The Raman Spectrum and Vibrational Frequencies of Methyl Acetylene

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atomic number of the combining element with the Mn. We may understand this by the following argument: The exchange force energy is nearly the same for all the compounds (MnO, MnS, MnSe, MnTe) and the perturbing energy needed to destroy this extra binding is also the same. Now in order to get a crystal with heavy elements into the required high energy state (lattice vibration) it requires a higher temperature than for a lighter crystal. This is considering the question from a Boltzmann statistical view point i.e., the number of heavy elements in a given high energy state is less than the number of lighter ones in such a state for a given temperature.

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The Raman spectrum of liquid methyl acetylene has been measured in connection with the research program on molecular vibrations now in progress in this laboratory. The apparatus used has been previously described;[1] the blue-violet mercury lines were used for excitation. The material was made available through the kindness of Professor G. B. Kistiakowsky. It was of extreme purity, having been prepared for use in the hydrogenation calorimeter; the preparation will be described in a future publication of the series on heats of hydrogenation.

The observed shifts are given in Table I, together with their intensities, polarization characters, and assignments.

TABLE I. *Observed Raman shifts.*

$\Delta\nu$, cm^{-1}	EXCITATION*	INTENSITY, POLARIZATION†	ASSIGNMENT
333	e, k, i	10 b, D	E fund.
642	e, k, g, i	4 b, D	E fund.
926	e, k, i	6, P	A_1 fund.
1035	e, k	0, —	E fund.
1380	e, k	2, $D?$	A_1 fund.
1444	e, k	2, —	E fund.
2125	e, k, f, g	12, P	A_1 fund.
2735	e, k	1, —	$1380^2 = 2760(A_1)$
2866	e, k	3, —	$1444^2 = 2888(A_1+A_2+E)$**
2927	e, k	8, P	A_1 fund.**
2975	e, k	2, —	E fund.
3300	e, k	3, —	A_1 fund.

* K. W. F. Kohlrausch's notation for the mercury lines is used: $e = 22938$, $f = 22995$, $g = 23039$, $i = 24516$, $k = 24705$ cm^{-1}.
† b=broad, P=polarized ($\rho \leq 6/7$), D=depolarized ($\rho = 6/7$).
** Resonance doublet.

TABLE II. *Fundamental frequencies of methyl acetylene.*

A_1	E
926	333
1380	642
2125	1035
2910	1444
3300	2975

The polarizations of the lines have not been previously studied, nor has the 1035 cm^{-1} shift been previously reported. Other shifts agree with those found by Glockler and Davis.[2]

The symmetry of the molecule (C_{2v}) yields the structure $\Gamma = 5A_1 + 5E$ for the representation formed by the normal coordinates. The selection rules allow both the non-degenerate (A_1) and degenerate (E) fundamentals to appear in the Raman effect; the A_1 fundamentals may be polarized. These considerations lead immediately to the assignment given in Table I, with the set of fundamentals shown in Table II. This assignment differs in several respects from that given by Glockler and Davis.[2] The figure of 2910 cm^{-1} for the symmetrical $C-H$ stretching frequency in the methyl group results from an arbitrary allowance for the effect of the resonance interaction with the overtone of the 1444 cm^{-1} fundamental. The presence of this interaction is shown by the intensity of the overtone.

Low temperature heat capacity measurements were made on the gas by Mr. W. W. Ransom, using the "hot-wire" method as developed in this laboratory.[3] The experimental values agree, within experimental error, with those calculated from the fundamental frequencies of Table II. (At 158°K, calculated value 8.247, observed value 8.24 cal./mole/degree; at higher temperatures the experimental data are as yet incomplete.)

A complete report, including thermodynamic calculations, will be published when a study of the infra-red absorption, now in prospect, has been completed.

In conclusion, I wish to express my thanks to Mr. Ransom for the use of his heat-capacity measurements, and especially to Professor E. B. Wilson, Jr., for suggesting the study of this molecule and for his continued interest in the work.

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