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The Infrared Absorption Bands of Acetylene

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The present interpretations of the overtone bands in the infrared spectrum of acetylene are unsatisfactory in that they either do not fulfill the known selection rules or else fail to give satisfactory numerical agreement between calculated and observed band positions. A new arrangement of the complete infrared spectrum of acetylene is given which is in accord with the selection rules and yields consistent numerical results. Several of the anharmonic and interaction constants are thus determined for the five fundamental frequencies. It is remarked that there is probably a direct connection between the magnitudes of these anharmonic constants and the intensities of the overtone bands.

It has been known for some time that the form of the acetylene molecule is linear and symmetrical. This was proved by the work of Levin and Meyer[1] and of Mecke and others[2] on its infrared absorption bands. Such being the case, it must possess five fundamental frequencies and it should be possible to interpret all of the observed infrared bands in terms of the allowed overtone and combination bands of these five fundamentals, the physical character of which is illustrated in Fig. 1. Several attempts have now been made to do this,[3] but none of them can be regarded as satisfactory. Those of Mecke, and of Lueg and Hedfield may be immediately disregarded since the selection rules given by Dennison[4] are fulfilled by neither of them, while that of Lochte-Holtgreven and Eastwood leads to flagrant discrepancies between the observed and calculated values of several combination frequencies.

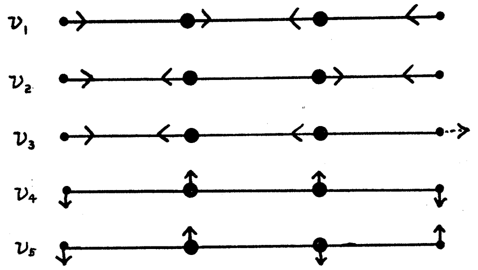

FIG. 1.

There is actually little doubt about the assignment of the five fundamental frequencies; these have been given their approximate values by Mecke, *viz.*

$$\nu_1=1975\text{ cm}^{-1},\quad \nu_2=3370\text{ cm}^{-1},\quad \nu_3=3277\text{ cm}^{-1},$$
$$\nu_4=\ 729\text{ cm}^{-1},\quad \nu_5=600\text{ cm}^{-1},$$

and we need not go into the arguments which show that this is the only possible choice. The difficulty comes in combining those to yield the other observed frequencies while conforming with Dennison's selection rules. The latter are given in Table I where n_3, n_4, n_5 are quantum numbers (taking any integral values) in the general expression for an overtone or combination band, *viz.*

$$\nu=n_1\nu_1+n_2\nu_2+n_3\nu_3+n_4\nu_4+n_5\nu_5.$$

TABLE I. *Dennison's selection rules.*

	Parallel Bands		Perpendicular Bands	
n_3	odd	even	even	odd
n_4	even	odd	odd	even
n_5	even	odd	even	odd

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[1] Levin and Meyer, J. Opt. Soc. Am. **16**, 137 (1928).

[2] Childs and Mecke, Zeits. f. Physik **64**, 162 (1930); Hedfield and Mecke, Zeits. f. Physik **64**, 151 (1930); Mecke, Zeits. f. Physik **64**, 173 (1930).

[3] Mecke, Zeits. f. physik. Chemie **B17**, 1 (1932); Hedfield and Lueg, Zeits. f. Physik **77**, 446 (1932); Lochte-Holtgreven and Eastwood, Zeits. f. Physik **79**, 450 (1932).

[4] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

TABLE II. *Observed bands and interpretations.*

Frequency observed (cm^{-1})	Arrangement		
	Mecke	Hedfield and Lueg	Lochte-Holgreven and Eastwood
730	ν_4	ν_4	ν_4
1326	$\nu_4+\nu_5$	$\nu_4+\nu_5$	$\nu_4+\nu_5$
2643	$\nu_2-\nu_4$	$\nu_2-\nu_4$	$\nu_2-\nu_4$
2670	$\nu_3-\nu_5$	$\nu_3-\nu_5$	$\nu_3-\nu_5$
2683	?	?	?
2702	$\nu_1+\nu_4$	$\nu_1+\nu_4$	$\nu_1+\nu_4$
3288	ν_3	ν_3	ν_3
3898	$\nu_3+\nu_5$	$\nu_3+\nu_5$	$\nu_3+\nu_5$
4092	$\nu_2+\nu_4$	$\nu_2+\nu_4$	$\nu_2+\nu_4$
4690	$\nu_2+\nu_4+\nu_5$	$\nu_2+\nu_4+\nu_5$	$\nu_2+\nu_4+\nu_5$
5250	$\nu_3+\nu_1$	$\nu_3+\nu_1$	$\nu_3+\nu_1$
6500	$\nu_3+\nu_2$	$2\nu_3$	$\nu_3+\nu_2$
8450	$\nu_1+\nu_2+\nu_3$	$\nu_1+\nu_2+\nu_3$	$\nu_1+\nu_2+\nu_3$
9641	$3\nu_3$	$3\nu_3$	$3\nu_3$
9835	—	$3\nu_3$ "ohne verstimmung"	$\nu_3+2\nu_2$
10400	—	$2\nu_3+2\nu_1$	$2\nu_3+2\nu_1$
11599	$3\nu_3+\nu_1$	$3\nu_3+\nu_1$	$3\nu_3+\nu_1$
11783	—	$4\nu_3-\nu_4$	$\nu_3+3\nu_2$
12676	$4\nu_3$	$4\nu_3$	$3\nu_3+\nu_2$
15600	—	$5\nu_3$	$3\nu_3+2\nu_2$
18430	—	$6\nu_3$	$3\nu_3+3\nu_2$

The observed bands together with the existing interpretations of them are given in Table II. Of these bands the positions of the last eight are known with great accuracy, since these have been observed photographically under very high dispersion.[5] The positions of the preceding four are not known with any accuracy, while the first nine are correct to within about one wave number.

Since the appearance of overtone and combination bands is due to an anharmonicity in the vibrational motions of the molecule the simple formula

$$\nu=n_1\nu_1+n_2\nu_2+n_3\nu_3+n_4\nu_4+n_5\nu_5$$

will only give the positions of the bands very approximately and to obtain accuracy we must introduce anharmonic correction terms depending on the second powers of the quantum numbers. Thus we write

$$\nu=n_1\nu_1+n_2\nu_2+n_3\nu_3+n_4\nu_4+n_5\nu_5+x_{11}n_1^2$$
$$x_{22}n_2^2+x_{33}n_3^2+x_{44}n_4^2+x_{55}n_5^2+x_{12}n_1n_2$$
$$+x_{13}n_1n_3+\cdots+x_{45}n_4n_5$$

and the observed fundamentals are no longer ν_1, ν_2, ν_3, ν_4 and ν_5 but ν_1+x_{11}, ν_2+x_{22}, etc. If now there exists a series of combination bands of, say, the two fundamental frequencies ν_2 and ν_3, then three of those will be sufficient to determine x_{22}, x_{33} and x_{23}; the positions of the others may then be predicted with great accuracy and the resulting agreement forms a test of the correctness of the assignment. This was the method employed by Lochte-Holtgreven and Eastwood whose results are summarized in Table III. The agreement between calculated and observed values is seen to be most unsatisfactory. It will now be shown that an alternative arrangement of the bands exists which yields very consistent results.

TABLE III. *Results of Lochte-Holtgreven and Eastwood.*

$\nu_2=3285n_2-56n_2^2$; $\nu_3=3308.4n_3-31.6n_3^2$; $x_{23}=-65.6$ cm^{-1}

Frequency	$\nu_3+\nu_2$	$\nu_3+2\nu_2$	$\nu_3+3\nu_2$	$3\nu_3+\nu_2$	$3\nu_3+2\nu_2$	$3\nu_3+3\nu_2$
Calculated	6440	9492	12,431	12,673	15,593	18,401
Observed	6500	9835	11,782	12,675	15,600	18,430

The essential point in this new interpretation is that the very strong band at 9641 cm^{-1} is no longer taken to be $3\nu_3$ but to be $\nu_3+2\nu_2$. While this may seem surprising at first sight the arguments for such an assignment are very strong for in addition to yielding consistent values for the anharmonic constants it explains several qualitative features which seemed rather puzzling on the old interpretation. For instance, it seemed surprising that if $3\nu_3$ (i.e., 9641 cm^{-1}) were so intense, no sign of $5\nu_3$ should be observed, but on the new arrangement $3\nu_3$ (i.e., 9835 cm^{-1}) is already a weak band and so one would not expect $5\nu_3$ to be observed. Again if $3\nu_3$ is an intense band one would expect to find signs of $3\nu_3+\nu_5$ since $\nu_3+\nu_5$ is quite a strong band (cf. $\nu_3+\nu_1$ and $3\nu_3+\nu_1$ which appear on either assignment). This is fulfilled by the new, but by none of the old arrangements. Another satis-

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[5] Lueg and Hedfield, reference 3.

TABLE IV. *New assignments of bands.*

$\nu_1 = 1974$ cm^{-1}; $\nu_2 = 3372$ cm^{-1}; $\nu_3 = 3288$ cm^{-1}; $\nu_4 = 730$ cm^{-1}; $\nu_5 = 605$ cm^{-1}.

Frequency observed cm^{-1}	Character† observed	Character predicted	Assignment	Frequency predicted cm^{-1}
730	Perpendicular	Perpendicular	ν_4	—
1326	Parallel	Parallel	$\nu_4+\nu_5$	—
2643	Perpendicular	Perpendicular	$\nu_2-\nu_4$	2642
2670	?	—	Overlapping bands	—
2683	Perpendicular	Perpendicular	$\nu_3-\nu_5$	—
2702	"	"	$\nu_1+\nu_4$	—
3288	Parallel	Parallel	ν_3	—
3882	Perpendicular	Perpendicular	$\nu_3+\nu_5$	3880
3910	Parallel (?)	Parallel	$3\nu_4+3\nu_5$	—
4092	Perpendicular	Perpendicular	$\nu_2+\nu_4$	—
4690	?	Parallel	$\nu_2+\nu_4+\nu_5$	—
5250	?	"	$\nu_3+\nu_1$	5253
6500	?	"	$\nu_3+\nu_2$	6513
8450	?	"	$\nu_3+\nu_2+\nu_1$	8435
9641*	Parallel V.S.	"	$\nu_3+2\nu_2$	9641
9835*	" S.	"	$3\nu_3$	9835
10,400*	? V.W.	Perpendicular	$3\nu_3+\nu_5$	10,400
11,599*	Parallel S.	Parallel	$\nu_3+2\nu_2+\nu_1$	11,599
11,783*	" M.	"	$3\nu_3+\nu_1$	11,783
12,676	" S.	"	$\nu_3+3\nu_2$	12,668
15,600	" M.	"	$\nu_3+4\nu_2$	15,598
18,430*	" M.	"	$\nu_3+5\nu_2$	18,430

* Abbreviations for intensity of photographed overtones: V.S. = very strong, S. = strong, M. = medium, V.W. = very weak.

† A "perpendicular" band possesses a Q branch while a "parallel" band possesses no Q branch.

factory feature of the new arrangement is that it explains the very weak band at 10,400 cm^{-1} which seemed to contradict Dennison's selection rules even in Lochte-Holtgreven and Eastwood's arrangement. It is unfortunate that its extreme weakness seems to have prevented even a determination of the general character of this band.

Table IV gives the new assignment. The experimental values are taken from Levin and Meyer (for the first nine frequencies), from Mecke (for the next four) and from Hedfield and Lueg (for the last eight). The values for the frequencies ν_1 and ν_2 are taken from the measurements of Bhagavantam[6] on the Raman spectrum of the gas; these are probably correct to within less than 2 cm^{-1}.

Six frequencies (marked with an asterisk) were required to determine the anharmonic constants x_{12}, x_{13}, x_{22}, x_{23}, x_{33} and x_{35} giving the values

$$x_{12} = -3 \text{ cm}^{-1}, \qquad x_{23} = -146.8 \text{ cm}^{-1},$$
$$x_{13} = -9 \text{ cm}^{-1}, \qquad x_{33} = -5 \text{ cm}^{-1},$$
$$x_{22} = -49.2 \text{ cm}^{-1}, \qquad x_{35} = -13 \text{ cm}^{-1}.$$

These constants then permitted a calculation of the positions of six other bands formed by combinations of the fundamentals ν_1, ν_2, ν_3 and ν_5. The agreement between calculated and observed positions is very satisfactory, considering the uncertainty with which some of the bands are known[7] and the assumptions involved in such a calculation. It is interesting to notice the variations in magnitude of these constants. The fact that x_{23} and x_{22} are so large compared with the others is in accordance with the observed intensity of the series of overtones $\nu_3+\nu_2$, $\nu_3+2\nu_2$, $\nu_3+3\nu_2$, $\nu_3+4\nu_2$ and $\nu_3+5\nu_2$. A similar phenomenon has been found by Adel and Dennison[8] in the overtone bands of carbon dioxide.

As regards the bands between 1300 cm^{-1} and 5000 cm^{-1} some modifications of Mecke's arrangement are proposed. The difference band

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[6] Bhagavantam, Indian J. Phys. **6**, 319 (1931).

[7] It is important that the bands at 6500 cm^{-1} and 8450 cm^{-1} be reexamined under high dispersion as a confirmation of the above assignments. Professor Imes of Fisk University informs me that he intends to undertake this work very shortly.

[8] Adel and Dennison, Phys. Rev. **43**, 716 (1933).

$\nu_3-\nu_5$ is associated with the frequency 2683 cm^{-1} instead of 2670 cm^{-1} yielding an accurate value for ν_5 of 605 cm^{-1}. When this is used along with the value of x_{35} determined from the band at 10,400 cm^{-1} to predict the position of the band $\nu_3+\nu_5$ we obtain a calculated value of 3880 cm^{-1}. This seems to fit the weak maximum observed at 3882 cm^{-1} much better than the strong one at 3898 cm^{-1}. Accordingly we take the latter to be the *P* branch of a parallel band with center at 3910 cm^{-1} and interpret it as $3\nu_4+3\nu_5$. The anomalously high intensity of the *P* branch is probably due to its having superimposed on it the *R* branch of the 3882 cm^{-1} band. The fact that, in the corresponding band at 1326 cm^{-1}, due to $\nu_4+\nu_5$ the convergence was in the *P* rather than the *R* branch, is important since a slight exaggeration of this effect in the "overtone" at $3\nu_4+3\nu_5$ would also tend to make the unresolved *P* branch appear stronger than the *R* branch.[9] If Mecke's assignment is correct then the accurate value of ν_5 is 618 cm^{-1} and the calculated position of $\nu_3+\nu_5$ is 3888 cm^{-1} (with $x_{35}=-18$ cm^{-1}). Since this seems to agree with neither of the maxima we would have to assume that the interpretation of the band at 10,400 cm^{-1} as $3\nu_3+\nu_5$ is wrong. A careful reexamination of the bands at 2670 cm^{-1}, 2683 cm^{-1}, 3882 cm^{-1}, 3898 cm^{-1} and 10,400 cm^{-1} would be very desirable in order to discriminate between these assignments.

Some of the other interaction constants may be determined from the remaining bands. Thus we obtain;

$$\begin{array}{llll} & \nu_4+\nu_5 & & x_{45}=-9\ \text{cm}^{-1},\\ & \nu_4+\nu_1 & & x_{14}=-2\ \text{cm}^{-1},\\ \text{from} & & \text{that} & \\ & \nu_4+\nu_2 & & x_{24}=-10\ \text{cm}^{-1},\\ & \nu_4+\nu_2+\nu_5 & & x_{25}=+2\ \text{cm}^{-1}.\end{array}$$

These values cannot be verified until more bands have been observed, the positions of which depend on them, but (with the exception of x_{25}) we may assume that the error is not more than one or two wave numbers. To determine x_{25} with this accuracy the position of the band at 4690 cm^{-1} requires to be known with a corresponding accuracy.

While the correct assignment of the overtone and combination bands in an infrared spectrum such as that of acetylene is of considerable interest as a verification of theoretical selection rules the question arises whether it will lead to further results of importance. We feel that this is the case since it allows a determination of the anharmonic constants x_{ij} which describe the behavior of the potential energy for amplitudes of vibration which are not infinitesimally small. It seems quite probable that these will prove to be of major importance in eventually furnishing the molecule with a potential function valid over a large range of the coordinates. Some progress has already been made in this direction by Adel and Dennison[9] in their study of the carbon dioxide molecule. The acetylene molecule being somewhat more complex, the necessary analysis has not as yet been made. One qualitative feature has already appeared however, for, as we have pointed out, there exists a direct connection between the magnitude of the anharmonic constants and the intensities of the combination bands.

I would gratefully acknowledge the benefit of much helpful discussion of this problem with Professor D. M. Dennison. I am also indebted to him and to Mr. Adel for permission to use their results on carbon dioxide before publication.

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[9] Cf. *The Infrared Spectrum of Carbon Dioxide, Part II* by Adel and Dennison (to appear shortly in The Physical Review) where it is shown that, when no resonance degeneracy exists, the factor giving the convergence of the rotation lines in a fundamental band has to be multiplied by three for the convergence in the second overtone.