uncertainties with a precision of 0.0001 cm$^{-1}$. This leads to transitions with upper $J$ and $K$ of 34 and 31, respectively. The $K = 0$ transition with $J = 8$ -- 7 is the most intense transition at 300 K. At 500 K and 1000 K, the corresponding transition with $J = 11$ -- 10 and $J = 14$ -- 14, respectively, is the most intense one. With phosphine being only a minor constituent in the atmospheres of Jupiter and Saturn, the current predictions should therefore contain sufficient ground state rotational transitions not only at 300 K, but also, after appropriate conversion of the intensities, for 500 K and likely for 1000 K. However, the neglect of rotational transitions in excited vibrational states may cause non-negligible errors already around 300 K, as can be seen below.

Intensities of the transitions with $\Delta K = 3$ should be viewed with some caution as indicated above. Predictions of transition frequencies with $\Delta K = 0$ should be reliable as long as the predicted uncertainties do not exceed 5 MHz. Predictions of transition frequencies with $\Delta K \neq 0$ should be viewed with caution if the predicted uncertainties are larger than 0.5 MHz. In these cases, the actual frequencies may differ from the predictions by more than five times the predicted uncertainties.

The partition function values given in the documentation of the CDMS entries do not include vibrational contributions; they are about 2.4 % at 300 K and amount to about 18.5 % at 500 K. Classically estimated vibrational contributions are intended to be provided through a link in the documentation file. It should be mentioned that the HITRAN entry takes into account vibrational contributions to the partition function. Moreover, the intensities at 300 K have been converted to those at 296 K, which is the default temperature in HITRAN.

Pickett’s SPFIT and SPCAT programs [23] use the total parity. This parity is therefore also used in the ASCII table version of the PH$_3$ entry in the CDMS. It differs both from the $A_1/A_2$ parity as well as from the $A_2/A_2$ parity. Levels with negative parity belong to $A_2$ for even $K$ and to $A_1$ for odd $K$. Levels with positive parity belong to $A_2$ for $J + K$ even and to $A_1$ for $J + K$ odd. Additional confusion may occur because the sign has been omitted, and transitions with rounded $A_1/A_2$ splitting of less than 0.1 kHz have been merged. These transitions are thus between two levels with negative parity designation. Moreover, since only 2 characters are available for each quantum number, $K$ values $\geq 10$ with negative parity are indicated by lower case characters; e.g. $a_2$, $a_5$, $a_8$, and $b_1$ are used for $-12$, $-15$, $-18$, and $-21$, respectively. The entry in HITRAN provides their common parity labels. It should be also mentioned that a process is under way to create a database version of the CDMS within the framework of the Virtual Atomic and Molecular Data Centre (VAMDC) [28]. The official release of a test version is still pending because very many entries need to be imported properly, and in many cases necessary auxiliary files need to be created. One of the goals of VAMDC is providing easily interpretable quantum numbers.

Fairly recently, dipole moment and potential energy surfaces were reported, and selected ground state rotational energies have been provided [26]. The deviations between their energies and the present ones are fairly small. They drop at $J = 10$ from 0.9164 cm$^{-1}$ for $K = 0$ to 0.4720 cm$^{-1}$ for $K = 9$. The deviations are larger at $J = 20$, where they drop from 3.4312 cm$^{-1}$ for $K = 0$ to 2.9680 cm$^{-1}$ for $K = 9$. Because of the extent of the experimental data, these deviations are probably predominantly due to insufficiencies in the calculated potential energy surface.

---

1 http://www.astro.uni-koeln.de/cdms/

2 http://www.astro.uni-koeln.de/cgi-bin/cdmsinfo?file=e034501.cat

3 http://www.vamdc.eu/
More recently, a very extensive and very accurate line list has been created for PH$_3$ [27]. The authors found a remarkably good agreement between their transition frequencies and the ones in the first CDMS entry which had been created in October 2008 and which has been recalculated in February of 2013 by lowering the intensity cut-offs to provide weaker transition frequencies which in part access higher quantum numbers. These predictions correspond essentially to the ones derived from the alternative fit in the present work. The authors mentioned that the deviations are below 0.003 cm$^{-1}$ for the strongest 100 transitions [27]. As these transitions involve $J$ values between 3 and 14 and $K$ values from 0 to 9, which are all covered by experimental data, the deviations are probably again predominantly due to insufficiencies in the calculated potential energy surface. Moreover, differences in the predicted frequencies generated from the preferred fit or the alternative fit are very small for these transitions. Even more remarkable are the deviations at low quantum numbers. The $J_K =$ $J_0$ − $J_0$ prediction from Ref. [27] is only 2.8 MHz lower than the experimental frequency as well as the frequency calculated from either present fit. The deviations decrease first with increasing $J$, until the frequency of the $8_0$ − $7_0$ transition is actually higher than the one predicted from the preferred fit. Similarly, the $2_2$ − $2_1$ transition frequency from Ref. [27] is only 3.6 MHz lower than the one predicted from the preferred fit. Again, the deviations decrease first for increasing $J$ until the $10_2$ − $10_1$ transition frequency is higher in frequency. The agreement is still rather good if all transitions from the previous CDMS predictions are compared with those from Ref. [27]; the authors give an rms value of 0.076 cm$^{-1}$. Because of the limitations in the experimental data as well as in the Hamiltonian model, it may well be that the predicted transition frequencies from the present study are eventually less reliable that those from Ref. [27].

The intensities from Ref. [27] agree very well with either prediction from the present fits for $\Delta K = 0$ transitions. The value for $\mu^2$ from the former work is 3.9 % larger than the experimental value from Ref. [15]; this deviation is almost canceled by the neglect of the vibrational contributions to the partition function at 300 K in the present work. However, there are larger deviations between the calculated intensities of $\Delta K \neq 3$ transitions; e.g., the intensity of the $2_2$ − $2_1$ transition from Ref. [27] is a factor of 1.85 weaker than the intensity from predictions generated from the preferred fit; it is even weaker by a factor of 2.5 if predictions generated from the alternative fit are used. Possible explanations for these deviations are insufficiencies in the calculations from Ref. [27], insufficiencies in the preferred Hamiltonian model, e.g. $\epsilon_K$ had to be constrained to zero, or the neglect of distortion corrections to the electric dipole moment. It may well be that each of these explanations is responsible in part.

3. Conclusion

Improved spectroscopic parameters of PH$_3$ have been determined from recent very accurate rotational transition frequencies combined with previous works. Predictions for the ground state rotational spectrum of PH$_3$ generated from the preferred fit and employing the permanent dipole moment of 0.57395 D [15] and in the new edition of HITRAN$^4$ [24,25] will be provided in the catalog section of the CDMS$^5$ [24,25] and in the new edition of HITRAN$^6$. Transition frequencies with assignments, uncertainties, and residuals between the observed frequencies and those calculated from the preferred parameter set as well as the predictions in the CDMS format will be provided as supplementary material. Line, parameter, and fit files along with various auxiliary files will be provided in the archive section of the CDMS catalog. The old predictions together with available auxiliary files will be available in the archive section of the CDMS$^5$.

Acknowledgements

I thank Cristina Puzzarini for providing the data files associated with Ref. [21]. Moreover, I am very grateful to the Bundesministerium für Bildung und Forschung (BMBF) for financial support through project FKZ 50OF0901 (ICC HIFI Herschel).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jqsrt.2013.xxx.yyy

References

[1] Ridgway ST, Wallace L, Smith GR. The 800–1200 inverse centimeter absorption spectrum of Jupiter. Astrophys J 1976;207:1002–06.
[2] Larson HP, Fink U, Treflers RR. Phosphine in Jupiter’s atmosphere – The evidence from high-altitude observations at 5 micrometers. Astrophys J 1977;211:972–79.
[3] Lellouch E, Encrènaz T, Combès F. Microwave observations of Jupiter and Saturn. Astron Astrophys 1984;140:216–19.
[4] Weissstein EW, Serabyn E. Detection of the 267 GHz J = 1-0 rotational transition of PH$_3$ in Saturn with a new fourier transfer spectrometer. Icarus 1994;109:367–81.
[5] Fletcher LN, Irwin PGJ, Teynay NA, Orton GS, Parrish PD, Calcutt SB, Bowles N, de Kok R, Howell C, Taylor FW. The meridional phosphine distribution in Saturn’s upper troposphere from Cassini/CIRS observations. Icarus 2007;188:72–88.
[6] Fletcher LN, Swinyard B, Salji C, Polehampton E, Fulton T, Sidor S, Lellouch E, Moreno R, Orton G, Cavaillo T, Courtn R, Rengel M, Sagawa H, Davis GR, Hartogh P, Nayrol D, Walker H, Lim T. Sub-millimetre spectroscopy of Saturn’s trace gases from Herschel/SPIRE. Astron Astrophys 2012;539:A44.
[7] Sharp CM, Burrows A. Atomic and molecular opacities for brown dwarf and giant planet atmospheres. Astrophys J Suppl Ser, 2007;168:140–66.
[8] Tenenbaum ED, Ziurys LM. A search for phosphine in circumstellar envelopes: PH$_3$ in IRC +10216 and CRL 2688? Astrophys J, 2008;680:L121–24.
[9] Agúndez M, Cernicharo J, Pardo JR, Guelin M, Phillips TG. Tentative detection of phosphine in IRC +10216. Astron Astrophys 2008;485:L33–L36.
[10] Dennison DM, Hardy JD. The parallel type absorption bands of ammonia. Phys Rev 1932;39:938–47.

---

$^4$http://www.astro.uni-koeln.de/cdms/catalog
$^5$http://www.cfa.harvard.edu/HITRAN/
$^6$http://www.astro.uni-koeln.de/site/vorhersagen/catalog/archive/PH3/version/1/
[11] Dennison DM, Uhlenbeck GE. The two-minima problem and the ammonia molecule. Phys Rev 1932;41:313–21.
[12] Burrus CA, Jache A, Gordy W. One-to-two millimeter wave spectroscopy. V. PH$_3$ and PD$_3$. Phys Rev 1954;95:706–08.
[13] Helmhinger P, Gordy W. Submillimeter-wave spectra of ammonia and phosphine. Phys Rev 1969;188:100–08.
[14] Burrus CA. Stark effect from 1.1 to 2.6 millimeters wavelength: PH$_3$, PD$_3$, DI, and CO. J Chem Phys 1958;28:427–29.
[15] Davies PB, Neumann RM, Wofsy SC, Klemperer W. Radio-frequency spectrum of phosphine (PH$_3$). J Chem Phys 1971;55:3564–68.
[16] Chu FY, Oka T. "Forbidden" rotational spectra of phosphine and arsine. J Chem Phys 1974;60:4612–18.
[17] Helms DA, Gordy W. "Forbidden" rotational spectra of symmetric-top molecules: PH$_3$ and PD$_3$. J Mol Spectrosc 1977;66:206–18.
[18] Belov SP, Burenin AV, Gerstein LI, Krupnov AF, Markov VN, Maslovsky AV, Shapin SM. Rotational spectrum and spectroscopic constants of the phosphine molecule in the ground vibrational state. J Mol Spectrosc 1981;86:184–92.
[19] Belov SP, Burenin AV, Polyansky OL, Shapin SM. A new approach to the treatment of rotational spectra of molecules with small moments of inertia applied to the PH$_3$ molecule in the ground state. J Mol Spectrosc 1981;90:579–89.
[20] Fusina L, Carlotti M. The far-infrared spectrum and spectroscopic parameters of PH$_3$ in the ground state. J Mol Spectrosc 1988;130:371–81.
[21] Cazzoli G, Puzzarini C. The Lamb-dip spectrum of phosphine: The nuclear hyperfine structure due to hydrogen and phosphorus. J Mol Spectrosc 2006;239:64–70.
[22] Tarrago G, Dang Nhu M. Ground state rotational energies of C$_3$, quasi-spherical top molecules: Applications to $^{16}$OF$_3$ and PH$_3$. J Mol Spectrosc 1985;111:425–39.
[23] Pickett HM. The fitting and prediction of vibration-rotation spectra with spin interactions. J Mol Spectrosc 1991;148:371–77.
[24] Müller HSP, Thorwirth S, Roth DA, Winnewisser G. The Cologne Database for Molecular Spectroscopy, CDMS. Astron Astrophys 2001;370:L49–L52.
[25] Müller HSP, Schlüter F, Stutzki J, Winnewisser G. The Cologne Database for Molecular Spectroscopy, CDMS: a useful tool for astronomers and spectroscopists. J Mol Struct 2005;742:215–27.
[26] Yurchenko SN, Carvajal M, Thiel W, Jensen P. Ab initio dipole moment and theoretical rovibrational intensities in the electronic ground state of PH$_3$. J Mol Spectrosc 2006;239:71–87.
[27] Sousa-Silva C, Yurchenko SN, Tennyson J. A computed room temperature line list for phosphine. J Mol Spectrosc 2013, in press; doi: 10.1016/j.jms.2013.04.002.
[28] Dubernet M L, Boudon V, Culhane J L, et al. Virtual atomic and molecular data centre. J Quant Spectrosc Radiat Transfer 2010;111:2151–9.