

### The Infrared Spectrum and Internuclear Distances of Methyl Acetylene\*

A parallel type band of methyl acetylene in the photographic infrared has recently been investigated by Herzberg, Patat and Verleger<sup>1</sup> who were able to obtain from it an accurate value of the large moment of inertia of the molecule. Assuming that all parameters except the C—C single bond distance have the values which have been found in other molecules they were obliged to conclude that this distance is about 1.463Å. This conclusion seems rather remarkable since the C—C single bond distance has been found to be approximately 1.54Å in a number of molecules, and it seemed worth while to check the result.

We have obtained very satisfactory pictures of the methyl acetylene band at  $\lambda 10,304$ , completely free from contamination by acetylene, in which the lines are visible right down to the origin except the first line of the *P* branch which is obscured by the strong *Q* branch. The lines have been measured by one of us directly on two plates and by the other on microphotometer curves of the same plates. The results are very self-consistent and agree well with those of the authors mentioned above. Indeed we even check quite well the measurements on lines near the origin of the band and in the vicinity of  $J=23$  so that the deviations of the points for these regions from the straight line of Fig. 2 of H. P. and V.<sup>1</sup> appear to be due to some systematic error which is duplicated in our work, and not to accident.

From the average of our two independent measurements and those of H. P. and V. we obtain as the most probable values for the rotational constants,  $B'=0.28231$  and  $B''=0.28496$ . These differ from those given by H. P. and V. by little more than their estimated error and leave the situation unchanged as regards the internuclear distances.

We have carefully considered various errors which might have entered into the measurements and their interpretation. The origin of the band appears to be uniquely determined by the *Q* branch but aside from this we believe we could pick the band center from the intensity distribution with an error of not more than two lines. The relative line numbering of the two branches also appears to be unique since the lines are visible clear down to the origin with one exception. Furthermore any other relative numbering leads to rotational constants which change more rapidly with  $J$  than is possible.

We have considered possible errors due to the contamination of the  $\lambda 10,304$  band by two weak bands which appear to arise from absorption by molecules in excited vibrational levels. Of these only the *Q* branches are visible and one is so weak that it can scarcely cause any disturbance except in its *Q* branch which makes the measurement of one line a little uncertain. The other, however, may possibly be as much as one-fifth as intense as the main band and appears to introduce some error in the measurement of lines near the origin of the latter. As mentioned above, the measurements of the lines with  $J<8$  appear to be systematically in error which might well be expected since they are very weak while the *R* branch of the overlying satellite band is near its maximum of in-

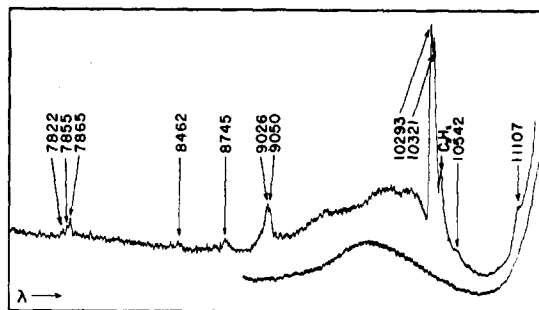


FIG. 1. The upper curve is a microphotometer tracing of the absorption spectrum of methyl acetylene in the photographic infrared taken under low dispersion. The wave-lengths of several maxima which appear to belong to bands of parallel type are given. The broad maximum in the region  $\lambda 9000-10,000$  is mainly due to a minimum in the plate sensitivity, as shown in the lower curve which gives the plate background, but it is possible that there may be two weak bands in this region, probably of perpendicular type.

tensity in this region. In the remainder of the measurements we do not find any evidence of appreciable errors of the same sort. In the *R* branch the lines with  $J>15$  should in any case be practically free from contamination, while in the *P* branch if the lines of the satellite band are strong enough to cause any disturbance we should expect the errors to alternate between negative and positive owing to the inequality of spacing of the main and satellite branches. Consequently the calculated rotational constants should also fluctuate, though the average value should be about correct. There seems to be no indication that this state of affairs exists and in comparing measurements with the line positions calculated from the average rotational constants one finds no evidence of special error in the *P* branch except possibly in a little region about  $J=23$ .

Consequently we are obliged to regard the short C—C distance in methyl acetylene as real. This result does not appear to us particularly surprising. In the first place, as has been known for some time, the C—H distance in acetylene is appreciably shorter than in methane. In the second place, in some considerations regarding the spectra of the substituted acetylenes made by one of us<sup>2</sup> it seemed necessary to assume that the C—C single bond force constant in dimethyl acetylene, etc., is somewhat larger than would be compatible with a distance of 1.54Å.

It would of course be very desirable to make measurements on other bands of methyl acetylene but we have not found it possible to do so with high dispersion. Under low dispersion we have observed a number of bands which are shown in the accompanying microphotometer tracing. One of these, at  $\lambda 9040$ , is moderately strong and appears to be of the same type as the  $\lambda 10,304$  band but it was just too weak to show up in spectrograms taken with the 21 ft. grating with the amount of material we had available.

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<sup>1</sup> Herzberg, Patat and Verleger, *J. Phys. Chem.* **41**, 123 (1937).  
<sup>2</sup> R. M. Badger, *J. Chem. Phys.* **5**, 178 (1937).