

l-Type Doubling in Linear Polyatomic Molecules

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The infra-red spectra of C_2H_2 , HCN, and CO_2 give evidence of a splitting of the Π vibrational levels (in which a \perp vibration is singly excited) into two components which is entirely analogous to the Λ -type doubling of the electronic states of diatomic molecules and is called here *l*-type doubling. The experimental data show that this *l*-type doubling may be represented by $\Delta\nu = q_i J(J+1)$ and that the constant q_i is of the same order as the constant α_i in $B_{[v]} = B_e - \sum \alpha_i (v_i + \frac{1}{2}d_i)$. The existence of the *l*-type doubling also explains the apparent discrepancy that the fundamental bands of HCN and C_2H_2 do not show a convergence of the *P* and *R* branches while the *Q* branch is distinctly shaded to shorter wave-lengths. A preliminary

theoretical treatment of the *l*-type doubling is also given. The doubling is due mainly to the fact that in the displaced position of a perpendicular vibration a linear molecule is a slightly asymmetric top, but to some extent also to the Coriolis interaction of different vibrations. The observed values of q_i are all larger than the calculated ones. Taking the *l*-type doubling into account the rotational constants α_i of CO_2 have been newly evaluated and from them and the value $B_{000} = 0.3895_0 \text{ cm}^{-1}$ the rotational constant B_e in the equilibrium position is found to be $0.3906 \pm 0.0002 \text{ cm}^{-1}$ which gives for the moment of inertia $I_e = 71.67 \cdot 10^{-40} \text{ g cm}^2$ and for the CO distance $r_e = 1.1615 \cdot 10^{-8} \text{ cm}$.

A. INTRODUCTION

IT is well known that the perpendicular vibrations of linear polyatomic molecules are doubly degenerate and that this double degeneracy is entirely analogous to the double degeneracy of Π , Δ , \dots electronic states of diatomic molecules except that in the first case we have a vibrational angular momentum l about the internuclear axis, in the second case an electronic angular momentum Λ . According to Mulliken¹ the vibrational states of linear polyatomic molecules are designated in the same way (Σ^+ , Σ^- , Π , Δ , \dots) as the electronic states of diatomic molecules, depending on the value of the quantum number l instead of Λ . If several perpendicular vibrations are excited or if one perpendicular vibration is multiply excited, the resultant l is obtained from the individual l_i 's in the same way as Λ is obtained from the individual λ_i 's. However, it must be realized that, for a given vibrational quantum number v_i of a perpendicular vibration, l_i can only assume the values v_i , $v_i - 2$, $v_i - 4$, \dots 1 or 0.

For diatomic molecules the double degeneracy of Π , Δ , \dots electronic states is removed with increasing rotation of the molecule on account of the interaction of rotation and electronic motion: we have the Λ -type doubling. Similarly one would expect the double degeneracy of the Π , Δ , \dots vibrational states of linear polyatomic

molecules to be removed with increasing rotation on account of the interaction of rotation and vibration, leading to *l*-type doubling. It appears that the possibility of this *l*-type doubling or at least its appreciable magnitude has not been recognized in recent theoretical work on the infra-red spectra of linear polyatomic molecules.^{2,3} But experimental evidence for it, in the case of C_2H_2 , was obtained six years ago by Funke and Herzberg⁴ and later by Funke and Lindholm.⁵

In what follows we shall summarize the experimental evidence for *l*-type doubling in the case of C_2H_2 , add further evidence for it in the cases of HCN and CO_2 , and attempt a preliminary theoretical discussion.

B. EXPERIMENTAL EVIDENCE

Just as for the Λ -type doubling of diatomic molecules, the *l*-type doubling of linear polyatomic molecules is of an appreciable magnitude only for Π states, for which it is proportional to $J(J+1)$. In other words the two components of a Π state have slightly different effective rotational constants B . In one Π substate (Π^+) the even rotational levels are positive, the odd

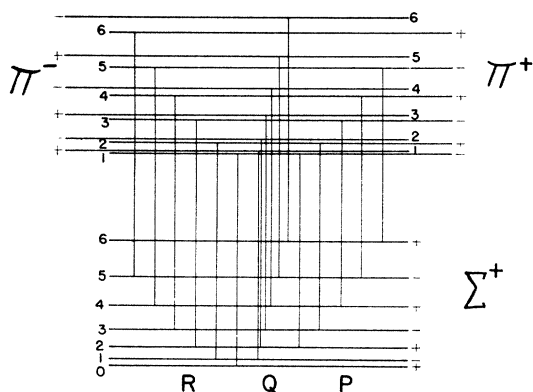
² D. M. Dennison, *Rev. Mod. Phys.* **12**, 175 (1940).

³ W. H. Shaffer and A. H. Nielsen, *J. Chem. Phys.* **9**, 847 (1941).

⁴ G. W. Funke and G. Herzberg, *Phys. Rev.* **49**, 100 (1936); G. W. Funke, *Zeits. f. Physik* **99**, 341 (1936); **104**, 169 (1936).

⁵ G. W. Funke and E. Lindholm, *Zeits. f. Physik* **106**, 518 (1937).

¹ R. S. Mulliken, *J. Phys. Chem.* **41**, 159 (1937).

FIG. 1. $\Pi-\Sigma^+$ vibrational transition.

negative, in the other (Π^-) the reverse is the case. Therefore and on account of the selection rule that positive rotational levels combine only with negative, in a $\Pi-\Sigma^+$ band (\perp band) the Q lines ($\Delta J=0$), as shown by Fig. 1, occur only for the $\Pi^- - \Sigma^+$ subband, the P and R lines only for the $\Pi^+ - \Sigma^+$ subband. If the l -type doubling is appreciable, therefore, a different B value in the upper state is obtained from the Q branch on the one hand and from P and R branches on the other. From the same reason the combination relation

$$R(J) - Q(J) = Q(J+1) - P(J+1)$$

is not exactly fulfilled but a combination defect appears which gives directly the sum of the splittings of the levels J and $J+1$. In $\Pi-\Pi$ bands (that is transitions in which a perpendicular vibration is excited in both upper and lower state) the P and R branches occur only for the $\Pi^+ - \Pi^+$ and $\Pi^- - \Pi^-$ subbands while the Q branches occur only for $\Pi^+ - \Pi^-$ and $\Pi^- - \Pi^+$. Thus a doubling of the lines occurs corresponding to the difference or the sum of the l -type doublings in the upper and lower states.

C_2H_2

In both these ways the l -type doubling has been established for C_2H_2 . The photographic infra-red $\Pi-\Sigma^+$ bands show the combination defect clearly. As an example Fig. 2 gives the splitting in the upper state of the band 9645A as a function of $J(J+1)$ according to Funke and Lindholm. Funke has also observed an

actual splitting in two $\Pi-\Pi$ bands. The measurements give values for the constant q of the l -doubling in the formula

$$\Delta\nu = qJ(J+1), \quad (1)$$

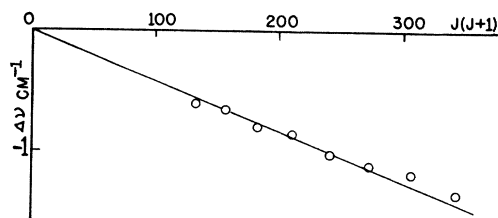
where, of course, q is the difference between the two effective B values referred to before. It is found that for the Π_g state in which the symmetrical perpendicular vibration ν_4 is singly excited $q_4 = 0.0059 \text{ cm}^{-1}$. This value is only very slightly changed when in addition various parallel vibrations are excited, with one exception, the upper state of the band 9600A for which $q = 0.0084 \text{ cm}^{-1}$ is found. The q value for the Π_u state in which only the antisymmetrical perpendicular vibration ν_5 is singly excited has not been directly obtained but it has been obtained for the upper state of the band 9645A in which $\nu_2 + 2\nu_3 + \nu_5$ is excited (see Fig. 2). For this state $q = 0.0038 \text{ cm}^{-1}$. It is very probable that the q value for the state ν_5 is close to this value. In all cases it is the Π^+ component that is the lower one.

It is interesting to compare the observed q values with the rotational constants α_i that occur in

$$B_{(v)} = B_e - \sum \alpha_i (v_i + \frac{1}{2}d_i) \quad (2)$$

and give the dependence of the average effective B values (that is, if the l -type doubling is neglected) on the vibrational quantum numbers v_i (d_i is the degree of degeneracy of the vibration ν_i). One finds $\alpha_4 = -0.0012$ and $\alpha_5 = -0.0015 \text{ cm}^{-1}$. Thus it is seen that the l -type doubling in the Π vibrational states of C_2H_2 is greater than the shift produced by the change of the average effective B values from that in the lowest state (B_0).

It is noteworthy that the fundamental ν_5 of C_2H_2 at 13.7μ shows no convergence in the P and R branches but a very distinct shading of

FIG. 2. l -type doubling in the upper state of the C_2H_2 band 9645A.

the (unresolved) *Q* branch toward shorter wave-lengths.⁶ This is immediately understood on the basis of the above data: The upper state of the *P* and *R* lines is Π^+ (see Fig. 1) whose *B* value is smaller than B_0 by the amount

$$\alpha_5 + \frac{1}{2}q_5 = -0.0015 + 0.0019 = 0.0004 \text{ cm}^{-1}.$$

Within the accuracy of the measurements⁷ this small difference does not cause any convergence. However, the upper state of the *Q* lines is Π^- whose *B* value is greater than B_0 by the amount $0.0015 + 0.0019 = 0.0034 \text{ cm}^{-1}$. This leads to a noticeable convergence of the *Q* branch toward shorter wave-lengths in agreement with observation.

HCN

For HCN Lindholm⁸ obtained from a $\Pi-\Pi$ band (without resolving the *l*-type doubling) a value $\alpha_2 = -0.0007$ for the change of *B* with ν_2 (the quantum number of the perpendicular vibration ν_2). On the other hand, from the measurements of the fundamental ν_2 by Bartunek and Barker⁹ using *P* and *R* lines only one obtains $B' - B'' = 0$ within the accuracy of the measurements (which corresponds perhaps to $\pm 0.0002 \text{ cm}^{-1}$ in *B*). The reason for this apparent discrepancy is not a lack of accuracy of the infra-red measurements, as Lindholm assumed, but lies in the *l*-type doubling. The determination of *B* from the $\Pi-\Pi$ band supplies an average of the *B* values of the two substates while the *P* and *R* branches of the fundamental ν_2 give the *B* value of the Π^+ substate which, in agreement with the behavior for C_2H_2 , is smaller than the average. The value of q_2 is twice the difference between B_{average} and $B(\Pi^+)$, that is approximately $q_2 = 0.0014 \text{ cm}^{-1}$. By this amount the *B* value of the Π^- substate should be greater than $B(\Pi^+)$. Therefore the *Q* branch should be shaded toward shorter wave-lengths and this has indeed been observed by Bartunek and Barker.

⁶ A. Levin and C. F. Meyer, J. Opt. Soc. Am. **16**, 137 (1928).

⁷ It should be remembered that $q_5 = 0.0038$ is probably somewhat too high since it is obtained from overtones. A smaller q_5 would lead to a still closer agreement of $B(\Pi^+)$ and B_0 .

⁸ E. Lindholm, Zeits. f. Physik **108**, 454 (1938).

⁹ P. F. Bartunek and E. F. Barker, Phys. Rev. **48**, 516 (1935).

TABLE I. Observed *B* values of the various vibrational levels of the CO_2 molecule.

Vibrational state			
ν_1	ν_2'	ν_3	$B_{[v]}$
0	0°	0	0.3895 ₀
0	1°(<i>PR</i>)	0	0.3899 ₅
0	2°	0	0.3899 ₆
1	0°	0	0.3897 ₁
0	0°	1	0.3866 ₀

CO_2

At the Ohio State symposium last year the author gave a reevaluation of the rotational constants of the CO_2 molecule. Table I gives the rotational constants obtained for the various vibrational levels using the usual numbering of the vibrations. The rotational constant α_3 is immediately obtained as the difference between B_{001} and B_{000} yielding $\alpha_3 = 0.0029_0$. The constants α_1 and α_2 may be obtained from the *B* values of the two resonating levels 02°0 and 10°0 if it is considered that these *B* values are the following mixtures of the unperturbed *B* values ($B_{[v]}^\circ$)

$$\begin{aligned} B_{02^\circ 0} &= a^2 B_{02^\circ 0}^\circ + b^2 B_{10^\circ 0}^\circ \\ B_{10^\circ 0} &= b^2 B_{02^\circ 0}^\circ + a^2 B_{10^\circ 0}^\circ, \end{aligned} \quad (3)$$

where *a* and *b* are the fractional contributions of the unperturbed to the perturbed vibrational eigenfunctions. By using the values $a^2 = 0.57$ and $b^2 = 0.43$ given by Adel and Dennison¹⁰ the values $\alpha_1 = 0.00056$ and $\alpha_2 = -0.00062 \text{ cm}^{-1}$ are obtained. On the other hand from the *B* value for the 01°0 state $\alpha_2 = -0.00045 \text{ cm}^{-1}$ would follow. The former α_2 value agrees much better with Dennison's² theoretical value -0.00069 than the latter. Again this apparent discrepancy is not due to any low accuracy of the measurements of the fundamental ν_2 but rather to the fact that only *P* and *R* lines have been used to evaluate the B_{010} value, that is, it refers to the Π^+ substate whereas the α_2 value obtained from B_{020} and B_{100} refers to the average of Π^+ and Π^- . The difference between the two α_2 values is half the constant $\frac{1}{2}q_2$ of the *l*-type doubling of the 01°0 state. The value of q_2 thus obtained is 0.00034 cm^{-1} . It should be realized that the possible error of this value is rather large since the coefficients a^2 and

¹⁰ A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933).

b^2 are somewhat uncertain and since the B values themselves are accurate only to within $\pm 0.00005 \text{ cm}^{-1}$. Using Dennison's theoretical value for α_2 one would obtain $q_2 = 0.00048 \text{ cm}^{-1}$ from the observed $B_{02^0_0}$ and $B_{10^0_0}$ without any assumption about a^2 and b^2 . At the same time one can then evaluate a^2 and b^2 and obtain $a^2 = 0.56$ and $b^2 = 0.44$. In this case α_1 would be 0.00071 cm^{-1} .

At any rate from the above an l -type doubling constant of the 01^1_0 state of CO_2 of the same order as the rotational constant α_2 seems to be established.

It may be mentioned that from the above α_i and B_{000} values the rotational constant B_e in the equilibrium position is found to be

$$B_e = 0.3906 \pm 0.0002 \text{ cm}^{-1},$$

where the stated error allows for the above-mentioned uncertainties of α_1 and α_2 . From B_e the moment of inertia and the internuclear distance in the equilibrium position are found to be

$$I_e = 71.67 \cdot 10^{-40} \text{ g cm}^2, \quad r_e = 1.1615 \cdot 10^{-8} \text{ cm},$$

while the effective values in the lowest vibrational state (obtained from B_{000}) are

$$I_0 = 71.87 \cdot 10^{-40} \text{ g cm}^2, \quad r_0 = 1.1632 \cdot 10^{-8} \text{ cm}.$$

It is believed that these values are more accurate than those hitherto published even though they are based on the same measurements.

C. THEORETICAL DISCUSSION

There are essentially three reasons for the change of the rotational constant B with the vibrational quantum numbers v_i , that is, three contributions to the rotational constants α_i : (1) the fact that even for strictly harmonic oscillations the mean value of $1/I$ is not equal to $1/I_e$ although the mean values of the internuclear distances are equal to their equilibrium values r_e ; (2) the fact that in consequence of the anharmonicity of the vibrations the mean values of the internuclear distances are in general larger than the equilibrium values, and (3) the influence of the Coriolis forces on the nuclei. For diatomic molecules only the first two reasons operate but for polyatomic molecules in addition

we have the effect of the Coriolis forces. We may therefore write

$$\alpha_i = \alpha_i^{(\text{harm})} + \alpha_i^{(\text{anharm})} + \alpha_i^{(\text{Cor})}. \quad (4)$$

It is now easy to see qualitatively that an l -type doubling is produced by the same reasons that produce the contributions $\alpha_i^{(\text{harm})}$ and $\alpha_i^{(\text{Cor})}$: If we consider that component of the perpendicular vibration in which the nuclei oscillate in a plane, σ_v^{\parallel} , through the axis of rotation of the whole molecule it is clear that the moment of inertia about the axis of rotation is not changed as long as the vibrations are harmonic since the nuclei move parallel to the axis of rotation. On the other hand for the component of the perpendicular vibration in a plane, σ_v^{\perp} , perpendicular to the axis of rotation, the moment of inertia is changed. We may therefore expect a splitting that is proportional to $J(J+1)$. This same effect may also be described as due to the fact that when a perpendicular vibration is excited the molecule is actually a slightly asymmetric top. For this asymmetric top the double degeneracy of levels with $K > 0$ of the symmetric top is removed (where, of course, K in our case is l).

In a similar way it is seen that a Coriolis force acts on the nuclei during a perpendicular vibration only when the vibration is in the plane σ_v^{\perp} but not when it is in the plane σ_v^{\parallel} . We expect therefore that the Coriolis interaction will produce a splitting that is proportional to $J(J+1)$.

Dennison² and Shaffer and Nielsen³ have derived formulae for the rotational constants α_i for CO_2 and C_2H_2 . From them one obtains for C_2H_2

$$\alpha_4^{(\text{harm})} + \alpha_4^{(\text{Cor})} = (B_e^2/\omega_4) + 4B_e^2\omega_4[\gamma^2/(\omega_1^2 - \omega_4^2) + \delta^2/(\omega_2^2 - \omega_4^2)], \quad (5)$$

$$\alpha_5^{(\text{harm})} + \alpha_5^{(\text{Cor})} = (B_e^2/\omega_5) + 4B_e^2\omega_5/(\omega_3^2 - \omega_5^2), \quad (6)$$

where γ^2 and δ^2 are constants depending on the masses, dimensions, and force constants of the molecule and where $\gamma^2 + \delta^2 = 1$. The formula for $\alpha_2^{(\text{harm})} + \alpha_2^{(\text{Cor})}$ for CO_2 results from (6) by changing the subscript 5 to 2. The formulae (5) and (6) have been derived without considering the possibility of l -type doubling. It appears, however, that the l -type doubling can be ob-

TABLE II. Comparison of observed and calculated q_i .

Mole- cule	Vibra- tion	q_i (observed)	q_i (calculated)
C ₂ H ₂	ν_4	0.0059 cm ⁻¹	0.0026-0.0032 cm ^{-1b}
	ν_5	0.0038	0.0023
CO ₂	ν_2	0.00034	0.00031
		-0.00048 ^a	

^a The two values correspond to two assumptions about α_2 (see above).
^b The two values correspond to $\gamma^2=1, \delta^2=0$, and $\gamma^2=0, \delta^2=1$, respectively. The correct value according to the above formula must be between the two limits given.

tained from Shaffer and Nielsen's Hamiltonian. It can easily be seen that non-diagonal matrix elements exist between the two mutually degenerate states $+l$ and $-l$ if (and only if) $l=1$. By taking this into account and following Van Vleck's treatment of the Λ -type doubling in diatomic molecules¹¹ it was found from a preliminary calculation that the constant of the l -type doubling in a state in which the perpendicular vibration ν_i is singly excited is given by

$$q_i = \alpha_i^{(\text{harm})} + \alpha_i^{(\text{Cor})}. \quad (7)$$

This result is confirmed by a calculation of the "harmonic" part of the splitting according to a formula given by Wang¹² for the splitting of the K doublets of a slightly asymmetric top. Wang's formula yields

$$q_i^{(\text{harm})} = \alpha_i^{(\text{harm})} = B_e^2 / \omega_i. \quad (8)$$

In Table II the observed q_i values for C₂H₂ and CO₂ are compared with those calculated on the basis of Eqs. (5) to (7). It is seen that in every case the observed q_i is greater than the calculated. In fact the observed q_i values, particularly the most reliable of the three, q_4 of C₂H₂, suggest that $q_i = 2[\alpha_i^{(\text{harm})} + \alpha_i^{(\text{Cor})}]$.

¹¹ J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

¹² S. C. Wang, Phys. Rev. **34**, 243 (1929).

It may be mentioned that in each case the contribution of $\alpha_i^{(\text{harm})}$ to q_i (calculated) is much greater than that of $\alpha_i^{(\text{Cor})}$, that is, the l -type doubling in linear molecules is predominantly an effect of the asymmetry of the molecule in the displaced position of a perpendicular vibration. However, the Coriolis forces will give a larger contribution when a suitable vibrational level is fairly close to the one considered. This is apparently the reason for the anomalously large l -type doubling in the upper state of the 9600A band of C₂H₂ mentioned previously.

Note added in proof: It should be noted that in Shaffer and A. H. Nielsen's paper³ the two terms in Eqs. (5) and (6) are written as one (with a common denominator). They are their $-b_{55}B_e$ and $-b_{44}B_e$, respectively. According to H. H. Nielsen and Shaffer (private communication) both terms, here called $\alpha_i^{(\text{harm})}$ and $\alpha_i^{(\text{Cor})}$ are due to Coriolis interaction. However there appears to be some room for divergence of opinion as to which terms are due to Coriolis interaction and which would occur even without it (harmonic terms). At any rate this difference of classification does not influence the actual theoretical formula for the l -type doubling given above which is based on Shaffer and A. H. Nielsen's Hamiltonian. But according to H. H. Nielsen and Shaffer it would not be correct to apply Wang's formula to obtain the harmonic part of the l -type doubling as has been done above as an alternative method. The writer still feels that the application of Wang's formula (which would certainly apply to a very slightly bent molecule) is justified even though not quite rigorous and gives a somewhat more easily visualizable explanation of the reason for the l -type doubling.