200. *On the Vibration Frequencies of Ethylene and Ethane.*

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WE summarise in this paper existing experimental data on the infra-red and Raman spectra and on the specific heats of ethylene and ethane, and hence derive sets of vibration frequencies for these two molecules. Although it cannot be claimed that these frequencies are final, we believe that they are the best that can be given at the present time. Our main reason for discussing them in detail is that we desire to make clear the basis of our calculation of the vibrational factors in the partition functions used in the preceding paper. In discussing the assignment of frequencies we have found it convenient to introduce a systematic notation for the molecular vibrations based as far as possible on the symmetry properties of the molecules.

[*] After this paper had been completed we were informed by Professor Kistiakowsky that the reliability of the direct thermal measurements of heats of hydrogenation has been confirmed by subsequent work with the calorimeter at Harvard; the discrepancy between theory and experiment is probably, in his opinion, to be attributed to an unexpectedly large restriction on the rotation of the methyl groups in ethane. On the other hand, we now hear from Professor Eucken that new work in his laboratory confirms the reliability of the method used by Eucken and Weigert to determine the magnitude of the restricting potential. The discrepancy therefore remains. It would be particularly interesting in this connexion to examine the spectra and the specific heats of the deutero-substituted ethylene and ethane, since that knowledge combined with existing data on the ordinary molecules would provide a valuable check on the actual values and the assignment of the vibration frequencies, and on the magnitude of the restricting potential in ethane.

The experimental data concerning the vibrations of ethylene are :—

(1) *The Raman spectrum of ethylene.* This was investigated by Dickinson, Dillon, and Rasetti (*Physical Rev.*, 1929, **34**, 582) in the gas. They found three strong Raman lines with the frequencies (expressed in wave-numbers) 1342, 1623, and 3019, and three weaker lines 2880, 3240, and 3272. Their results agree satisfactorily with those of Daure (*Ann. Physique*, 1929, **12**, 375), done with less accuracy and upon liquid ethylene.

(2) *The infra-red spectrum of ethylene.* The most recent measurements in the spectral region relevant for the fundamental frequencies are by Levin and Meyer (*J. Opt. Soc. Amer.*, 1928, **16**, 137). Strong absorption was found at 950, 2990, 1444, and 3110. The rotational structure of the bands shows that in the first two of these vibrations the change of electric moment is perpendicular to the C–C axis, and in the last two it is parallel to this axis. Two weaker bands were found at 1890 and 2047, also arising from parallel vibration of the dipole moment. Additional absorption regions at wave-lengths less than 3μ exist, but are not important for the present purpose; they correspond to combination- and over-tones which might be composed out of the fundamental frequencies in a number of different ways.

(3) *The specific heat of ethylene.* This was measured by Eucken and Parts (*Z. physikal. Chem.*, 1933, *B*, **20**, 184) in the temperature range 178·6—464·0° Abs. The limits of error are given as less than 1%. The results are only 0·5—1·0% higher than those of Heuse (*Ann. Physik*, 1919, **59**, 86), which cover the range 182·2—291·2° Abs. There are also measurements by Haas and Stegeman (*J. Physical Chem.*, 1932, **36**, 2127) from 275·5° to 339·8° Abs.; above room temperature their results are 2—3% lower than the values interpolated from the data of Eucken and Parts, to which we attach most weight in our further discussion.

The interpretation of the infra-red and Raman spectra * can be considerably simplified by taking into account the symmetry properties of the molecule and the vibrations.

The plane model usually adopted for ethylene has three symmetry planes. One is the plane of the molecule; we denote it by γ. A second symmetry plane, α, is perpendicular to the C–C bond. The remaining plane, β, is perpendicular to the other two. The molecular vibrations can be classified by making use of their relationship to the planes of symmetry. We shall use the subscript t to denote the fact that a vibration is symmetrical with respect to all three planes, *i.e.*, that it is " totally symmetrical." For the other vibrations we shall use as subscripts the symbols of the planes to which the vibration is anti-symmetrical. This symbolism relating to the symmetry is not in itself sufficient to describe all the vibrations in a unique way, for in some cases more vibrations than one have the same symmetry character. Therefore we extend our notation by introducing as indices symbols which describe in a qualitative way the form of vibration. We shall use the index CH to indicate that the vibration is one involving a considerable change of the C–H distances. It is a general (empirical) rule that such frequencies lie in the region of 3μ. Similarly the index CC will indicate a vibration of the C–C bond. If the valency distances remain almost constant during the vibration, and the main displacement is a change of the valency angle in the CH_2 group, we use the index CH_2. Finally, if, in addition to the valency distances, the internal angle of the CH_2 group also remains practically unchanged, and the vibration consists of an alteration of the orientation of the CH_2 group within the molecule, we shall use the index M.

It must, however, be emphasised that the only differences between the vibrations that can be formulated rigorously are those relating to the symmetry.

In our notation the 12 ethylene frequencies are: ν_t^{CH}, ν_t^{CC}, $\nu_t^{CH_2}$, ν_γ^{M}, ν_α^{CH}, $\nu_\alpha^{CH_2}$, ν_β^{CH}, ν_β^{M}, $\nu_{\alpha\gamma}^{M}$, $\nu_{\alpha\beta}^{CH}$, $\nu_{\alpha\beta}^{M}$, $\nu_{\alpha\beta\gamma}^{M}$.

The vibrations ν_t^{CH}, ν_t^{CC}, $\nu_t^{CH_2}$, $\nu_{\alpha\gamma}^{M}$, $\nu_{\alpha\beta}^{CH}$, and $\nu_{\alpha\beta}^{M}$ should appear in the Raman spectrum. In the vibrations ν_β^{CH}, ν_β^{M}, and ν_γ^{M} there is a change of the electric moment perpendicular to the C–C axis, and it is therefore to be expected that these frequencies will give rise to infra-red bands with a " perpendicular " rotational structure. ν_α^{CH} and $\nu_\alpha^{CH_2}$ should appear

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* The spectra have been interpreted by Mecke (*Z. physikal. Chem.*, 1932, *B*, **17**, 1). We arrive at conclusions not very different from his.

as " parallel " bands in the infra-red spectrum. On this basis, the following interpretation of the infra-red spectrum can be given : the " perpendicular " band at 2990 is ν_β^{CH}. The band at 950 will be either ν_β^M or ν_γ^M, or else (as assumed by Mecke, *loc. cit.*) both ν_β^M and ν_γ^M are equal to 950. The two " parallel " frequencies ν_α^{CH} and $\nu_\alpha^{CH_2}$ are to be identified with the strong " parallel " bands at 3110 and 1444. The two weaker " parallel " bands at 1890 and 2047 must be interpreted as combination tones.* As these bands are not very weak, we shall try to interpret them as summation tones of not more than two frequencies. According to the selection rules for combination tones, the following pairs of frequencies may give rise to a " parallel " band in the infra-red spectrum : $\nu_t + \nu_\alpha$, $\nu_\beta + \nu_{\alpha\beta}$, $\nu_\gamma + \nu_{\alpha\gamma}$. The first of these pairs can be ruled out, because the two ν_α frequencies of ethylene are 3110 and 1444, so that it would be necessary to assume a value of about 603 ($1444 + 603 = 2047$) or about 446 ($1444 + 446 = 1890$); but such a frequency would give rise to higher specific-heat values at low temperatures than were observed by Eucken and Parts and by Heuse. Consequently, the two bands at 1890 and 2047 must correspond to $\nu_\beta^M + \nu_{\alpha\beta}^M$ and $\nu_\gamma^M + \nu_{\alpha\gamma}^M$. If we assume with Mecke that $\nu_\beta^M = \nu_\gamma^M = 950$, then we obtain for $\nu_{\alpha\beta}^M$ and $\nu_{\alpha\gamma}^M$ the two values 940 and 1097. These frequencies were first suggested by Eucken and Parts. If, however, we assume one of the two frequencies ν_β^M or ν_γ^M to be different from 950, then one of the frequencies assigned to $\nu_{\alpha\beta}^M$ and $\nu_{\alpha\gamma}^M$ must be changed.

Of the group of four Raman frequencies 2880, 3019, 3240, and 3272, two must correspond to CH vibrations, and the other two will be combination- or over-tones. The most intense line 3019 may reasonably be taken as a fundamental frequency, and 2880 is probably the overtone of $\nu_\alpha^{CH_2} = 1444$. We have therefore no reason to reject the assignment made by Mecke, *viz.*, $\nu_t^{CH} = 3019$, $\nu_{\alpha\beta}^{CH} = 3240$. In connection with the preceding paper, it may be remarked that the CH frequencies are not very much excited even at the highest temperatures employed in the equilibrium measurements, so that for the purpose of that paper it is not very important which of these four Raman lines correspond to the fundamental frequencies.

The two remaining Raman lines at 1623 and 1342 may be interpreted, in agreement with Mecke, as ν_t^{CC} and $\nu_t^{CH_2}$.† $\nu_{\alpha\beta\gamma}^M$ was calculated by Eucken and Parts from the specific heats, assuming for all other vibrations the values given above. They found $\nu_{\alpha\beta\gamma}^M = 803$. Frost changed this frequency to 950 in order to obtain better agreement with the specific heat at the higher temperatures, but the agreement at low temperatures is thereby made less satisfactory. Eucken and Parts have proposed a second set of frequencies which agree better with the specific heats, but disregard the requirements that $\nu_\beta + \nu_{\alpha\beta}$ and $\nu_\gamma + \nu_{\alpha\gamma}$ should be equal to 1890 and 2047.

We have found it possible to obtain a better fit with the specific-heat data by assuming that only one of the two frequencies ν_β^M and ν_γ^M is equal to 950. The set of frequencies we have actually used in the statistical-mechanical calculation is $\nu_t^{CH} = 3019$; $\nu_\alpha^{CH} = 2990$; $\nu_\beta^{CH} = 3110$; $\nu_{\alpha\beta}^{CH} = 3240$; $\nu_t^{CC} = 1623$; $\nu_\alpha^{CH_2} = 1444$; $\nu_t^{CH_2} = 1342$; $(\nu_\beta^M, \nu_\gamma^M, \nu_{\alpha\beta}^M, \nu_{\alpha\gamma}^M) = (950, 1097, 730, 1160)$;‡ $\nu_{\alpha\beta\gamma}^M = 1110$. These frequencies are in agreement with all the specific-heat data, except those of Haas and Stegeman (*loc. cit.*). We do not think

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* Besides the argument from the intensities, there are two reasons which prevent us from assuming that the 1890 and 2047 bands correspond to fundamental frequencies. First, analogous molecules usually do not exhibit strong absorption in this region. Secondly, such an assumption would involve taking the frequency 1444 as a combination tone, and this in turn would necessitate the existence of some normal vibrations with frequencies so low as to be incompatible with the specific-heat measurements at low temperatures.

† It must be pointed out, however, that the line 1342 might correspond to $\nu_{\alpha\gamma}^M$ or $\nu_{\alpha\beta}^M$; thus Trumpy (*Z. Physik*, 1934, **88**, 226; **90**, 133) found in the Raman spectrum of dichloro- and dibromo-ethane a line in the region of 1400 which was strongly depolarised and therefore could not correspond to a totally symmetrical vibration. On the other hand, a calculation by Sutherland and Dennison (*Proc. Roy. Soc.*, 1935, **148**, 250) based on a special model of the ethylene molecule was in agreement with $\nu_t^{CH_2} = 1342$. On the whole, this assignment seems probable but not quite certain.

‡ Apart from the conditions that ν_β^M or ν_γ^M should be 950 and that the two sums $\nu_\beta^M + \nu_{\alpha\beta}^M$ and $\nu_\gamma^M + \nu_{\alpha\gamma}^M$ should be 1890 and 2047 (or inversely), there is no restriction as to the order in which these four vibrations should be associated with the four frequencies.

that the four frequencies taken as 1097, 730, 1160, 1110 are uniquely determined; other frequencies, *e.g.*, the sets used by Eucken and Parts or by Frost, are also possible.*

The experimental data concerning the vibrations of ethane are:

(1) The Raman spectrum was studied in the liquid state by Daure (*loc. cit.*), and in the gas by Bhagavantam (*Indian J. Physics*, 1930, **6**, 545) and Lewis and Houston (*Physical Rev.*, 1934, **44**, 903). In each case lines were found at 993, 2899, and 2955. A weaker line found by Daure at 1460 was not found by the other investigators, except Bhagavantam, who attributed it to impurity.

(2) The infra-red spectrum, according to Levin and Meyer (*loc. cit.*), consists of three bands of the " perpendicular " type at 827, 1480, and 2890, and two " parallel " bands at 1370 and 3020. The band at 1480 has rather an irregular appearance: it extends from about 1450 to 1510. The 1370 band is weak.

(3) The specific heats were measured by Eucken and Parts (*loc. cit.*) between 189·1° and 323·5° Abs., by Heuse (*loc. cit.*) between 191·2° and 288·2° Abs., and by Thayer and Stegeman (*J. Physical Chem.*, 1931, **35**, 1505) between 275·7° and 337·4° Abs. As with ethylene, Heuse's results are slightly lower than those of Eucken and Parts. Thayer and Stegeman's results are rather lower. The same limits of error are given by the authors as with ethylene; we shall give most weight to the measurements by Eucken and Parts. Eucken and Weigert (*Z. physikal. Chem.*, 1933, *B*, **23**, 265) measured the specific heat of ethane down to 143° Abs. by a comparison of the heat conductivity of ethane and ethylene; the specific heat of the latter at such low temperatures is not in doubt. Applying to their results Teller and Weigert's calculations (*Nachr. Ges. Wiss. Göttingen*, 1933, 218) of the specific heat of a restricted rotator, they concluded that the difference between the maximum and minimum potentials during the rotation of a methyl group is 315 ± 60 cals. A consequence of this is that above 250° Abs. the specific heat due to internal rotation of the methyl groups becomes equal (within the experimental error) to that of a free rotator, *i.e.*, $\frac{1}{2}R$. We cannot, however, rely upon this conclusion as certainly as upon the specific-heat data of Eucken and Parts, because Eucken and Weigert's measurements required for their interpretation the assumption that ethane and ethylene have the same accommodation coefficients. This was made very probable by measurements at higher temperatures, where the specific heats of the two gases are independently known, but it cannot be regarded as definitely proved.†

To derive the selection rules from the molecular symmetry, we should need to include a discussion of the effect of the free internal rotation upon the symmetry. We do not, however, propose to discuss this fully here, and will state the selection rules only for a special configuration, in which the two methyl groups can be interchanged by reflection in a plane perpendicular to the C–C axis. We call this symmetry plane α. The modifications required in the selection rules on account of the free rotation will be indicated afterwards.

Whilst with ethylene the symmetry of the molecule did not give rise to any degenerate frequencies, the trigonal symmetry axis of ethane (*i.e.*, the C–C axis) causes some of the ethane vibrations to have a two-fold degeneracy. These frequencies we will indicate by the notation $^2\nu$. In other respects the notation used for the ethane vibrations will be similar to that used for ethylene. The ethane frequencies are: ν_t^{CH}, ν_t^{CC}, $\nu_t^{CH_3}$, ν_a^{CH}, $\nu_a^{CH_3}$, $^2\nu^{CH}$, $^2\nu^{CH_3}$, $^2\nu^{M}$, $^2\nu_a^{CH}$, $^2\nu_a^{CH_3}$, $^2\nu_a^{M}$. There are five non-degenerate and six two-fold degenerate vibrations, and these, together with the internal rotation, make up the eighteen degrees of freedom possessed by the ethane molecule in addition to its translation and rotation as a whole.

Of these vibrations, ν_t^{CH}, ν_t^{CC}, $\nu_t^{CH_3}$, $^2\nu_a^{CH}$, $^2\nu_a^{CH_3}$, and $^2\nu_a^{M}$ should appear in the Raman spectrum, and ν_a^{CH}, $\nu_a^{CH_3}$, $^2\nu^{CH}$, $^2\nu^{CH_3}$, $^2\nu^{M}$ in the infra-red. The non-degenerate vibrations give rise to " parallel " bands, the degenerate to " perpendicular " bands.

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* We are indebted to Mr. G. B. B. M. Sutherland for discussing with us the interpretation of the spectroscopic data for ethylene.

† Since completing this paper, we have been informed by Professor Eucken that new measurements by Mr. Bertram (unpublished) by the conductivity method give strong support to the applicability of the method in the case of ethylene and ethane.

When we take into account the free rotation, the selection rules concerning the non-degenerate frequencies are unchanged,[*] whereas we should expect all the degenerate frequencies to appear both in the Raman and in the infra-red spectrum. It is not to be expected, however, that the non-preservation of the symmetry plane α will give rise to additional regions of absorption or new Raman lines of any considerable intensity. Any such new regions of infra-red absorption of small intensity should have a " perpendicular " rotational structure.

The two " parallel " infra-red bands at 3020 and 1370 must be interpreted as ν_a^{CH} and $\nu_a^{CH_3}$ respectively. Although the band at 1370 is weak, it cannot be considered as a combination- or over-tone because this could not be reconciled with the specific-heat measurements at low temperatures.[†]

The three " perpendicular " bands observed at 2890, 1480, and 827 will correspond respectively to ${}^2\nu^{CH}$, ${}^2\nu^{CH_3}$, and ${}^2\nu^{M}$. The assignment of ${}^2\nu^{CH_3}$ is justified by the analogy with the methyl halide spectra.

The complicated region extending from 1450 to 1510 was interpreted by Mecke (*loc. cit.*) as the superposition of two bands, *viz.*, ${}^2\nu^{CH_3}$ and $\nu_a^{CH_3}$; but, as stated above, we have good reason to assign $\nu_a^{CH_3}$ to another frequency; possibly the complication in this region is caused by the free rotation removing the prohibition of the band ${}^2\nu_a^{CH_3}$.

The two frequencies ν_t^{CH} and ${}^2\nu_a^{CH}$ must be identified with the two Raman lines 2955 and 2899. The analogy with the CH bands appearing in the infra-red spectrum suggests that this is the correct order.

The Raman frequency 993 must be identified with ν_t^{CC} because C–C bands as a general rule are associated with frequencies in the region of 1000. The vibrations $\nu_t^{CH_3}$ and ${}^2\nu_a^{CH_3}$ were identified by Mecke with the line 1460 found by Daure; this line may possibly be due to impurity, but we do not reject this assignment since, by analogy with the methyl halides, it is clear that the vibration frequencies in question should lie in this region.

The remaining frequency ${}^2\nu_a^{M}$ is missing from the Raman spectrum.[‡] It has been calculated from the specific heats by Eucken and Parts (*loc. cit.*), on the basis of the other frequencies as given by Mecke, to be 712. The changes we have made in the other frequencies being taken into account, ${}^2\nu_a^{M}$ becomes 750.

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