

On the Interpretation of the Rotational Structure of the CO₂ Emission Bands

By ROBERT S. MULLIKEN

Ryerson Physical Laboratory, University of Chicago

(Received September 17, 1932)

Schmid's analysis of the rotational structure of a number of the ultraviolet CO₂ emission bands is discussed, and it is pointed out that in spite of uncertainties, some definite conclusions can be drawn, notably that the molecule in equilibrium is nearly linear, or probably strictly linear, in both initial and final states, that B' is nearly equal to B'' , and that the values of both are approximately known (cf. Schmid). It is also shown that the bands are most probably of the type ${}^1\Pi \rightarrow {}^1\Pi$, but possibly ${}^1\Sigma \rightarrow {}^1\Sigma$ or (much less likely) ${}^2\Sigma \rightarrow {}^2\Sigma$ or some other type. If ${}^2\Sigma \rightarrow {}^2\Sigma$ the emitter must be CO₂⁺, otherwise CO₂. It is proposed to designate by κ the quantum number corresponding to the angular momentum of rotation of the carbon atom relative to the O atoms around the O-C-O axis. It is pointed out that in electronic bands, one expects predominantly $\Delta\kappa=0$. This rule is then applied to possible interpretations of the band structures. Some suggestions are also made concerning the vibrational analysis. Evidence from the values of B and ν_1 is stated, which supports Smyth's interpretation of the a and c series as ν_1' progressions. It is suggested that the isolated bands $\lambda\lambda 2896, 2883$ may be the (0,0) band of a ${}^2\Pi \rightarrow {}^2\Pi$ transition of CO₂⁺ with B' and B'' almost equal.

RECENT work by Schmid¹ in this laboratory on the rotational structure of a number of ultraviolet CO₂ emission bands has revealed an unexpectedly simple structure. Schmid's work indicates that the spectrum contains at least three band systems. The bands whose analysis he has published probably all belong to one system. They consist of P -form and R -form branches of about equal intensity, each showing staggering, i.e., being composed of doublets but with alternately the high- and low-frequency component of each doublet missing.

The observed structures are consistent with a molecular structure which when at rest is linear in both initial and final states. Small departures from linearity would apparently not affect the qualitative nature of the energy level scheme nor, for most practical purposes, the selection rules, but a large departure in either or both states would surely give rise to a less regular and simple band structure.²

For a symmetrical linear molecule, the electronic states can be classed as ${}^1\Sigma_g^+$, ${}^1\Sigma_g^-$, ${}^3\Pi_u$, etc., just as for a diatomic molecule, and the selection rules for electronic quantum numbers should be the same. The existence of three characteristic vibrations (quantum numbers ν_1 , ν_2 , and ν_3) does not affect in any essential way the structures of individual bands, although the fact that levels with given electronic and rotational quantum numbers change

¹ R. F. Schmid, Phys. Rev. **41**, 732 (1932).

² D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931) for the basis of these statements. Also Phys. Rev. **41**, 304 (1932).

from symmetrical in the nuclei to antisymmetrical, or *vice versa*, when v_3 changes from even to odd,² is essential in deciding which particular rotational levels and lines are present, which missing, in any given band.

The rotational energy is given for a diatomic molecule without electronic angular momentum by:

$$E_r/hc = \text{const.} + BK(K+1) + \dots$$

If $\Lambda > 0$ and $S > 0$ this is still essentially true, but every level is split up into a fine doublet (Λ -type doubling), the width of this increasing in general with K .³ If the molecule has two equal nuclei without spin, one component of each double level, alternately the upper and the lower, is missing. If $S > 0$, the case is more complicated, unless the spin is very loosely coupled. (This is usually true only for $\Lambda = 0$.) For a linear triatomic molecule like CO₂ there is an added complication in the existence² of a quantum number κ associated with, roughly speaking, the rotation of the C nucleus around the line joining the two O atoms.⁴ Λ and κ play similar roles. If $\Lambda = 0$, we expect κ -type doubling, with one component of each doublet missing, when $\kappa > 0$.² In analogy with Λ -type doubling, we might expect to find the doubling usually largest for $\kappa = 1$, much smaller for $\kappa = 2$, and so on. If $\Lambda > 0$ and $\kappa > 0$, the matter is more complicated (see below).

In general, Λ and κ are expected to obey the selection rules $\Delta\Lambda = 0, \pm 1$ and $\Delta\kappa = 0, \pm 1$. But since there is relatively little interaction, "coupling," between the nuclear motion connected with κ and the electron motions, one may expect in the case of an electronic band system to find practically only bands with $\Delta\kappa = 0$. This rule is similar to the rule $\Delta M_S = 0$ for atoms in the Paschen-Back effect and to the rule $\Delta\Sigma = 0$ for diatomic molecules in Hund's case *a*.³

With $\Delta\kappa = 0$, one expects band structures and intensity relations of exactly the same types as for diatomic molecules, except for some complications in the fine structure of $\kappa > 0, \Lambda > 0$. For instance, we can speak of cases, *a, b, c, d* of Hund.³ The bands analyzed by Schmid can hardly be case *a* bands, since these would show multiplet structure (e.g., heads all in pairs, or in triplets with approximately constant spacing), and in all probability would show noticeable Zeeman effects at high quantum numbers, contrary to Schmid's observations. Nor are they of the type with one state case *a*, the other case *b*.³

The bands must then be case *b*, with $S > 0$, or else be singlet bands ($S = 0$). Other cases (*c* and *d*) can safely be excluded for a molecule such as CO₂. The observed *P*-form and *R*-form branches are then surely actual *P* and *R* branches ($\Delta K = \pm 1$). Bands having *P* and *R* branches and no *Q* branches (or very weak *Q* branches) have $\Delta\Lambda = 0$, and an electric moment vibrating parallel

³ R. S. Mulliken, Rev. Mod. Phys. **3**, 89 (1931).

⁴ The symbol κ has been chosen here after some consideration in preference to Dennison's *l*. Since it is likely to be of considerable importance, it seems desirable to have a unique symbol for this quantum number. The use of a Greek letter for a rotation around the figure axis of a molecule is in accordance with diatomic usage; the choice of κ suggests that, as with K , we are dealing with a nuclear rotation.

to the axis (here the O-C-O line). If $S > 0$, the band lines should almost certainly show evidence of fine structure if $\Lambda > 0$, and very probably even if $\Lambda = 0$. Only in the higher energy states of very light molecules (H_2 , He_2) is such fine structure so narrow as to escape observation (case b') for $\Lambda > 0$. For $\Lambda = 0$, $S = \frac{1}{2}$ (${}^2\Sigma \rightarrow {}^2\Sigma$ transition) there might possibly be an unobserved fine structure for CO_2 , since ${}^2\Sigma$ states of NO and CO^+ are known with separations that are barely detectable or not detectable. But it is much more likely that, if the bands were really ${}^2\Sigma \rightarrow {}^2\Sigma$, some evidence of fine structure would have been found among the many bands and band-lines examined. Actually there is no evidence whatever of splitting or broadening of the lines in the absence of a magnetic field,—other than the staggered-doubling, which cannot possibly be a spin effect, since with spin doubling both components of a double line would be present or absent together.³ The possibility ${}^3\Sigma \rightarrow {}^3\Sigma$ can be practically excluded, since in diatomic molecules (O_2 , NH , N_2 , etc.), except He_2 , this gives a fine structure too large to be missed.

One concludes then that very probably $S = 0$, but that possibly the bands are ${}^2\Sigma \rightarrow {}^2\Sigma$. Of course if the emitter is CO_2 , as Smyth considers probable,⁵ the latter possibility is excluded. On the other hand, $S = 0$, is excluded if it is CO_2^+ .

The bands correspond, then, very probably to one of the types ${}^1\Sigma \rightarrow {}^1\Sigma$, ${}^1\Pi \rightarrow {}^1\Pi$, ${}^1\Delta \rightarrow {}^1\Delta$, etc. Schmid's result that no Zeeman splitting or measurable broadening is observed even in strong fields¹ excludes all but ${}^1\Sigma \rightarrow {}^1\Sigma$ and ${}^1\Pi \rightarrow {}^1\Pi$. His definite observation that the low-numbered P lines are probably broadened (*apparently* weakened) agrees with what would be expected for the Zeeman effect of ${}^1\Pi \rightarrow {}^1\Pi$. (The corresponding low-numbered R lines are obscured by other lines.) The fact that weak Q branches would be expected (just a few lines at low J values) for ${}^1\Pi \rightarrow {}^1\Pi$, etc., but not for ${}^1\Sigma \rightarrow {}^1\Sigma$, is no objection to the ${}^1\Pi \rightarrow {}^1\Pi$ interpretation, since Schmid could not have detected these Q lines amid the strong and crowded R lines. A possible real objection, connected with the expected simultaneous occurrence of Λ and κ -type doubling, will be mentioned later. ${}^1\Sigma \rightarrow {}^1\Sigma$ should show no Zeeman effect, or at most a slight broadening at *high* quantum numbers. The same is true of ${}^2\Sigma \rightarrow {}^2\Sigma$ if, as we must suppose here in order to consider this case at all as a possibility, the spin is very loosely coupled, since then $\Delta M_S = 0$.

From the foregoing it would seem most probable that the bands are ${}^1\Pi \rightarrow {}^1\Pi$, with ${}^1\Sigma \rightarrow {}^1\Sigma$ as a second important possibility in case some unexpected explanation of the magnetic behavior of the low-numbered P lines can be found, and with ${}^2\Sigma \rightarrow {}^2\Sigma$ as a rather remote possibility.

The bands analyzed by Schmid all show exactly the same type of structure, except for differences in the magnitude of the staggering. The strongest bands analyzed are three bands of the a progression of Smyth ($\lambda\lambda 3247$, 3370 and 3503) and three bands of Smyth's c progression ($\lambda\lambda 3254$, 3377 and 3511). The c bands show staggering, the a bands none within the experimental error,

⁵ H. D. Smyth, Phys. Rev. **38**, 2000 (1931); **39**, 380 (1932); cf. also H. J. Henning, Ann. d. Physik **13**, 599 (1932).

but as Schmid shows, we may assume that a very small staggering is actually present.

Now as will be seen by reference to reproductions given by Smyth,⁵ and by Fox, Duffendack and Barker, each of the *a* bands above mentioned is the first, and also the strongest, member of a well-marked group of bands extending toward longer wave-lengths. No bands which could be associated with the group, except a few of much lower intensity, occur on the short wave-length side of the *a* band of each of these groups. Following each *a* band closely on its long wave-length side, and nearly as strong as the *a* band, is a *c* band. At longer wave-lengths in each group is a more or less irregular distribution of weaker bands (members of Smyth's series *b*, *d*, *n* and *j*). A few of these have been analyzed by Schmid; they include two examples with no observable staggering ($\lambda\lambda 3546$ and 3674), one with small staggering ($\lambda 3534$), and one with rather large staggering ($\lambda 3839$); one or two of these (especially $\lambda 3839$) may, however, perhaps not belong to the same system as the others.

The most natural interpretation of the above results consistent with the rule $\Delta\kappa=0$ and a ${}^1\Pi\rightarrow{}^1\Pi$ electronic transition is that the strong bands *a* and *c* correspond to low values, presumably 0 and 1, of κ and also of the related² quantum number v_2 ($\kappa=v_2$ for $v_2=0, 1$), the other bands to higher v_2 or κ values. Since $\kappa'=\kappa''$, the intensity distribution among different κ values would be determined by the initial (κ') distribution. The fact that each group starts suddenly with a strong band (*a*) is most easily understood if this band has $\kappa=0$, and $v_2=0$. With $\kappa=0$, we should have pure Λ -type doubling, with alternate components of each doublet missing, giving staggering. The fact that each branch (*P*, *R*) appears in the *a* bands to consist of a single series of lines without staggering is not unreasonable, since the Λ -type doublets might happen to be very narrow. (In the angstrom bands of CO, for instance the Λ -type doubling in the ${}^1\Pi$ states is too small to detect except for very high *J* values.) This is especially true (cf. Schmid's Fig. 2) since the observed band-line displacements depend on *differences* of displacements in the initial and final ${}^1\Pi$ states. With $\kappa=v_2=1$, assumed in the *c* bands, we might have κ -type doubling to explain the observed staggering; or the fact that $\kappa, v_2>0$ may increase the Λ -type doubling. [For a nonlinear molecule, a ${}^1\Pi$ state must split into two electronic states; and $\kappa>0$ or $v_2>0$, since it throws the C atom out of line with the O atoms, should induce such a splitting, giving Λ -type doubling even without rotation. Such a constant splitting might, however, escape observation.] With $\kappa=1, \Lambda=1$, there should be a quadrupling of each rotational level but with two components of each level missing; and unless they should more or less accidentally coincide, it would seem that each of the observed band-lines should be double (i.e., each line theoretically quadruple but with two components missing, alternately one pair and the other pair in adjacent lines; it can easily be shown theoretically that quadruple levels should give here quadruple lines, not more complex groups). The fact that only a staggered series of simple lines, not of doublets, is observed, tends to discredit the present interpretation. But until theoretical calcula-

tions have been made on the nature of combined κ - and Λ -type doubling, it seems worth considering. Another difficulty, however, is the fact that one would expect bands for which $\kappa = v_2$ has the values 0, 1, 2, \dots to form a nearly uniformly-spaced series, since the levels associated with v_2' and v_2'' should have approximately the uniform spacings characteristic of the harmonic oscillator; actually, the bands a , c , and so on, in each group are irregularly spaced.

An alternative interpretation may be attempted as follows. Disregarding as not quite conclusive the Zeeman effect evidence in favor of ${}^1\Pi \rightarrow {}^1\Pi$, suppose the bands are ${}^1\Sigma \rightarrow {}^1\Sigma$ (or ${}^2\Sigma \rightarrow {}^2\Sigma$). In this case there is no Λ -type doubling, only κ -type doubling, and if $\kappa > 0$ everything is consistent with the observed band structures. But for $\kappa = 0$, with $\Lambda = 0$, the rotational levels must be single, and now the requirement that every other level shall be missing means that for every other J value no level at all exists (with $\Lambda > 0$ or $\kappa > 0$, at least one level is present for every J value). This would give bands with alternate missing lines, i.e., with a spacing apparently twice as large as for bands with $\Lambda > 1$ or $\kappa > 1$. But the bands without appreciable staggering, to which we have tentatively assigned $\kappa = 0$, are in all other respects the same as the bands with staggering, so that the idea of alternate missing lines must be rejected (cf. also Schmid's evidence based on intensity measurements).¹ Hence if $\Lambda = 0$ for the a bands, we must rule out $\kappa = 0$. If $\kappa = 0$ does not apply to the a bands, then presumably there are other bands somewhere with $\kappa = 0$, since there is no theoretical reason why the transition $\kappa = 0 \rightarrow \kappa = 0$ should not occur. One might assume, for instance, $v_2 = 3$, $\kappa = 3$, for the a bands, $v_2 = 3$, $\kappa = 1$ for the c bands, and suppose that $v_2 = 2$, $\kappa = 2$; $v_2 = 2$, $\kappa = 0$; $v_2 = 1$, $\kappa = 1$; $v_2 = 0$, $\kappa = 0$ are among the weaker bands in the group. But this would require a rather surprising initial distribution (v_2' , κ'), as well as an improbable arrangement of the initial and final energy levels associated with v_2 and κ , such as to form a kind of band-group head just at the a band, with both lower and higher numbered bands at longer wave-lengths. Everything considered, the ${}^1\Pi \rightarrow {}^1\Pi$ interpretation seems more probable than a $\Sigma \rightarrow \Sigma$ interpretation, but both interpretations are tentative and far from satisfactory.

We may turn next to some other points connected with Schmid's analysis. Usually when a diatomic spectrum is analyzed, the correctness of the analysis is not considered as proved until conclusive combination agreements, i.e., agreeing sets of ΔT values, have been found for both initial and final electronic states. But when one is sure that the bands belong to a definite type, or to one of a few closely similar types, these requirements can be relaxed in some respects. In the case of Schmid's analysis of three of the c bands, combination agreements within experimental error are found for any of two or three different interpretations. According to these all the c bands may have a common initial state, or all may have a common final state in agreement with Smyth's vibrational analysis,⁵ or two may have a common initial, two a common final state. Corresponding statements hold for the three a bands analyzed by Schmid. One might think then that the analysis proves nothing, but this is far from being true. Schmid's results determine

within one or at most two units the correct rotational quantum numbers (K) of the band lines, and also determine the values of the rotational constants B' and B'' , and the moment of inertia and dimensions of the excited molecule, within a few percent. That is, we know that the correct values of B' and B'' must be chosen from just a few possible sets whose values do not differ much. Also, the difference $B' - B''$ is accurately known from the band structure, so that with the B values themselves approximately known, we can definitely conclude that B' and B'' are *nearly equal*. Further, Schmid's work shows definitely that neither B' nor B'' can be *exactly* the same in any of the a as in any of the c bands, but also that they are certainly very *nearly* the same in the a and c series. Schmid's work also indicates, but somewhat less conclusively, that the B' and B'' values are nearly the same in all the bands he has analyzed. These results are in agreement with the present interpretation according to which the a and c bands, since $\Delta\kappa = 0$, must differ in both initial and final states in respect to v_2 and κ at least. They do not support Smyth's assignment of a common final level to the a and c series but are not inconsistent with his formulation of the a and c series each as a v_1' progression.

Of the three or four possible combinations (ΔT sets), of which just one must be correct, indicated by Schmid's analysis for the series a and c , certain ones give almost exact integers for the effective rotational quantum numbers, the others almost exact half-integers.¹ The best agreement comes for one of the half-integral sets in each case. But the agreement is only slightly poorer for one of the integral sets. Since for a diatomic or linear polyatomic molecule the theory appears absolutely to demand integral K values for case b and for singlet transitions ($^1\Sigma \rightarrow ^1\Sigma$, $^2\Sigma \rightarrow ^2\Sigma$, $^1\Pi \rightarrow ^1\Pi$, or any other singlet or $\Sigma \rightarrow \Sigma$ transitions), it seems necessary to rule out the possible combinations which would give half-integral rotational quantum numbers. (In speaking of integral K values, we are using the formula $BK(K+1) + \dots$ for the rotational energy.) Half-integral values would be expected only for J values, in case a with S half-integral, but as has been mentioned above, the bands show no evidence of the multiple-headed structure necessary for this case, nor of the Zeeman effects probably to be expected (because of partial going-over to case b at high J values). Nevertheless, in view of the difficulties experienced in interpreting the bands as singlet or case b bands, it may be well not to exclude absolutely the possibility of case a bands. The most likely case a type, consistent with the observed P , R structure, would be $^2\Pi \rightarrow ^2\Pi$.

Ruling out half-integral numbers would restrict the possible combinations considerably. If one could be perfectly sure from the vibrational analysis that the a bands all have a common final state and constitute a v_1' progression, and the c bands likewise, as indicated by Smyth's tentative analysis, the correct combinations could be given with considerable confidence. New evidence in favor of the interpretation of the a and c bands as v_1' progressions, in spite of the difficulty in understanding an intensity distribution involving a range of v_1' values and only one v_1'' value, can be given as follows.

The well-known empirical relation that the quantity ω_e/B_e is very nearly

a constant for all states of a single diatomic molecule might reasonably be expected to be capable of extension to the linear CO_2 molecule, at least if we use ν_1/B , where ν_1 refers to the symmetrical vibration. Taking ν_1/B for the normal state of CO_2 ,⁶ one finds almost the same value as one obtains for the upper level of the ultraviolet emission bands using $\nu_1' = 1137$ (cf. Eq. (1) below) and using the most probable B' value of Schmid. No such good agreement is obtained if one uses Schmid's B'' and uses for ν_1 a value secured by reinterpreting the a or c series as ν_1'' progressions. Hence Smyth's interpretation of these ν_1' progressions receives strong support.

The reader may wonder why, in spite of his very accurate measurements, Schmid's analysis does not permit a decision between several different possible sets of combination differences. This is because of the fact, shown by Schmid's analysis, that if for instance we agree with Smyth that the a (or c) bands constitute a ν_1' progression, then the constant B' varies only very slightly with ν_1' . That is, if we write $B = B_0 - \alpha_1\nu_1 - \alpha_2\nu_2 - \alpha_3\nu_3 + \dots$ in analogy with the diatomic relation $B = B_0 - \alpha v + \dots$, we find that the ratio α_1'/B' is very much smaller than the usual values of α/B for diatomic molecules,—although it has the same sign as is usual in the diatomic case. The former fact causes several sets of possible combination differences to agree so closely that the differences between them cannot be certainly distinguished from experimental error.

If we should assume that the a (or c) bands have a common *upper* level and a set of lower levels differing by unit steps of ν_1'' , we would conclude that α_1''/B'' is very much smaller than α/B for diatomic molecules, so that the same difficulty as before would arise for the analysis. In this case α'' has the opposite sign to that usual in diatomic molecules, i.e., α in the above equation is negative.

With the assumption of a common lower level for the bands of the a (or c) series, the vibrational analysis⁵ gives an equation of the form

$$\nu = \text{const.} + 1136.85\nu' - 1.85\nu'^2. \quad (1)$$

Here the ratio x of the coefficients of ν'^2 and ν' is much smaller than in diatomic molecules, in agreement with the behavior of the ratio α/B . In diatomic molecules too the ratios x and α/B are closely related, and in the only two known diatomic cases where x has a negative sign, and only in these cases, α also has a negative sign. If, contrary to Smyth's analysis, and in spite of the evidence given above based on the value of ν_1/B , the a and c series should turn out to be ν_1'' progressions, x and α would have negative signs. Although this case is rare in diatomic, there is evidence that it is less so in polyatomic molecules. That the a and c series are *either* ν' progressions or ν'' progressions, and that the variable v is ν_1 , seem to have been fairly well established.⁵

Since Schmid's analysis shows that B' and B'' are nearly equal, so that the dimensions of the molecule change very little in emitting the ultraviolet

⁶ Martin and Barker, Phys. Rev. **41**, 291 (1932). For ν_1 we may take the *average* of the two observed frequencies which result from the interaction of ν_1 and $2\nu_2$ ($\nu_2 = 2$, $\kappa = 0$).

bands, we can make by means of the Franck-Condon principle some predictions in regard to the intensities for various vibrational transitions. The most probable changes should be those conforming to $\Delta v_1=0$, $\Delta v_2=0$, $\Delta v_3=0$, except in case one or more of the v 's has a large initial value or large initial values. Apparently this is true of v_1 . The fact that the band system is not more complicated than it is suggests that perhaps $v_3'=0$ mostly, and $\Delta v_3=0$, that v_2' (and κ') are confined mostly to a few small values, and that $\Delta v_2=0$ only (incidentally, $\Delta \kappa=0$ requires $\Delta v_2=\text{even}$, in view of the fact that κ is limited to the values $v_2, v_2-2, \dots 0$ or 1).

An initial distribution involving one or several fairly large v_1' values can be understood if it is produced⁵ by electron impacts on unexcited molecules having mostly $v_1=0$, $v_3=0$, $v_2=0$ or 1 (the frequency ν_2 is the smallest of the three, and molecules with $v_2>0$ might be moderately abundant in the unexcited gas). Since the equilibrium dimensions of the molecule, which is linear in both states, are considerably different before and after electron impact in this case,^{1,6} the latter should tend mainly to excite v_1 , but v_3 not at all, and v_2 only indirectly through coupling of v_1 and v_2 .

Something further needs now to be said about the Λ -type or κ -type doubling found by Schmid. As Schmid has shown for the band $\lambda 3839$, the combination differences ΔT are surely of one of two classes. (Since $\lambda 3839$ has no state in common with any of the other bands analyzed, it is impossible to make tests of the possible combination differences by comparison with other bands; but by analogy considerations the numbering of the lines can be established within a few units;¹ all the possible combinations then fall into these two classes.) Corresponding remarks apply, Dr. Schmid has informed the writer, to the other bands measured by him but not belonging to the a and c series. In one of the two classes, the effective rotational quantum numbers are approximately integral (exactly so where the staggering is small), in the other approximately or exactly half-integral. If the analysis is carried through assuming integral quantum numbers, it shows that the Λ -type or κ -type doubling is moderately large, but if half-integral quantum numbers are assumed, it must be much smaller. In view of theoretical considerations presented above, showing that the rotational quantum numbers ought almost certainly to be integers, it appears necessary to accept one of the sets of possible combination differences which involve integral quantum numbers. But whether one of the integral or of the half-integral sets is adopted, Schmid's work shows perfectly definitely that the Λ -type or κ -type doublet-widths are not greatly different in the initial and final states, also that the departures of the positions of the two doublet components x and y from the positions given by $BK(K+1)$ are of the form $\text{const.}_i + a_i K + b_i K(K+1)$, with $a_x = -a_y$; and that b_x and b_y differ considerably, although only $b_x - b_y$ is determinable from the data. These details may prove of considerable value for the analysis of the system.

The definite fact, established by Schmid's work, that the doubling is nearly the same in the initial and final states suggests that the two states are closely similar in respect to the wave functions and energy levels dependent

on ν_2 and κ , in agreement with conclusions stated above based on the near-equality of B' and B'' . A difficulty in the way of this conclusion, however, is the fact that there is a considerable interval (about 65 cm^{-1}) between each a band and the nearest c band. If ν_2 is about 600 cm^{-1} , as in the infrared or Raman spectra of CO_2 , and if for the a bands $\nu_2 = \kappa = 0$ for both initial and final states while for the c bands $\nu_2 = \kappa = 1$, then ν_2 must be about 10 percent different for the initial and final states, which is rather surprisingly large. Consideration of the bands in each group other than a and c increases this difficulty (cf. above).

In conclusion, it may be remarked that a great deal remains to be done before the problem of the structure of this system of CO_2 bands will be completely solved.

A rather casual suggestion concerning the interpretation of the two strong CO_2 bands near $\lambda 2896$ and 2883 may be worth making. The evidence of those who have worked on these bands shows rather clearly that they do not belong to the same system as those discussed above. Duncan's measurements,⁵ and those of Schmid, show probable P , Q and R branches, and Schmid's work shows also that all the band lines have pronounced Zeeman effects. The doublet structure ($\lambda 2896$, 2883) can be interpreted by a transition ${}^2\Pi \rightarrow {}^2\Pi$ (or possibly by some other transition between doublet states) in CO_2^+ . The doublet width has a reasonable value for a molecule like CO_2^+ . The fact that only a single isolated double band is found can be understood by the Franck-Condon principle if the constants of the molecule (assumed linear) are practically identical in initial and final states. The band is then to be interpreted as having $\nu_1' = \nu_2' = \nu_3' = 0 = \nu_1'' = \nu_2'' = \nu_3''$, probably with weaker bands superposed having one or more quantum numbers greater than zero. This interpretation is supported by the band structure, which is of a type expected when B' and B'' are very nearly equal. Several cases like this are known among diatomic band spectra, e.g., the NH band at $\lambda 3360$, which is a strong $(0,0)$ band with a $(1,1)$ and other weaker bands superposed.