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 $\Delta k = \pm 1$ transition is given as

$$S = (\theta_{z''})_{\text{eff}}(J \pm k)(J \pm k - 1)(J \pm k - 2)(J \pm k + 1)(J \pm k + 2) \times (J \pm k + 3)(2J + 1)/4J(J + 1)$$

where

$$(\theta_{z''})_{\text{eff}} = \theta_{z''} + \hbar^2 r_{zz'} \mu_d/2\hbar(B - C).$$

An approximate calculation using the normal coordinate analysis (4) indicates that the first term is about $1.6 \times 10^{-4}$ D and the second term is about $8.3 \times 10^{-5}$ 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

<table>
<thead>
<tr>
<th>Transitions $\Delta k = \pm 3$ Transitions of PH$_3$</th>
<th>Observed Frequency (MHz)</th>
<th>$\Delta \nu$ (MHz)$^a$</th>
<th>Calculated intensity (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = \pm 1$</td>
<td></td>
<td>$J = \pm 2$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>47390.3 ± 0.8</td>
<td>0.4</td>
<td>2.3 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>7</td>
<td>47177.9 ± 0.6</td>
<td>-0.3</td>
<td>3.5 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>8</td>
<td>46938.4 ± 0.3</td>
<td>0.1</td>
<td>4.5 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>9</td>
<td>46671.2 ± 0.3</td>
<td>0.2</td>
<td>5.3 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>10</td>
<td>46377.3 ± 0.3</td>
<td>0.0</td>
<td>5.6 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>11</td>
<td>46057.8 ± 0.4</td>
<td>-0.1</td>
<td>5.3 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>12</td>
<td>45713.8 ± 0.6</td>
<td>-0.3</td>
<td>4.8 $\times$ 10$^{-4}$</td>
</tr>
</tbody>
</table>

$^a \Delta \nu = \nu_{obs} - \nu_{calc}$.

The sensitivity of our sp of 3 sec. From the ober to be $7.2 \times 10^{-4}$ D. The information on the rot: molecular axis. The folk $B - C$

Using the previously r

$C = 117489$.

Further work in millin work together with the establish the possibility of region. We should also top molecules without a Stark modulation is not molecules (9).

We would like to thank information and discussions I.

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6. P. Helmingen and W. Gc
7. R. F. Culy, T. Oka, and

Division of Physics
National Research Council of
Ottawa, Ontario, Canada
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The sensitivity of our spectrometer is estimated to be $1 \times 10^{-6} \text{ cm}^{-1}$ at a time constant of 3 sec. From the observed signal to noise ratio, we estimate the magnitude of $(\theta^2)_{ab}$ to be $7.2 \times 10^{-6}$ 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

$$B - C + 5D_K - 21H_K = 16011.59 \pm 0.1 \text{ MHz},$$

$$D_{JK} - 5H_{JJK} = -5.177 \pm 0.005 \text{ MHz},$$

$$H_{JJK} = -0.0014 \pm 0.0001 \text{ MHz}.$$

Using the previously reported values of $B$ (6), $D_K$, and $H_{JJK}$ (7), we obtain

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

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. Nakahari Rao, P. K. L. Yin, J. K. G. Watson, and F. Shimizu for information and discussions leading to this work.

REFERENCES


F. Y. Chu
T. Oka

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Calculated intensity (cm$^{-1}$)

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\begin{align*}
2.3 \times 10^{-4} \\
3.5 \times 10^{-4} \\
4.5 \times 10^{-4} \\
5.3 \times 10^{-4} \\
5.6 \times 10^{-4} \\
5.3 \times 10^{-4} \\
4.8 \times 10^{-4}
\end{align*}
\]

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