THE

PHYSICAL REVIEW

A Journal of Experimental and Theoretical Physics Established by E. L. Nichols in 1893

VOL. 60, NO. 4 AUGUST 15, 1941 SECOND SERIES

The Structure of Electronic Bands of Polyatomic Molecules

I. Prolate Approximation for XY_2 Molecules

N. METROPOLIS
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

(Received June 18, 1941)

A study has been made of the rotational structure of electronic bands of polyatomic molecules whose moments of inertia are related approximately like those of a symmetrical top, with the object of facilitating the interpretation of observed (resolved or unresolved) structures. The present discussion concerns non-linear XY_2 molecules, but it is also valid for all polyatomic molecules that come approximately under the prolate symmetrical top classification. The four characteristic cases of changes in dimensions during the electronic transition are considered and yield four typically different band structures. The variation in band structure with bond distance and apex angle is worked out in detail for SO_2 molecules and theoretical quantitative diagrams of band structures are given, for a temperature of 200°K. The intensity distributions shown in these diagrams are valid (for some adjusted temperature) for any polyatomic molecules in which the moments of inertia of the ground state have the same ratio as those in SO_2. If, in addition, the same is true of the moments of inertia in the upper states, then the entire band structure is identical at some adjusted scale. The correlation between rotational structure and vibrational intensity distribution is worked out, from which conclusions about the changes in dimensions of the XY_2 molecule in the transition can be made. It is shown how a qualitative examination of the observed (resolved or unresolved) rotational structure may guide or confirm the associated vibrational analysis. Finally a comparison with the available data on SO_2 and ClO_2 is made.

INTRODUCTION

THE problem of analyzing electronic bands of non-linear molecules is, at best, a complicated one. One reason for this is the fact that the expressions for the rotational energy levels of non-linear, as compared to linear, molecules contain a second rotational quantum number. As is well known, the expressions are those derived by the quantum mechanics for a freely rotating top, either symmetrical or asymmetrical.[1] The most suitable approximations will depend, for a particular molecule, upon the relative values of its three principal moments of inertia. Following the notation used by Mulliken,[2] let these be I_a, I_b, I_c with $I_a \leq I_b \leq I_c$. For planar molecules, and in particular non-linear XY_2 molecules, $I_c = I_a + I_b$, so that, in general, non-linear triatomic molecules are of the asymmetrical top type. However, there is a particular value, say $2\alpha_{ob}$, of the YXY apex angle 2α, dependent only on the masses of the X and Y atoms, such that

$$I_a = I_b = \tfrac{1}{2} I_c$$

holds, yielding an oblate-symmetrical top. Now

---

[1] D. M. Dennison, Phys. Rev. **28**, 318 (1926); F. Hund, Zeits. f. Physik **43**, 805 (1927); H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **58**, 217 (1929); O. B. Klein, Zeits. f. Physik **58**, 730 (1929); S. C. Wang, Phys. Rev. **34**, 243 (1929); D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931); W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939).

[2] A complete discussion of top and species classifications of non-linear triatomic molecules has been given recently by R. S. Mulliken, Phys. Rev. **59**, 873 (1941).

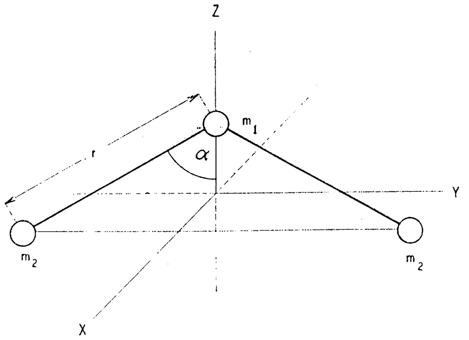

FIG. 1. XY_2 molecule.

then, if the actual value of 2α is near to $2\alpha_{ob}$, the molecule, strictly speaking, rotates like an asymmetrical top; nevertheless its wave functions and energy level patterns approximate those of the oblate-symmetrical top (see Fig. 4 of reference 2), and accordingly one may speak of the molecule as belonging to the near-oblate top classification. For 2α sufficiently far from $2\alpha_{ob}$, prolate top approximations to the wave functions and energy levels become valid. The acute near-prolate top or the obtuse near-prolate top case[2] obtains according as $\alpha \ll \alpha_{ob}$ or $\alpha \gg \alpha_{ob}$. For intermediate values of α, both symmetrical top approximations are poor.

The present discussion primarily concerns electronic spectra of non-linear XY_2 molecules in which the molecule in both upper and lower states belongs to the near-prolate top classification. Since, almost exclusively, the obtuse near-prolate case occurs in practice, the following discussion, for the most part, refers to this case. The changes necessary to cover the acute near-prolate case are quite simple and are given in the footnotes. A study of molecules which are of the near-oblate top classification in both states and of the mixed case where the top classification is different in the two states is in preparation.

For a particular XY_2 molecule, the values of the rotational constants [see Eqs. (2) below] depend, of course, on the values of the XY bond distance and of the apex angle. In an electronic transition the bond distance and angle will, in general, change. Two questions immediately arise: (1) How do the rotational constants depend upon the shape of the molecule? (2) What is the appearance of the resulting band structure for various possibilities as to shapes in upper and lower states? It was these points that had to be considered for SO_2, when the rotational spectrum of the λ3880 system was first photographed. Spectrograms of this system,[3] taken in first and second order of the 30-foot grating spectrograph, exhibited a curious shading toward both shorter and longer wave-lengths. Consideration of the above questions soon showed that an increase in bond distance and in angle could account for the two-sided shading. Because of the rather interesting results obtained, a systematic investigation has been carried through.

Hypothetical band structures for SO_2 have been computed and plotted, with symmetrical top formulas to approximate the rotational levels.[4] Electron diffraction values were used for the dimensions of the ground state and various reasonable assumptions were made about the dimensions in the excited state. Both parallel- and perpendicular-type bands have been considered.

A study of these plots showed that these band structures are examples of four general types whose qualitative aspects depend only on the signs of the changes in dimensions. Furthermore, such band structures are not limited to SO_2 and SO_2-like molecules, but must occur quite generally for XY_2 and other molecules, provided only that the moments of inertia in both states are related approximately like those of prolate symmetrical top.

For XY_2 molecules which satisfy the latter condition, it turns out that a qualitative treatment of the observed (resolved or unresolved) band structures may lead to definite conclusions concerning (1) relative values of bond distances and of angles of the molecule in upper and lower states; (2) direction of quantum-mechanical dipole moment; (3) intensity distribution to be expected in the associated vibrational structure in case the latter has not yet been analyzed: for there exist definite relations, based on the Franck-Condon principle, between the rotational and vibrational structures; or on the other hand,

---

[3] N. Metropolis and H. Beutler, Phys. Rev. **57**, 1078A (1940).

[4] G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934), and L. Harris and G. W. King, J. Chem. Phys. **8**, 775 (1940).

a vibrational analysis already made can be confirmed.

ROTATIONAL STRUCTURES AND BAND SHADING

In infra-red band spectra of diatomic molecules, the equilibrium nuclear separation, r_e, remains nearly constant in transitions to higher vibrational and rotational states. As a result, each band appears as a series of nearly evenly spaced lines on both sides of the origin. In rare cases, heads may be formed. In marked contrast, electronic bands are transitions in which the equilibrium nuclear separations are usually different in the two states, so that heads are formed. For diatomic molecules, it is well known that the bands degrade toward the ultraviolet or the red according as $r_e' < r_e''$ or $r_e' > r_e''$.

In polyatomic molecules, there is greater complexity in band structures, together with a greater variety of possibilities in band shading. To a good approximation, the rotational terms of an asymmetrical top molecule, if two moments of inertia are even roughly equal and differ markedly from the third (unique) moment, may be written

$$F = BJ(J+1) + CK^2 \qquad (1)$$

where, for the near-prolate case,[5]

$$\begin{aligned} B &= (h/8\pi^2c)\tfrac{1}{2}(1/I_b + 1/I_c); \\ C &= (h/8\pi^2c)[1/I_a - \tfrac{1}{2}(1/I_b + 1/I_c)]. \end{aligned} \qquad (2)$$

J is the total angular momentum quantum number, and K is the approximately valid quantum number associated with the component of the total angular momentum along the axis of the unique moment of inertia (quasi-symmetrical-top axis). Necessarily $J \geqq K$.

The rotational levels of the normal and excited states in a spectroscopic transition are given by Eq. (1) with B', C' for the upper levels and B'', C'' for the lower. The allowed transitions[1] are given by $\Delta J = 0, +1, -1$, which correspond respectively to the Q, R and P branches of the "J structure," and by $\Delta K = 0, \pm 1$, which correspond to the q, r and p branches of the "K structure." The two cases, $\Delta K = 0$ and $|\Delta K| = 1$, which usually occur only in separate vibrational or electronic transitions, are referred to as "parallel-type" and "perpendicular-type" transitions because of the orientation of the quantum-mechanical dipole moment parallel or perpendicular to the unique axis of the symmetrical or quasi-symmetrical top.

It is convenient to write

$$\nu_{KJ} = \nu_0 + \nu_K + \nu_J, \qquad (3)$$

where ν_0 is the band origin, and where

$$\nu_K = C'K'^2 - C''K''^2, \qquad (4)$$

giving the K structure, and

$$\nu_J = B'J'(J'+1) - B''J''(J''+1), \qquad (5)$$

giving the J structure. Usually the distance between lines is much smaller for one structure than for the other. This fact makes it convenient

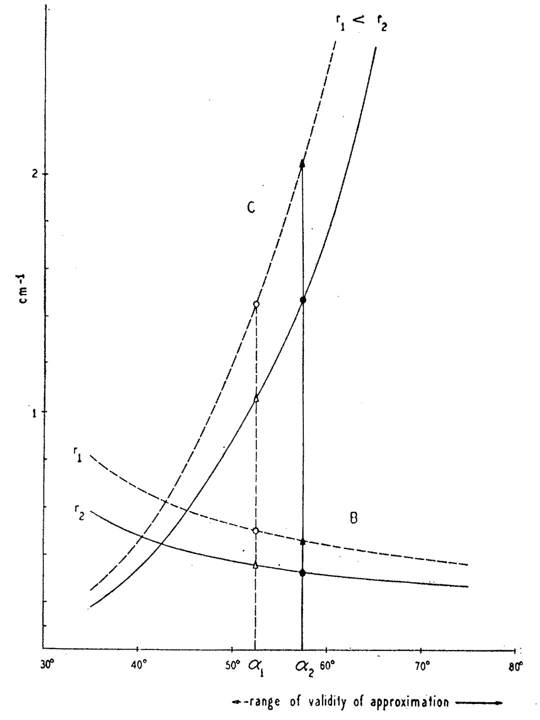

FIG. 2. Graphs showing the behavior of the rotational constants B and C of Eq. (1) as functions of the half-angle α at the apex for *constant bond distance*. The solid curves are for a state having a bond distance r_2, the dashed curves are for a state having $r_1 = 0.85r_2$. Other r_1/r_2 ratios would give similar curves. α_1 and α_2 are two sample values of α. The scale for ordinates applies to SO_2; the value of r_2 is 1.43A, the experimental value for the normal state. For any other XY_2 molecule belonging to the obtuse near-prolate top classification, the curves have approximately the same shape. Although no sharply defined limit exists for the range of validity, this extends approximately to 50°. As α approaches 90°, C tends toward infinity, while B approaches $h/8\pi^2c(2m_2r^2)$; all C curves cross the α-axis at $\alpha = \tan^{-1}[\sqrt{2}(1+2m_2/m_1)]^{-\frac{1}{2}}$.

---

[5] It is easily seen that for XY_2 molecules $I_b = 2m_2r^2 \sin^2\alpha$, and $I_a = (2m_1m_2/m_1 + 2m_2)r^2 \cos^2\alpha$.

to regard the frequencies of the coarser structure as giving the positions of sub-band origins, e.g., the frequencies $\nu_0+\nu_K$ of Eq. (4) if the K structure is the coarser, as for molecules like SO_2.[6] The sub-bands themselves are made up of sets of lines constituting fine structure, the frequencies being given by ν_J of Eq. (5).

In infra-red studies, the coefficients B' and B'' are nearly equal in the two states, just as in the diatomic case. Similarly C' and C'' are nearly equal. Hence the series of lines and sub-bands forming the band structure due to $|\Delta K|=1$ or $|\Delta J|=1$ exhibit slow convergence, if any, while series corresponding to $\Delta K=0$ or $\Delta J=0$ exhibit little if any *divergence*. On the other hand, the values of B and C may be quite different in the two states if a transition involves a change in the electronic state. This is the case in which we are interested.

Dependence of Rotational Coefficients upon Bond Distance and Apex Angle

Special cases to be treated

The available experimental data show that a number of non-linear XY_2 molecules belong to the obtuse near-prolate top type. This follows from the fact that 2α (see Fig. 1) is usually large enough so that $I_c \approx I_b > I_a$. Thus in the normal states of SO_2, NO_2 and ClO_2, the values of 2α from electron diffraction studies and spectroscopic data are approximately 120°, 154° and 122° respectively. For these values of the angles, the following ratios are obtained

	SO_2	NO_2	ClO_2
I_c/I_a	7.00	7.16	7.23
I_c/I_b	1.17	1.16	1.16

(In Fig. 1 for XY_2, the moments of inertia I_c, I_b and I_a are those about the x, y and z axes respectively.)

TABLE I. *Character of band structures in four special cases for* XY_2 *molecules belonging to the obtuse near-prolate top classification.*

	Case	B	C	J Structure Degrades Toward	K Structure Degrades Toward
I	$\alpha'>\alpha'', r'=r''$	$B'<B''$	$C'>C''$	red	violet
II	$\alpha'<\alpha'', r'=r''$	$B'>B''$	$C'<C''$	violet	red
III	$\alpha'=\alpha'', r'>r''$	$B'<B''$	$C'<C''$	red	red
IV	$\alpha'=\alpha'', r'<r''$	$B'>B''$	$C'>C''$	violet	violet

As an aid to analyzing actual spectra, it is useful to work out the band structures for the four following cases:

$$\begin{array}{rll} \text{I.} & \alpha'>\alpha'', & r'=r'' \\ \text{II.} & \alpha'<\alpha'', & r'=r'' \\ \text{III.} & \alpha'=\alpha'', & r'>r'' \\ \text{IV.} & \alpha'=\alpha'', & r'<r''. \end{array} \qquad (6)$$

In a discussion of these cases, it is useful to consider Fig. 2. The solid curves show the behavior of B and C [cf. Eq. (2)] for SO_2 as functions of the half-angle at the apex, for a *constant bond distance* $r_2=1.43$A. The dashed curves are similar functions for a bond distance $r_1=0.85r_2$. Curves for other XY_2 molecules are qualitatively the same as these for SO_2; the C curves are always monotonic increasing and the B curves monotonic decreasing functions.[6a] In Fig. 2, α_1 and α_2 are two sample values of α such that $\alpha_1<\alpha_2$.

For cases I and II, where only the angle changes in the transition, the behavior of B and C is immediately apparent; if α increases in an absorption transition (suppose $\alpha''=\alpha_1$, $\alpha'=\alpha_2$) C increases markedly but B decreases slightly, whereas for $\alpha'<\alpha''$, the directions of the changes in B and C are reversed.

For cases III and IV, where only the bond distance changes in the transition, it is easy to show that $B'=[(r''/r')^2]B''$ and $C'=[(r''/r')^2]C''$. Hence a change in bond distance alone increases both B and C if $r'<r''$, decreases both if $r'>r''$. If, for example, in Fig. 2, $\alpha''=\alpha'=\alpha_2$ and $r''=r_2$ and $r'=r_1$, all that is necessary is to move along the vertical from the solid circles to the solid triangles. The foregoing relations are summarized in Table I; the direction toward which each

---

[6] A convenient qualitative method for comparing the relative coarseness of spacing of J and K structures is the following: (i) For parallel-type bands, the span of, say, the first ten Q lines from the head may be compared with that of the first ten q transitions. (ii) For perpendicular-type transitions, the span of the first ten lines from the head of the J structure (P or R branch) in some strong sub-band may be compared with that of the first ten transitions from the head of the K structure (p or r branch). Using this criterion for case II in SO_2 (see Fig. 4) one finds that the K structure is about five and seven times as coarse as the J structure for the parallel- and perpendicular-types, respectively.

[6a] The corresponding curves for the acute near-prolate top case are approximately those obtained by reflecting the curves in Fig. 2 at $\alpha=45°$. Consequently the present discussion applies to the acute form provided the inequality signs in $\alpha'<\alpha''$ and in $\alpha'>\alpha''$, wherever used, are reversed.

structure degrades in each of the four cases is also indicated.

Characteristic patterns of bands

The four representative cases considered above yield four characteristic band structures.[7] For case I, where $\alpha' > \alpha''$ results in $C' > C''$ and $B' < B''$, the K structure degrades toward the violet, whereas the J structure goes off toward the red. Case II with $\alpha' < \alpha''$ reverses both directions of shading. Cases I and II will thus exhibit a shading of K structure to one side with a superposition of J structure shaded to the other. The band as a whole will not have a

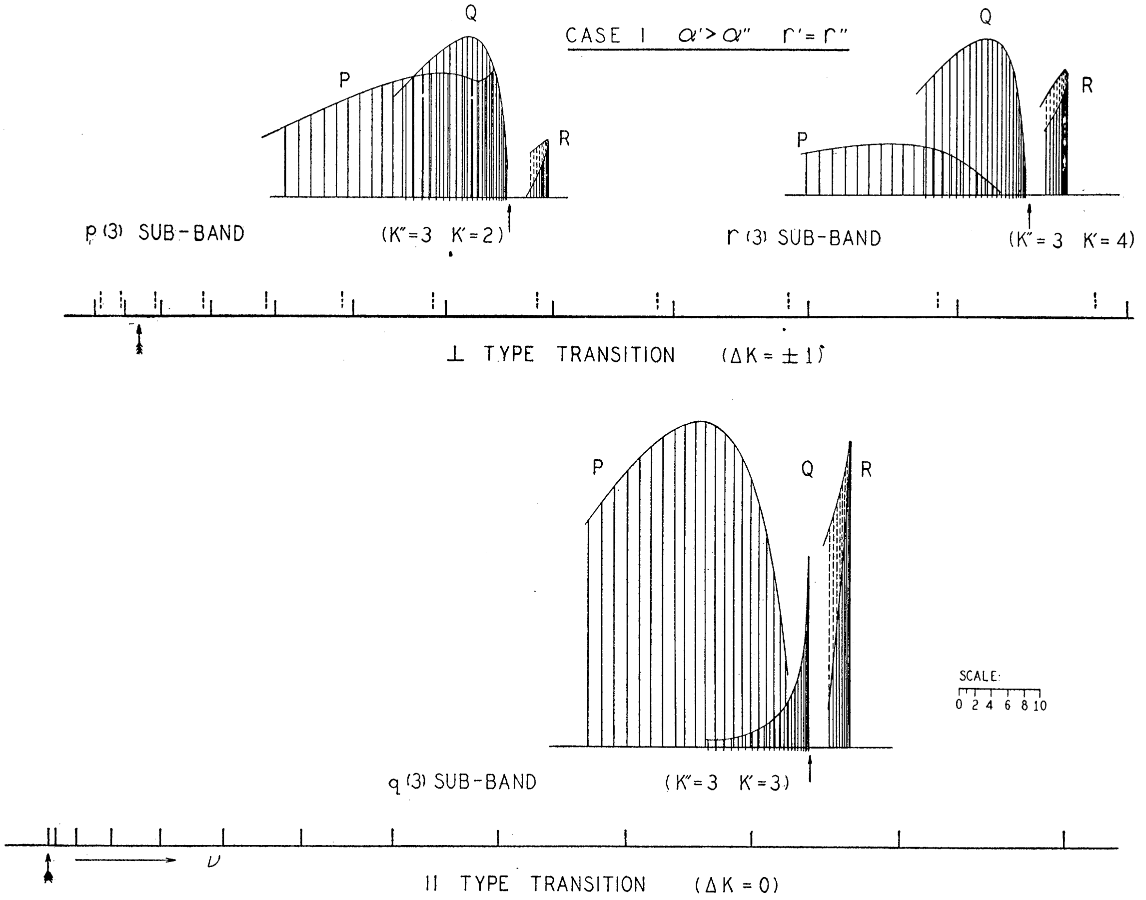

FIG. 3. Schematic representation of typical band structures of SO_2-like molecules, showing the "component parts" of both parallel- and perpendicular-type transitions when the only change in dimensions is (for absorption) an increase in the apex angle (case I). The K structure, which forms a set of origins for the sub-bands (J structure), is shown by lines of uniform height. Returning branches in the perpendicular-type K structures and in the J structures are shown by dashed lines. Lines of the Q branches are drawn below the axis. The feathered arrows correspond to origins of bands, unfeathered arrows to sub-band origins. The intensities correspond to a temperature of 200°K for the case of SO_2. For any other XY_2 molecule having the same ratio of moments of inertia I_b/I_c as SO_2, a change in scale combined with an appropriate temperature T' would yield an identical plot; T' is given by $T(I_b/I_b')$. Since $K''=3$ has been chosen for all three sub-bands exhibited here, the first lines in the P, Q and R branches shown are $P(3)$, $Q(3)$ and $R(3)$ where, as usual, the numbers in parentheses refer to J''. The J'' values run to 25.

---

[7] Explicit band formulas for the two types of transitions are as follows. For the perpendicular type ($\Delta K = \pm 1$), the formula [cf. Eq. (3)] may be written

$$\nu = \nu_0 + \tfrac{1}{2}(C'-C'') + (C'+C'')k + (C'-C'')k^2 + \left\{ \begin{matrix} (B'+B'')m + (B'-B'')m^2 \\ (B'-B'')J + (B'-B'')J^2 \end{matrix} \right\}.$$

Here k is a convenient index number with the value $k = K + \frac{1}{2}$ for the r branch and $k = -K + \frac{1}{2}$ for the p branch of the K structure [cf. Eq. (4)]. The bracketed expressions represent ν_J of Eq. (5). The lower expression for ν_J corresponds to the Q branch; in the upper expression, the index number m with $m = J+1$ gives the R branch, and with $m = -J$ the P branch. For parallel-type transitions, the formula may be written

$$\nu = \nu_0 + (C'-C'')K^2 + \left\{ \begin{matrix} (B'+B'')m + (B'-B'')m^2 \\ (B'-B'')J + (B'-B'')J^2 \end{matrix} \right\}.$$

In all the foregoing formulas, K means K'', J means J''.

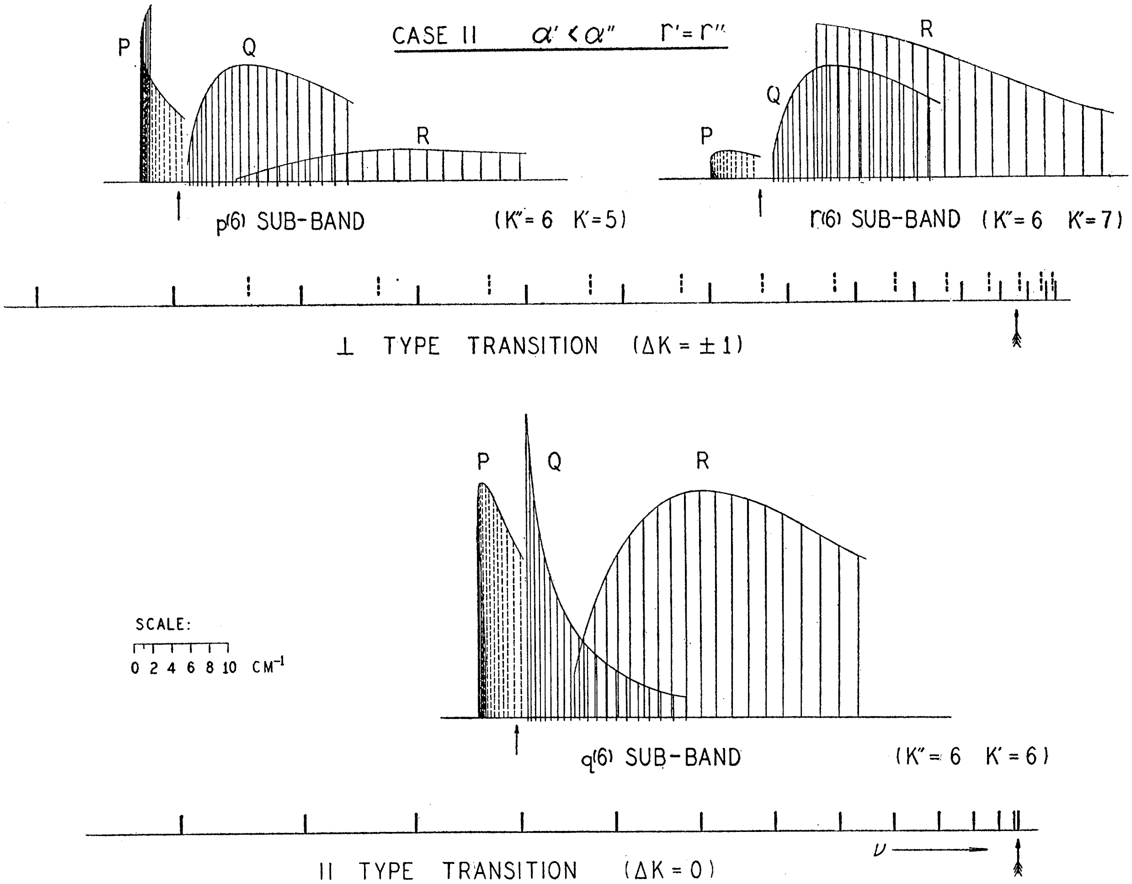

FIG. 4. Band structures for the case (in absorption) of a decrease in angle without change in bond distance (case II). In this instance the *J* and *K* structures degrade toward the ultraviolet and red respectively. See Fig. 3 for other details.

characteristic sharp edge, but will spread out on both sides.

In distinct contrast to the foregoing, cases III and IV will exhibit a shading of both *J* and *K* structures in the same direction; the whole band will possess a characteristic edge[8]—rather sharp in most instances—on the violet or red side according as $r' > r''$ or $r' < r''$.

The foregoing applies equally to parallel- and perpendicular-type transitions; in fact, it is only with some difficulty that one can expect to distinguish between these two types by observing the qualitative features of the bands. A returning branch of the *K* structure would distinguish a ⊥ from a || type transition, the latter having no returning branch. However, the considerable overlapping should make it difficult to ascertain whether or not a returning branch of the *K* structure is present (cf. *K* structures of Figs. 3–6 where returning branches are shown by dashed lines); both ⊥ and || types exhibit a convergence in the *K* structure. However, a plot of sub-band intensities should be of considerable aid.

More general cases

The four cases just treated are, of course, very special; in general, both angle and bond distance change in going from one electronic state to another. In the preceding sections, the discussion of the coefficients was limited to a change in only one parameter (either α or r). To understand the effects of a change in both parameters, one considers first the effect of a change in one parameter, and using the results as a starting

---

[8] It may, of course, happen that the convergence in both structures is rather slow so that the intensity is small at the heads.

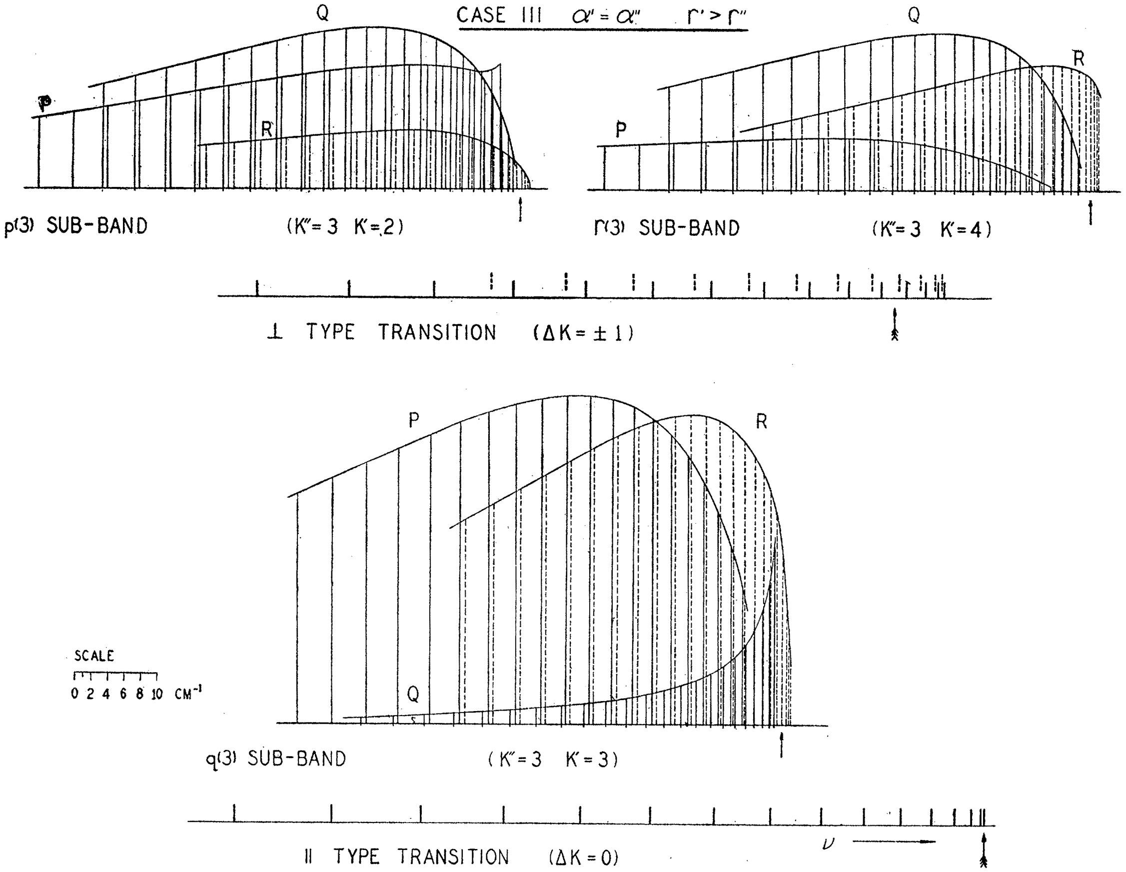

FIG. 5. Band structures for the case (in absorption) of an increase in bond distance without change in angle (case III). Note that both J and K structures degrade toward the red.

point, one may study the effect of a change in the second parameter.

From Fig. 2 one may obtain an insight into a variety of cases. As an example, let $\alpha''=\alpha_2$, $r''=r_2$ and $\alpha'=\alpha_1$, $r'=r_1$, and consider an absorption transition. B'' and C'' values are given by solid circles in Fig. 2, B' and C' by open circles. The effect of the decrease in angle alone (from α_2 to α_1) would be a movement along the solid curves from the solid circles to the open triangles. To obtain also the change in bond distance $r_2 \rightarrow r_1$, a shift is now necessary along the vertical at α_1 from the solid to the dashed curves, i.e., from the open triangles to the open circles. The net result is seen to be a considerable increase in B and a slight decrease in C for the example selected.

The fact that B and C change in opposite directions for a change in angle alone affords some interesting possibilities. In the example just given, $C' \approx C''$ resulted, yielding non-convergent K structure. This might suggest that $\alpha' \approx \alpha''$, $r' \approx r''$. However, inspection of the J structure, which (in our example) forms heads at relatively small quantum numbers, indicates $B' > B''$ definitely, since $-\Delta\alpha$, $-\Delta r$ both decrease B.

If the dimensions of the molecule should be practically unchanged in a transition, this fact would be immediately evident by the absence of heads in *both* J and K structures.

TYPICAL ELECTRONIC BANDS

Detailed diagrams of spectra of SO_2 and SO_2-like molecules have been worked out for each of the four special cases [Eqs. (6)] treated above, for values of J up to twenty-five and of K up to fifteen, for temperatures of 200° and of 300°K. Equations (1) and (2) were used to calculate the positions of lines, and the intensities were calculated from formulas taken from Dennison's review;[1] the frequency factor ν for absorption (or ν^4 for emission) was, however, omitted.

Since the oxygen nucleus has zero resultant spin, only one of the two possible levels associated with $|K|$ exists for $K>0$; for $K=0$, lines with alternate J values are missing.

Representative parts of the spectra of SO_2-like molecules for the four special cases are shown in Figs. 3–6. The ground state dimensions, $\alpha''=60°$, $r''=1.43\text{A}$, were taken to agree with electron diffraction values for SO_2;[9] for the excited states the following assumptions were made:

$$\begin{aligned} \text{Case}\quad \text{I.}\ & \alpha'=65°, & r'&=r'', \\ \text{II.}\ & \alpha'=55°, & r'&=r'', \\ \text{III.}\ & \alpha'=\alpha'', & r'&=1.15r'', \\ \text{IV.}\ & \alpha'=\alpha'', & r'&=0.85r''. \end{aligned} \tag{7}$$

In each figure, the K (coarser) structure is shown for a parallel-type transition ($\Delta K=0$) and gives the origins of a set of sub-bands [cf. Eqs. (3)–(5)]; in addition, the structure of one sample sub-band is shown to the same scale. In each figure also, the K structure of a perpendicular-type transition ($\Delta K=\pm 1$) is similarly exhibited together with one sample sub-band from each of the two K branches (p and r). (A sub-band origin, shown by unfeathered arrow in the sample sub-band, should be brought into coincidence with the line representing each K transition.) It is, of course, necessary to make appropriate changes in relative intensity for the various sub-bands and to delete lines with $K>J$.

As a supplement to Figs. 3–6, Figs. 7 and 8 have been constructed to help in visualizing the change in intensity from one sub-band to the next. In the cases of both parallel- and perpendicular-type transitions, the intensity of the *most intense line* for each branch of the J structure has been plotted as a function of K. The dashed segments at $K=0$ have been inserted to remind one that the sub-bands having either K'' or K' equal to zero contain only half as many lines as other sub-bands, since lines with alternate J values are missing.

Returning to Figs. 3–6, one observes that in cases I and II, the J and K structures degrade in opposite directions, whereas in cases III and IV the two structures are shaded in the same direction; it is clear that the bands in the latter two

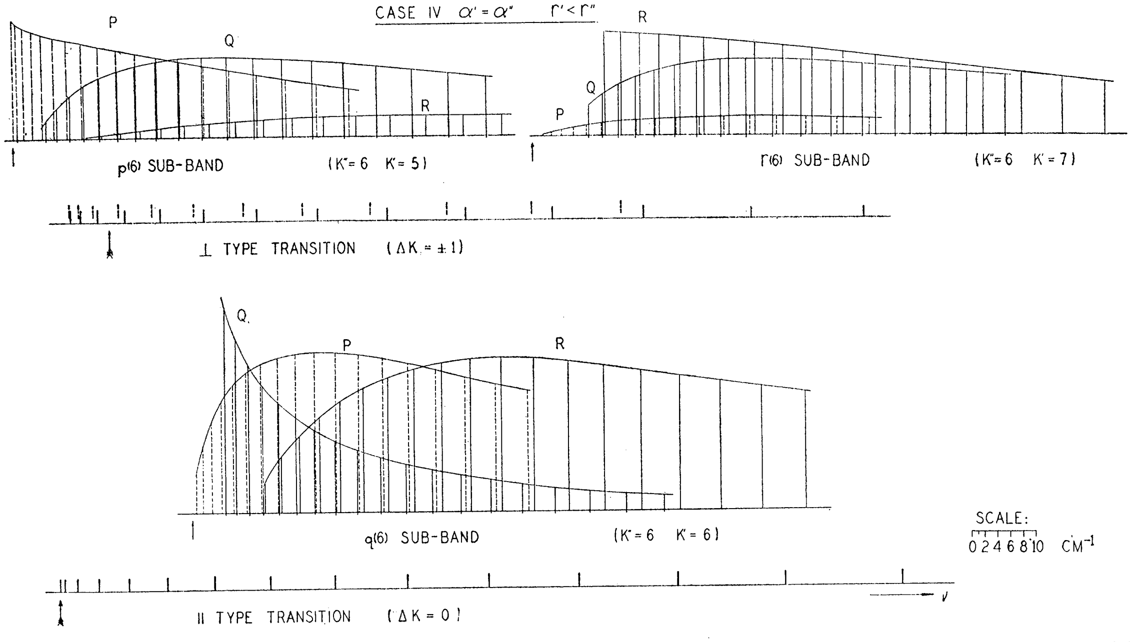

FIG. 6. Band structures typical of a decrease in bond distance without change in angle in an absorption transition (case IV). As in case III (Fig. (5)), J and K structures both degrade in the same direction, but here the direction is toward the ultraviolet.

---

[9] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 62, 1270 (1940).

cases must have a characteristic sharp edge.[8] In view of the considerable overlapping of the sub-bands and the usually large moments of inertia, the band may be so complicated that the only characteristic feature is the presence or absence of a sharp edge. However, even such meager information as the qualitative shape of the band envelope is valuable both for itself and as a help in the corresponding vibrational analysis; this latter point is discussed in the next section.

APPLICATION TO VIBRATIONAL ANALYSIS

In this last section the correlation of the qualitative characteristics of electronic bands with the intensity distribution in the associated vibrational structure is discussed. As a result of the interrelations that exist between rotational and vibrational structures, it is convenient to carry out the two analyses side by side. In the following, only absorption bands arising from the vibrationless level of the ground state will be considered. The fundamental frequencies of the normal state are usually known (mostly from infra-red and Raman work), so that transitions from excited vibrational levels in the ground state are easily recognized. However, in the event that these frequencies are not known, the temperature-sensitiveness of such bands makes them easy to pick out; or they can be made quite faint by lowering the temperature.

In making (or confirming) a vibrational analysis for an XY_2 molecule, two factors are to be considered: (1) the direction toward which the K structure (here the coarser) and the J (here the sub-band) structure degrade, (2) the intensity distribution in the vibrational structure. These two factors can be correlated by means of the Franck-Condon principle.

In the simplest instance there is one strong band, the vibrationless transition, accompanied by a few weaker ones. This intensity distribution is expected if the dimensions of the molecule are not appreciably changed in the transition to the excited state; the latter relation would be confirmed by slow convergence, if any, of both J and K structures.

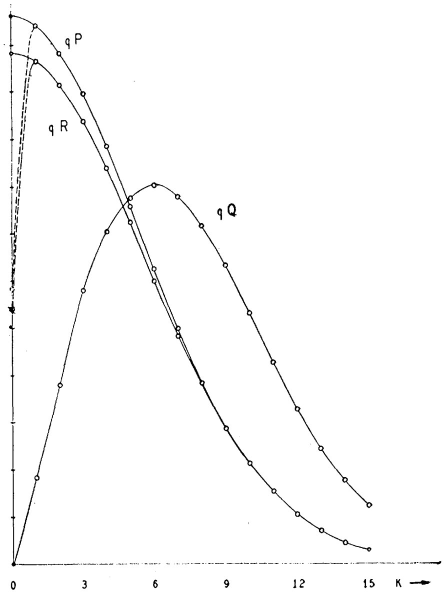

FIG. 7. The intensity of the strongest line of each branch (branches P, Q, R) of each sub-band is plotted as a function of K (i.e., K'') for a parallel-type transition, for SO_2 and SO_2-like molecules. The dashed segments from $K=1$ to $K=0$ are to remind one that only lines with alternate J values are present for $K=0$, so that the total intensity of each sub-band with $K=0$ is halved.

If, on the other hand, there is one prominent series of quite evenly spaced bands, then by the Franck-Condon principle one may conclude that either the angle or bond distance has changed. If the bands exhibit a two-sided shading (cf. Figs. 3–4), it is primarily a change in angle that has occurred; but if both J and K structures degrade in the same direction so that the band as a whole possesses a sharp edge (cf. Figs. 5–6), then it is principally a change in bond distance that has taken place.

If the intensity distribution is more complicated, then the bond distance and angle must both have suffered appreciable changes, Δr (i.e., $r'-r''$) and $\Delta\alpha$ ($\alpha'-\alpha''$) in the electronic transition. Before attempting to discuss the interpretation of such cases with complicated intensity relations in terms of molecular changes, it is useful to consider first the converse problem of determining the directions toward which the J and K structures degrade for each of four possible types of transition in respect to the signs of the changes in r and α. For convenience let J and K with the subscripts + or − be used to denote whether the J or K rotational structure degrades toward the violet or the red. Referring to Table II, one observes that to each of the four types of changes in molecular dimensions (A, B, C, D)

there correspond two rotational-structure subtypes. In type A, the J structure is necessarily J_-; for, referring to Fig. 2, one observes that an increase in either α or r decreases B, hence certainly $B'<B''$. On the other hand, the K structure may be either K_+ or K_-, giving the two subtypes A_1 and A_2. This follows from the fact that an increase in α tends to increase C but an increase in r tends to decrease it; if the effect of the increase in r more than compensates that of the change in α, K is K_-; if not, then it is K_+. The discussion of the other types proceeds in similar fashion.

Returning to the original problem, one desires to determine the signs of the changes in molecular dimensions for a given type of band shading. Referring to Table III, one sees that for each of the K and J shading cases, there are two possible interpretations in terms of molecular changes. To ascertain which of the two possibilities is at hand, it would be necessary to determine which structure, J or K, converges more rapidly to form a head. This could be done easily if both structures are resolved. Usually the J structure is not completely resolved; however, the second differences in the J structure may be evaluated from resolved lines with high J values far from the head. From these evaluations, combined with a knowledge of B'', one can determine B'. Analogously, the second differences in the K structure can be determined, and finally C', since C'' is usually known. Hence the expressions $|(B'-B'')/(B'+B'')|$ and $|(C'-C'')/(C'+C'')|$ can be evaluated. Their numerical values indicate the rate of convergence (or divergence) in the respective structures. A comparison of these serves as a criterion to distinguish between the two possibilities in Table III.

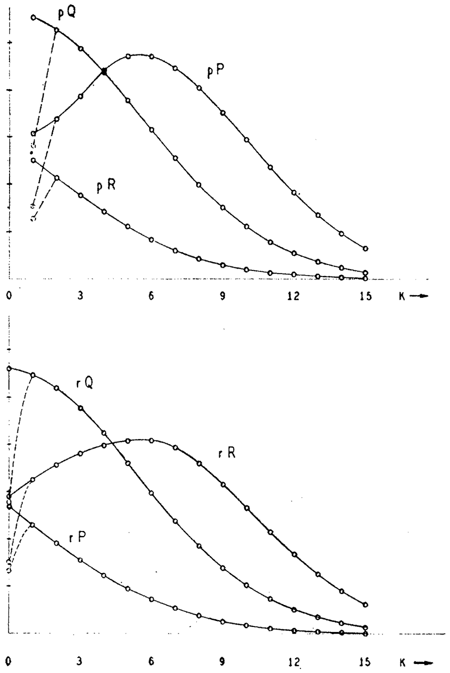

FIG. 8. Analogous to Fig. 7. Here a perpendicular-type transition is considered.

TABLE II. *Possibilities for shading of K and J structures for various Δα, Δr types where Δα and Δr are changes in molecular dimensions.* ($\Delta\alpha=\alpha'-\alpha''$, $\Delta r=r'-r''$.) *The signs in column 3 indicate directions of shading* (+, *toward ultraviolet,* −, *toward red*).

			BAND SHADING	
TYPE	Δα	Δr	K STRUC.	J STRUC.
A_1	+	+	+	−
A_2			−	−
B_1	−	−	−	+
B_2			+	+
C_1	+	−	+	−
C_2			+	+
D_1	−	+	−	+
D_2			−	−

However, in practice it is usually not necessary to use this quantitative method because many spectra show such markedly dissimilar rates of divergence of the two structures that a mere inspection suffices. This situation occurs when both α and r change considerably. In the absence of marked differences, one has recourse to another criterion, taken from the vibrational intensity distribution. This situation arises from a change principally in only one of the two parameters, α and r (cf. p. 291).

As an example, suppose the spectrum observed is the case J_-K_-. Then definitely the bond distance has increased, but it remains to determine whether α has increased or decreased. If the J structure converges relatively more rapidly than the K, then $\alpha'>\alpha''$; if the opposite is observed, then $\alpha'<\alpha''$.

If one succeeds in determining the signs of the changes in dimensions, one is interested in knowing more explicitly how these changes are correlated with the vibrational intensity distribution. As yet, a quantitative treatment of the Franck-Condon principle for triatomic molecules is lacking, but some conclusions may be reached if simplifying assumptions are made.

Suppose, first, that the equilibrium bond distance increases by an amount Δr as a result of the electronic transition. Qualitative application of the Franck-Condon principle then shows that a pure v_1 vibrational progression should be developed (ν_1 = breathing frequency). Let us denote the quantum number of the strongest band in this series by $(v_1)_{\max}$. Evidently $(v_1)_{\max}$ is larger the larger is Δr.[10]

Again, suppose that $\Delta r = 0$ but that the equilibrium angle increases by an amount $\Delta\alpha$. In this event, a pure v_2 progression should be developed, whose strongest member may be designated by $(v_2)_{\max}$ (ν_2 = deformation frequency). Finally, suppose both Δr and $\Delta\alpha$ differ from zero. Then both pure v_1 and pure v_2 progressions should be developed; and in addition mixed progressions. Further, for any given Δr value there is some corresponding $\Delta\alpha$ value such that $(v_1)_{\max}$ and $(v_2)_{\max}$ are equal.

If now a plane is defined by plotting $\Delta\alpha$ as ordinate against $\Delta r/r'$ as abscissa (it is found that $\Delta r/r'$ is more convenient for this purpose than Δr itself), then curves can be plotted in this plane passing through points where Δr and $\Delta\alpha$ are so related that $(v_1)_{\max} = (v_2)_{\max}$: see Fig. 9. If some simple assumptions are made,[10] it turns out that these curves are approximately straight lines passing through the origin (dashed lines in Fig. 9), given roughly by

$$\Delta\alpha = \pm 2^{\frac{1}{2}}(\Delta r/r').$$

These lines evidently divide the plane into four regions, in two of which $(v_2)_{\max} > (v_1)_{\max}$ (dotted regions in Fig. 9), while in the other two $(v_1)_{\max} > (v_2)_{\max}$ (undotted regions in Fig. 9).

The $\Delta\alpha$, Δr plane can be divided into regions not only with respect to vibrational intensity distribution in the manner just discussed, but also with respect to rotational structure types. The rotational structure regions, like the vibrational distribution regions, are four in number. In the terminology introduced earlier, the four rotational regions may be labeled J_+K_+, J_+K_-, J_-K_+, and J_-K_-. The boundary between any two of these regions corresponds either to $B' = B''$ (J_+, J_- boundary) or to $C' = C''$ (K_+, K_- boundary). These boundaries can be located with the help of considerations used in plotting Fig. 2, and are given, for the case of absorption by SO_2 in its normal state, in Fig. 9.

TABLE III. *Interpretation of various K and J shading cases in terms of changes in molecular dimensions $\Delta\alpha$ and Δr.*

	BAND SHADING			
CASE	*K* STRUC.	*J* STRUC.	$\Delta\alpha$	Δr
I	+	−	+	+
			+	−
II	−	+	−	−
			−	+
III	−	−	+	+
			−	+
IV	+	+	−	−
			+	−

Now then, if it is known which mode of vibration is more strongly excited and if the *J*, *K* shading can be determined, the possible changes in dimensions are limited to a region of the

---

[10] It is to be expected that for a given total intensity the number of bands in a v_1 progression (pure breathing series) is greater the larger the change in bond distance. If harmonic motion is assumed, one can estimate $(v_1)_{\max}$, the quantum number of the strongest band in such a series. It turns out that $(v_1)_{\max}$ is related to the frequency and the change in bond distance approximately according to

$$(v_1)_{\max} = c(\Delta r)^2\nu_1. \qquad \text{(a)}$$

where ν_1 is the symmetrical valence or breathing frequency and c is a constant factor. It is interesting to observe that some deformation vibration is excited even though only the bond distance changes. If the angular change in a transition is $\Delta\alpha$, the distance of the Y atom in its normal state position, measured perpendicularly to the X−Y bond distance, from the excited state equilibrium position is approximately $\Delta s = r'\Delta\alpha$, where r' is the bond distance in the excited state. Then

$$(v_2)_{\max} = c(\Delta s)^2\nu_2, \qquad \text{(b)}$$

where v_2 is the quantum number associated with ν_2, the deformation frequency, and c is the same as in Eq. (*a*). Empirically, $\nu_1 = 2\nu_2$ is found to be roughly true for the normal states of several XY_2 molecules. Hence from Eqs. (a) and (b)

$$(v_1)_{\max} = (v_2)_{\max} \qquad \text{(c)}$$

provided

$$(\Delta s) = \sqrt{2}(\Delta r).$$

In other words, Eq. (a) is true in case the change in α has the special value $\Delta_v\alpha$ given by

$$\Delta_v\alpha = \sqrt{2}(\Delta r)/r'. \qquad \text{(d)}$$

diagram where these properties overlap. For example, suppose the v_1 vibration is the stronger and the rotational structure is J_-K_-, then the possible changes in dimensions are represented by the area common to the vertically shaded region and the undotted region in the neighborhood of the positive $\Delta r/r'$ axis. At first it may appear that there still remains a considerable range of allowed changes in dimensions. However, a closer study should confine the region still more. For clearly, near the lower boundary (dashed line) of the region in the foregoing example, $(v_1)_{\max} \approx (v_2)_{\max}$. In addition, the J structure converges relatively slowly. For changes corresponding to points near the $\Delta r/r'$ axis, $(v_1)_{\max} > (v_2)_{\max}$ definitely, and both J and K structures degrade approximately at the same rate. Finally, in the vicinity of the upper boundary (solid line) the coarse K structure should degrade rather slowly, if at all.

A more favorable case occurs when the v_2 vibration is the more prominent and both J and K structures degrade in the same direction. In this instance, the overlapping regions are quite small.

If, for some molecule, the dotted region should coincide with the vertically-shaded region, one could determine from the J, K shading which vibration would be more prominent. Conversely, if the vibrational intensity were known, the J, K shading could be determined. Finally, from the figure the remarks made in connection with Tables II and III can be confirmed.

Some actual cases may be considered. Recent photographs of the absorption spectrum of ClO_2 taken on the 30-foot grating spectrograph by J. B. Coon in this laboratory[11] provide an interesting example to show the correlation between vibrational and rotational analysis. Here the structure is J_-K_- and both structures converge approximately at the same rate. On the basis of the present work it was seen that this indicates an increase in bond distance as the principal change in the transition and identifies the long series of some twenty bands as belonging to the breathing rather than the deformation frequency. The subsequent analysis proved this.

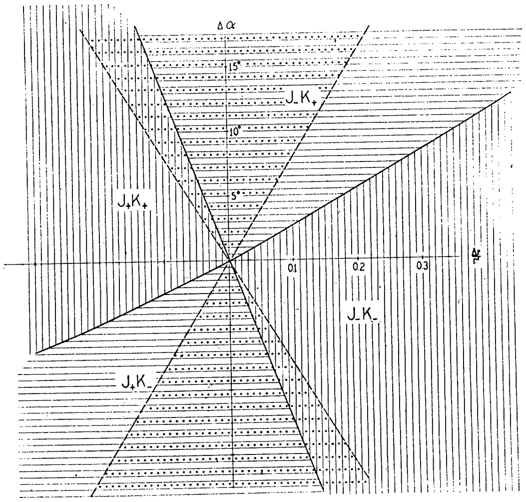

FIG. 9. A schematic diagram showing the directions of shading of the J and K structures for simultaneous changes in angle and in bond distance. As before, the subscripts indicate direction of shading (+, toward ultraviolet; −, toward red). Change in the value of the apex half-angle in degrees is plotted as ordinate, and $\Delta r/r'$ as abscissa, where $\Delta r = r' - r''$. The whole field is divided by two intersecting full heavy curved lines into four regions J_+K_+, J_-K_+, J_-K_-, J_+K_- indicated by horizontal or vertical hatching. The field is also divided in another way into four regions by two intersecting dashed lines: in the dotted region, the deformation is more prominent than the symmetrical valence vibration, whereas the opposite is true in the undotted region.

Photographs of the λ3880 system of SO_2 taken by Metropolis and Beutler[3] show quite other characteristics. Here the structure is J_-K_+. Of the two possibilities, case C_1 of Table II ($+\Delta\alpha$, $-\Delta r$) is excluded because long progressions of the deformation frequency are not evident. Hence it must be case A_1 ($+\Delta\alpha$, $+\Delta r$), and this is confirmed by the fact that the K structure converges more slowly than the J. That the changes are small is confirmed by the fact that the combination band having one quantum of each of the totally symmetrical vibrations is the strongest.

ACKNOWLEDGMENTS

The author is indebted to Professor Robert S. Mulliken, Dr. Hans G. Beutler and Dr. Wave H. Shaffer for their suggestions and encouragement and for many helpful discussions. Dr. Shaffer was also kind enough to help with the calculations of the intensity factors which were used for Figs. 3–6.

---

[11] J. B. Coon, Phys. Rev. **58**, 926(L) (1940).