

**GROUND STATE MOLECULAR PARAMETERS OF PHOSPHINE,
PH₃, FROM THE SIMULTANEOUS ANALYSIS
OF THE HIGH-RESOLUTION INFRARED, MICROWAVE
AND SUBMILLIMETERWAVE SPECTRA**

Soňa PŘÁDNÁ^a, Dušan PAPOUŠEK^a, Jyrki KAUPPINEN^b, Sergei P. BELOV^c,
Andrei F. KRUPNOV^c, Flavio SCAPPINI^d and Gianfranco Di LONARDO^d

^a *The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6, Czechoslovakia,*

^b *Department of Physics, University of Oulu, Finland,*

^c *Institute for Applied Physics, Academy of Sciences, Gorkii, U.S.S.R. and*

^d *Istituto di Spettroscopia Molecolare del C.N.R., I-40126 Bologna, Italy*

Received January 23th, 1985

Fourier transform spectra of the ν_2 band of PH₃ have been remeasured with 0.0045 cm^{-1} resolution. Ground state combination differences from these data have been fitted simultaneously with the microwave and submillimeterwave data to determine the ground state spectroscopical parameters of PH₃ including the parameters of the $\Delta k = \pm 3n$ interactions. The correlation between the latter parameters has been discussed from the point of view of the existence of two equivalent effective rotational operators which are related by a unitary transformation. The $\Delta J = 0, \pm 1$, $\Delta K = 0$ ($A_1 \leftrightarrow A_2, E \leftrightarrow E$) rotational transitions in the ν_2 and ν_4 states have been measured for the first time by using a microwave spectrometer and a radiofrequency spectrometer with acoustic detection.

Phosphine, PH₃, is a spectroscopically interesting molecule. Because of the relatively small value of $C - B$ ($\sim -0.533 \text{ cm}^{-1}$ for the ground vibronic state), the higher-order vibrational-rotational interactions which in a given vibrational state connect rotational states differing by $\Delta k = \pm 3n$ ($n = 1, 2, \dots$) are rather important. This effect leads to a significant mixing of the corresponding rotational wavefunctions and consequently many $\Delta k = \pm 3$ perturbation allowed transitions have been detected in the submillimeterwave¹⁻⁵ as well as infrared spectra⁶⁻⁸ of this molecule.

The ground state molecular parameters of PH₃ have been recently determined by a least squares fit to the ground state microwave and submillimeterwave data taking into account these interactions, by using a standard approach⁴ as well as the representation of the effective rotational Hamiltonian in the form of a Pade operator⁵. In both cases, however, the results have not been quite satisfactory, especially as for the determination of the centrifugal distortion parameters D_J, H_{JJJ} etc., because only a few $\Delta J = +1$ transitions have been observed in the submillimeterwave spectra of PH₃.

A simultaneous fit to the submillimeterwave and infrared data should obviously improve the situation. So far such a fit has been reported by Maki, Sams and Olson⁶, but these authors have not taken into account the $\Delta k = \pm 3n$ interactions in the analysis.

In this paper, we report the determination of the ground state molecular parameters of PH_3 by a simultaneous least squares fit to the submillimeterwave and high-resolution infrared data taking into account the $\Delta k = \pm 3n$ interactions in the ground vibronic state of this molecule. Although the high-resolution infrared spectra of PH_3 have been investigated in detail by several authors⁶⁻⁹, the resolution of the previous measurement was not better than 0.03 cm^{-1} and the accuracy of the infrared data was therefore much below the accuracy of the microwave and submillimeterwave data.

We have therefore remeasured the high-resolution infrared spectra of a substantial part of the ν_2 band of PH_3 using a Fourier transform spectrometer built at the University of Oulu^{10,11} and working with 0.0045 cm^{-1} resolution. The microwave and submillimeterwave data¹⁻⁵ have been analyzed simultaneously with the ground state combination differences from our Fourier transform measurement, the precise ν_2 band transition wavenumbers obtained by using an off-set locked waveguide CO_2 laser system¹², and infrared-microwave two-photon transition wavenumbers¹³.

A set of the ground state spectroscopical parameters has been obtained in this way which includes also the "spectroscopically forbidden" parameters C_0 , D_K^0 , H_K^0 and the parameters of the $\Delta k = \pm 3n$ interactions. The correlation of the latter parameters has been discussed from the point of view of the two equivalent effective rotational operators which are related by a unitary transformation.

We have also measured for the first time certain $\Delta J = 0, +1$, $\Delta K = 0$ ($A_1 \leftrightarrow A_2$, $E \leftrightarrow E$) transitions in the ν_2 and ν_4 excited states of PH_3 by using a microwave spectrometer at the Institute for Spectroscopy in Bologna and a submillimeterwave spectrometer RAD built at the Institute for Applied Physics in Gorkii¹⁹. By combining the ν_2 and ν_4 band transition wavenumbers with the calculated ground state energy levels, we have been able to predict precisely the wavenumbers of these transitions and assign the microwave and submillimeterwave data.

EXPERIMENTAL

The apodized Fourier spectrum of the ν_2 band of PH_3 has been measured in a cell with 1 m absorption path length, the pressure of the sample was about 1 000 Pa (7 Torr). The spectrum has been measured with a $2.5 \mu\text{m}$ Mylar beamsplitter in $830-1\,100 \text{ cm}^{-1}$ wavenumber range. Because of the Mylar beamsplitter selfabsorption at $1\,050 \text{ cm}^{-1}$, the measurement is confined to $J = 7$ in the R branch. The wavenumber scale was calibrated with the aid of the ν_2 lines of CO_2 (ref.¹¹). Resolution was 0.0045 cm^{-1} , the precision of the line positions was better than 10^{-3} cm^{-1} for unblended narrow lines. The results of measurements are given in Table I (see also Fig. 1).

TABLE I
Transition wavenumbers in the ν_2 band of PH_3 (see^a, in cm^{-1})

P		P		P	
J	K	J	K	J	K
ν_{exp}^d		ν_{exp}^d		ν_{exp}^d	
1	0	9	5	13	6
2	0	9	6	13	7
2	1	9	7	13	8
2	1	9	8	13	9
3	0	10	0	13	10
3	1	10	1	13	11
3	2	10	2	13	12
4	0	10	3	14	0
4	1			14	1
4	2	10	4	14	2
4	3	10	5	14	3
5	0	10	6		
5	1	10	7	14	4
5	2	10	8	14	5
5	2	10	9	14	6
5	3	11	0	14	7
5	3	11	1	14	8
5	4	11	2	14	9
6	0	11	3	14	10
6	1			14	11
6	1	11	4	14	12
6	2	11	5	14	13
6	3	11	6	15	0
6	4	11	7	15	1
6	5	11	8	15	2
7	0	11	9	15	3
7	0	11	10		
7	1	12	0	15	4
7	1	12	1	15	5
7	2	12	2	15	6
7	3	12	3	15	7
7	3			15	8
7	4	12	4	15	9
7	5	12	5	15	10
7	6	12	6	15	11
8	0	12	7	15	12
8	1	12	8	15	13
8	2	12	9	15	14
8	3	12	10	16	4
8	4	12	11	16	5

TABLE I
(Continued)

<i>P</i>			<i>P</i>			<i>P</i>		
<i>J</i>	<i>K</i>	ν_{exp}^d	<i>J</i>	<i>K</i>	ν_{exp}^d	<i>J</i>	<i>K</i>	ν_{exp}^d
8	5	916·39287(10)	13	0	854·42058(10)	16	6	823·29853(500)
8	6	918·46208(10)	13	1	854·56131(20)	16	7	824·99600(3000)
8	7	920·99322(10)	13	2	854·98479(10)	16	8	827·00109(1000)
9	0	900·71177(10)	13	3	855·68068(10)	16	9	829·33945(100)
9	1	900·87870(10)			855·70972(10)	16	10	832·03913(3000)
9	2	901·38223(10)	13	4	856·70139(20)	16	11	835·12352(3000)
9	3	902·22963(80)	13	5	858·01507(20)	16	12	838·71180(200)
9	4	903·43371(20)						
<i>Q</i>			<i>Q</i>			<i>Q</i>		
<i>J</i>	<i>K</i>	ν_{exp}^d	<i>J</i>	<i>K</i>	ν_{exp}^d	<i>J</i>	<i>K</i>	ν_{exp}^d
1	1	991·97985(3000)	10	6	980·95731(70)	14	7	969·33164(10)
2	1	991·27386(60)	10	7	983·20072(150)	14	8	971·51921(20)
2	2	991·88261(3000)	10	7	983·20073(25) ^b	14	9	973·07316(20)
3	1	990·22949(200)	10	8	985·88078(250)	14	10	977·03214(20)
3	2	990·82259(100)	10	9	989·04784(300)	14	11	980·44571(50)
3	3	991·83228(3000)	10	9	989·04902(25) ^b	14	12	984·38170(0) ^{e,c}
4	1	988·86143(30)	10	10	992·76790(150)	14	12	984·38183(25) ^b
4	2	989·44327(300)	11	2	972·75667(200)	14	13	988·92495(1500)
4	3	990·42701(1000)	11	3	973·48579(150)	14	14	994·17842(30)
4	4	991·82143(3000)			973·52502(80)	15	2	959·78591(50)
5	1	987·19581(10)	11	4	974·58710(20)	15	3	960·21395(80)
5	2	987·76273(100)	11	5	975·99976(20)			960·40853(100)
5	3	988·71873(500)	11	6	977·76297(40)	15	4	961·23920(1000)
5	4	990·07769(150)	11	6	977·76304(25) ^b	15	5	962·41717(200)
5	5	991·87289(3000)	11	7	979·90174(50)	15	6	963·89267(250)
6	1	985·25471(10)	11	8	982·44984(30)	15	7	965·67416(30)
6	2	985·80419(20)	11	9	985·45201(100)	15	8	967·72265(100)
6	3	986·73001(150)	11	10	988·96942(250)	15	9	970·14543(10)
6	4	988·04801(100)	11	11	993·07014(50)	15	10	972·94607(200)
6	5	989·78342(200)	11	11	993·06988(25) ^b	15	11	976·15758(100)
6	6	991·96252(3000)	12	2	969·63911(1000)	15	12	979·84447(20)
7	1	983·06343(30)	12	3	970·34288(80)	15	13	984·00135(250)
7	2	983·59491(20)			970·39874(80)	15	14	989·04784(500)
7	3	984·49044(200)	12	4	971·40578(60)	15	15	994·60540(30)
7	4	985·76175(50)	12	5	972·75667(100)	16	6	960·17937(150)
7	5	987·43193(80)	12	6	974·43992(50)	16	7	961·89425(200)
7	6	989·53602(400)	12	7	976·47841(100)	16	8	963·88225(1000)

TABLE I
(Continued)

<i>Q</i>			<i>Q</i>			<i>Q</i>		
<i>J</i>	<i>K</i>	ν_{exp}^d	<i>J</i>	<i>K</i>	ν_{exp}^d	<i>J</i>	<i>K</i>	ν_{exp}^d
7	7	992·09792(250)	12	8	978·89894(50)	16	9	966·17248(100)
8	1	980·64458(30)	12	8	978·89852(25) ^b	16	10	968·82070(200)
8	2	981·15931(20)	12	9	981·74317(150)	16	11	971·85263(100)
8	3	982·02174(100)	12	10	985·06210(30)	16	12	975·31283(60)
8	4	983·24662(350)	12	11	988·92495(1500)	16	13	979·26716(10)
8	4	983·24731(25) ^b	12	12	993·40788(100)	16	14	983·80094(20)
8	5	984·85330(200)	13	2	966·41914(1000)	16	15	989·04784(450)
8	6	986·86770(250)	13	3	967·07826(500)	16	16	995·05631(50)
8	7	989·32735(250)			967·16169(300)	17	9	962·16434(200)
8	8	992·28245(350)	13	4	968·10967(50)	17	10	964·67334(200)
9	1	978·03030(50)	13	5	969·40098(50)	17	12	970·79122(100)
9	2	978·52363(10)	13	6	971·01124(100)	17	14	978·70643(100)
9	3	979·34697(100)	13	7	972·94607(200)	17	15	983·54577(200)
		979·35859(100)	13	8	975·24905(50)	17	17	995·52669(50)
9	4	980·52943(20)	13	9	977·94402(150)	18	11	963·23089(200)
9	5	982·07075(30)	13	10	981·07658(40)	18	13	969·77603(200)
9	5	982·07155(25) ^b	13	10	981·07695(25) ^b	18	14	973·69179(500)
9	6	984·00135(200)	13	11	984·70678(30)	18	15	978·15316(30)
9	7	986·35196(100)	13	12	988·91555(1500)	18	18	996·01315(50)
9	8	989·16796(150)	13	13	993·77747(50)	19	14	968·75040(2000)
9	9	992·50380(300)	14	2	963·10148(20)	19	15	972·94607(200)
10	2	975·71074(30)	14	3	963·70930(150)	19	16	977·63525(400)
10	3	976·49587(300)			963·83095(150)	19	17	982·95881(1000)
		976·51708(300)	14	4	964·71543(150)	19	18	989·35009(1000)
10	4	977·63525(250)	14	5	965·95015(150)	19	19	996·51140(500)
10	5	979·11170(50)	14	6	967·48272(50)	20	20	997·016632(1000)

<i>R</i>			<i>R</i>			<i>R</i>		
<i>J</i>	<i>K</i>	ν_{exp}^d	<i>J</i>	<i>K</i>	ν_{exp}^d	<i>J</i>	<i>K</i>	ν_{exp}^d
0	0	1 000·68263(70)	4	4	1 034·56475(1000)	6	6	1 051·77127(500)
1	0	1 008·87760(300)	5	0	1 038·38725(3000)	7	0	1 051·44664(700)
1	1	1 009·07964(200)	5	1	1 038·57710(2000)	7	1	1 051·62809(1000)
2	0	1 016·73237(1000)	5	2	1 039·12674(1000)	7	2	1 052·14274(1000)
2	1	1 016·93134(3000)	5	3	1 040·06444(3000)	7	3	1 053·01639(1500)
2	2	1 017·52903(500)	5	4	1 041·40024(1000)	7	4	1 054·26335(500)
3	0	1 024·25916(3000)	5	5	1 043·14891(2000)	7	5	1 055·89213(1000)
3	1	1 024·44955(1000)	5	5	1 043·14873(25) ^b	7	6	1 057·95075(1000)
3	2	1 025·03731(3000)	6	0	1 045·04217(1000)	7	7	1 060·43561(1000)

TABLE I
(Continued)

		R		R		R	
<i>J</i>	<i>K</i>	ν_{exp}^d		<i>J</i>	<i>K</i>	ν_{exp}^d	
3	3	1 026·02068(3000)		6	1	1 045·21623(3000)	
4	0	1 031·46947(3000)		6	2	1 045·76464(1000)	
4	1	1 031·65839(1000)		6	3	1 046·66561(3000)	
4	2	1 032·23110(1000)		6	4	1 047·95824(1000)	
4	3	1 033·19305(3000)		6	5	1 049·64914(500)	
				8	3	1 059·15095(25) ^b	
						1 059·13994(25) ^b	
				9	7	1 071·89507(25) ^b	
				9	8	1 074·62651(25) ^b	
				10	4	1 071·91139(25) ^b	

^a Our Fourier transform measurements unless stated otherwise; values in parentheses are the estimated experimental uncertainties; ^b ref.¹³; ^c ref.¹²; ^d for $K = 3$, the larger ν_{exp} corresponds to a transition $A_1 \leftarrow A_2$ for J odd, $A_2 \leftarrow A_1$ for J even (it is assumed that $\eta' = \eta''$), only one value corresponds to a nonresolved transition; ^e $\nu_{\text{exp}}(14, 12) = 984\cdot38170(50)$ from our FTIR spectra.

The microwave measurements of the transitions in the ν_4 state have been carried out using a 8400C Hewlett-Packard spectrometer. The Stark cell has been operated at room temperature with a gas pressure of about 6·7 Pa (0·050 Torr).

The high sensitivity submillimeterwave spectrometer¹⁹ RAD has been used with a system employing phase-sensitive frequency stabilization of the backward wave oscillator to measure the rotational transition frequencies in the ν_2 and ν_4 states of PH₃. The absolute accuracy of the measurements of frequencies is ± 10 kHz for lines with signal-to-noise ratios higher than 600; for the weakest lines the experimental accuracy can reach $\pm 0\cdot5$ MHz. However, there are pressure induced frequency shifts of the line center which lead to the experimental uncertainty of the line frequencies about ± 1 MHz for sample pressures used in our measurements. The results of the microwave and submillimeterwave measurements are given in Table III, see also Fig. 2).

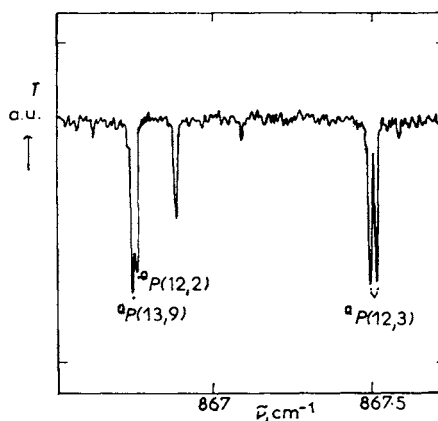


FIG. 1
Part of the Fourier spectrum of the ν_2 band

The combination differences formed from the infrared bands wavenumbers have been used together with the ground state microwave and sumillimeterwave data in a simultaneous least squares fit. The data have been weighted as $1/\delta^2$, where δ is the estimated experimental uncertainty. We have used $\delta = \pm 1$ MHz for the ground state data which is slightly more pessimistic than the authors estimates but probably better reflects the effects of the pressure induced shifts. The infrared data have been weighted as indicated above.

THEORETICAL

The effective rotational Hamiltonian for a nondegenerate vibronic state of a symmetric top C_{3v} molecule can be written in the following form²⁰ (which includes the sixth powers of the angular momentum operators):

$$\begin{aligned} H'_{\text{rot}} = & B'J^2 + (C' - B')J_z^2 - D'_1J^4 - D'_{JK}J^2J_z^2 - D'_KJ_z^4 + H'_{JJJ}J^6 + \\ & + H'_{JJK}J^4J_z^2 + H'_{JKK}J^2J_z^4 + H'_{KKK}J_z^6 + H'_{\text{split}}, \end{aligned} \quad (1)$$

where

$$\begin{aligned} H'_{\text{split}} = & \alpha[J_+^3 + J_-^3, J_z]_+ + \alpha J^2[J_+^3 + J_-^3, J_z]_+ + \\ & + \alpha_K[J_+^3 + J_-^3, J_z^3]_+ + \eta'(J_+^6 + J_-^6). \end{aligned} \quad (2)$$

In Eq. (1), B' and C' are the rotational constants, D' and H' are the quartic and sextic centrifugal distortion constants, respectively. The angular momentum operators J^2 and J_z ($\alpha = x, y, z$) are measured in units of $\hbar/2\pi$, energy (H'_{rot}) is measured in units of cm^{-1} .

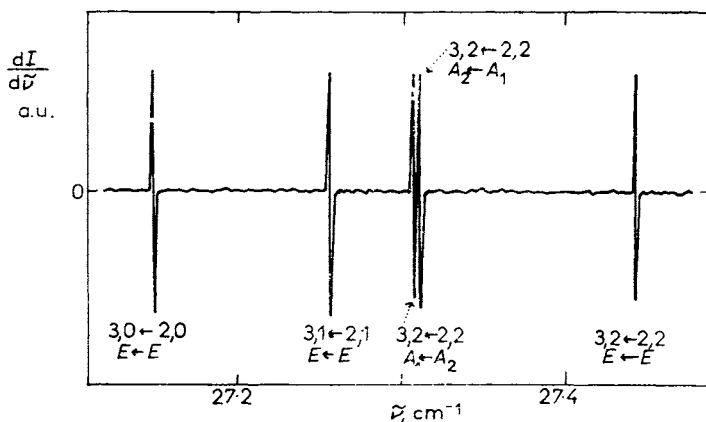


FIG. 2

Part of the rotational spectrum in the ν_4 state of PH_3

In Eq. (2)

$$J_{\pm} = J_x \pm iJ_y \quad (3)$$

and

$$[A, B]_{+} = AB + BA \quad (4)$$

is the anticommutator of operators **A** and **B**.

A complete factorization of the matrix representation of H'_{rot} in Eq. (1) can be achieved in the basis of the symmetric top rotational wavefunctions obtained by the Wang transformation¹⁴. In this basis, the operator $H'_{\text{rot}} - H'_{\text{split}}$ [cf. Eq. (1)] is purely diagonal; H'_{split} contains the term $\eta'(J_{+}^6 + J_{-}^6)$ which connects states with $\Delta k = \pm 6$, hence for $K(\equiv |k|) = 3$ contributes to the diagonal. On the other hand, rotational operators with the coefficients α , α_j , and α_K are purely off-diagonal because they connect states with $\Delta k = \pm 3$. A detailed discussion of the matrix representation of H'_{rot} including the discussion of the phase convention in the definition of the rotational wavefunctions can be found in ref.¹⁴.

It is therefore possible to apply a unitary transformation to the effective rotational Hamiltonian H'_{rot} such that the α -containing terms are transformed into the term $\eta(J_{+}^6 + J_{-}^6)$ and into other terms containing the even powers of **J** and J_z (refs¹⁵⁻²⁰ for more details):

$$\begin{aligned} H_{\text{rot}} = \exp(i\lambda S) H'_{\text{rot}} \exp(-i\lambda S) = & BJ^2 + (C - B)J_z^2 - D_J J^4 - \\ & - D_{JK} J^2 J_z^2 - D_K J_z^4 + H_{JJJ} J^6 + [H_{JJK} J^4 J_z^2 + H_{JKK} J^2 J_z^4 + H_{KKK} J_z^6 + \\ & + \eta(J_{+}^6 + J_{-}^6)]. \end{aligned} \quad (5a)$$

Relations between the parameters of the reduced Hamiltonian in Eq. (5a) and the parameters in H'_{rot} (Eq. (1)) can be found *e.g.* in ref.²⁰.

This means that the parameters α , α_j and α_K are correlated with the parameters occurring in the reduced form of the Hamiltonian given by Eq. (5a), which makes it difficult to determine the α - and η -parameters separately by fitting the experimental data (see also ref.¹⁵).

In our least squares fit to the experimental data, we have extended the effective Hamiltonian by certain octic terms:

$$L_{JJJJ} J^8 + L_{JJJK} J^6 J_z^2 + L_{JJKK} J^4 J_z^4 + L_{JKKK} J^2 J_z^6 + L_{KKKK} J_z^8 \quad (5b)$$

for the centrifugal distortion parameters and

$$\eta_j J^2 (J_{+}^6 + J_{-}^6) + \eta_K [J_{+}^6 + J_{-}^6, J_z^2]_{+} \quad (5c)$$

for the higher order $\Delta k = \pm 6$ interaction terms (Table II).

TABLE II
Ground state spectroscopic parameters of PH₃ (in cm⁻¹)

Parameter	Set I ^a	Set II ^b	Set III ^c	Set IV ^b	Set V ^b
<i>B</i>	4·45241770(416)	4·45241730(50)	4·45241590(43)	4·45241610(58)	4·45241670(47)
<i>C</i> - <i>B</i>	-0·53338580(55)	-0·53338615(45)	-0·53338548(41)	-0·53339047(69)	-0·53339094(60)
<i>D</i> _J · 10 ⁴	1·313252(6530)	1·312431(59)	1·312085(50)	1·312081(192)	1·312445(58)
<i>D</i> _{JK} · 10 ⁴	-1·722171(48)	-1·722230(30)	-1·722183(36)	-1·725001(109)	-1·725105(75)
<i>D</i> _K · 10 ⁴	1·412927(353)	1·412966(289)	1·413034(270)	1·414369(337)	1·414297(333)
<i>H</i> _{JJ} · 10 ⁸	1·3772(30901)	1·0358(20)	1·0288(16)	1·2807(145)	1·3098(20)
<i>H</i> _{JK} · 10 ⁸	-2·1464(30)	-2·1490(24)	-2·1518(22)	-4·7948(45)	-4·7976(40)
<i>H</i> _{KK} · 10 ⁸	1·6997(125)	1·7015(96)	1·7310(84)	5·9668(277)	5·9356(140)
<i>H</i> _{KKK} · 10 ⁸	0·4282(722)	0·4385(588)	0·3841(547)	-1·5749(674)	-1·5528(640)
<i>L</i> _{JJJ} · 10 ¹⁰	0 ^d	0 ^d	0 ^d	0·0065(32)	0 ^d
<i>L</i> _{JJK} · 10 ¹⁰	0 ^d	0 ^d	0 ^d	0·0363(10)	0·0355(8)
<i>L</i> _{JJKK} · 10 ¹⁰	0 ^d	0 ^d	0 ^d	-0·0143(114)	0 ^d
<i>L</i> _{JKKK} · 10 ¹⁰	0 ^d	0 ^d	0 ^d	-0·0842(211)	-0·0939(187)
<i>L</i> _{KKKK} · 10 ¹⁰	0 ^d	0 ^d	0 ^d	0 ^d	0 ^d
<i>η</i> _J · 10 ¹²	0 ^d	0 ^d	0 ^d	0·16258(709)	0·15748(585)
<i>η</i> _K · 10 ¹⁰	0 ^d	0 ^d	0 ^d	-0·1483(31)	-0·1463(26)
<i>η</i> _K · 10 ⁵	0 ^d	0 ^d	0 ^d	-0·2081(782)	-0·1517(646)
<i>α</i> _J · 10 ⁵	2·76000(62)	2·75986(50)	2·75997(47)	0 ^d	0 ^d
<i>α</i> _J · 10 ⁸	-0·5401(18)	-0·5400(14)	-0·5405(13)	0 ^d	0 ^d
<i>α</i> _K · 10 ⁸	0·736(14)	0·748(11)	0·757(10)	0 ^d	0 ^d
No of Data	75	357	2 920	357	357
Std. dev. of the fit	1·3 · 10 ⁻⁵	3·7 · 10 ⁻⁵	2·9 · 10 ⁻⁴	3·7 · 10 ⁻⁵	3·7 · 10 ⁻⁵

^a Fit to the microwave and submillimeterwave data only¹⁻⁵. ^b Fit to the microwave and submillimeterwave data¹⁻⁵ simultaneously with the *v*₂ band data measured in this work and the precise data given in refs^{12,13}. ^c Fit to the same data as specified in footnote^b, extended by the data given in refs⁶⁻⁹. ^d Constrained value.

The results concerning the reduction of the effective Hamiltonian remain of course valid also for this case.

RESULTS AND DISCUSSION

Although we made several attempts to determine the parameters α and η' separately in the same fit to the experimental data, we never succeeded. We converged either to unrealistic values of the spectroscopical parameters or to parameters with rather large indeterminacy and poor standard deviations of the fit. This is of course in agreement with the results of the previous section concerning the correlation of the parameters α and η' (see²² for similar results obtained for AsH₃).

We have therefore fit the data either by constraining the parameters η to zero or α to zero (Table II). In both cases we arrived at approximately the same standard deviation of the fit. Furthermore, we found by fitting the parameters α , α_j , and α_k that the octic centrifugal distortion coefficients L (Table II) are not well determined and hence only the sextic centrifugal distortion constants H have been included into the fit. It can be seen by comparing sets *I*, *II*, and *III* in Table II that especially the parameters B , D_J , and H_J are much better determined if the microwave data are processed simultaneously with the infrared data.

On the other hand, fitting the same data by constraining the parameters α , α_j , and α_k (Sets *IV* and *V* in Table II) required to include some of the octic centrifugal distortion coefficients in the fit, in order to arrive at a quantitative description of the data.

It should be noted that the signs of the interaction parameters α and η depend on the arbitrary choice of the phase factors in the rotational wavefunctions (see ref.¹⁴ for more details). However, there is a difference between α and η as for the possibility to determine their signs for a given phase convention from the experimental data. As for the coefficients of the $\Delta k = \pm 3$ interactions, we can only determine the relation of the signs of α_j and α_k with respect to α but not their absolute signs. On the other hand, the sign of η can be determined for a given phase convention, if the $\Delta k = \pm 3$ "forbidden" transitions are processed simultaneously with the usual $\Delta k = 0$ transition wavenumbers (see ref.¹⁵ for more details).

The matrix elements of $\eta(J_+^6 + J_-^6)$ are

$$\eta \langle J, 3; \pm | (J_+^6 + J_-^6) | J, 3; \pm \rangle = \pm \eta \cos(6\omega) (J+3)! / (J-3)!, \quad (6)$$

where

$$|J, 3; \pm \rangle = 2^{-1/2} [|J, +3 \rangle \pm |J, -3 \rangle], \quad (7)$$

ω is the phase factor^{14,21} and the signs are correlated on both sides of Eqs (6) and (7).

TABLE III

Wavenumbers of the rotational transitions in the ν_2 and ν_4 vibrational states of PH_3 (in cm^{-1})^a

Assignment $J', K' \leftarrow J'', K''$	ν_{exp}	ν_{calc} (see ^b)
ν_2 state		
1,0 \leftarrow 0,0	8·5483655	8·54823(403)
2,0 \leftarrow 1,0	17·1000327	17·09991(105)
3,0 \leftarrow 2,0	25·655468	25·65710(140)
4,0 \leftarrow 3,0	34·223623	34·22464(111)
2,1 \leftarrow 1,1	17·098387	17·09757(304)
3,1 \leftarrow 2,1	25·657818	25·65530(300)
4,1 \leftarrow 3,1	34·220714	34·22099(36)
3,2 \leftarrow 2,2	25·648266	25·64874(54)
4,2 \leftarrow 3,2	34·211778	34·21145(28)
4,3 \leftarrow 3,3 ^c	34·196267	34·19529(36)
4,3 \leftarrow 4,3 ($A_2 \leftarrow A_1$) ^d	0·00012	—
9,3 \leftarrow 9,3 ($A_1 \leftarrow A_2$) ^d	0·01059	0·01031(28)
ν_4 state		
1,0 \leftarrow 0,0	9·10872268	9·084(30)
2,0 \leftarrow 1,0	18·1710314	18·171(3)
3,0 \leftarrow 2,0	27·151103	27·150(4)
2,1 \leftarrow 1,1 ($-l \leftarrow -l, E \leftarrow E$)	18·215577	18·225(15)
2,1 \leftarrow 1,1 ($+l \leftarrow +l, A_2 \leftarrow A_1$)	17·8635733	17·869(21)
2,1 \leftarrow 1,1 ($+l \leftarrow +l, A_1 \leftarrow A_2$)	18·5564116	18·556(4)
3,1 \leftarrow 2,1 ($-l \leftarrow -l, E \leftarrow E$)	27·256931	27·253(12)
3,1 \leftarrow 2,1 ($+l \leftarrow +l, A_1 \leftarrow A_2$)	26·788386	26·786(28)
3,1 \leftarrow 2,1 ($+l \leftarrow +l, A_2 \leftarrow A_1$)	27·809304	27·809(4)
3,2 \leftarrow 2,2 ($+l \leftarrow +l, E \leftarrow E$)	27·452011	27·452(3)
3,2 \leftarrow 2,2 ($-l \leftarrow -l, A_1 \leftarrow A_2$)	27·317905	27·320(10)
3,2 \leftarrow 2,2 ($-l \leftarrow -l, A_2 \leftarrow A_1$)	27·321892	27·320 (10)
1,1 \leftarrow 1,1 ($+l \leftarrow +l, A_2 \leftarrow A_1$) ^e	0·35020561	0·345(5)
2,1 \leftarrow 2,1 ($+l \leftarrow +l, A_1 \leftarrow A_2$) ^e	1·0430443	1·031(20)
3,1 \leftarrow 3,1 ($+l \leftarrow +l, A_2 \leftarrow A_1$) ^e	2·0639628	2·056(10)
4,1 \leftarrow 4,1 ($+l \leftarrow +l, A_1 \leftarrow A_2$) ^f	3·3986759	3·410(15)
9,2 \leftarrow 9,2 ($-l \leftarrow -l, A_2 \leftarrow A_1$) ^g	0·205959	0·205(4)
11,2 \leftarrow 11,2 ($-l \leftarrow -l, A_2 \leftarrow A_1$) ^g	0·329391	0·330(7)
9,4 \leftarrow 9,4 ($+l \leftarrow +l, A_2 \leftarrow A_1$) ^g	0·192200	0·191(3)
10,4 \leftarrow 10,4 ($+l \leftarrow +l, A_1 \leftarrow A_2$) ^g	0·265890	0·267(3)
11,4 \leftarrow 11,4 ($+l \leftarrow +l, A_2 \leftarrow A_1$) ^g	0·3512557	0·352(4)
13,4 \leftarrow 13,4 ($+l \leftarrow +l, A_2 \leftarrow A_1$) ^g	0·5601435	0·544(22)

^a Our submillimeterwave measurements unless stated otherwise (see footnote^g). ^b Calculated as the weighted average from the ν_2, ν_4 band wavenumber (Table I and refs^{7,9}). ^c A_1, A_2 splitting has not been resolved. ^d Ref.¹⁶. ^e Ref.¹⁷. ^f Ref.¹⁸. ^g Our microwave measurements.

For $\omega = 0$, $|J, 3; +\rangle$ is of the species A_2 for J even and A_1 for J odd, and $|J, 3; -\rangle$ is of the species A_1 for J even and A_2 for J odd. For this phase convention, the analysis of the data gives $\eta > 0$ (Table II).

From the ground state parameters of PH_3 given in Table II, it is possible to calculate precise values of the ground state energies of PH_3 . We have combined these calculated values with the experimental data on the ν_2 band transitions given in Table I and the ν_4 band data^{7,12,13} to obtain the ν_2 and ν_4 state energy levels of PH_3 . These energy levels have been used to predict wavenumbers of the rotational transitions in the ν_2 and ν_4 states of PH_3 which we have measured in the microwave and submillimeterwave regions (Table III).

When this paper was finished, we received a preprint of an interesting paper of Tarrago and Dang Nhu²³ in which the ground state spectroscopic parameters of PH_3 have been determined. Tarrago and Dang Nhu used only the microwave and submillimeterwave data in their fit (the same 75 frequencies as in our work). As for the possibility of determining the coefficients α and η' in a separate fit, they arrived at the same conclusions as discussed in our paper.

We are grateful to Dr V. Špirko and Dr Š. Urban for many helpful discussions and to Dr G. Tarrago for sending us her results prior to publication.

REFERENCES

1. Helminger P., Gordy W.: *Phys. Rev.* **188**, 100 (1969).
2. Chu F. Y., Oka T.: *J. Chem. Phys.* **60**, 4612 (1974).
3. Helms D. A., Gordy W.: *J. Mol. Spectrosc.* **66**, 206 (1977).
4. Belov S. P., Burenin A. V., Gershtein L. I., Krupnov A. F., Markov V. N., Maslovsky A. V., Shapin S. M.: *J. Mol. Spectrosc.* **86**, 184 (1981).
5. Belov S. P., Burenin A. V., Polyanskii O. L., Shapin S. M.: *J. Mol. Spectrosc.* **90**, 579 (1981).
6. Maki A. G., Sams R. L., Olson W. B.: *J. Chem. Phys.* **58**, 4502 (1973).
7. Tarrago G., Dang-Nhu M., Goldman A.: *J. Mol. Spectrosc.* **88**, 311 (1981).
8. Baldacci A., Devi Malathy V., Rao Narahari K., Tarrago G.: *J. Mol. Spectrosc.* **81**, 179 (1980).
9. Yin P. K. L., Rao Narahari K.: *J. Mol. Spectrosc.* **51**, 199 (1974).
10. Kauppinen J.: *Appl. Opt.* **18**, 1788 (1979).
11. Kauppinen J., Jolma K., Horneman V.-M.: *Appl. Opt.* **21**, 3332 (1982).
12. Crocker D., Butcher R. J.: *Int. J. Infrared Millimeter Waves* **3**, 409 (1982).
13. Tanimura S., Takagi K.: *J. Mol. Spectrosc.* **104**, 414 (1984).
14. Urban Š., D'Cunha R., Rao Narahari K., Papoušek D.: *Can. J. Phys.* **62**, 1775 (1984).
15. Papoušek D., Urban Š.: *J. Mol. Spectrosc.*, in press.
16. Carlotti M., Di Lonardo G., Trombetti A.: *J. Chem. Phys.* **78**, 1670 (1983).
17. Guarnieri A., Scappini F., Di Lonardo G.: *Chem. Phys. Lett.* **82**, 321 (1981).
18. Belov S. P., Krupnov A. F., Papoušek D., Urban Š., Cazzoli G.: *J. Mol. Spectrosc.* **98**, 265 (1983).
19. Krupnov A. F. in the book: *Modern Aspects of Microwave Spectroscopy* (G. W. Chantry, Ed.). Academic Press, London 1979.

20. Watson J. K. G. in the book: *Vibrational Spectra and Structure* (J. Durig, Ed.), Vol. 6, p. 1. Elsevier, Amsterdam 1977.
21. Yamada K.: *Z. Naturforsch.* *38a*, 821 (1983).
22. Carlotti M., Di Lonardo G., Fusina L.: *J. Mol. Spectrosc.* *102*, 310 (1983).
23. Tarrago G., Dang Nhu M.: *J. Mol. Spectrosc.* *111*, 425 (1985).

Translated by the author (D.P.).