JOURNAL OF MOLECULAR SPECTROSCOPY 48, 612–613 (1973)

LETTER TO THE EDITORS

Microwave Spectrum of $\Delta k = \pm 3$ Transitions of PH_3

Recently the existence of $\Delta k = \pm 3$ rotational transitions in symmetric top molecules with a C_{3v} symmetry has been pointed out and the possible role of such transitions in the equilibration of interstellar NH_3 molecules has been discussed (*1*, *2*). In this letter we report a laboratory observation of such transitions in PH_3.

The $\Delta k = \pm 3$ transitions are caused by a small induced dipole moment perpendicular to the molecular axis due to centrifugal distortion. According to Watson (*3*), the line strength of a Q-type $\Delta k = \pm 3$ transition is given as

$$S = (\theta_x^{xx})_{\rm eff}^2 (J \mp k)(J \mp k - 1)(J \mp k - 2)(J \pm k + 1)(J \pm k + 2) \times (J \pm k + 3)(2J + 1)/4J(J + 1)$$

where

$$(\theta_x^{xx})_{\rm eff} = \theta_x^{xx} + \hbar^4 \tau_{xxxz} \mu_z / 2hc(B - C).$$

An approximate calculation using the normal coordinate analysis (*4*) indicates that the first term is about 1.6×10^{-5} D and the second term is about 8.3×10^{-5} D. These considerations suggested that the $\Delta k = \pm 3$, $\Delta J = 0$ transitions for $5 < J < 15$ are sufficiently strong to be observed with a conventional microwave spectrometer. The $\Delta k = \pm 3$ vibration-rotation transitions of PH_3 have been studied by Maki, Sams, and Olson (*5*) in the infrared region and the frequencies of the microwave transition could be predicted to within 40 MHz by using their molecular constants.

The observation was made with a 3 m K-band Stark modulation spectrometer. The observed lines are given in Table I together with the estimated absorption coefficients.

TABLE I

OBSERVED $\Delta k = \pm 3$ TRANSITIONS OF PH_3

Transitions $(J, \pm 1) \leftarrow (J, \mp 2)$	Observed Frequency (MHz)	$\delta\nu$ (MHz)[a]	Calculated intensity (cm^{-1})
6	47390.3 ± 0.8	0.4	2.3×10^{-9}
7	47177.9 ± 0.6	−0.3	3.5×10^{-9}
8	46938.4 ± 0.3	0.1	4.5×10^{-9}
9	46671.2 ± 0.3	0.2	5.3×10^{-9}
10	46377.3 ± 0.3	0.0	5.6×10^{-9}
11	46057.8 ± 0.4	−0.1	5.3×10^{-9}
12	45713.8 ± 0.6	−0.3	4.8×10^{-9}

[a] $\delta\nu = \nu_{\rm obs.} - \nu_{\rm calc.}$.

The sensitivity of our spectrometer is estimated to be 1×10^{-9} cm^{-1} at a time constant of 3 sec. From the observed signal to noise ratio, we estimate the magnitude of $(\theta_x^{zx})_{eff}$ to be 7.2×10^{-5} D. The measured frequencies of the $\Delta k = \pm 3$ transitions give accurate information on the rotational parameters associated with the rotation around the molecular axis. The following constants are determined from the observed frequencies

$$B - C + 5D_K - 21H_K = 16011.59 \pm 0.1 \text{ MHz},$$
$$D_{JK} - 5H_{JKK} = -5.177 \pm 0.005 \text{ MHz},$$
$$H_{JJK} = -0.0014 \pm 0.0001 \text{ MHz}.$$

Using the previously reported values of B (*6*), D_K, and H_{JKK} (*5*), we obtain

$$C = 117489.0 \pm 2.1 \text{ MHz and } D_{JK} = -5.165 \pm 0.006 \text{ MHz}.$$

Further work in millimeterwave region and for other molecules is in progress. This work together with the recent observation of the microwave spectrum of CH_4 (*7, 8*) establish the possibility of observing "forbidden" rotational transitions in the microwave region. We should also be able to observe rotational spectrum of nonpolar symmetric top molecules without a center of symmetry such as BH_3, BF_3, allene, etc., although Stark modulation is not easily applied due to the lack of first order Stark effect in these molecules (*9*).

We would like to thank K. NARAHARI RAO, P. K. L. YIN, J. K. G. WATSON, AND F. SHIMIZU for information and discussions leading to this work.

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Received August 22, 1973