

# BAND CONTOURS OF INFRARED VAPOUR SPECTRA OF SOME DIHALOGENEBENZENE MOLECULES

By G. VARSÁNYI

Department for Physical Chemistry of the Technical University, Budapest,  
Central Research Institute for Chemistry of the Academy of Sciences, Budapest

*To Professor Dr. Árpád Kiss on his 70<sup>th</sup> birthday*

*(Received December 28, (1959))*

## *Introduction*

The bands of the infrared vapour spectra of symmetric rotor show two kinds of rotational structures depending on the circumstances whether the transition moment of the vibration occur to be parallel to the main axis of symmetry or perpendicular to it (parallel and perpendicular bands). An asymmetrical rotor showing a symmetry plane and at least one twofold in-plane axis has three kinds of band shapes accordingly whether the transition moment lies parallel to the rotational axis with the smallest moment of inertia or with the axes with mean or highest moments of inertia (*A*, *B* and *C* bands). With rotational lines of bands of polyatomic molecules thus generally with a relatively large moment of inertia the individual registration can only be accomplished with extremely high dispersion, therefore in general we have to be content by measuring and interpreting the envelope curves of the bands [1].

All of the dihalogenobenzene molecules belong to the asymmetric top, in fact, mixed substituted *o*- and *m*-dihalogenobenzenes do not even possess a single twofold axis, so that at the separation of the band *A* and *B* an especial consideration is required. This consideration was however found to be rather productive just for the determination of the direction of the transition moments in these molecules and by the aid of this for the assignment of the frequencies to the corresponding normal vibrations.

The indirect aim of our achieved computations is to determine approximately the force constants of the individual bonds in molecules. Since, however, in first approximation the force constants were found to be proportional to the band forces, complementary data to the theory of the covalent bond can be obtained by this.

## *Terms of asymmetric rotors*

One of the relatively simple approximations of the terms of asymmetric rotor appeared to be the graphical method on the basis of which the molecule is considered to be a transition of two symmetric rotors [2]: The rota-

tional constants of the two symmetric rotors agree with  $A$  and  $C$ , the greatest and smallest rotational constants of the asymmetric rotors in question, but while in the one it is  $A$  referring to the principal axis of symmetry, in the other it is  $C$ . Consequently the first is the prolate type, the other the oblate type. The symmetric rotor chosen for these two boundary cases differs thus only in the rotational constant  $B$  from the asymmetric rotor, in so far as  $B=C$  in the prolate type,  $B=A$  in the oblate type, while  $B$  appears as value between these two in reality. Also for the asymmetric rotor it holds true that by giving the complete angular momentum in units of  $h/2\pi$  it becomes equal to  $\sqrt{J(J+1)}$ . Further, when the molecule occupies a position where the rotational axis of the smallest moment of inertia is directed towards the  $x$ -axis and that with the greatest towards the  $z$ -axis, then, according to the quantum restrictions, the sum of the vector components  $p_x$  and  $p_z$  of the angular momentum has to be equivalent with  $\sqrt{J(J+1)}$  or  $\sqrt{(J+1)(J+2)}$ . The projection of the angular momentum falling on any rotational axis expressed in  $h/2\pi$ -units is, also in case of the asymmetric rotor, equivalent to the rotational quantum number about the axis in question. When as a boundary case the rotational quantum number of the prolate type is designed with  $K$  and that of the oblate type with  $L$ , then the above quantum restrictions were found to be in agreement with the expression  $K+L=J$  or  $K+L=J+1$ . Terms of the asymmetric rotor are obtainable when, on the terms belonging to the identical  $J$  values of the two symmetric rotors, weighted averaging is achieved individually in the order of the growing term values by taking into consideration also the value  $B$ . This may be achieved by a summation of the spaces of the prolate types multiplied with  $x$  and those of the oblate types multiplied with  $(1-x)$  after the sign of  $x = \frac{A-B}{A-C}$  had been introduced. The index  $J_{K,L}$  was used for a general designation of the term, where thus  $L$  is equal either to  $(J-K)$  or to  $(J-K+1)$ . The general term formula obtained by the graphical interpolation appeared to be the following:

$$T_r = x[CJ(J+1) + (A-C)K^2] + (1-x)[AJ(J+1) + (C-A)L^2]. \quad (1)$$

#### *Selection rules of the infrared spectrum of the asymmetric rotor*

The most convenient view of the selection rules for infrared spectra of polyatomic molecules is obtainable on the basis of symmetry conditions also with regard to the rotational structure of the bands. Here too we may start from the general rule that, with rotational axes of the molecule simultaneously being axes of symmetry the eigenfunction-product belonging to the ground and excited rotational state of the rotation around the axis lying in the direction of the transition moment has to be symmetrical and the function products of the rotation about the axis being perpendicular to it must be asymmetrical.

The selection rules are very easy to survey in case of bi-indexical term-symbols. These two indices indicate, according to an original formulation, the quantum numbers  $K$  and  $L$  of the prolate and oblate type, respectively,

as boundary cases, *i.e.* in due succession, those referring to the rotation about the axes with the smallest and the greatest moment of inertia. Thus, on the basis of the indices the symmetry of the rotational transitions can be observed directly with regard to the axis with the smallest and greatest moment of inertia, by which also a definition for the symmetry of the third axis is attained. If namely the rotational eigenfunction is symmetrical to two axes perpendicular to each other it becomes evident that it must be symmetrical to the third too. If it is symmetrical only with respect to the one but anti-symmetrical to the second, it also has to be antisymmetrical to the third. Finally, if it is antisymmetrical to both the axes designed, then it becomes symmetrical to the third.

Consequently the selection rules proved to be the following:

1. If the transition moment comes to lie in the direction of the axis with the smallest moment of inertia (A-band) then by applying the index  $J_{K,L}$  the  $\Delta K$  becomes even and  $\Delta L$  odd.

2. If the direction of the transition moment is the axis with the greatest moment of inertia (C-band) then the  $\Delta K$  becomes odd and  $\Delta L$  even. Finally, with the transition moment occurring in the direction of the axis with a mean magnitude of the moment of inertia (B-band) both quantum numbers vary with odd numbers.

For the intensity of rotational lines of symmetric rotors likewise no explicit formulae can be derived for the terms. By KRAMERS and ITTMAN [3] a method has been elaborated for the determination of intensities which however was found to be extremely complicated and lengthy even for small  $J$ -s. Recently CROSS, HAINER and KING [4] have extended detailed computations to  $J=12$  for different  $K$ -s, while SCHWENDEMAN and LAURIE [5] expanded the accuracy of the calculations to seven valid signs with the help of a computing device. With polyatomic molecules of a great moment of inertia however, with a considerable intensity there appear also lines with the quantum numbers  $J$  essentially higher than 12, since, however, with the growth of  $J$  the complexity of computation increases rapidly, thus in the practice no rigorous calculation can be achieved. Numerous experiments have been carried out in order to elaborate approximate computation methods, among which the method of RANDALL, DENNISON and coworkers [6] was found to be the most applicable on account of its relative simplicity and smaller inaccuracy. In this, the formulae\* [7] concerning the symmetric rotor are

$$* \quad \Delta J = +1; \Delta K = 0 (Rq \text{ branch}) \quad F = \frac{(J+1)^2 - K^2}{(J+1)(2J+1)}$$

$$\Delta J = 0; \Delta K = 0 (Qq \text{ branch}) \quad F = \frac{K^2}{J(J+1)}$$

$$\Delta J = +1; \Delta K = \pm 1 (Rr, Rp \text{ branch}) \quad F = \frac{(J+2 \pm K)(J+1 \pm K)}{(J+1)(2J+1)}$$

$$\Delta J = 0; \Delta K = +1 (Qr \text{ branch}) \quad F = \frac{(J+1+K)(J-K)}{J(J+1)}$$

approximately accepted so that, depending on the quantum numbers  $K$  and  $L$  which are characteristic to the rotational state of the asymmetric rotor the quantum numbers  $K$  or  $L$  of the symmetric rotor are substituted into the place of  $K$  in the formula, *i.e.* in some cases the molecule may be considered a prolate type, in other cases an oblate type. At the values  $K$  being near to  $J$  the angular momentum of the rotation encloses a small angle with the axis of the smallest inertia and with the axis of the greatest inertia at the small values of  $K$  and accordingly of  $L$  being in the vicinity of  $J$ . In this way, when a small angle is enclosed by the angular momentum with one of the axes, the neglectation is generally permissible by which the two other axes of the ellipsoid of inertia are taken as equivalent and with this the molecule as a symmetric rotor. At the mean  $K$  and  $L$  values the molecule represents the transition of the two symmetric rotors.

### *Applied branch-formulae*

By starting from (1) a special branch-formula had to be elaborated for each sub-branch separately. Since it is question of an asymmetric rotor, most of the sub-branches split into further components. (see Table 1.)

With this, however, the discussion on all the possibilities for sub-branches is not yet exhausted. However, by taking into consideration that with enough large quantum numbers  $J$  the sub-branches  $Pp$ ,  $Pr$ ,  $Qp$  and  $Pq$ , respectively appeared to be the corresponding images of the sub-branches  $Rr$ ,  $Rp$ ,  $Qr$  and  $Rq$ , respectively, we may be content in computing the half band-form. With the simplifying reservation all this is permitted by neglecting the alteration in the rotational constants caused by the change of the vibrational state. This neglectation has been applied in the deduction of all branch formulae. The form of the experimental bands shows that, with regard to the fundamentals this neglectation is rather rough, since the bands are more or less asymmetrical. Since, however, the alterations in the three rotational constants, which was brought about with the excitation of the vibrations, are found to be proportional, on the whole, relative to the symmetric ones, the branches decline in the same direction and "as a consequence of this" the maximum distances in question, for example, remain unchanged.

The five kinds of sub-branches discussed above represent the half of the bands  $A$ ,  $B$  and  $C$ .

### *Method for the computation of the intensities*

With polyatomic molecules also a value  $J$  considerably higher than 100 has to be taken into consideration, thus a rigorous computation of intensities is not possible. We used at our computations the method of RANDALL, DENNISON and coworkers by applying further simplifications in which the averaging range was abandoned with applied ranges of the intensity formulae of prolate and oblate types touching each other. This was necessary because in our case only a vibration rotation spectrum with considerably more com-

Table 1.

$$\begin{aligned}
\Delta\tilde{\nu}_{Rr_pC} &= 2B(J+1) + (A-B)(2K+1) \\
\Delta\tilde{\nu}_{Rr_pB I} &= 2C(J+1) + (A-C)(2K+1) \\
\Delta\tilde{\nu}_{Rr_pB II} &= 2(2B-C)(J+1) + (A+C-2B)(2K+1) \\
\Delta\tilde{\nu}_{Rp_pC} &= 2(2C-B)(J+1) + (3B-A-2C)(2K-1) \\
\Delta\tilde{\nu}_{Rp_pB I} &= 2(3C-2B)(J+1) + (4B-A-3C)(2K-1) \\
\Delta\tilde{\nu}_{Rp_pB II} &= 2C(J+1) + (2B-A-C)(2K-1) \\
\Delta\tilde{\nu}_{Qr_pB} &= 2(B-C)(J+1) + (A+C-2B)(2K+1) + (C-B) \\
\Delta\tilde{\nu}_{Qr_pC I} &= (A-B)(2K+1) \\
\Delta\tilde{\nu}_{Qr_pC II} &= 4(B-C)(J+1) + (2C+A-3B)(2K+1) + 2(C-B) \\
\Delta\tilde{\nu}_{Rq_p} &= 2C(J+1) + 2(B-C)K \\
\Delta\tilde{\nu}_{Qq_p} &= 2(C-B)(J+1) + (B-C)(2K+1) \\
\Delta\tilde{\nu}_{Rr_oA} &= 2B(J+1) + (C-B)(2L+1) \\
\Delta\tilde{\nu}_{Rr_oB I} &= 2A(J+1) + (C-A)(2L+1) \\
\Delta\tilde{\nu}_{Rr_oB II} &= 2(2B-A)(J+1) + (A+C-2B)(2L+1) \\
\Delta\tilde{\nu}_{Rp_oA} &= 2(2A-B)(J+1) + (3B-2A-C)(2L-1) \\
\Delta\tilde{\nu}_{Rp_oB I} &= 2(3A-2B)(J+1) + (4B-3A-C)(2L-1) \\
\Delta\tilde{\nu}_{Rp_oB II} &= 2A(J+1) + (2B-A-C)(2L-1) \\
\Delta\tilde{\nu}_{Qr_oB} &= 2(B-A)(J+1) + (A+C-2B)(2L+1) + (A-B) \\
\Delta\tilde{\nu}_{Qr_oA I} &= (C-B)(2L+1) \\
\Delta\tilde{\nu}_{Qr_oA II} &= 4(B-A)(J+1) + (2A+C-3B)(2L+1) + 2(A-B) \\
\Delta\tilde{\nu}_{Rq_o} &= 2A(J+1) + 2(B-A)L \\
\Delta\tilde{\nu}_{Qq_o} &= 2(A-B)(J+1) + (B-A)(2L+1)
\end{aligned}$$

plicated rotational structure has been available while RANDALL, DENNISON and cow. were able to determine the boundary of the transition range on the basis of experimental data of well separated far infrared pure rotational spectra. In order to eliminate the inaccuracy arising from this a comparison was made of the intensities computed from the formulae of the symmetric rotor with the intensities of the corresponding lines in the Table of SCHWENDEMAN—LAURIE and by the quotient of both the correction factor  $q$  was obtained. By an extrapolation beyond the value  $J=12$  it was rendered possible that the expression for the intensities summarized in the formulae, with enough high values  $J$ , could be given as the functions of the quotient  $K/J$  (in the

following:  $S$ ), which holds also for the line intensities of asymmetric rotors computed with rigorous methods. With  $J$  being great enough, 1 and 2 may be neglected compared to  $J$  in the formulae and by dividing all numerators and denominators by  $J^2$  and introducing the variable  $S$  more simple formulae are obtained.

The value  $s$  being characteristic for every individual molecule ( $s$  represent the boundary value of  $S$  from which given prolate and oblate rotors, respectively, are computable.) has been determined in our computations after KRAMERS and ITTMAN with the following formula:

$$s_K = \frac{2}{\pi} \arctg \sqrt{\frac{B-C}{A-B}} \quad (2)$$

and for the oblate type, respectively:

$$s_L = \frac{2}{\pi} \arctg \sqrt{\frac{A-B}{B-C}} \quad (2/a)$$

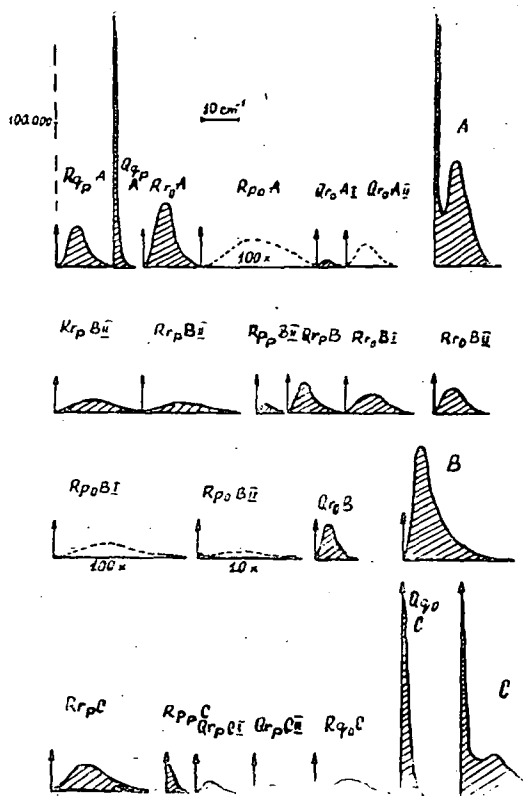


Fig. 1

### Infrared band contours of *m*-difluorobenzene

The moments of inertia and rotational constants of the *m*-difluorobenzene molecule were computed on the basis of the bond-distances measured with electron diffraction. The center of gravity of the molecule appears in the axis of symmetry in a distance of 0,96 Å from the one carbon and in a distance of 1,82 Å from the other one lying likewise in the axis of symmetry. The smallest axis of inertia is perpendicular to the axis, of the greatest symmetry, as in all planar molecules, is perpendicular

to the plane and the moment of inertia computed about this is as likewise in all planar molecules, the sum of the other two moments of inertia. In good approximation the ratio of the three rotational constants is 3:1,5:1. Consequently on the basis of (2):  $s_K = 1/3$  and  $s_L = 2/3$ .

The envelope curves of the sub-branches multiplied by the correction factor are given in Figure 1. Some branches proved to be quite weak so they could only be given with ordinate values augmented by 1—2 orders of magnitude. In the Figure theoretical band contours obtained from the summation of the sub-branches are also represented.

Figure 2 shows the bands computed for the spectral slit width of  $2\text{ cm}^{-1}$  and Figure 3 represents the infrared band contours measured experimentally by FERGUSON, COLLINS and NIELSEN [8]. It can be stated that not only the form of the bands but also the distance of the partial-maximums in the the theoretical and experimental bands are in good agreement.

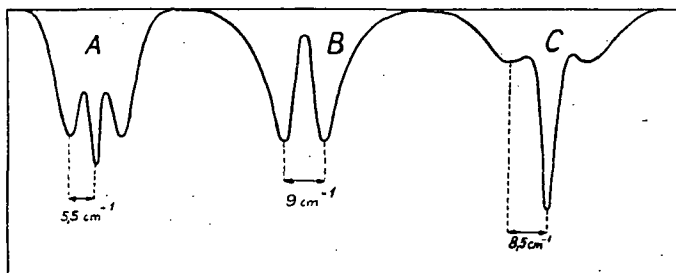


Fig. 2

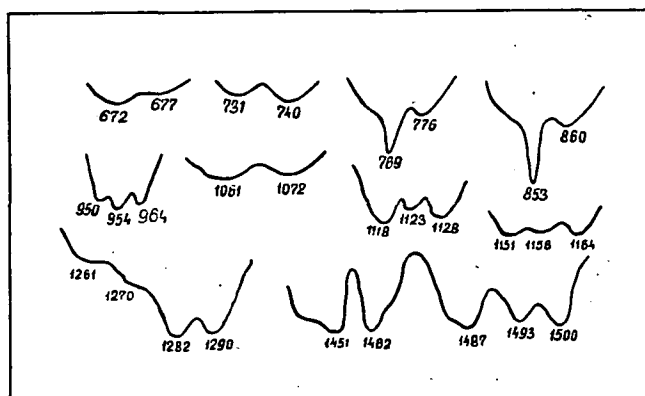


Fig. 3

### *Infrared band contours of o- and m-bromofluorobenzene*

The only symmetry element of the mixed substituted dihalogenobenzenes in ortho and meta position is the plane of the molecule. Thus, among the three axes of inertia only one can be distinguished on the basis of symmetry conditions, *i.e.*, the one being perpendicular to the plane of the molecule and consequently the C-bands in the spectra were found to be typical ones. Those bands, however, whose the corresponding transition moment lies within the plane of the molecule appear more or less as the transitions of the A and B bands. The aim of our work is to carry out an approximate determination

of the angle enclosed by the transition moment and the axis with the minimum moment of inertia from the form of such "hybrid" bands. The component of the vibration moment in any direction of the axis can be obtained by multiplying the moment with the cosine of the angle enclosed by the axis in question,

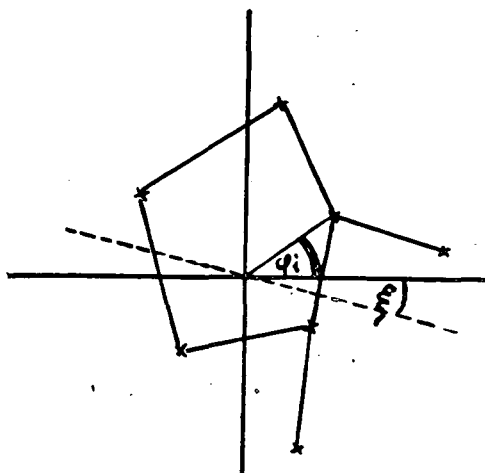


Fig. 4

so in general the vibration moment within the plane shows a component in both the axis  $A$  and  $B$ . Since, however, the square of the transition moment occurs in the formulae of the intensities, the contours of the hybrid bands corresponding to the transition are deducible from the bands  $A$  and  $B$  when the two bands after having them multiplied with the square of the cosine of the angle enclosed by the given axis and the transition moment are summed. We accomplished these computations for three remarkable cases with the transition moment enclosing the angles of  $30^\circ$ ,  $45^\circ$  and  $60^\circ$  with axes of the smallest moment of inertia. The averaging was carried out in the first case

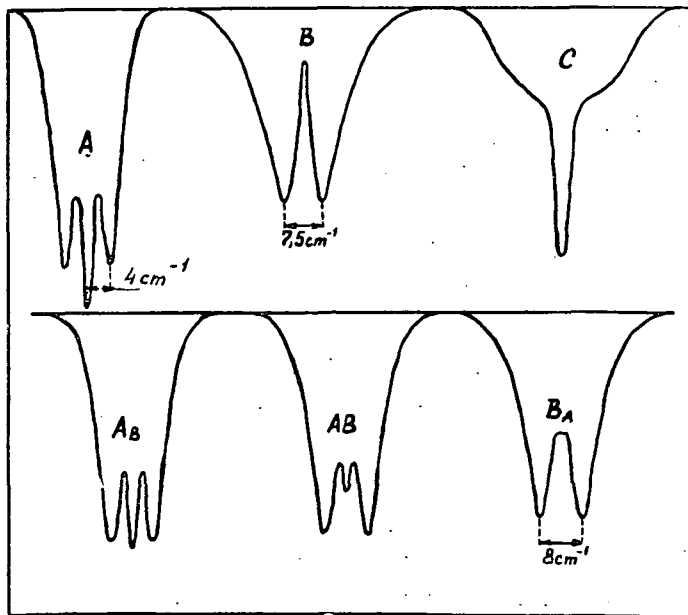


Fig. 5





on the bands *A* and *B* with the weight 3:1, in the second case 1:1, in the third case 1:3.

First the direction of the axis with the smallest moment of inertia has to be established. Let us place the molecule into an arbitrary system of coordinates with the center of gravity of the molecule being in the origin. Let  $\xi$  be the angle enclosed by the axis with the smallest moment of inertia and

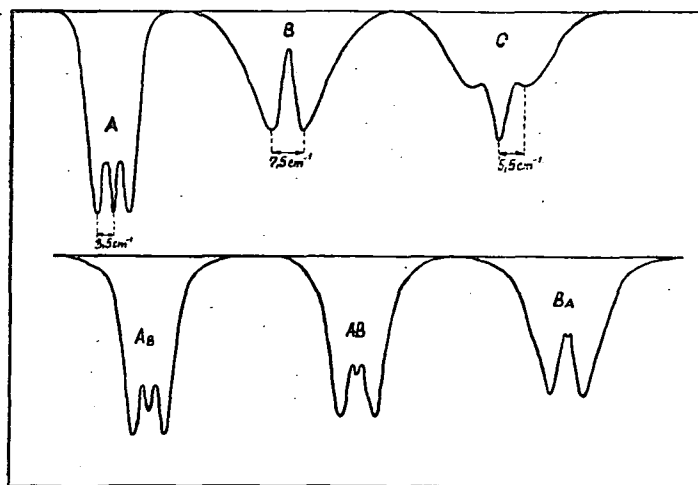


Fig. 7

the *x*-axis of the adopted co-ordinate system. (Figure 4.) Any *i*-th mass point is the directional angle  $\varphi_i$  referred to the *x*-axis of the adopted co-ordinate system. In this case the distance of the *i*-th mass point from the axis with the smallest moment of inertia becomes  $r_i \sin(\varphi_i + \xi)$ . From here the smallest moment of inertia is

$$I = \sum m_i r_i^2 \sin^2(\varphi_i + \xi). \quad (3)$$

Let us search the angle at which the moment of inertia becomes minimum. On differentiating (3) and putting it equal to 0 we get:

$$\operatorname{tg} 2\xi = - \frac{\sum m_i r_i^2 \sin 2\varphi_i}{\sum m_i r_i^2 \cos 2\varphi_i}. \quad (4)$$

*O*-bromofluorobenzene: The ratio of the three rotational constants is approximately 1:1, 3:4. With these  $s_K = 1/5$  and  $s_L = 4/5$ .

The theoretical form of pure and hybrid bands of bromofluorobenzene is given in Figure 5 where also the spectral slit width of  $2 \text{ cm}^{-1}$  has been taken into account. The band signed with  $A_B$  is corresponding to the transition in which an angle of  $30^\circ$  is enclosed by the transition moment with the

axis  $A$ . With the band signed with  $AB$  the enclosed angle is  $45^\circ$  with that of the sign  $B_A$   $60^\circ$ .

*M-bromofluorobenzene*: The ratio of the three rotational constants was found to be approximately 1:1,25:6. Computing with these:  $s_K = 1/7$  and  $s_L = 6/7$ .

The envelope curves of the sub-branches and theoretical bands are given in Figure 6, the band forms computed for finite slit width may be seen from Figure 7. Some details of infrared vapour spectra prepared in our investigations are presented in Figure 8 with a designation of the character of the bands for both bromofluorobenzene isomers. The distances of the partial maxima show a good agreement with those computed theoretically. By com-

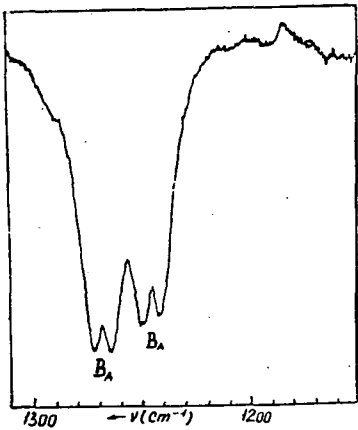


Fig. 8a

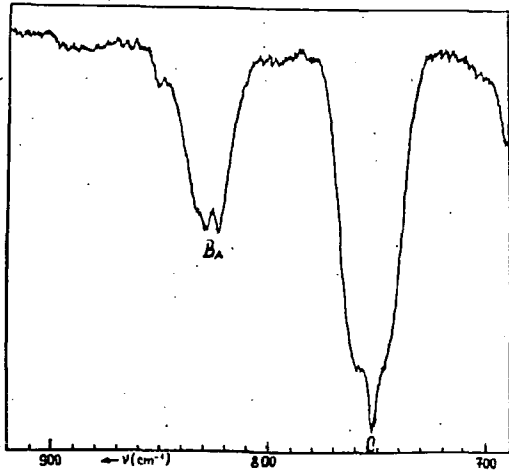


Fig. 8c

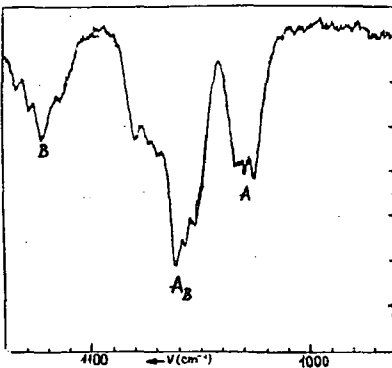


Fig. 8b

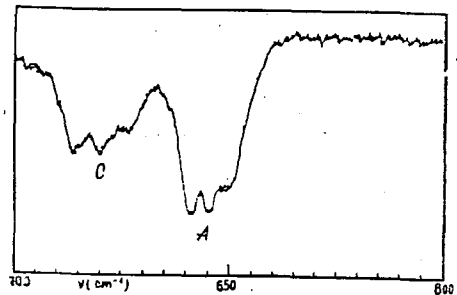


Fig. 8d

paring the experimental and theoretical forms of bands an approximate determination of the angle enclosed by the transition moment and the axis of the smallest moment of inertia in the corresponding transition can be given.

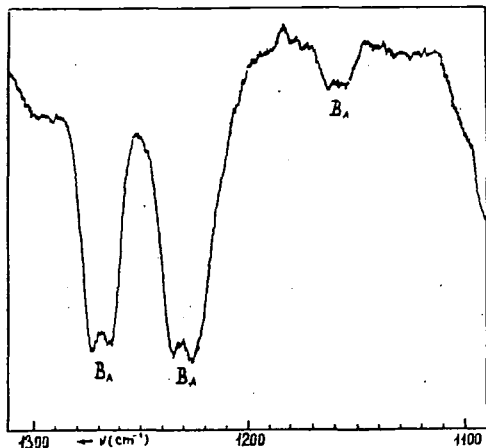


Fig. 8e

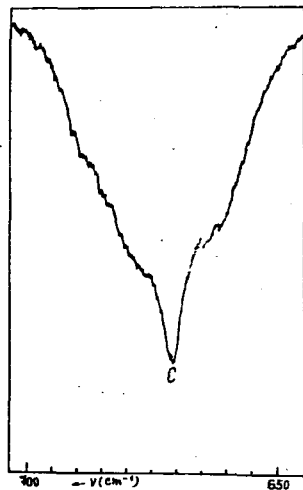


Fig. 8f

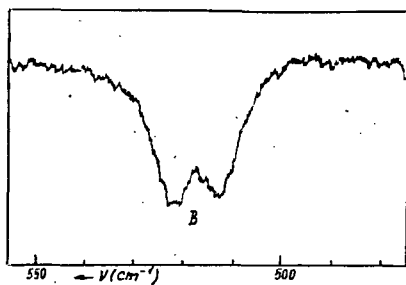


Fig. 8g

### References

- [1] Badger, R. M., L. R. Zumwalt: *J. Chem. Phys.* **6**, 711 (1938).
- [2] Herzberg, G.: *Molecular Spectra and Molecular Structure II.*, 42—60, 414—433, 460—484.
- [3] Kramers, H. A., G. P. Ittmann: *Z. Physik*, **58**, 217 (1929).
- [4] Cross, P. C., R. M. Hainer, G. W. King: *J. Chem. Phys.* **12**, 210 (1944).
- [5] Schwendeman, R. H., V. W. Laurie: *Tables of Line Strengths for Rotational Transitions of Asymmetric Rotor Molecules*, Pergamon Press.
- [6] Randall, H. M., D. M. Dennison, N. Ginsburg, L. R. Weber: *Phys. Rev.* **52**, 160 (1937).
- [7] Dennison, D. M.: *Rev. Mod. Phys.* **3**, 280 (1931).
- [8] Ferguson, E. E., R. L. Collins, J. R. Nielsen: *J. Chem. Phys.* **21**, 1470, (1953).