Rotational l-Type Doubling in the $kl = +1$ Levels of the ν_4 State of PH_3

High resolution infrared and microwave studies of rotational l-type doubling in symmetric top molecules give valuable information on the anharmonicity of the molecular potential function (*1, 2*). It has also been shown recently that transitions between the l-type doublets are suitable for interesting microwave–infrared double resonance experiments (*3, 4*).

Scappini and Schwarz (*5*) and Guarnieri *et al.* (*6*) have recently measured the first three direct ($\Delta J = 0$) l-doublet transitions in the $\nu_4 = 1$ state of PH_3 ($kl = +1$; $J = 1, 2, 3$). In the present paper we have extended this measurement to the $J = 4$ state and to the $J + 1 \leftarrow J$ transitions for $J = 1, 2$. The microwave ($\Delta J = 0$) and submillimeterwave ($\Delta J = +1$) transition frequencies are internally consistent within the accuracy of experiment (Table I); they are also consistent with the assignments of the ν_4 band transition frequencies published by Tarrago *et al.* (*7*).

The microwave l-type doubling transition frequency has been measured using the O.K.I. 35 V 12 klystron (third harmonic, approximately 102 GHz). The klystron was locked to the suitable harmonic of a Fluke synthesizer 6160 B driven by a Commodore PET microcomputer 2001. The microcomputer also provided an improvement in the signal to noise ratio of the spectrum by averaging of the digital signal coming from the output of the lock-in amplifier connected to the detector.

A P-band Stark cell 1.5 m long has been employed and the modulation frequency was 33.3 kHz. The absorption cell was operated at room temperature and the pressure of the gas in the cell was about 4 Pa (30 mTorr).

The submillimeterwave spectrometer RAD with an acoustic detector and a system employing phase-sensitive frequency stabilization of the backward wave oscillator (*8, 9*) has been used to measure the $\Delta J = +1$ transition frequencies in the $kl = +1$ levels. The $J = 2 \leftarrow 1$ transitions have been measured at 16 Pa (0.12 Torr), the $J = 3 \leftarrow 2$ transitions at 53 Pa (0.4 Torr) of the PH_3 gas. The pressure induced frequency shift has been estimated to be approximately +0.3 MHz/Torr for the $J = 2 \leftarrow 1$ transition and smaller than this for the $J = 3 \leftarrow 2$ transition.

It is convenient to use the D_{3h} permutation-inversion group for the symmetry classification of the energy levels in PH_3, i.e., to consider PH_3 as an ammonia-like molecule in a classification scheme allowing for a separate classification of the energy levels split by the inversion tunneling (*2, 10*). Of course, we could use the C_{3v} group of a semirigid PH_3 model equally as well. However, ultrahigh resolution spectroscopists have a continuing interest in detecting the inversion splitting of the energy levels in PH_3 (cf. (*10*)) and we want to show how to avoid the pitfall that there is an easily measurable true separation of the symmetric s and antisymmetric a (with respect to inversion) sublevels in the $\nu_4 = 1$, $kl = +1$ levels of PH_3.

In the notation $|v_2^{(i)}, v_4^{\pm l_4}; J, k\rangle$ (see (*11*)), we can write the stabilized wavefunctions of the $kl = +1$ states as

$$|{}^{(i)}A_{\pm}^{(4)}(+l; J, K = 1)\rangle = 2^{-1/2}[|0^{(i)}, 1^{+1}; J, +1\rangle \pm |0^{(i)}, 1^{-1}; J, -1\rangle] \tag{1}$$

where in the D_{3h} group (using conventions defined in (*2*)), $|{}^{(s)}A_{+}^{(4)}\rangle$ is A_2'' for J even, A_2'' for J odd; $|{}^{(a)}A_{+}^{(4)}\rangle$ is A_2' for J even, A_1' for J odd; $|{}^{(s)}A_{-}^{(4)}\rangle$ is A_2'' for J even, A_1'' for J odd; $|{}^{(a)}A_{-}^{(4)}\rangle$ is A_1' for J even, A_2' for J odd. For PH_3, only the A_2 states have nonzero spin statistical weight 4. The overall selection rule for the allowed transitions is $\Gamma(\psi') \times \Gamma(\psi'') \in A_1''$.

Note that the l-type doubling effect in PH_3 splits each $kl = +1$ level into two levels s and a. However, this is not the "true" inversion splitting due to the tunneling between the symmetrically equivalent configurations of PH_3 separated by the inversion barrier of about 12 000 cm^{-1} (10). Because the A_1' and A_1'' states have zero spin statistical weights in PH_3, the s and a sublevels in the $kl = +1$ level of PH_3 (Fig. 1) do not belong to the same inversional doublet. This is obvious from the comparison of the PH_3 energy level diagram with that of PD_3 (Fig. 1).

TABLE I

Wavenumbers of the $\Delta J = +1, 0$ Transitions between the $kl = +1$ Levels in the ν_4 State of PH_3 (cm^{-1})

J	$\nu_J^{(l)}(exp)$	$\nu_J^{(l)}(exp) - \nu_J^{(l)}(calc)^d$		
		I	II	III
1	0.35020561^a $(0.345)^c$	-1.5604×10^{-4}	-0.1230×10^{-4}	-1.3761×10^{-4}
2	1.04304425^a $(1.035)^c$	1.1937×10^{-4}	2.1488×10^{-4}	0.9829×10^{-4}
3	2.06396276^a $(2.048)^c$	-0.4669×10^{-4}	-1.9540×10^{-4}	-0.3440×10^{-4}
4	3.3986759^b $(3.405)^c$	0.0789×10^{-4}	0.5474×10^{-4}	0.0492×10^{-4}
5	5.008^c	-0.027	-0.027	-0.030
6	6.925^c	-0.037	-0.048	-0.064
7	9.014^c	-0.153	-0.220	-0.272
8	11.413^c	-0.198	-0.463	-0.590
9	13.962^c	-0.229	-1.038	-1.313
10	16.752^c	0.074	-2.022	-2.559
ν_{12}	17.8635733^b $(17.870)^c$	$\nu_2^{(l)} - \nu_1^{(l)}$	0.6928386	
ν'_{12}	18.5564116^b $(18.554)^c$	$\nu'_{12} - \nu_{12}$	0.6928383	
ν_{23}	26.788386^b $(26.786)^c$	$\nu_3^{(l)} - \nu_2^{(l)}$	1.0209185	
ν'_{23}	27.809304^b $(27.8095)^c$	$\nu'_{23} - \nu_{23}$	1.020918	
ν_{34}	35.689^c	$\nu_4^{(l)} - \nu_3^{(l)}$	1.334713	
ν'_{34}	37.040^c	$\nu'_{34} - \nu_{34}$	1.351	

[a] References (5, 6).

[b] Our measurement; $c = 2.99792458 \times 10^8$ ms^{-1} has been used in converting the frequency units into wavenumber units.

[c] Calculated from the data in (7).

[d] I, II: Simultaneous least squares fit of the microwave and infrared data (Eq. (3)), $w(MW) = 1$, $w(IR) = 4 \times 10^{-8}$; I: $\beta_1 = 0.17590849(3843)$, $\beta_2 = -3.7208(648) \times 10^{-4}$, $\beta_3 = 4.1758(3008) \times 10^{-6}$, $\beta_4 = -2.5463(4369) \times 10^{-8}$; II: $\beta_1 = 0.17579386(7890)$, $\beta_2 = -3.4793(1189) \times 10^{-4}$, $\beta_3 = 2.7396(4121) \times 10^{-6}$; III: Fit to the microwave data only, $\beta_1 = 0.17588452(2713)$, $\beta_2 = -3.6300(416) \times 10^{-4}$, $\beta_3 = 3.2726(1450) \times 10^{-6}$.

According to Tarrago et al. (7), the ν_4 band $^RP(J, 0)$ and $^RR(J - 2, 0)$ transitions go to the upper sublevel of the l-doublet, while the $^RQ(J - 1, 0)$ go to the lower sublevel (Fig. 1, Table I). Thus the following relation should hold between the submillimeterwave and microwave transition frequencies.

$$\nu'_{12} - \nu_{12} = \nu_2^{(l)} - \nu_1^{(l)} \qquad (2a)$$

$$\nu'_{23} - \nu_{23} = \nu_3^{(l)} - \nu_2^{(l)} \qquad (2b)$$

with the notation for the transition frequencies defined by Fig. 1. The data in Table I are in excellent agreement with (2).

The J dependence of the l-type doubling effect is usually described by the following expansion (1, 2).

$$\nu_J^{(l)} = \beta_1 J(J + 1) + \beta_2 J^2(J + 1)^2 + \beta_3 J^3(J + 1)^3 + \cdots . \qquad (3)$$

The results of a simultaneous least squares fit of the infrared and microwave data are given in Table I (I is a four-parameter fit; II a three-parameter fit; III is a three-parameter fit to the microwave data only).

It is obvious from these results that (3) does not lend itself to a quantitative description of the experimental data on the rotational l-type doubling in PH_3. The matrix element of the l-type doubling operator H_l

$$\langle 0^{(i)}, 1^{+1}; J, +1|H_l|0^{(i)}, 1^{-1}; J, -1\rangle = \beta J(J + 1) \qquad (4)$$

indicates that the J dependence of the l-type doubling of the $kl = +1$ levels should be basically $2\beta J(J + 1)$. However, there are many other higher-order interactions which perturb the $kl = +1$ levels in the ν_4 state, as e.g., the Coriolis interaction between the ν_2 and ν_4 states

$$\langle 1^{(4)}, 0^0; J, k|H_{Cor}|0^{(4)}, 1^{\pm 1}; J, k \pm 1\rangle = \pm\alpha[J(J + 1) - k(k \pm 1)]^{1/2} \qquad (5)$$

the K-type doubling or the $\Delta k = \pm 3n$ interactions (12).

Because of the close coincidence of the energy levels with the same J value in PH$_3$, the ν_4 state energy levels are strongly perturbed by these interactions and a simultaneous variational analysis of the ν_2, ν_4 band data, together with the ground and ν_2, ν_4 state microwave and submillimeterwave data, should be used instead of a simple polynomial approach represented by (3). In the former approach, the rotational l-type doubling transition frequencies in the ν_4 state are useful data for determining the effective molecular parameters of these interactions. For example, for $J = K = 1$, only the l-type and Coriolis interactions described by (4) and (5) occur. By an algebraic treatment of the corresponding interaction matrices, the following relation can be found to hold between α and β.

$$\beta = \frac{1}{8}[\pm(d^2 - 16\alpha^2)^{1/2} - 2\nu_1^{(l)} + d] \qquad (6)$$

where d is the difference between the perturbed $J = K = 1$ A_2' level of the ν_4 state and the $J = 1$, $K = 0$ level of the ν_2 state.

For example, for $\alpha = 1.952$ cm^{-1} obtained by Yin and Rao (12) and for $d = 129.8405$ cm^{-1}, which can be obtained from the data in (7), we arrive at $\beta = 32.3432$ or -0.0582 cm^{-1}. The former value of β is
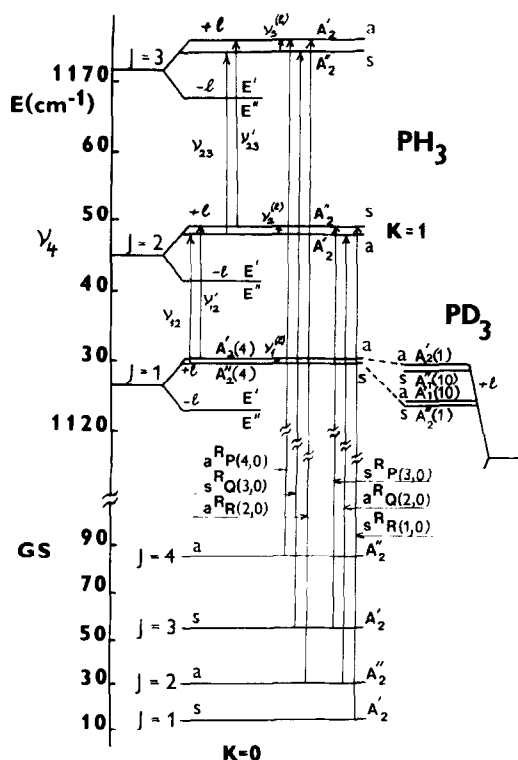

FIG. 1. Energy level diagram for the $\nu_4 = 1$, J, $K = 1$ states of PH$_3$ (PD$_3$ energy levels are not drawn to scale).

obviously not physically acceptable; Yin and Rao (*12*) reported $\beta = +0.0531$ cm^{-1}, which should probably have the opposite sign in their paper.

A complete quantitative analysis of these higher-order interactions in the ν_2, ν_4 states of PH_3 is a formidable task requiring a simultaneous treatment of the microwave, submillimeterwave, and infrared data. Work is now in progress in our labs using this approach and the data sets extended by additional submillimeterwave and Fourier transform measurements.

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