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THE FORCE CONSTANTS OF SOME POLYATOMIC MOLECULES AND IONS

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ABSTRACT

The force constants of the molecules phosphorous oxybromide and thiophosphoryl bromide and the ions GaBr_4^- , InBr_4^- , TlBr_4^- and CdBr_4^- have been evaluated using the known fundamental vibration frequencies. The matrix method of Wilson was used in all the cases. The value of the P = O force constant was nearly the same as found in the molecule OPCl_3 and the P-Br force constant was also nearly the same in OPBr_3 and SPBr_3 . However, there was some difference between the values of the P = S force constant in SPBr_3 and SPCl_3 .

INTRODUCTION

The present investigation deals with the determination of the force constants of the molecules phosphorous oxybromide (OPBr_3) and thiophosphoryl bromide (SPBr_3) and the ions GaBr_4^- , InBr_4^- , TlBr_4^- and CdBr_4^- using known values of their fundamental vibration frequencies. The molecules OPBr_3 and SPBr_3 belong to the point group C_{3v} . The vibration spectrum of OPBr_3 has been studied by Gerding and van Driel (1942) and that of SPBr_3 by Delwaille and Francois (1947). The electron diffraction measurements on these molecules have been carried out by Secrist and Brockway (1944).

From a consideration of the vibration spectra, the ions GaBr_4^- , InBr_4^- , TlBr_4^- and CdBr_4^- are supposed to have tetrahedral symmetry T_d . The investigation of the Raman spectrum of GaBr_4^- by Woodward and Nord (1955), of InBr_4^- by Woodward and Bill (1955), of TlBr_4^- by Delwaille (1954) and of CdBr_4^- by Delwaille, Francois and Wiemann (1939) and Rolfe, Sheppard and Woodward (1954) support the view that the ions are tetrahedral.

The Wilson's matrix method has been used to evaluate the force constants.

THE POTENTIAL ENERGY FUNCTION

In the case of the tetrahedral ions, even though there are only four distinct vibration frequencies available for calculating the force constants, a general valence force potential function containing all the interaction terms has been assumed. This contains seven force constants. When we factorise the secular equation and obtain the F matrices corresponding to each species, the elements of these matrices occur as combination of the force constants. Hence to determine the individual force constants certain approximations have to be made.

The potential energy function can be written as follows:

$$\begin{aligned}
 2V = & f_a \sum_i \Delta d_i^2 + f_a \sum_{i,j} (d\Delta a_{ij})^2 + 2f_{aa} \sum_{i,j} \Delta d_i \Delta d_j \\
 & + 2f_{aa} \sum_{i,j} (d\Delta a_{ij}) (\sum_{kl} d\Delta a_{kl}) + 2f'_{aa} \sum_{i,j,m,n} (d\Delta a_{ij}) (d\Delta a_{mn}) \\
 & + 2f_{aa} \sum_i \Delta d_i [(\sum_{i,j} (d\Delta a_{ij}))] + 2f'_{aa} \sum_i \Delta d_i (\sum_{i,k} (d\Delta a_{ik})).
 \end{aligned}$$

where $i, j = 1, \dots, 4$ and $i \neq j$

$k, l = 1, \dots, 4$ but k or l may be equal to i or j and $k \neq l$.

Similarly $m \neq n$, and m or n not equal to either i or j

d_i denotes the X - Y_i distance

α_{ij} the angle Y_iX Y_j assuming the ion to be X Y₄.

The factored F matrices are:

For type A₁

$$F_{11} = f_a + 3f_{aa}.$$

For type E

$$F_{22} = d^2 (f_a + f'_{aa} - 2f_{aa})$$

and for type T₂

$$F_{33} = d^2 (f_a - f'_{aa})$$

$$F_{34} = F_{43} = \sqrt{2} d (f_{aa} - f'_{aa});$$

$$F_{44} = f_a - f_{aa}.$$

In order to determine the force constants separately, a procedure due to Voelz Meister and Cleveland (1951) has been adopted. In this f_{aa} is given a series of values, each a small fraction of f_a . For each value of f_{aa} the corresponding f_a was obtained from F_{11} and substituted in F_{44} . Knowing F_{44} we can get values of F_{33} and F_{34} . In each case we get two sets of values for F_{33} and F_{34} . If we neglect f'_{aa} in the first approximation we get f_a from F_{33} and f_{aa} from F_{34} . We cannot, however, get the separate values of f_{aa} and f'_{aa} . From the series of values of the force constants thus obtained we can fix the most probable limits within which the force constants will lie even though it is not possible to choose a unique set.

The potential function for the two molecules OPBr₃ and SPBr₃ is assumed as

$$\begin{aligned}
 2V = & f_D \Delta D^2 + f_a \sum_i \Delta d_i^2 + f_\alpha \sum_{i,j} (d\Delta\alpha_{ij})^2 + f_\beta \sum_i (d\Delta\beta_i)^2 \\
 & + 2f_{ad} \sum_{i,j} \Delta d_i \Delta d_j + 2f_{\alpha\alpha} \sum_{i,j,l} (d\Delta\alpha_{ij}) (d\Delta\alpha_{il}) \\
 & + 2f_{\beta\beta} \sum_{i,j} (d\Delta\beta_i) (d\Delta\beta_j)
 \end{aligned}$$

$i, j, l = 1, 2, 3; i \neq j \neq l$. If we denote the molecules as XY₃ Z D = X - Z distance, $d_i = X - Y_i$ distance, $\alpha_{ij} = Y_i \hat{X} Y_j$, $\beta_i = Y_i \hat{X} Z$. For a series of molecules of the type XY₃Z which includes OPBr₃ Venkateswarulu and Sundaram (1956) have assumed a similar function containing six constants. The interaction constant of the type f_{Dd} is included while the constants $f_{\alpha\alpha}$ and $f_{\beta\beta}$ are neglected. Of course it is true that only six fundamental frequencies are available and we can determine only six force constants. Since f_{Dd} occurs as a non-diagonal element, it is not included and instead, the interaction terms $f_{\alpha\alpha}$ and $f_{\beta\beta}$ which occur in the diagonal elements are included. The F matrix elements for the two species A₁ and E are

For A₁ $F_{11} = f_D; \quad F_{22} = f_a + 2f_{ad}$
 $F_{33} = \frac{1}{2} d^2 (f_\alpha + f_\beta + 2f_{\alpha\alpha} + 2f_{\beta\beta})$

For E $F_{44} = f_a - f_{ad} \quad F_{55} = d^2 (f_\beta - f_{\beta\beta})$
 $F_{66} = d^2 (f_\alpha - f_{\alpha\alpha})$.

From these, the values of f_D, f_a and f_{ad} can be easily determined. If we neglect either $f_{\alpha\alpha}$ or $f_{\beta\beta}$ we can get the values of the other three constants.

The fundamental vibration frequencies and the parameters of the molecule and ions are given in Tables I and II.

TABLE I

| Molecule | $\nu_1(A_1)$ | $\nu_2(A_1)$ | $\nu_3(A_1)$ | $\nu_4(E)$ | $\nu_5(E)$ | $\nu_6(E)$ | d in ÅU | D in ÅU | α | β |
|----------------------|--------------|--------------|--------------|------------|------------|------------|-----------|---------|----------|---------|
| OPBr ₃ .. | 173 | 340 | 1260 | 118 | 267 | 488 | 2.06 | 1.41 | 108 | 110 |
| SPBr ₃ .. | 165 | 299 | 718 | 115 | 179 | 438 | 2.13 | 1.81 | 106 | 112°47' |

TABLE II

| Ion | $\nu_1(A_1)$ | $\nu_2(E)$ | $\nu_3(T_2)$ | $\nu_4(T_2)$ |
|--------------------------------|--------------|------------|--------------|--------------|
| GaBr ₄ ⁻ | 210 | 71 | 102 | 278 |
| InBr ₄ ⁻ | 197 | 55 | 79 | 239 |
| TlBr ₄ ⁻ | 190 | 51 | 64 | 209 |
| CdBr ₄ ⁻ | 166 | 53 | 62 | 181 |

TABLE III

| Molecule | $F_{11} \times 10^5$ | $F_{22} \times 10^5$ | $F_{33} \times 10^{-11}$ | $F_{44} \times 10^5$ | $F_{55} \times 10^{-11}$ | $F_{66} \times 10^{-11}$ |
|-------------------|----------------------|----------------------|--------------------------|----------------------|--------------------------|--------------------------|
| OPBr ₃ | 9.6 | 2.834 | 0.886 | 1.4 | 1.039 | 0.939 |
| SPBr ₃ | 3.755 | 2.828 | 1.388 | 1.3 | 1.147 | 0.916 |

TABLE IV

Force Constants in 10⁵ dynes/cm.

| Molecule | f_D | f_d | f_{da} | $J_\beta - f_{\beta\beta}$ | $f_a - f_{aa}$ | $f_a + f_\beta + 2f_{da}$ $+ 2f_{\beta\beta}$ |
|-------------------|-------|-------|----------|----------------------------|----------------|--|
| OPBr ₃ | 9.6 | 1.878 | 0.478 | 0.2447 | 0.221 | 0.4178 |
| SpBr ₃ | 3.75 | 1.81 | 0.509 | 0.2527 | 0.202 | 0.6117 |

If we neglect $f_{\beta\beta}$ we get $f_a = 0.205 \times 10^5$ dynes/cm.

$$f_{aa} = -0.016 \quad ,,$$

$$f_\beta = 0.2447 \quad ,,$$

and if we neglect f_{aa} we get $f_\beta = 0.2287 \times 10^5$ dynes/cm.

$$f_{\beta\beta} = -0.016 \quad ,,$$

$$f_a = 0.221 \quad ,,$$

The values of the force constants corresponding to the bonds P = O and P — Br are in good agreement with those obtained by Venkateswarulu and Sundaram (*loc. cit.*). There is rather large difference between the force constants of the P = S bond between the molecules SPCL₃ and SPBr₃. For the former the value obtained is 5.36×10^5 dynes/cm. while for the latter the value is 3.75×10^5 .

For the tetrahedral ions, the two sets of constants for a series of values of f_{da} are given in Tables V to VIII. The force constants are given in 10⁵ dynes/cm.

Between the two sets of values for the force constants given in the above tables the A set gives rather high values for the bending constants.

Since all the frequencies have been used in evaluating the force constants it is not possible to choose a unique set by this method. However, it can be seen that for a certain range of values of f_{da} the variation in f_a and f_{aa} is very small and the values of the force constants within this range can be taken as the most

TABLE V

 $GaBr_4^{2-}$

| f_{aa} | f_a | $f_{aa} - f'_{aa}$ A set | $f_{aa} - f'_{aa}$ B set | $f_a - f'_{aa}$ A set | $f_a - f'_{aa}$ B set | f_{aa} |
|----------|-------|-----------------------------|-----------------------------|--------------------------|--------------------------|----------|
| 0 | 2.08 | 0.841 | 0.266 | 0.757 | 0.145 | 0.033 |
| 0.02 | 2.02 | 0.832 | 0.233 | 0.773 | 0.134 | 0.027 |
| 0.04 | 1.96 | 0.839 | 0.183 | 0.804 | 0.106 | 0.013 |
| 0.08 | 1.84 | 0.793 | 0.144 | 0.809 | 0.114 | 0.017 |
| 0.1 | 1.78 | 0.776 | 0.118 | 0.813 | 0.111 | 0.016 |
| 0.12 | 1.72 | 0.759 | 0.094 | 0.82 | 0.111 | 0.0158 |
| 0.15 | 1.63 | 0.726 | 0.061 | 0.82 | 0.113 | 0.0169 |
| 0.2 | 1.48 | 0.668 | 0.014 | 0.82 | 0.125 | 0.023 |
| 0.22 | 1.42 | 0.641 | -0.002 | 0.82 | 0.133 | 0.027 |
| 0.25 | 1.33 | 0.578 | -0.002 | 0.788 | 0.168 | 0.044 |
| 0.3 | 1.18 | 0.514 | -0.045 | 0.783 | 0.186 | 0.053 |

TABLE VI

 $InBr_4^{2-}$

| f_{aa} | f_a | $f_{aa} - f'_{aa}$ A set | $f_{aa} - f'_{aa}$ B set | $f_a - f'_{aa}$ A set | $f_a - f'_{aa}$ B set | f_{aa} |
|----------|-------|-----------------------------|-----------------------------|--------------------------|--------------------------|----------|
| 0 | 1.83 | .. | .. | .. | .. | .. |
| 0.01 | 1.8 | 0.62 | 0.202 | 0.488 | 0.104 | 0.028 |
| 0.02 | 1.77 | 0.625 | 0.179 | 0.506 | 0.096 | 0.024 |
| 0.04 | 1.71 | 0.629 | 0.138 | 0.537 | 0.085 | 0.019 |
| 0.06 | 1.65 | 0.629 | 0.101 | 0.564 | 0.078 | 0.015 |
| 0.08 | 1.59 | 0.626 | 0.068 | 0.587 | 0.075 | 0.014 |
| 0.1 | 1.53 | 0.618 | 0.038 | 0.608 | 0.075 | 0.014 |
| 0.12 | 1.47 | 0.608 | 0.012 | 0.6258 | 0.0775 | 0.015 |
| 0.14 | 1.41 | 0.595 | -0.0119 | 0.641 | 0.082 | 0.017 |
| 0.16 | 1.35 | 0.580 | -0.0335 | 0.654 | 0.089 | 0.021 |
| 0.18 | 1.29 | 0.562 | -0.0525 | 0.665 | 0.099 | 0.025 |
| 0.2 | 1.23 | 0.542 | -0.0692 | 0.673 | 0.111 | 0.031 |

TABLE VII

 $TlBr_4^-$

| f_{aa} | f_a | $f_{aa} - f'_{aa}$ A set | $f_{aa} - f'_{aa}$ B set | $f_a - f'_{aa}$ A set | $f_a - f'_{aa}$ B set | a_a |
|----------|-------|-----------------------------|-----------------------------|--------------------------|--------------------------|-------|
| 0 | 1.7 | .. | .. | .. | .. | .. |
| 0.01 | 1.67 | .. | .. | .. | .. | .. |
| 0.02 | 1.64 | 0.357 | 0.228 | 0.235 | 0.141 | 0.05 |
| 0.04 | 1.58 | 0.423 | 0.133 | 0.312 | 0.103 | 0.031 |
| 0.06 | 1.52 | 0.452 | 0.074 | 0.363 | 0.09 | 0.024 |
| 0.08 | 1.46 | 0.47 | 0.028 | 0.405 | 0.087 | 0.023 |
| 0.1 | 1.4 | 0.478 | 0.009 | 0.442 | 0.089 | 0.024 |
| 0.12 | 1.34 | 0.482 | 0.046 | 0.474 | 0.096 | 0.027 |
| 0.14 | 1.28 | 0.48 | 0.069 | 0.503 | 0.106 | 0.032 |
| 0.16 | 1.22 | 0.475 | 0.092 | 0.529 | 0.117 | 0.038 |
| 0.18 | 1.16 | 0.466 | 0.112 | 0.552 | 0.134 | 0.047 |

TABLE VIII

 $CdBr_4^-$

| f_{aa} | f_a | $f_{aa} - f'_{aa}$ A set | $f_{aa} - f'_{aa}$ B set | $f_a - f'_{aa}$ A set | $f_a - f'_{aa}$ B set | f_{aa} |
|----------|-------|-----------------------------|-----------------------------|--------------------------|--------------------------|----------|
| 0 | 1.298 | .. | .. | .. | .. | .. |
| 0.03 | 1.208 | .. | .. | .. | .. | .. |
| 0.04 | 1.178 | 0.334 | 0.210 | 0.207 | 0.11 | 0.033 |
| 0.05 | 1.148 | 0.338 | 0.170 | 0.241 | 0.085 | 0.02 |
| 0.06 | 1.118 | 0.349 | 0.14 | 0.265 | 0.071 | 0.013 |
| 0.08 | 1.058 | 0.359 | 0.093 | 0.301 | 0.055 | 0.005 |
| 0.1 | 0.998 | 0.359 | 0.056 | 0.328 | 0.051 | 0.003 |
| 0.12 | 0.938 | 0.353 | 0.025 | 0.349 | 0.025 | -0.009 |
| 0.15 | 0.748 | 0.334 | 0.011 | 0.372 | 0.052 | -0.0037 |

probable ones. These are given in Table IX. A similar method has been applied by Voelz, Meister and Cleveland (*loc. cit.*) in the case of SiF₄.

TABLE IX

| Ion | f_{da} | f_a | $f_{da} - f'_{da}$ | f_a | f_{aa} |
|--------------------------------|------------|-------------|--------------------|--------------|--------------|
| GaBr ₄ ⁻ | 0.08 | 1.84 | 0.144 | 0.114 | 0.0176 |
| | to 0.15 | to 1.63 | to 0.061 | to 0.113 | to 0.0169 |
| InBr ₄ ⁻ | 0.06 | 1.65 | 0.101 | 0.0786 | 0.0156 |
| | to 0.12 | to 1.47 | to 0.012 | to 0.0776 | to 0.0150 |
| TlBr ₄ ⁻ | 0.06 | 1.52 | 0.074 | 0.09 | 0.0248 |
| | to 0.12 | to 1.34 | to 0.046 | to 0.096 | to 0.0276 |
| CdBr ₄ ⁻ | 0.06 | 1.118 | 0.14 | 0.071 | 0.0137 |
| | to 0.1 | to 0.998 | to 0.056 | to 0.051 | to 0.0036 |

For the ions GaBr₄⁻, InBr₄⁻ and TlBr₄⁻, the orbital valency force field developed by Heath and Linnet (1948) was also applied. This contains four force constants, a stretching constant f_r , a bending constant f_a and two others corresponding to the interaction between non-bonded atoms, viz., $A = \frac{1}{2} d^2V/dr^2$ and $B = -dV/dr$ where $V = a/r^n$, a being a constant and r the interatomic distance. n is generally taken as 12 if the bonded atoms resemble electronically the inert gas atoms. Heath and Linnet have applied such a function for the ions ClO₄⁻, SO₄⁻, SeO₄⁻ and PO₄⁻ and find it satisfactory.

The stretching force constants obtained in the present case are: for GaBr₄⁻, $f_r = 1.345 \times 10^6$ dynes/cm. for InBr₄⁻, $f_r = 1.357 \times 10^6$ and for TlBr₄⁻, $f_r = 1.296 \times 10^6$. These values are lower than those obtained using a valence force potential function. The difference is to be expected because the values of the individual force constants depend to a certain extent on the potential functions used.

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