



**GROUND STATE MOLECULAR PARAMETERS OF PHOSPHINE,  
 $\text{PH}_3$ , FROM THE SIMULTANEOUS ANALYSIS  
 OF THE HIGH-RESOLUTION INFRARED, MICROWAVE  
 AND SUBMILLIMETERWAVE SPECTRA**

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Fourier transform spectra of the  $\nu_2$  band of  $\text{PH}_3$  have been remeasured with  $0\cdot0045 \text{ cm}^{-1}$  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  $\text{PH}_3$  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  $\Delta J = 0, +1$ ,  $\Delta K = 0$  ( $A_1 \leftrightarrow A_2$ ,  $E \leftrightarrow E$ ) rotational transitions in the  $\nu_2$  and  $\nu_4$  states have been measured for the first time by using a microwave spectrometer and a radiofrequency spectrometer with acoustic detection.

Phosphine,  $\text{PH}_3$ , is a spectroscopically interesting molecule. Because of the relatively small value of  $C - B$  ( $\sim -0\cdot533 \text{ cm}^{-1}$  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 submillimeterwave<sup>1-5</sup> as well as infrared spectra<sup>6-8</sup> of this molecule.

The ground state molecular parameters of  $\text{PH}_3$  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 approach<sup>4</sup> as well as the representation of the effective rotational Hamiltonian in the form of a Pade operator<sup>5</sup>. 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  $\text{PH}_3$ .

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 Olson<sup>6</sup>, 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  $\text{PH}_3$  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  $\text{PH}_3$  have been investigated in detail by several authors<sup>6-9</sup>, the resolution of the previous measurement was not better than  $0.03 \text{ cm}^{-1}$  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  $v_2$  band of  $\text{PH}_3$  using a Fourier transform spectrometer built at the University of Oulu<sup>10,11</sup> and working with  $0.0045 \text{ cm}^{-1}$  resolution. The microwave and submillimeterwave data<sup>1-5</sup> have been analyzed simultaneously with the ground state combination differences from our Fourier transform measurement, the precise  $v_2$  band transition wavenumbers obtained by using an off-set locked waveguide  $\text{CO}_2$  laser system<sup>12</sup>, and infrared-microwave two-photon transition wavenumbers<sup>13</sup>.

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  $v_2$  and  $v_4$  excited states of  $\text{PH}_3$  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 Gorkii<sup>19</sup>. By combining the  $v_2$  and  $v_4$  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  $v_2$  band of  $\text{PH}_3$  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  $830-1100 \text{ cm}^{-1}$  wavenumber range. Because of the Mylar beamsplitter selfabsorption at  $1050 \text{ cm}^{-1}$ , the measurement is confined to  $J'' = 7$  in the  $R$  branch. The wavenumber scale was calibrated with the aid of the  $v_2$  lines of  $\text{CO}_2$  (ref.<sup>11</sup>). Resolution was  $0.0045 \text{ cm}^{-1}$ , the precision of the line positions was better than  $10^{-3} \text{ cm}^{-1}$  for unblended narrow lines. The results of measurements are given in Table I (see also Fig. 1).

TABLE I  
Transition wavenumbers in the  $\nu_2$  band of  $\text{PH}_3$  (see<sup>a</sup>, in  $\text{cm}^{-1}$ )

<i>P</i>			<i>P</i>			<i>P</i>		
<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$	<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$	<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$
1	0	983·23044(400)	9	5	905·01296(20)	13	6	859·65261(10)
2	0	973·97320(50)	9	6	906·99396(10)	13	7	861·63554(50)
2	1	974·17562(50)	9	7	909·41455(10)	13	8	863·99301(30)
2	1	974·17535(25) <sup>b</sup>	9	8	912·32049(10)	13	9	866·75689(250)
3	0	964·37284(100)	10	0	889·33567(20)	13	10	870·00103(50)
3	1	964·57181(200)	10	1	889·49621(20)	13	11	873·77178(50)
3	2	965·17421(80)	10	2	889·97949(20)	13	12	878·15122(50)
4	0	954·44407(100)	10	3	890·78882(400)	14	0	842·59430(10)
4	1	954·63992(50)			890·79541(400)	14	1	842·72869(10)
4	2	955·23166(100)	10	4	891·94561(50)	14	2	843·13299(10)
4	3	956·22846(200)	10	5	893·45736(50)	14	3	843·79020(30)
5	0	944·20988(50)	10	6	895·35070(20)			843·83218(20)
5	1	944·40042(30)	10	7	897·65872(50)	14	4	844·77050(50)
5	2	944·97750(20)	10	8	900·42299(20)	14	5	846·02293(20)
5	2	944·97844(25) <sup>b</sup>	10	9	903·70088(10)	14	6	847·58045(20)
5	3	945·94959(30)	11	0	877·81262(20)	14	7	849·46379(20)
5	3	945·95144(25) <sup>b</sup>	11	1	877·96634(20)	14	8	851·69718(20)
5	4	947·33741(10)	11	2	878·42929(10)	14	9	854·31450(20)
6	0	933·69168(20)	11	3	879·20194(80)	14	10	857·35982(100)
6	1	933·87743(20)			879·21349(80)	14	11	860·89463(50)
6	1	933·87824(25) <sup>b</sup>	11	4	880·31118(20)	14	12	864·98864(50)
6	2	934·43824(50)	11	5	881·75538(10)	14	13	869·73277(400)
6	3	935·38524(100)	11	6	883·56105(20)	15	0	830·70642(100)
6	4	936·72934(50)	11	7	885·75725(30)	15	1	830·83491(100)
6	5	938·50123(10)	11	8	888·38195(20)	15	2	831·22118(100)
7	0	922·91744(20)	11	9	891·48632(10)	15	3	831·83853(150)
7	0	922·91749(0) <sup>c</sup>	11	10	895·13366(40)			831·89768(100)
7	1	923·09739(20)	12	0	866·16682(10)	15	4	832·78249(100)
7	1	923·09751(25) <sup>b</sup>	12	1	866·31387(10)	15	5	833·97493(80)
7	2	923·63998(10)	12	2	866·76418(300)	15	6	835·45665(50)
7	3	924·55396(50)	12	3	867·49135(20)	15	7	837·24453(100)
7	3	924·55479(25) <sup>b</sup>			867·51042(20)	15	8	839·36131(150)
7	4	925·85538(20)	12	4	868·55537(10)	15	9	841·83344(50)
7	5	927·56665(20)	12	5	869·93310(10)	15	10	844·69966(100)
7	6	929·71988(10)	12	6	871·65350(20)	15	11	848·00953(250)
8	0	911·91461(20)	12	7	873·74068(50)	15	12	851·83121(250)
8	1	912·08830(20)	12	8	876·22953(50)	15	13	856·25422(500)
8	2	912·61196(20)	12	9	879·16393(10)	15	14	861·37138(3000)
8	3	913·49334(50)	12	10	882·60292(30)	16	4	820·74191(300)
8	4	914·74654(20)	12	11	886·61766(10)	16	5	821·87910(300)

TABLE I  
(Continued)

<i>P</i>			<i>P</i>			<i>P</i>		
<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$	<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$	<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$
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>	$\nu_{\text{exp}}^d$	<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$	<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$
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) <sup>b</sup>	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) <sup>b</sup>	14	12	984·38170(0) <sup>e,c</sup>
4	1	988·86143(30)	10	10	992·76790(150)	14	12	984·38183(25) <sup>b</sup>
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) <sup>b</sup>	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) <sup>b</sup>	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>	$\nu_{\text{exp}}^d$	<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$	<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$
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) <sup>b</sup>	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) <sup>b</sup>	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) <sup>b</sup>	13	10	981·07695(25) <sup>b</sup>	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>	$\nu_{\text{exp}}^d$	<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$	<i>J</i>	<i>K</i>	$\nu_{\text{exp}}^d$
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) <sup>b</sup>	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		
J	K	$\nu_{\text{exp}}^d$	J	K	$\nu_{\text{exp}}^d$	J	K	$\nu_{\text{exp}}^d$
3	3	1 026.02068(3000)	6	1	1 045.21623(3000)	8	3	1 059.15095(25) <sup>b</sup>
4	0	1 031.46947(3000)	6	2	1 045.76464(1000)			1 059.13994(25) <sup>b</sup>
4	1	1 031.65839(1000)	6	3	1 046.66561(3000)	9	7	1 071.89507(25) <sup>b</sup>
4	2	1 032.23110(1000)	6	4	1 047.95824(1000)	9	8	1 074.62651(25) <sup>b</sup>
4	3	1 033.19305(3000)	6	5	1 049.64914(500)	10	4	1 071.91139(25) <sup>b</sup>

<sup>a</sup> Our Fourier transform measurements unless stated otherwise; values in parentheses are the estimated experimental uncertainties; <sup>b</sup> ref.<sup>13</sup>; <sup>c</sup> ref.<sup>12</sup>; <sup>d</sup> for  $K = 3$ , the larger  $\nu_{\text{exp}}$  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; <sup>e</sup>  $\nu_{\text{exp}}(14, 12) = 984.38170(50)$  from our FTIR spectra.

The microwave measurements of the transitions in the  $\nu_4$  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 spectrometer<sup>19</sup> 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  $\nu_2$  and  $\nu_4$  states of  $\text{PH}_3$ . The absolute accuracy of the measurements of frequencies is  $\pm 10$  kHz for lines with signal-to-noise ratios higher than 600; for the weakest lines the experimental accuracy can reach  $\pm 0.5$  MHz. However, there are pressure induced frequency shifts of the line center which lead to the experimental uncertainty of the line frequencies about  $\pm 1$  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).

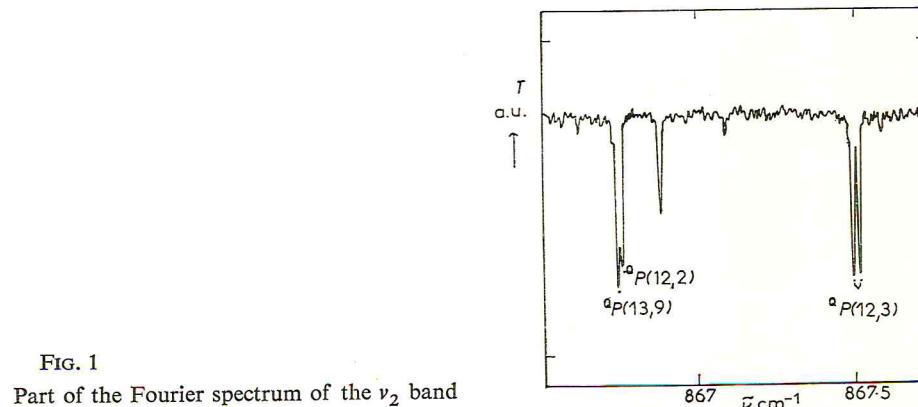


FIG. 1  
Part of the Fourier spectrum of the  $\nu_2$  band

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  $\delta$  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 form<sup>20</sup> (which includes the sixth powers of the angular momentum operators):

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

where

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

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 ( $H'_{\text{rot}}$ ) is measured in units of  $\text{cm}^{-1}$ .

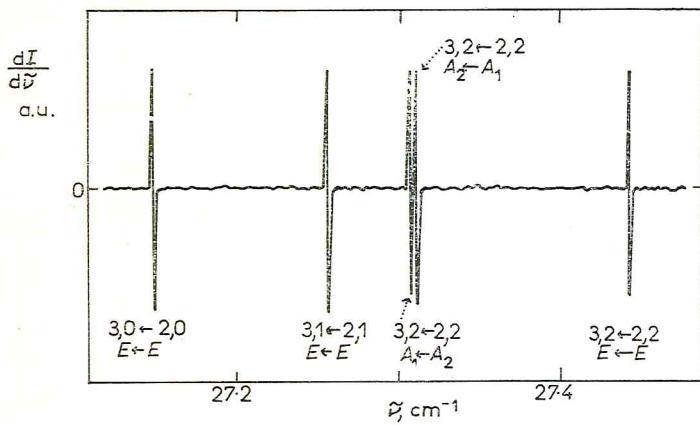


FIG. 2  
Part of the rotational spectrum in the  $\nu_4$  state of  $\text{PH}_3$

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  $H'_{\text{rot}}$  in Eq. (1) can be achieved in the basis of the symmetric top rotational wavefunctions obtained by the Wang transformation<sup>14</sup>. In this basis, the operator  $H'_{\text{rot}} - H'_{\text{split}}$  [cf. Eq. (1)] is purely diagonal;  $H'_{\text{split}}$  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  $\alpha$ ,  $\alpha_J$ , and  $\alpha_K$  are purely off-diagonal because they connect states with  $\Delta k = \pm 3$ . A detailed discussion of the matrix representation of  $H'_{\text{rot}}$  including the discussion of the phase convention in the definition of the rotational wavefunctions can be found in ref.<sup>14</sup>.

It is therefore possible to apply a unitary transformation to the effective rotational Hamiltonian  $H'_{\text{rot}}$  such that the  $\alpha$ -containing terms are transformed into the term  $\eta(J_+^6 + J_-^6)$  and into other terms containing the even powers of  $J$  and  $J_z$  (refs<sup>15-20</sup> for more details):

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

Relations between the parameters of the reduced Hamiltonian in Eq. (5a) and the parameters in  $H'_{\text{rot}}$  (Eq. (1)) can be found e.g. in ref.<sup>20</sup>.

This means that the parameters  $\alpha$ ,  $\alpha_J$  and  $\alpha_K$  are correlated with the parameters occurring in the reduced form of the Hamiltonian given by Eq. (5a), which makes it difficult to determine the  $\alpha$ - and  $\eta$ -parameters separately by fitting the experimental data (see also ref.<sup>15</sup>).

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 PH<sub>3</sub> (in cm<sup>-1</sup>)

Parameter	Set I <sup>a</sup>	Set II <sup>b</sup>	Set III <sup>c</sup>	Set IV <sup>b</sup>	Set V <sup>b</sup>
<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<sub>J</sub></i> · 10 <sup>4</sup>	1.313252(6530)	1.312431(59)	1.312085(50)	1.312081(192)	1.312445(58)
<i>D<sub>JK</sub></i> · 10 <sup>4</sup>	-1.722271(48)	-1.722230(30)	-1.722183(36)	-1.725001(109)	-1.725105(75)
<i>D<sub>K</sub></i> · 10 <sup>4</sup>	1.412927(353)	1.412966(289)	1.413034(270)	1.414369(337)	1.414297(333)
<i>H<sub>JJ</sub></i> · 10 <sup>8</sup>	1.37772(30901)	1.0358(20)	1.0288(16)	1.2807(145)	1.3098(20)
<i>H<sub>JK</sub></i> · 10 <sup>8</sup>	-2.1464(30)	-2.1490(24)	-2.1518(22)	-4.7948(45)	-4.7976(40)
<i>H<sub>JKK</sub></i> · 10 <sup>8</sup>	1.6997(125)	1.7015(96)	1.7310(84)	5.9668(277)	5.9356(140)
<i>H<sub>KKK</sub></i> · 10 <sup>8</sup>	0.4282(722)	0.4385(588)	0.3841(547)	-1.5749(674)	-1.5528(640)
<i>L<sub>JJJ</sub></i> · 10 <sup>10</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0.0065(32)	0 <sup>d</sup>
<i>L<sub>JKK</sub></i> · 10 <sup>10</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0.0363(10)	0.0355(8)
<i>L<sub>JKK</sub></i> · 10 <sup>10</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>d</sup>	-0.0143(114)	0 <sup>d</sup>
<i>L<sub>KKK</sub></i> · 10 <sup>10</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>d</sup>	-0.0842(211)	-0.0939(187)
<i>L<sub>KKKK</sub></i> · 10 <sup>10</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>d</sup>
<i>n</i> · 10 <sup>8</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0.16258(709)	0.15748(585)
<i>n<sub>J</sub></i> · 10 <sup>12</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>d</sup>	-0.1483(31)	-0.1463(26)
<i>n<sub>K</sub></i> · 10 <sup>10</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>d</sup>	-0.2081(782)	-0.1517(646)
<i>α</i> · 10 <sup>5</sup>	2.76000(62)	2.75986(50)	2.75997(47)	0 <sup>d</sup>	0 <sup>d</sup>
<i>α<sub>J</sub></i> · 10 <sup>8</sup>	-0.5401(18)	-0.5400(14)	-0.5405(13)	0 <sup>d</sup>	0 <sup>d</sup>
<i>α<sub>K</sub></i> · 10 <sup>8</sup>	0.736(14)	0.748(11)	0.757(10)	0 <sup>d</sup>	0 <sup>d</sup>

No of Data      75      357      2 920      357      357  
Std. dev. of the fit      1·3 · 10<sup>-5</sup>      3·7 · 10<sup>-5</sup>      2·9 · 10<sup>-4</sup>      3·7 · 10<sup>-5</sup>      3·7 · 10<sup>-5</sup>

<sup>a</sup> Fit to the microwave and submillimeterwave data only<sup>1-5</sup>. <sup>b</sup> Fit to the microwave and submillimeterwave data<sup>1-5</sup> simultaneously with the ν<sub>2</sub> band data measured in this work and the precise data given in refs<sup>12,13</sup>. <sup>c</sup> Fit to the same data as specified in footnote<sup>b</sup>, extended by the data given in refs<sup>6-9</sup>. <sup>d</sup> 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  $\alpha$  and  $\eta'$  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  $\alpha$  and  $\eta'$  (see<sup>22</sup> for similar results obtained for AsH<sub>3</sub>).

We have therefore fit the data either by constraining the parameters  $\eta$  to zero or  $\alpha$  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  $\alpha$ ,  $\alpha_J$ , and  $\alpha_K$  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  $\alpha$ ,  $\alpha_J$ , and  $\alpha_K$  (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  $\alpha$  and  $\eta$  depend on the arbitrary choice of the phase factors in the rotational wavefunctions (see ref.<sup>14</sup> for more details). However, there is a difference between  $\alpha$  and  $\eta$  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  $\alpha_J$  and  $\alpha_K$  with respect to  $\alpha$  but not their absolute signs. On the other hand, the sign of  $\eta$  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.<sup>15</sup> 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

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

$\omega$  is the phase factor<sup>14,21</sup> and the signs are correlated on both sides of Eqs (6) and (7).

TABLE III  
Wavenumbers of the rotational transitions in the  $v_2$  and  $v_4$  vibrational states of  $\text{PH}_3$  (in  $\text{cm}^{-1}$ )<sup>a</sup>

Assignment $J', K' \leftarrow J'', K''$	$v_{\text{exp}}$	$v_{\text{calc}} (\text{see}^b)$
$v_2$ 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 <sup>c</sup>	34.196267	34.19529(36)
4,3 $\leftarrow$ 4,3 ( $A_2 \leftarrow A_1$ ) <sup>d</sup>	0.00012	—
9,3 $\leftarrow$ 9,3 ( $A_1 \leftarrow A_2$ ) <sup>d</sup>	0.01059	0.01031(28)
$v_4$ 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 ( $+l \leftarrow +l, A_2 \leftarrow A_1$ ) <sup>e</sup>	0.35020561	0.345(5)
2,1 $\leftarrow$ 2,1 ( $+l \leftarrow +l, A_1 \leftarrow A_2$ ) <sup>e</sup>	1.0430443	1.031(20)
3,1 $\leftarrow$ 3,1 ( $+l \leftarrow +l, A_2 \leftarrow A_1$ ) <sup>e</sup>	2.0639628	2.056(10)
4,1 $\leftarrow$ 4,1 ( $+l \leftarrow +l, A_1 \leftarrow A_2$ ) <sup>f</sup>	3.3986759	3.410(15)
9,2 $\leftarrow$ 9,2 ( $-l \leftarrow -l, A_2 \leftarrow A_1$ ) <sup>g</sup>	0.205959	0.205(4)
11,2 $\leftarrow$ 11,2 ( $-l \leftarrow -l, A_2 \leftarrow A_1$ ) <sup>g</sup>	0.329391	0.330(7)
9,4 $\leftarrow$ 9,4 ( $+l \leftarrow +l, A_2 \leftarrow A_1$ ) <sup>g</sup>	0.192200	0.191(3)
10,4 $\leftarrow$ 10,4 ( $+l \leftarrow +l, A_1 \leftarrow A_2$ ) <sup>g</sup>	0.265890	0.267(3)
11,4 $\leftarrow$ 11,4 ( $+l \leftarrow +l, A_2 \leftarrow A_1$ ) <sup>g</sup>	0.3512557	0.352(4)
13,4 $\leftarrow$ 13,4 ( $+l \leftarrow +l, A_2 \leftarrow A_1$ ) <sup>g</sup>	0.5601435	0.544(22)

<sup>a</sup> Our submillimeterwave measurements unless stated otherwise (see footnote<sup>g</sup>). <sup>b</sup> Calculated as the weighted average from the  $v_2$ ,  $v_4$  band wavenumber (Table I and refs<sup>7,9</sup>). <sup>c</sup>  $A_1$ ,  $A_2$  splitting has not been resolved. <sup>d</sup> Ref.<sup>16</sup>. <sup>e</sup> Ref.<sup>17</sup>. <sup>f</sup> Ref.<sup>18</sup>. <sup>g</sup> 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  $\text{PH}_3$  given in Table II, it is possible to calculate precise values of the ground state energies of  $\text{PH}_3$ . We have combined these calculated values with the experimental data on the  $v_2$  band transitions given in Table I and the  $v_4$  band data<sup>7,12,13</sup> to obtain the  $v_2$  and  $v_4$  state energy levels of  $\text{PH}_3$ . These energy levels have been used to predict wavenumbers of the rotational transitions in the  $v_2$  and  $v_4$  states of  $\text{PH}_3$  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 Nhu<sup>23</sup> in which the ground state spectroscopic parameters of  $\text{PH}_3$  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  $\alpha$  and  $\eta'$  in a separate fit, they arrived at the same conclusions as discussed in our paper.

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