Absence of Spin Effects in the Heat Capacity of Ethane Gas

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Hunsmann[1] has suggested that the low value of the heat capacity of ethane gas at 100°K does not necessarily prove the existence of a high potential barrier in this molecule because of the possibility that the calculations have been incorrectly made, since no consideration was taken of the fact that there are several noncombining nuclear spin species, analogous to ortho- and parahydrogen. Because of the relatively large moment of inertia of ethane, this suggestion seemed inherently unreasonable, but on account of the importance of this problem, a detailed calculation of the partition function and heat capacity of each of the spin species of ethane has been made for several different barriers and temperatures, in which full account was taken of the statistical weights of each individual rotational energy level. The method used to find these weights was an extension of that described earlier for the general problem.[2] The rotational group for ethane has 18 elements and 9 irreducible representations. Some of these occur as conjugate pairs, however, so that there are only six possible spin species of ethane. At 90°K the over-all rotation of the molecule is classically excited with the result that these six species can be divided into two sets, the members of each set having the same partition functions. The partition function for one set involves the state sum over those levels of the internal motion which are nondegenerate, while the partition function for the other set involves the sum over the degenerate levels of the internal torsional motion. For very high barriers the levels of the two species become identical and for very low barriers the levels go over into those for free rotation. In each of these limiting cases the two partition functions are negligibly different at 90°K. A detailed calculation for a barrier of 300 cal. yields the same result. This means that the equilibrium proportions of the two species have practically attained their high temperature limiting values at 90°K. Furthermore the heat capacities of the two species are identical at this temperature or higher. Consequently, the usual method[3] of calculation which involves the neglect of spin and symmetry effects is entirely justified.

This eliminates one possible explanation of the heat capacity of ethane gas at low temperatures and seems to leave the existence of a high barrier as the only alternative.

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Carbon Isotope Effect in the Raman Spectrum of Dimethylacetylene

For dimethylacetylene Glockler and Davis[1] reported a pair of strong Raman frequencies, 2235 and 2313 cm^{-1} which were accompanied by two overlapping pairs of weak lines, 2201 and 2280 cm^{-1}, 2179 and 2258 cm^{-1}, all excited by Hg 4358A. (Fig. 1.) They divided these lines into two
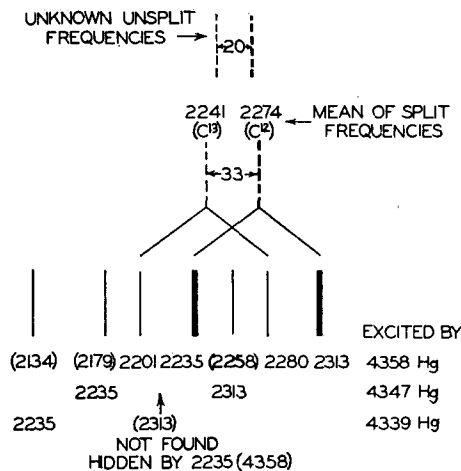

FIG. 1. Raman frequencies of the triple bond in dimethylacetylene (cm^{-1}).

groups, one consisting of the higher members of the pairs, the other of the lower frequency members. Each group was considered to represent a strong vibration accompanied by weaker components which were the first members of P rotation series. Such a lopsided rotation-vibration band had been proposed by Bonino and Cella[2] to account for a similar group of lines in α-pinene. In both substances excellent checks on observed separations were obtained by assuming that the rotating portions of the molecules were simple rotators with one degree of freedom. In dimethylacetylene it was assumed that the six hydrogen atoms were rotating about the figure axis.

Of course there were objections to the above interpretation. The restricted nature of the rotator calculations and the absence of R branches caused doubt. Recently in studies conducted here on other low molecular weight hydrocarbons[3] measurements were made on the weak Raman shifts due to molecules containing the C^{13} isotope. In continuing this study reference was made to the available plates on dimethylacetylene in a search for lines of isotopic origin. The first pair of weak lines listed, giving a separation of 33 cm^{-1} from the corresponding members of the strong pair, were considered to be due to molecules containing C^{13}.

The elimination of the first component in each rotation series necessitated another explanation for the other members. It was then found that the 2179 and 2258 cm^{-1} weak lines were exactly in position to be the 2235 and 2313 cm^{-1} strong shifts excited by the 4347.5A member of the mercury triplet. In the paper mentioned no further weak lines were reported; however, in an enlargement of one of the plates by Davis a faint line was discernible which was in position to be the 2235 cm^{-1} shift excited by the 4339.2A member of the triplet; the 2313 cm^{-1} shift thus excited would not be visible because of coincidence with a strong line. In consequence of these measurements the rotational interpretation of the faint lines is to be discarded.

Subsequent to the studies of Glockler and Davis the

pair of strong lines, 2235 and 2313 cm^{-1} were explained by Badger[4] as manifestations of a single fundamental vibration interacting with an overtone of a lower fundamental in Fermi resonance due to accidental degeneracy. As a result, this carbon-carbon triple bond vibration frequency of the normal molecule appears split into two components, the actual fundamental frequency lying near the mean value of the pair. Similarly the weak pair of lines, 2201 and 2280 cm^{-1}, are now considered to result from the interaction of the carbon-carbon triple bond fundamental of isotopic molecules with an overtone of a lower fundamental of these isotopic molecules.

By considering the normal molecule to be a simple harmonic two-body oscillator with reduced mass of $1/\mu = 1/25 + 1/25$ and the isotopic molecule to have similar properties with a reduced mass of $1/\mu = 1/25 + 1/26$ it is possible to calculate a separation of 20 cm^{-1} for the carbon-carbon triple-bond frequencies of the normal and the isotopic molecules. This is not checked very well by the experimental measurement of 33 cm^{-1} separating the mean values of the resonance split pairs. Of course this calculation is only an approximation. However, it must be emphasized that a close check is not to be expected since the separation of mean values of split frequencies does not give an accurate measure on separations of the "unsplit" carbon-carbon triple bond frequencies. The resonance split values observed depend not only on the "unsplit" fundamentals but also on the overtone of the lower fundamentals likewise engaged in the resonance interaction.[5] Because the isotopic shift for the lower frequency will differ from that for the higher frequency, the separation of mean values of split frequencies necessarily will vary from the separation of the true, "unsplit" fundamental vibrations in normal and isotopic molecules.

In the present approximate treatment no consideration was given to location of the C^{13}. In dimethylacetylene roughly four percent of the molecules are isotopic with half of these having isotopic triple bond carbons, the other half possessing C^{13} in the methyl groups.

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Raman Effect in Liquid Ethylene and Ethane

In the Raman spectrum of liquid ethylene two lines, 943 and 3075 cm^{-1} have been observed[1] which have not been found in the gas on very long exposures at high pressure.[2] Since the work of Bonner[3] on Raman effect in the liquid and infra-red absorption in the gas, it has been customary in theoretical treatments[4] to use these lines (950 and 3069 cm^{-1}) as fundamental vibrations along with other frequencies including 940, 950, and 3107 cm^{-1} which are infra-red active. According to the selection rules derived

for gases,[5] in molecules having a center of symmetry frequencies which are infra-red active should not appear in Raman effect. Of course there exists the possibility of an accidental coincidence of values. However, it is our belief that the appearance of the two lines mentioned in the Raman spectrum of liquid ethylene constitutes a violation of the selection rules since it seems likely that similar values in the infra-red absorption spectrum arise from the same vibrations.

The 3075 cm^{-1} line is somewhat diffuse but is of such a strength that it certainly should be visible on reasonable exposures in the gas, if permitted there. The line cannot be interpreted readily as a combination or overtone. Hence it seems convenient to relate this line to the strong 3107 cm^{-1} vibration observed in the infra-red. Of course, some increase in value is expected in going from liquid to gas for high frequencies. The increase here seems large, but does not appear excessive.

The 943 cm^{-1} shift in Raman effect for the liquid is very diffuse, and it seems natural to identify this with the 940 and 950 cm^{-1} lines in the infra-red. For low frequencies no great drop in value is observed generally in passing from gas to liquid.

Moreover, a similar comparison of data is possible with the Raman spectrum of liquid ethane and its infra-red absorption spectrum for the gas. In pure liquid ethane the Raman line 1463 cm^{-1}, though diffuse, is well established.[6] However, in the gas Lewis and Houston[7] could not find it and although Bhagavantam[8] measured a shift in this neighborhood he was using an impure sample and considered the line observed to be due to a contaminant. Now in infra-red absorption experiments[9] strong bands are observed at 1465 and 1495 cm^{-1}. Perhaps the mean value of 1480 cm^{-1} for the gas corresponds to the 1463 cm^{-1} Raman shift observed in the liquid.

In addition there are indications of a faint, diffuse Raman shift of 813 cm^{-1} in liquid ethane which may be related to the infra-red band 827 cm^{-1}.

Now it is possible that the failure to observe these Raman lines in the gas is due to their low intensities. But other lines of comparable strength (frequently of lower intensity) have been recorded in the gas. For this reason it seems likely that the Raman lines discussed are permitted only in the liquid state. The shifts are of nearly the same magnitude as infra-red active frequencies (see Table I), which fact may not be accidental. The presence of the C^{13} isotope has been shown to be responsible for slightly altered Raman shifts of low intensity accompanying corresponding strong lines excited in the normal molecules. The presence of this isotope contributes a small degree of asymmetry to the molecules which would cause infra-red active frequencies to be permitted in the Raman effect. However, such manifestations should be visible on long exposures in the gas as well as in the liquid. Since this condition has not been observed, it seems more reasonable to suppose that if the Raman and infra-red frequencies do belong to identical fundamentals, then a breakdown in selection rules in the liquid state for certain lines is indicated and must be due to the more strenuous environment existing there. Thompson and Linnett[4] have offered this