

# VIBRATION-ROTATION BANDS OF $AsH_3$ IN THE $2\mu$ REGION

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TECHNICAL REPORT 1093-41  
25 July 1968

Grant Number NsG-74-60

GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) 3.00

Microfiche (MF) .65

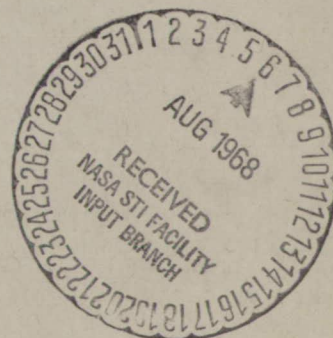
ff 653 July 65

National Aeronautics and Space Administration  
Office of Grants and Research Contracts  
Washington, D.C. 20546

**N68-31469**

FACILITY FORM 602

|  |                         |
|--|-------------------------|
| _____<br>(ACCESSION NUMBER)                      | _____<br>(THRU)         |
| <u>22</u><br>(PAGES)                             | <u>1</u><br>(CODE)      |
| <u>CR-95985</u><br>(NASA CR OR TMX OR AD NUMBER) | <u>06</u><br>(CATEGORY) |



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REPORT

by

The Ohio State University ElectroScience Laboratory  
(Formerly Antenna Laboratory)  
Columbus, Ohio 43212

Sponsor                      National Aeronautics and Space Administration  
                                 Office of Grants and Research Contracts  
                                 Washington, D.C. 20546

Grant Number                NsG-74-60

Investigation of             Receiver Techniques and Detectors for  
                                 Use at Millimeter and Submillimeter  
                                 Wave Lengths

Subject of Report            Vibration-Rotation Bands of  $\text{AsH}_3$  in the  
                                  $2\mu$  Region

Submitted by                P.K.L. Yin  
                                 ElectroScience Laboratory  
                                 Department of Electrical Engineering

Date                            25 July 1968

## ABSTRACT

The vibration-rotation bands of  $\text{AsH}_3$  in the  $2\mu$  region have tentatively been analyzed. The resonance effect, especially the  $\nu_1$  and the  $\nu_3$  bands for the K-type doubling and the Giant  $l$ -type doubling in the  $4\mu$  region have been described briefly. Some new combination difference relations in obtaining ground state constants from a perpendicular band have also been presented.

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# VIBRATION-ROTATION BANDS OF $\text{AsH}_3$ IN THE $2\mu$ REGION

## I. INTRODUCTION

It seems from a preliminary investigation that there is a possibility of laser action from an  $\text{AsH}_3$ - $\text{N}_2$  system. However, aside from other problems that might arise we must first of all have enough information on the molecular potential so that vibrational levels can be predicted to see if there is indeed a level close to that of  $\text{N}_2$  ( $v_2 = 1$ ).

Arsine ( $\text{AsH}_3$ ) is a pyramidal-type molecule similar to ammonia with the three hydrogen atoms forming the base of the pyramid and the As atom located at the apex. There are four fundamental vibration-rotation bands, two of which (designated as  $\nu_1$  and  $\nu_3$ ) occur in the region of  $5\mu$  and the other two (designated as  $\nu_2$  and  $\nu_4$ ) are doubly degenerate and are observed in the region of  $10\mu$ . All four fundamental bands plus some overtones have been studied in a series of reports by McConaghie and Nielsen<sup>1,2,3,4</sup> in 1948 with very low resolution.

In the past thirty years or so, many interesting features of the symmetric top molecule have been discovered. The inversion doubling in  $\text{NH}_3$  has been studied in considerable details both experimentally<sup>5,6,7,8</sup> and theoretically.<sup>9,10</sup> The Coriolis interaction which splits the degenerate vibrational levels was first realized by Teller and Tisza<sup>11</sup> in 1932. More recently, due to the availability of high resolution spectrometers the higher order interaction of two different vibrations due to Coriolis forces have been observed, namely the Giant  $l$ -type doubling and the K-type doubling. The theoretical developments are due to Nielsen<sup>12</sup> and Hoffman<sup>13</sup> respectively.

We shall report here the first clear observation of K-type doubling in a symmetric top molecule and the first observation of Giant  $l$ -type doubling in the  $\nu_3$  band of  $\text{AsH}_3$ . These doublings have been observed through the transitions of  $^R\text{P}(J, K)$  and  $^P\text{R}(J, K)$ . We have also been able to derive some new combination difference relations by utilizing these transitions to obtain ground state molecular constants from a perpendicular band.

In the  $2\mu$  region there are three possible bands which lie close together. These are the  $2\nu_1$ , a parallel band of species A,  $\nu_1 + \nu_3$ , a doubly degenerate perpendicular band of species E, and  $2\nu_3$ , a triply degenerate band of species A + A + E. Owing to the complex appearance of the spectrum, they have been only tentatively analyzed and we have not been able to obtain all the molecular constants.

## II. K-TYPE DOUBLING IN THE $\nu_3$ BAND

The doublets of  ${}^P P(J, 3)$  and  ${}^P R(J, 3)$  transitions are indicated in the partial spectrum presented in Fig. 1. It can be seen from an energy level diagram that the spacing between the doublets  ${}^P P(J, 3)$  and  ${}^P R(J-2, 3)$  should be equal if these splittings are due to the resonance effect of K-type doubling between  $\nu_1$  and  $\nu_3$ . The experimental finding which is given below indicates that this is indeed the case.

TABLE I  
OBSERVED K-TYPE DOUBLING SPLITTINGS

|                                      | ${}^P P(8, 3), {}^P R(6, 3)$ | ${}^P P(9, 3), {}^P R(7, 3)$ | ${}^P P(10, 3), {}^P R(8, 3)$ | ${}^P P(11, 3), {}^P R(9, 3)$ |
|--------------------------------------|------------------------------|------------------------------|-------------------------------|-------------------------------|
| $\Delta \nu$<br>( $\text{cm}^{-1}$ ) | 0.115, 0.090                 | 0.173, 0.174                 | 0.275, 0.261                  | 0.402, 0.388                  |

This doubling was indicated in the  $\nu_4$   ${}^R R(J, 3)$  transitions of  $\text{PH}_3$  molecule in Hoffman's work.<sup>13</sup> He found that the matrix elements which will split  $K = 2$  and  $K = 4$  A + A levels are the following.

$$\begin{aligned}
 (1) \quad & \langle \nu_s - 1, \nu_t, \ell_t, K | H^{(2)} / \hbar c | \nu_s, \nu_t - 1, \ell_t \bar{+}, K \pm 2 \rangle \\
 & = \langle \nu_s, \nu_t - 1, \ell_t \bar{+} 1, K \pm 2 | H^{(2)} / \hbar c | \nu_s - 1, \nu_t, \ell_t, K \rangle \\
 & = \gamma [\nu_s (\nu_s \pm \ell_t)]^{\frac{1}{2}} [(J \bar{+} K) (J \bar{+} K - 1) (J \pm K + 1) (J \pm K + 2)]^{\frac{1}{2}} .
 \end{aligned}$$

In the case of  ${}^P P(J, 3)$  transitions the following determinant governs the splittings

$$(2) \quad \begin{vmatrix} -\Delta + E & [J(J+1)]^{\frac{1}{2}} \alpha & [J(J+1)(J+2)(J-1)]^{\frac{1}{2}} \gamma \\ [J(J+1)]^{\frac{1}{2}} \alpha & 1 + E + J(J+1)\beta & 0 \\ [J(J+1)(J+2)(J-1)]^{\frac{1}{2}} \gamma & 0 & -2 + E \end{vmatrix} = 0 .$$

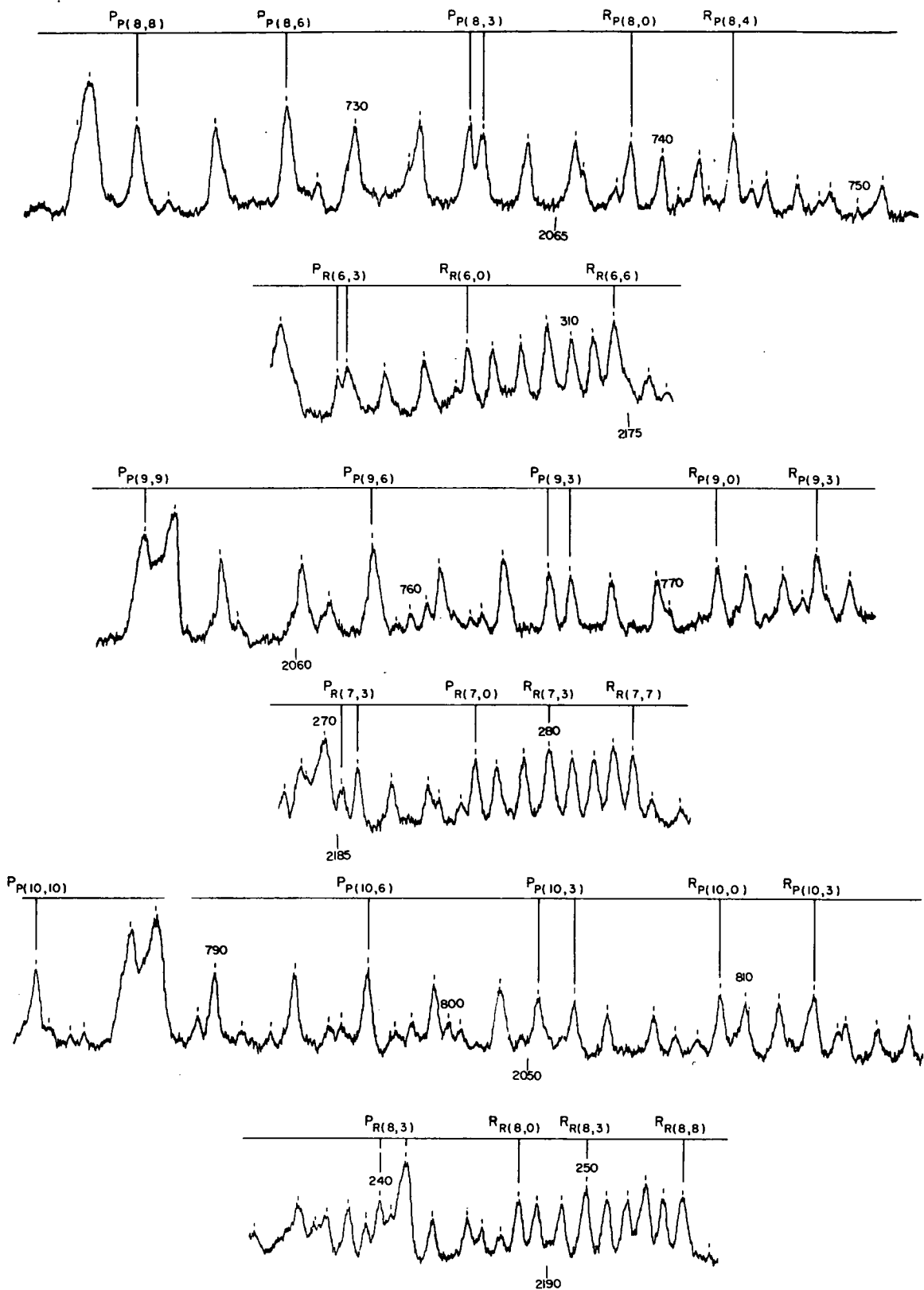


Fig. 1. K-type doubling and Giant  $l$ -type doubling in  $\nu_3$  of  $\text{AsH}_3$ .



To determine the parameter  $\gamma$  associated with K-type doubling, one could first employ the second order perturbation technique to obtain an approximate value of  $\gamma$ . Then by iteration one would eventually arrive at a best value for  $\gamma$  which, in this case, comes out to be  $1.91 \times 10^{-2} \text{ cm}^{-1}$ . These results are tabulated in Table II.

TABLE II  
OBSERVED AND CALCULATED  $P_{P(J, 3)}$  SPLITTINGS

|                                    | $P_{P(8, 3)}$ | $P_{P(9, 3)}$ | $P_{P(10, 3)}$ | $P_{P(11, 3)}$ | $P_{P(12, 3)}$ | $P_{P(13, 3)}$ | $P_{P(14, 3)}$ | $P_{P(15, 3)}$ |
|------------------------------------|---------------|---------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Observed<br>( $\text{cm}^{-1}$ )   | 0.115         | 0.174         | 0.275          | 0.402          | 0.614          | 0.832          | 0.995          | 1.174          |
| Calculated<br>( $\text{cm}^{-1}$ ) | 0.114         | 0.200         | 0.285          | 0.416          | 0.632          | 0.775          | 1.002          | 1.252          |

### III. COMBINATION DIFFERENCE RELATIONS AND THE GIANT $l$ -TYPE DOUBLING

The most desirable way of obtaining the ground state constants is to use certain combination relations in which the perturbation in the upper state energy levels is not involved. Therefore, in the past the ground state constants are obtained from parallel bands since the upper state of a parallel band is nondegenerate. However, if the transitions of  $P_{R(J, K)}$  and  $R_{P(J, K)}$  are observed in a perpendicular band one can obtain some combination difference relations which only involve the ground state levels. The fact that each pair of the transitions [ $R_{P(J+2, K)}$ ,  $R_{R(J, K)}$ ] and [ $P_{R(J-2, K)}$ ,  $P_{P(J, K)}$ ] do have a common upper state energy level leads to the following relations.

$$(3) \quad \frac{R_{R(J-1, K)} - R_{P(J+1, K)}}{2J+1} = 2B'' - 4D_J''(J^2 + J + 1) - 2D_{JK}'' K^2$$

$$\frac{P_{R(J-1, K)} - P_{P(J+1, K)}}{2J+1} = 2B'' - 4D_J''(J^2 + J + 1) - 2D_{JK}'' K^2 \quad .$$

The ground state constants obtained from  $\nu_3$  ( $\perp$ ) band by using the relations given by Eq. (3) and that obtained from  $\nu_2$  ( $\parallel$ ) band are very close as can be seen in Table III.

TABLE III  
GROUND STATE CONSTANTS OBTAINED  
FROM  $\nu_2$  AND  $\nu_3$

|                            | $\nu_2$                | $\nu_3$                |
|----------------------------|------------------------|------------------------|
| $B''(\text{cm}^{-1})$      | 3.7512                 | 3.7510                 |
| $D_J''(\text{cm}^{-1})$    | $9.4 \times 10^{-5}$   | $9.3 \times 10^{-5}$   |
| $D_{JK}''(\text{cm}^{-1})$ | $-1.16 \times 10^{-4}$ | $-1.20 \times 10^{-4}$ |

In addition, these  $P_R(J, K)$ ,  $R_P(J, K)$  transitions provide the relations

$$(4) \quad R_{R(J-1, 0)} + R_{P(J, 0)} = 2[\nu_0 - A' + B'] + 4[A'(1 - \xi) - B'] \\ + 2(B' - B'' - D_J' + D_J'' + \frac{1}{2}q)J^2 - 2(D_J' - D_J'')J^4$$

and

$$(5) \quad \frac{R_{R(J, 0)} - R_{P(J, 0)}}{2J+1} = (2B' + q) - 4D_J'(J^2 + J + 1)$$

which can be used in obtaining better values for the parameter  $q$  of the Giant  $\ell$ -type doubling as well as the band center.

The following matrix element which give rise to Giant  $\ell$ -type doubling has been derived by Nielsen.<sup>12</sup>

$$\begin{aligned}
(6) \quad & \langle v_{s-1}, v_t, l_t, K | H^{(1)}/\hbar c | v_s, v_{t-1}, l_{t+1}, K+1 \rangle \\
& = \langle v_s, v_{t-1}, l_{t+1}, K+1 | H^{(1)}/\hbar c | v_{s-1}, v_t, l_t, K \rangle \\
& = \frac{1}{2} \frac{\omega_s + \omega_t}{(\omega_s \omega_t)^{\frac{1}{2}}} [v_s(v_t + l_t)]^{\frac{1}{2}} [(J+K)(J+K+1)]^{\frac{1}{2}} \\
& \quad (\zeta_{st}^x B_e)
\end{aligned}$$

The effect of these matrix elements is to split the  $K=1$  upper state levels. However, owing to its selection rule, only one transition of the split levels is allowed. Therefore the appearance of this effect on the spectrum is the shift of  $R_R(J, 0)$  and  $R_P(J, 0)$  transitions. These shifts can be seen in Fig. 1.

#### IV. VIBRATION-ROTATION BAND IN THE $2\mu$ REGION

The spectrum in this region is shown in Fig. 2. One can see that it is complex and puzzling as far as a complete analysis is concerned. As already mentioned in the introduction, there are three possible bands which lie very close to each other. For the convenience of the following discussion we shall list them again.

$2\nu_1$  : a parallel band of species A

$\nu_1 + \nu_3$ : a doubly degenerate perpendicular band of species E

$2\nu_3$  : a triply degenerate band of species A+A+E which has two components, one of which is a parallel band of species A, while the other is a doubly degenerate perpendicular band of species E. We shall designate them as  $2\nu_3(\parallel)$  and  $2\nu_3(\perp)$  respectively.

From the theoretical point of view, one sees first of all that Fermi type resonance can occur between the parallel component of the  $2\nu_3$  band and the parallel band of  $2\nu_1$  through the cubic anharmonic force constants in the molecular potential. However, the perpendicular component of the  $2\nu_3$  band and the perpendicular band  $\nu_1 + \nu_3$  can give rise to Fermi type resonance only through very high order anharmonic terms. Therefore the observation of this effect is very unlikely. Secondly, according to John's rule all three bands will be coupled through Coriolis force.

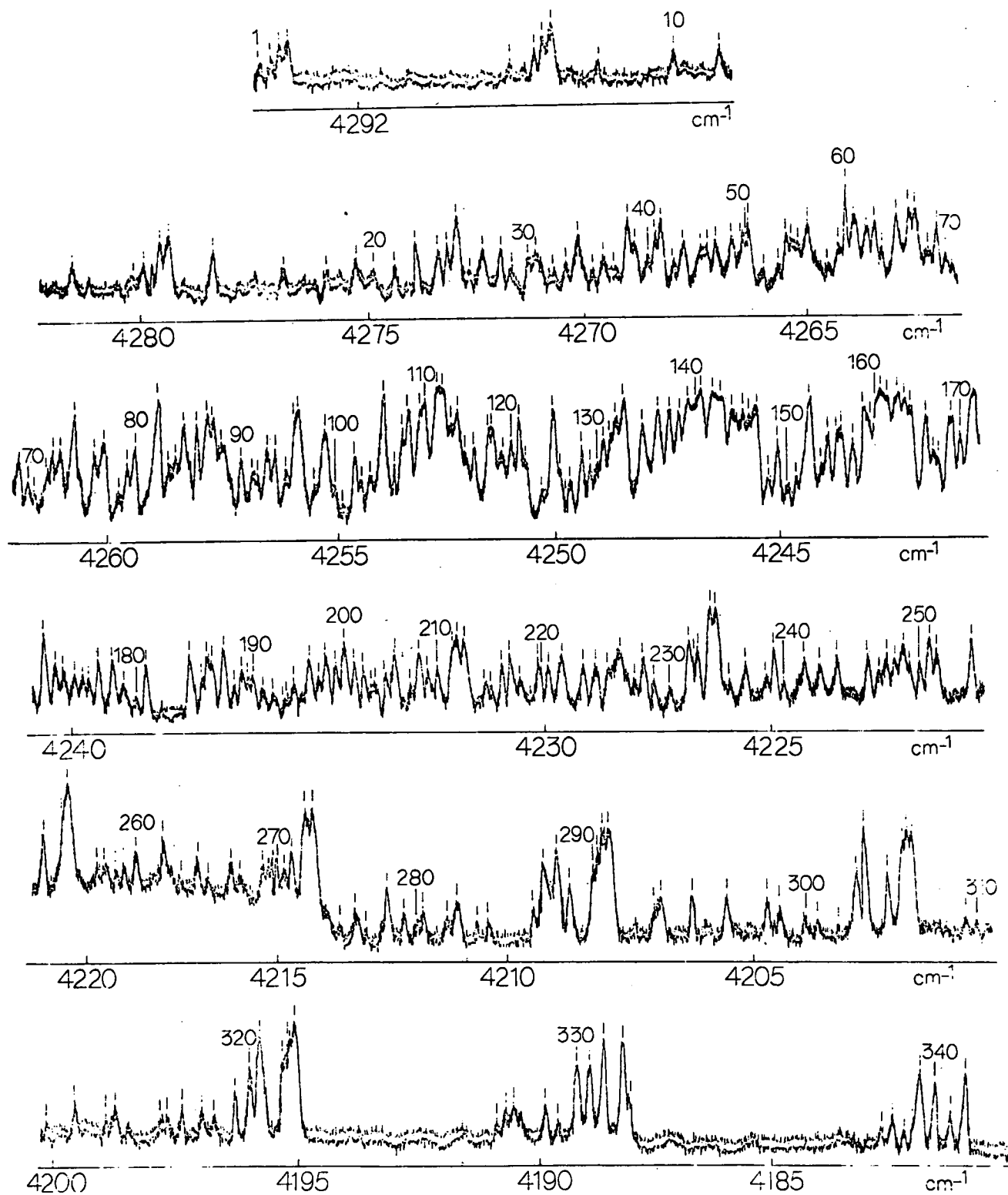


Fig. 2. Absorption spectrum of  $\text{AsH}_3$  in the  $2\mu$  region.

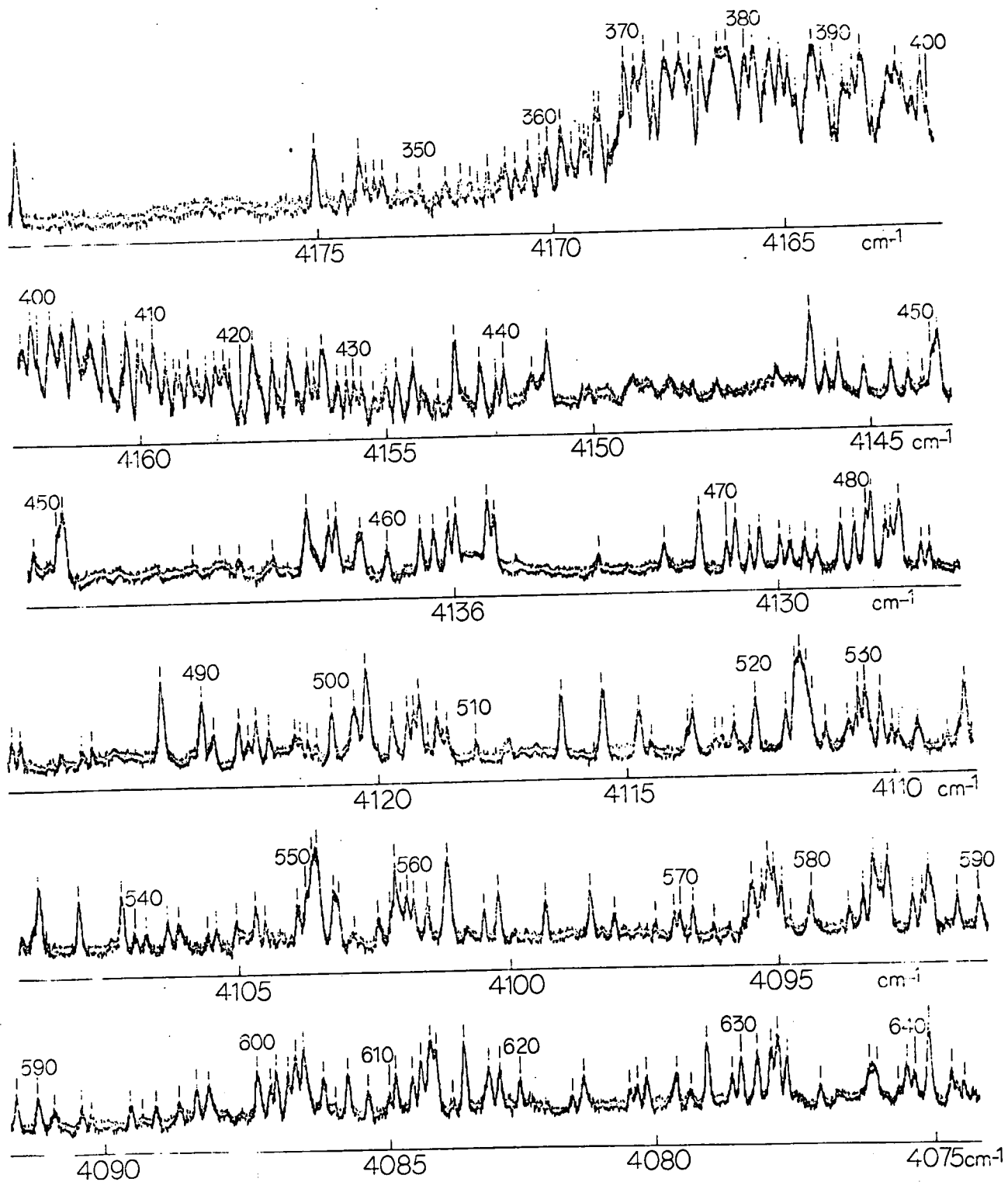


Fig. 2. (Cont.)

Hence the  $K = 1, 2, 4$  upper state levels of  $\nu_1 + \nu_3$  band will split through the interactions with both  $2\nu_1$  and the parallel component of the  $2\nu_3$ . However, there is no direct interaction between  $2\nu_1$  and  $2\nu_3(\perp)$  as one can easily see from the matrix elements given by Eqs. (1) and (6). Nonetheless, splitting of some of the levels of  $2\nu_3(\perp)$  will be possible through  $\nu_1 + \nu_3$ , namely the  $K=2, 4, 5$  levels, and  $K=3$ , and will be shifted. From group theory consideration, the  $2\nu_3(\perp)$  upper state rotational levels have the species given in Table IV in which  $p$  is any integer.

TABLE IV  
SYMMETRY OF THE ROTATIONAL LEVELS  
OF  $2\nu_3(\perp)$

| $K=0$ | $K=3p$ | $K=3p+2$             | $K=3p-2$              |
|-------|--------|----------------------|-----------------------|
| E     | E + E  | $\ell=2$ $A_1 + A_1$ | $\ell=-2$ $A_1 + A_1$ |
|       |        | $\ell=-2$ E          | $\ell=2$ E            |

Accordingly, the splitting of  $K=2, 5$  levels will be seen at  $R_R(J, 1)$  and  $R_R(J, 4)$  transitions respectively and that of  $K=4$  level will be seen at  $P_P(J, 5)$  transitions. These predicted splittings are not clearly shown in the spectrum except perhaps in the one instance of  $P_P(8, 5)$  and  $P_P(9, 5)$  which correspond to line numbers (541, 542) and (567, 568) in Fig. 2.

In assigning the rotational quantum numbers we have found Eq. (3) to be extremely useful since the ground state constants are known from the analysis of the fundamental bands. Table V gives all the lines that are tentatively identified.

It appears from the spectrum there is another band whose band center is around  $4247 \text{ cm}^{-1}$ .

## V. CONCLUSIONS

The detailed analysis of the four fundamental bands of  $\text{AsH}_3$ , their spectra and frequencies can be obtained in Reference 14. Table VI gives the molecular constants from this analysis. The vibration-rotation band in the  $2\mu$  region whose frequencies are given in Table VII is far from being completely analyzed. The author believes that further theoretical study must be done before thorough analysis can be attempted.

From the analysis of the four fundamentals of  $\text{AsH}_3$ , it seems that the K-type doubling as well as the Giant  $l$ -type doubling can be observed more readily in  $\nu_3$  than  $\nu_4$  because of the fact that the K structure of  $\nu_1$  which lies very close to  $\nu_3$  does not spread out as does that of  $\nu_2$  so that the rotational lines of  $\nu_3$  are left clean. It is therefore interesting to further confirm the findings of this work by studying the  $\nu_1$  and  $\nu_3$  vibration-rotation bands of similar molecules, namely  $\text{PH}_3$ .

#### ACKNOWLEDGEMENT

The author is indebted to the Infrared Laboratory, Physics Department, The Ohio State University where the data was taken. He also wishes to express his sincere gratitude to Professors K.N. Rao, and H.H. Nielsen who have spent many hours in guiding the author throughout this work.

TABLE V  
 ASSIGNED TRANSITIONS OF THE VIBRATION-ROTATION  
 BANDS OF AsH<sub>3</sub> IN THE 2μ REGION

| Serial No. | Transition | Serial No. | Transition | Serial No. | Transition |
|------------|------------|------------|------------|------------|------------|
| 213        | R(9, K)    | 328        | PR(2, 1)   | 494<br>495 | PP(6, 3)   |
| 235        | R(8, K)    | 330        | RR(2, 0)   |            |            |
| 255        | R(7, K)    | 331        | RR(2, 1)   | 501        | RP(6, 0)   |
| 274        | R(6, K)    | 332        | RR(2, 2)   | 502        | RP(6, 1)   |
| 294        | R(5, K)    | 337        | PR(1, 1)   | 503        | RP(6, 2)   |
| 308        | R(4, K)    | 339        | RR(1, 0)   | 504        | RP(6, 3)   |
| 325        | R(3, K)    | 340        | RR(1, 1)   | 511        | PP(7, 7)   |
| 333        | R(2, K)    | 343        | RR(0, 0)   | 512        | PP(7, 6)   |
| 342        | R(1, K)    | 406        | PP(1, 1)   | 513        | PP(7, 5)   |
| 345        | R(0, 0)    | 437        | PP(2, 2)   | 516        | PP(7, 4)   |
| 410        | P(1, 0)    | 438        | PP(2, 1)   | 520        | PP(7, 3)   |
| 442        | P(2, K)    | 440        | RP(2, 0)   | 521        | PP(7, 2)   |
| 451        | P(3, K)    | 443        | PP(3, 3)   | 526        | PP(7, 1)   |
| 465        | P(4, K)    | 445        | PP(3, 2)   | 536        | PP(8, 8)   |
| 485        | P(5, K)    | 446        | PP(3, 1)   | 537        | PP(8, 7)   |
| 506        | P(6, K)    | 447        | RP(3, 0)   | 538        | PP(8, 6)   |
| 530        | P(7, K)    | 448        | RP(3, 1)   | 541        | PP(8, 5)   |
| 557        | P(8, K)    | 456        | PP(4, 4)   | 544        | PP(8, 4)   |
| 583        | P(9, K)    | 458        | PP(4, 3)   | 546        | PP(8, 3)   |
| 613        | P(10, K)   | 459        | PP(4, 2)   | 550        | PP(8, 2)   |
| 267        | RR(6, 0)   | 460        | PP(4, 1)   | 562        | PP(9, 9)   |
| 278        | PR(5, 5)   | 461        | PR(4, 0)   | 564        | PP(9, 8)   |
| 281        | PR(5, 4)   | 462        | PR(4, 1)   | 565        | PP(9, 7)   |
| 283        | PR(5, 3)   | 464        | PR(4, 2)   | 564        | PP(9, 6)   |
| 286        | RR(5, 0)   | 469        | PP(5, 5)   | 585        | PP(10, 10) |
| 297        | PR(4, 4)   | 471        | PP(5, 4)   | 588        | PP(10, 9)  |
| 298        | PR(4, 3)   | 473        | PP(5, 3)   | 590        | PP(10, 8)  |
| 300        | PR(4, 2)   | 474        | PP(5, 2)   | 592        | PP(10, 7)  |
| 303        | RR(4, 0)   | 476        | PP(5, 1)   | 594        | PP(10, 6)  |
| 307        | RR(4, 4)   | 478        | RP(5, 0)   | 608        | PP(11, 11) |
| 317        | PR(3, 2)   | 479        | RP(5, 1)   | 612        | PP(11, 10) |
| 320        | RR(3, 0)   | 480        | RP(5, 2)   | 617        | PP(11, 9)  |
| 321        | RR(3, 1)   | 481        | RP(5, 3)   | 620        | PP(11, 8)  |
| 322        | RR(3, 2)   | 489        | PP(6, 6)   | 621        | PP(11, 7)  |
| 323        | RR(3, 3)   | 490        | PP(6, 5)   |            |            |
| 327        | PR(2, 2)   | 492        | PP(6, 4)   |            |            |



TABLE VI  
MOLECULAR CONSTANTS FOR AsH<sub>3</sub> (in cm<sup>-1</sup>)

|                          | Ground State           | $\nu_1$               | $\nu_2$                | $\nu_3$                | $\nu_4$ | $2\nu_1$              | $2\nu_3$ |
|--------------------------|------------------------|-----------------------|------------------------|------------------------|---------|-----------------------|----------|
| B                        | 3.7513                 | 3.7108                | 3.5848                 | 3.7153                 | 3.886   | 3.639                 | 3.688    |
| DJ                       | $9.4 \times 10^{-5}$   | $1.10 \times 10^{-4}$ | $-1.13 \times 10^{-4}$ | $0.86 \times 10^{-4}$  |         | $-3.6 \times 10^{-4}$ |          |
| DJK                      | $-1.18 \times 10^{-4}$ |                       | $3.71 \times 10^{-4}$  | $-2.19 \times 10^{-4}$ |         |                       |          |
| DK                       | $1.58 \times 10^{-4}$  |                       |                        | $2.05 \times 10^{-4}$  |         |                       |          |
| A                        | 3.4866                 |                       |                        | 3.4273                 | 3.571   |                       |          |
| D $\bar{K}$ -D $\bar{K}$ |                        |                       | $-2.66 \times 10^{-4}$ |                        |         |                       |          |
| A'-A''                   |                        |                       | 0.0243                 |                        |         |                       |          |
| (1- $\xi$ )A             |                        |                       |                        | 3.5076                 | 5.088   |                       |          |
| q                        |                        |                       |                        | $-7.0 \times 10^{-4}$  | 0.061   |                       | - .0433  |
| Y                        |                        |                       |                        | $1.91 \times 10^{-2}$  |         |                       | 3.477    |
| $\nu_1$                  |                        | 2115.191              |                        |                        |         |                       |          |
| $\nu_2$                  |                        |                       | 906.736                |                        |         |                       |          |
| $\nu_3$                  |                        |                       |                        | 2126.402               |         |                       |          |
| $\nu_4$                  |                        |                       |                        |                        | 999.409 |                       |          |
| $2\nu_1$                 |                        |                       |                        |                        |         | 4167.01               |          |
| $2\nu_3$                 |                        |                       |                        |                        |         |                       |          |

TABLE VII  
MEASURED FREQUENCIES OF AsH<sub>3</sub> BANDS  
IN THE 2 $\mu$  REGION

| Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) | Serial No | Wave No.<br>(in vacc. cm <sup>-1</sup> ) |
|------------|--|-----------|--|
| 1          |  | 36        | 4269.53                                  |
| 2          |  | 37        |  |
| 3          | 4292.34                                  | 38        | 4268.99                                  |
| 4          | 4292.15                                  | 39        | 4268.84                                  |
| 5          | 4286.83                                  | 40        | 4268.54                                  |
| 6          | 4286.53                                  | 41        | 4268.38                                  |
| 7          | 4286.29                                  | 42        | 4268.25                                  |
| 8          | 4286.11                                  | 43        | 4267.98                                  |
| 9          | 4285.92                                  | 44        | 4267.75                                  |
| 10         | 4283.06                                  | 45        | 4267.38                                  |
| 11         | 4282.03                                  | 46        | 4267.25                                  |
| 12         | 4280.18                                  | 47        | 4267.05                                  |
| 13         | 4279.92                                  | 48        | 4266.68                                  |
| 14         | 4279.70                                  | 49        | 4266.42                                  |
| 15         | 4279.52                                  | 50        | 4266.30                                  |
| 16         | 4278.52                                  | 51        | 4266.22                                  |
| 17         | 4276.91                                  | 52        | 4265.90                                  |
| 18         | 4275.95                                  | 53        | 4265.55                                  |
| 19         | 4275.31                                  | 54        | 4265.35                                  |
| 20         | 4274.91                                  | 55        | 4265.25                                  |
| 21         | 4274.44                                  | 56        | 4265.09                                  |
| 22         | 4273.88                                  | 57        | 4264.90                                  |
| 23         | 4273.63                                  | 58        | 4264.46                                  |
| 24         | 4273.17                                  | 59        | 4264.21                                  |
| 25         | 4272.96                                  | 60        | 4264.03                                  |
| 26         | 4272.67                                  | 61        | 4263.79                                  |
| 27         | 4272.37                                  | 62        | 4263.53                                  |
| 28         | 4271.97                                  | 63        | 4263.36                                  |
| 29         | 4271.75                                  | 64        | 4263.22                                  |
| 30         | 4271.37                                  | 65        | 4262.88                                  |
| 31         | 4271.21                                  | 66        | 4262.60                                  |
| 32         | 4270.70                                  | 67        | 4262.46                                  |
| 33         | 4270.41                                  | 68        | 4262.17                                  |
| 34         | 4270.13                                  | 69        | 4261.98                                  |
| 35         | 4269.77                                  | 70        | 4261.78                                  |

TABLE VII (Cont.)

| Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) | Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) |
|------------|--|------------|--|
| 71         | 4261.64                                  | 111        | 4252.56                                  |
| 72         | 4261.34                                  | 112        | 4252.48                                  |
| 73         | 4261.17                                  | 113        | 4252.29                                  |
| 74         | 4260.97                                  | 114        | 4252.15                                  |
| 75         | 4260.68                                  | 115        | 4251.98                                  |
| 76         | 4260.22                                  | 116        | 4251.78                                  |
| 77         | 4260.01                                  | 117        | 4251.45                                  |
| 78         | 4259.67                                  | 118        | 4251.38                                  |
| 79         | 4259.50                                  | 119        | 4251.17                                  |
| 80         | 4259.20                                  | 120        | 4250.96                                  |
| 81         | 4258.85                                  | 121        | 4250.77                                  |
| 82         | 4258.61                                  | 122        | 4250.64                                  |
| 83         | 4258.46                                  | 123        | 4250.25                                  |
| 84         | 4258.15                                  | 124        | 4250.03                                  |
| 85         | 4257.92                                  | 125        | 4249.88                                  |
| 86         | 4257.66                                  | 126        | 4249.67                                  |
| 87         | 4257.66                                  | 127        | 4249.57                                  |
| 88         | 4257.54                                  | 128        | 4249.30                                  |
| 89         | 4257.35                                  | 129        | 4249.13                                  |
| 90         | 4256.95                                  | 130        | 4248.99                                  |
| 91         | 4256.69                                  | 131        | 4248.82                                  |
| 92         | 4256.59                                  | 132        | 4248.67                                  |
| 93         | 4256.36                                  | 133        | 4248.57                                  |
| 94         | 4256.22                                  | 134        | 4248.40                                  |
| 95         | 4255.96                                  | 135        | 4248.00                                  |
| 96         | 4255.75                                  | 136        | 4247.67                                  |
| 97         | 4255.70                                  | 137        | 4247.43                                  |
| 98         | 4255.35                                  | 138        | 4247.23                                  |
| 99         | 4255.12                                  | 139        | 4247.03                                  |
| 100        | 4254.92                                  | 140        | 4246.85                                  |
| 101        | 4254.73                                  | 141        | 4246.77                                  |
| 102        | 4254.47                                  | 142        | 4246.49                                  |
| 103        | 4254.35                                  | 143        | 4246.29                                  |
| 104        | 4254.14                                  | 144        | 4246.07                                  |
| 105        | 4253.87                                  | 145        | 4245.82                                  |
| 106        | 4253.54                                  | 146        | 4245.69                                  |
| 107        | 4253.33                                  | 147        | 4245.55                                  |
| 108        | 4253.19                                  | 148        | 4245.28                                  |
| 109        | 4252.94                                  | 149        | 4245.08                                  |
| 110        | 4252.86                                  | 150        | 4244.87                                  |

TABLE VII (Cont.)

| Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) | Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) |
|------------|--|------------|--|
| 151        | 4244.68                                  | 191        | 4236.12                                  |
| 152        | 4244.39                                  | 192        | 4235.89                                  |
| 153        | 4244.14                                  | 193        | 4235.64                                  |
| 154        | 4244.02                                  | 194        |  |
| 155        | 4243.80                                  | 195        | 4235.46                                  |
| 156        | 4243.72                                  | 196        | 4235.12                                  |
| 157        | 4243.47                                  | 197        | 4234.93                                  |
| 158        | 4243.20                                  | 198        | 4234.77                                  |
| 159        | 4243.10                                  | 199        | 4234.56                                  |
| 160        | 4242.80                                  | 200        | 4234.38                                  |
| 161        | 4242.74                                  | 201        | 4234.17                                  |
| 162        | 4242.63                                  | 202        | 4233.98                                  |
| 163        | 4242.42                                  | 203        | 4233.81                                  |
| 164        | 4242.25                                  | 204        | 4233.75                                  |
| 165        | 4242.11                                  | 205        | 4233.52                                  |
| 166        | 4241.79                                  | 206        | 4233.33                                  |
| 167        | 4241.63                                  | 207        | 4232.97                                  |
| 168        | 4241.52                                  | 208        | 4232.80                                  |
| 169        | 4241.24                                  | 209        | 4232.62                                  |
| 170        | 4241.05                                  | 210        | 4232.41                                  |
| 171        | 4240.79                                  | 211        | 4232.08                                  |
| 172        | 4240.55                                  | 212        | 4232.00                                  |
| 173        | 4240.38                                  | 213        | 4231.85 R(9, K)                          |
| 174        | 4240.14                                  | 214        | 4231.39                                  |
| 175        | 4239.98                                  | 215        | 4231.29                                  |
| 176        | 4239.85                                  | 216        | 4231.05                                  |
| 177        | 4239.63                                  | 217        | 4230.85                                  |
| 178        | 4239.33                                  | 218        | 4230.66                                  |
| 179        | 4239.11                                  | 219        | 4230.28                                  |
| 180        | 4238.85                                  | 220        | 4230.20                                  |
| 181        | 4238.62                                  | 221        | 4229.95                                  |
| 182        | 4237.68                                  | 222        | 4229.67                                  |
| 183        | 4237.43                                  | 223        | 4229.21                                  |
| 184        | 4237.31                                  | 224        | 4228.95                                  |
| 185        | 4237.24                                  | 225        | 4228.67                                  |
| 186        | 4236.97                                  | 226        | 4228.46                                  |
| 187        | 4236.75                                  | 227        | 4228.13                                  |
| 188        | 4236.57                                  | 228        | 4227.93                                  |
| 189        | 4236.44                                  | 229        | 4227.60                                  |
| 190        | 4236.35                                  | 230        | 4237.28                                  |

TABLE VII (Cont.)

| Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) | Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) |
|------------|--|------------|--|
| 231        | 4226.85                                  | 271        | 4214.76                                  |
| 232        | 4226.74                                  | 272        | 4214.62                                  |
| 233        | 4226.56                                  | 273        | 4214.31                                  |
| 234        | 4226.30                                  | 274        | 4214.15                                  |
| 235        | 4226.16                                  | 275        | 4213.64                                  |
| 236        | 4225.88                                  | 276        | 4213.29                                  |
| 237        | 4225.54                                  | 277        | 4213.11                                  |
| 238        | 4225.09                                  | 278        | 4212.63                                  |
| 239        | 4224.94                                  | 279        | 4212.28                                  |
| 240        | 4224.74                                  | 280        | 4212.02                                  |
| 241        | 4224.30                                  | 281        | 4211.89                                  |
| 242        | 4223.97                                  | 282        | 4211.39                                  |
| 243        | 4223.63                                  | 283        | 4211.19                                  |
| 244        | 4222.97                                  | 284        | 4210.68                                  |
| 245        | 4222.73                                  | 285        | 4210.44                                  |
| 246        | 4222.59                                  | 286        | 4209.49                                  |
| 247        | 4222.41                                  | 287        | 4209.28                                  |
| 248        | 4222.25                                  | 288        | 4209.02                                  |
| 249        | 4222.12                                  | 289        | 4208.74                                  |
| 250        | 4221.88                                  | 290        | 4208.25                                  |
| 251        | 4221.68                                  | 291        | 4208.14                                  |
| 252        | 4221.55                                  | 292        | 4208.04                                  |
| 253        | 4220.82                                  | 293        | 4207.91                                  |
| 254        | 4220.37                                  | 294        | 4207.00                                  |
| 255        | 4220.28                                  | 295        | 4206.84                                  |
| 256        | 4219.66                                  | 296        | 4206.21                                  |
| 257        | 4219.49                                  | 297        | 4205.43                                  |
| 258        | 4219.27                                  | 298        | 4204.59                                  |
| 259        | 4219.11                                  | 299        | 4204.33                                  |
| 260        | 4218.86                                  | 300        | 4203.81                                  |
| 261        | 4218.16                                  | 301        | 4203.57                                  |
| 262        | 4217.79                                  | 302        | 4203.13                                  |
| 263        | 4217.47                                  | 303        | 4202.70                                  |
| 264        | 4217.25                                  | 304        | 4202.49                                  |
| 265        | 4216.77                                  | 305        | 4202.01                                  |
| 266        | 4216.58                                  | 306        | 4201.71                                  |
| 267        | 4216.10                                  | 307        | 4201.61                                  |
| 268        | 4215.95                                  | 308        | 4201.53                                  |
| 269        | 4215.81                                  | 309        | 4200.43                                  |
| 270        | 4215.40                                  | 310        | 4200.21                                  |

TABLE VII (Cont.)

| Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) | Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) |
|------------|--|------------|--|
| 311        | 4199.62                                  | 351        | 4172.26                                  |
| 312        | 4198.96                                  | 352        | 4172.96                                  |
| 313        | 4198.76                                  | 353        | 4171.74                                  |
| 314        | 4197.83                                  | 354        | 4171.56                                  |
| 315        | 4197.68                                  | 355        | 4171.39                                  |
| 316        | 4197.41                                  | 356        | 4171.00                                  |
| 317        | 4196.92                                  | 357        | 4170.80                                  |
| 318        | 4196.65                                  | 358        | 4170.53                                  |
| 319        | 4196.20                                  | 359        | 4170.27                                  |
| 320        | 4195.92                                  | 360        | 4170.13                                  |
| 321        | 4195.73                                  | 361        | 4169.83                                  |
| 322        | 4195.19                                  | 362        | 4169.64                                  |
| 323        | 4195.11                                  | 363        | 4169.41                                  |
| 324        | 4195.02                                  | 364        | 4169.33                                  |
| 325        | 4190.92                                  | 365        | 4169.23                                  |
| 326        | 4190.74                                  | 366        | 4169.02                                  |
| 327        | 4190.56                                  | 367        | 4168.96                                  |
| 328        | 4189.92                                  | 368        | 4168.75                                  |
| 329        | 4189.65                                  | 369        | 4168.48                                  |
| 330        | 4189.27                                  | 370        | 4168.30                                  |
| 331        | 4189.02                                  | 371        | 4168.06                                  |
| 332        | 4188.76                                  | 372        | 4167.83                                  |
| 333        | 4188.35                                  | 373        | 4167.63                                  |
| 334        | 4188.22                                  | 374        | 4167.38                                  |
| 335        | 4183.02                                  | 375        | 4167.08                                  |
| 336        | 4182.79                                  | 376        | 4166.87                                  |
| 337        | 4182.52                                  | 377        | 4166.64                                  |
| 338        | 4182.35                                  | 378        | 4166.28                                  |
| 339        | 4182.24                                  | 379        | 4166.10                                  |
| 340        | 4181.93                                  | 380        | 4165.74                                  |
| 341        | 4181.60                                  | 381        | 4165.57                                  |
| 342        | 4181.32                                  | 382        | 4165.33                                  |
| 343        | 4175.09                                  | 383        | 4165.22                                  |
| 344        | 4174.50                                  | 384        | 4165.02                                  |
| 345        | 4174.15                                  | 385        | 4164.86                                  |
| 346        | 4174.00                                  | 386        | 4164.72                                  |
| 347        | 4173.84                                  | 387        | 4164.50                                  |
| 348        | 4173.68                                  | 388        | 4164.35                                  |
| 349        | 4173.38                                  | 389        | 4164.15                                  |
| 350        | 4172.80                                  | 390        | 4163.93                                  |

TABLE VII (Cont.)

| Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) | Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) |
|------------|--|------------|--|
| 391        | 4163.71                                  | 431        | 4155.46                                  |
| 392        | 4163.53                                  | 432        | 4155.22                                  |
| 393        | 4163.37                                  | 433        | 4154.97                                  |
| 394        | 4163.15                                  | 434        | 4154.74                                  |
| 395        | 4162.81                                  | 435        | 4154.41                                  |
| 396        | 4162.67                                  | 436        | 4153.91                                  |
| 397        | 4162.54                                  | 437        | 4153.54                                  |
| 398        | 4162.36                                  | 438        | 4153.04                                  |
| 399        | 4162.16                                  | 439        | 4152.73                                  |
| 400        | 4162.05                                  | 440        | 4152.56                                  |
| 401        | 4161.76                                  | 441        | 4151.96                                  |
| 402        | 4161.53                                  | 442        | 4151.62                                  |
| 403        | 4161.29                                  | 443        | 4146.33                                  |
| 404        | 4160.95                                  | 444        | 4146.04                                  |
| 405        | 4160.66                                  | 445        | 4145.77                                  |
| 406        | 4160.31                                  | 446        | 4145.27                                  |
| 407        | 4160.20                                  | 447        | 4144.72                                  |
| 408        | 4159.98                                  | 448        | 4144.38                                  |
| 409        | 4159.87                                  | 449        | 4144.07                                  |
| 410        | 4159.66                                  | 450        | 4143.88                                  |
| 411        | 4159.43                                  | 451        | 4143.79                                  |
| 412        | 4159.24                                  | 452        | 4140.24                                  |
| 413        | 4159.16                                  | 453        | 4140.02                                  |
| 414        | 4158.97                                  | 454        | 4139.62                                  |
| 415        | 4158.81                                  | 455        | 4139.35                                  |
| 416        | 4158.63                                  | 456        | 4138.96                                  |
| 417        | 4158.44                                  | 457        | 4138.52                                  |
| 418        | 4158.27                                  | 458        | 4138.38                                  |
| 419        | 4158.16                                  | 459        | 4137.97                                  |
| 420        | 4157.94                                  | 460        | 4137.39                                  |
| 421        | 4157.68                                  | 461        | 4136.76                                  |
| 422        | 4157.29                                  | 462        | 4136.49                                  |
| 423        | 4157.16                                  | 463        | 4136.22                                  |
| 424        | 4156.95                                  | 464        | 4136.07                                  |
| 425        | 4156.57                                  | 465        | 4135.84                                  |
| 426        | 4156.44                                  | 466        | 4135.71                                  |
| 427        | 4156.26                                  | 467        | 4133.53                                  |
| 428        | 4155.95                                  | 468        | 4132.23                                  |
| 429        | 4155.77                                  | 469        | 4131.53                                  |
| 430        | 4155.62                                  | 470        | 4130.98                                  |

TABLE VII (Cont.)

| Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) | Serial No. | Wave No.<br>(in vacc. cm <sup>-1</sup> ) |
|------------|--|------------|--|
| 471        | 4130.81                                  | 511        | 4116.40                                  |
| 472        | 4130.52                                  | 512        | 4115.62                                  |
| 473        | 4130.32                                  | 513        | 4114.87                                  |
| 474        | 4129.91                                  | 514        | 4114.64                                  |
| 475        | 4129.72                                  | 515        | 4113.98                                  |
| 476        | 4129.43                                  | 516        | 4113.88                                  |
| 477        | 4129.19                                  | 517        | 4113.45                                  |
| 478        | 4128.73                                  | 518        | 4113.34                                  |
| 479        | 4128.46                                  | 519        | 4113.10                                  |
| 480        | 4128.22                                  | 520        | 4112.70                                  |
| 481        | 4128.14                                  | 521        | 4112.13                                  |
| 482        | 4127.77                                  | 522        | 4111.92                                  |
| 483        | 4127.65                                  | 523        | 4111.86                                  |
| 484        | 4127.49                                  | 524        | 4111.78                                  |
| 485        | 4127.04                                  | 525        | 4111.71                                  |
| 486        | 4126.87                                  | 526        | 4111.40                                  |
| 487        | 4125.60                                  | 527        | 4110.81                                  |
| 488        | 4125.33                                  | 528        | 4110.69                                  |
| 489        | 4124.01                                  | 530        | 4110.55                                  |
| 490        | 4123.27                                  | 531        | 4110.26                                  |
| 491        | 4122.95                                  | 532        | 4110.07                                  |
| 492        | 4122.48                                  | 533        | 4109.95                                  |
| 493        | 4122.30                                  | 534        | 4109.60                                  |
| 494        | 4122.15                                  | 535        | 4108.81                                  |
| 495        | 4121.88                                  | 536        | 4108.72                                  |
| 496        | 4121.41                                  | 537        | 4107.90                                  |
| 497        | 4121.33                                  | 538        | 4107.10                                  |
| 498        | 4121.16                                  | 539        | 4106.85                                  |
| 499        | 4121.01                                  | 540        | 4106.66                                  |
| 500        | 4120.72                                  | 541        | 4106.27                                  |
| 501        | 4120.28                                  | 542        | 4106.06                                  |
| 502        | 4120.05                                  | 543        | 4105.75                                  |
| 503        | 4119.58                                  | 544        | 4105.52                                  |
| 504        | 4119.30                                  | 545        | 4105.01                                  |
| 505        | 4119.17                                  | 546        | 4104.65                                  |
| 506        | 4119.05                                  | 547        | 4104.48                                  |
| 507        | 4118.91                                  | 548        | 4103.87                                  |
| 508        | 4118.73                                  | 549        | 4103.71                                  |
| 509        | 4118.55                                  | 550        | 4103.59                                  |
| 510        | 4118.01                                  |            |  |



TABLE VII (Cont.)

| Serial No. | Wave No.<br>(in vacc. $\text{cm}^{-1}$ ) | Serial No. | Wave No.<br>(in vacc. $\text{cm}^{-1}$ ) |
|------------|--|------------|--|
| 551        | 4103.53                                  | 591        | 4091.04                                  |
| 552        | 4103.21                                  | 592        | 4090.47                                  |
| 553        | 4103.15                                  | 593        | 4090.29                                  |
| 554        | 4102.85                                  | 594        | 4089.61                                  |
| 555        | 4102.37                                  | 595        | 4089.40                                  |
| 556        | 4102.12                                  | 596        | 4089.16                                  |
| 557        | 5102.01                                  | 597        | 4088.74                                  |
| 558        | 4101.93                                  | 598        | 4088.41                                  |
| 559        | 4101.77                                  | 599        | 4088.18                                  |
| 560        | 4101.64                                  | 600        | 4087.32                                  |
| 561        | 4101.40                                  | 601        | 4087.10                                  |
| 562        | 4101.01                                  | 602        | 4086.99                                  |
| 563        | 4100.37                                  | 603        | 4086.78                                  |
| 564        | 4100.11                                  | 604        | 4086.64                                  |
| 565        | 4099.24                                  | 605        | 4086.49                                  |
| 566        | 4098.41                                  | 606        | 4086.14                                  |
| 567        | 4097.98                                  | 607        | 4085.98                                  |
| 568        |  | 608        | 4085.70                                  |
| 569        | 4096.89                                  | 609        | 4085.33                                  |
| 570        | 4096.80                                  | 610        | 4084.96                                  |
| 571        | 4096.55                                  | 611        | 4084.84                                  |
| 572        | 4096.18                                  | 612        | 4084.54                                  |
| 573        | 4095.62                                  | 613        | 4084.39                                  |
| 574        | 4095.47                                  | 614        | 4084.22                                  |
| 575        | 4095.29                                  | 615        | 4084.13                                  |
| 576        | 4095.17                                  | 616        | 4083.83                                  |
| 577        | 4095.08                                  | 617        | 4083.61                                  |
| 578        | 4094.93                                  | 618        | 4083.18                                  |
| 579        | 4094.80                                  | 619        | 4082.99                                  |
| 580        | 4094.40                                  | 620        | 4082.52                                  |
| 581        | 4093.69                                  | 621        | 4081.39                                  |
| 582        | 4093.45                                  | 622        | 4081.24                                  |
| 583        | 4093.26                                  | 623        | 4080.54                                  |
| 584        | 4093.13                                  | 624        | 4080.43                                  |
| 585        | 4093.00                                  | 625        | 4080.27                                  |
| 586        | 4092.56                                  | 626        | 4079.66                                  |
| 587        | 4092.37                                  | 627        | 4079.40                                  |
| 588        | 4092.26                                  | 628        | 4079.07                                  |
| 589        | 4091.74                                  | 629        | 4078.61                                  |
| 590        | 4091.33                                  | 630        | 4078.45                                  |

TABLE VII (Cont.)

| Serial No. | Wave No.<br>(in vacc. $\text{cm}^{-1}$ ) | Serial No. | Wave No.<br>(in vacc. $\text{cm}^{-1}$ ) |
|------------|--|------------|--|
| 631        | 4078.16                                  | 638        | 4075.64                                  |
| 632        | 4077.91                                  | 639        | 4075.51                                  |
| 633        | 4077.80                                  | 640        | 4075.37                                  |
| 634        | 4077.64                                  | 641        | 4075.10                                  |
| 635        | 4077.05                                  | 642        | 4074.71                                  |
| 636        | 4076.12                                  | 643        | 4074.48                                  |
| 637        | 4076.07                                  |            |  |

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