Viscosity, Self-Diffusion, and Allied Effects in Solid Polymers*

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An attempt has been made to explain the observed viscous behavior of bulk polymers. It is found that the viscosity and diffusion may be represented by a theory which takes into account the coupling together of the molecules. Two equivalent treatments are given. One makes use of a segmental friction factor in the same manner as the common formulation of dilute solution viscosity of polymers. The second method uses the concept of segmental jumping. Since both are equivalent, an expression for the friction factor is found in terms of the segmental jumping frequency. Using this fact it is possible to calculate the segmental jumping frequency from bulk viscosity data. A simple application leads to the result that the jumping frequency is about 0.3 sec⁻¹ at the transition temperature in polystyrene.

In addition a simple relation is found to hold between bulk viscosity and diffusion constant. The proportionality constant is easily evaluated and so one is now able to obtain self-diffusion constants directly from viscosity data.

INTRODUCTION

MANY data are now at hand concerning the basic flow properties of polymers over a wide range of temperature, molecular weight, and plasticizer concentration. Until now there has been no quantitative molecular theory to explain the observed behavior.[1] The purpose of this paper is to show how it is possible to obtain at least a semiquantitative theory for the bulk viscosity and self-diffusion of polymers.

In order to illustrate the simplicity of the concepts involved, no effort is made in this paper to maintain exceptional mathematical rigor. Physically reasonable approximations are made with the understanding that a more precise treatment is possible. It is to be expected that a more exact derivation of the relations found here will not alter the results to any great extent.

I. RELATION BETWEEN VISCOSITY AND DIFFUSION

The essential difference between the viscosity mechanism in a solid polymer and in a dilute solution of a polymer is that in the former case the solvent is composed of polymer molecules. Since most theories of dilute solution viscosity of polymers make no assumptions as to the character of the solvent, it is possible to apply them almost directly to the case of bulk polymers. One must only keep in mind that in this case the polymer and solvent are identical.

There are essentially two types of calculations for the viscosity of dilute polymer solutions. The first of these assumes that the polymer molecule does not distort the flow lines in the solvent.[2] This is often referred to as

the "free draining" approximation since it is the case which would apply if the solvent flowed freely through the polymer molecule. Unfortunately, the term "free draining" does not tell the whole story. (It is possible to imagine instances where the molecules are far from free draining, and still the flow lines of the solvent are not distorted appreciably by the presence of the polymer molecule. For this reason, it would be preferable to refer to the calculations of that type as "zero-distortion" calculations of viscosity.) The second type of calculation[3] of dilute solution viscosity recognizes that the flow lines of the solvent may be distorted by the presence of the polymer molecule. In the extreme limit, such a calculation leads to the viscosity of hard spheres in a low molecular weight solvent.

It is apparent that if the solvent itself is a polymer, one has the case of a bulk polymer. Moreover, since all points in the bulk are equivalent, the flow lines in such a "solution" will be essentially undistorted about any single molecule in the "solution." For this reason the "zero-distortion" calculation of dilute solution viscosity may be applied providing one recognizes that the solvent is itself the polymer.

The theory for dilute solutions amounts essentially to a calculation of the frictional energy loss between polymer and solvent. One therefore needs to calculate the product of the velocity of each segment of a molecule with respect to the solvent and the frictional force resisting this motion. The sum of all such products for all segments of the molecule times the number of molecules per cc gives the energy loss per cc which is due to the presence of the polymer molecules. This quantity is equal to the polymeric contribution to the solution viscosity provided the velocity gradient in the solution is taken as unity.

In a low molecular weight solvent, the frictional force on a segment of a polymer molecule is due to the fact that it is sliding past the solvent molecules. In addition

[1] R. E. Powell and H. Eyring have presented an interpretation of some low molecular weight data on polyesters in *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1947), Vol. I, p. 199.

[2] M. L. Huggins, J. Phys. Chem. **43**, 439 (1939); W. and H. Kuhn, Helv. Chim. Acta **26**, 1394 (1943); P. Debye, J. Chem. Phys. **14**, 636 (1946).

[3] W. Kuhn, Kolloid-Z. **68**, 2 (1934); J. Kirkwood and J. Riseman, J. Chem. Phys. **16**, 565 (1948); P. Debye and A. M. Bueche, J. Chem. Phys. **16**, 573 (1948).

to this effect, one also has another effect if the solvent is polymeric. This second type of friction force is due to the fact that polymer molecules may be intertwined to such an extent that in order for one polymer molecule to move it must drag others with it.

The sliding friction force may be represented as usual as a constant times the velocity of the segment. This may also be done for the second force just mentioned. However, if the molecule is undergoing rotation as well as translation, this second friction constant may depend upon the position of the segment in the molecule as well as upon its velocity. Whether this positional dependence is important or not is intimately related with the manner of coupling between molecules. It may be shown that if the coupling is not extremely rigid this variation will not cause very serious trouble. For the present purposes we shall assume that the friction constant per chain segment is the same for all segments of the chain.

If this is done, one may follow through Debye's free draining calculation of viscosity to give the following expression for the bulk viscosity:

$$\eta = \frac{R^2}{M} \frac{N\rho A}{36} f, \tag{1}$$

where R^2 is the average square end-to-end chain distance, N is the number of chain segments per molecule, A is Avogadro's number, ρ is the density of polymer, M is the molecular weight, and f is the friction constant, which is evaluated more critically in Sec. II.

Since N and R^2 are both proportional to M, one might at first thought assume that the bulk viscosity should vary proportionally to the first power of M. This is not found to be true experimentally. The reason for this is that f, the friction factor, is also a function of the molecular weight. This functionality will be derived in a later section.

Fortunately, it is possible to obtain a relation between the diffusion constant D and the bulk viscosity, which does not contain f. This is done most simply by remembering the classical Einstein relation, which says

$$D = kT/\text{molecular friction constant.}$$

The molecular friction constant is defined as the force needed to pull a single molecule through the solvent with unit velocity. From the definition of f one sees that this will be just Nf. Therefore,

$$D = kT/Nf. \tag{2}$$

Taking the product between D and η one obtains

$$D\eta = (A\rho kT/36)(R^2/M). \tag{3}$$

Since R^2/M is essentially a constant for any bulk polymer and since its value is readily found from light scattering or dilute solution viscosity measurements

near the precipitation point,[4] it is possible to predict D if η is known. This is of considerable interest since, although D is the more easily interpreted physical quantity, η is far easier to measure.

The diffusion constant D has been measured along with η over a wide variety of conditions. These data are given in the preceding paper. They confirm the above relation within the experimental error of the measurements. Incidentally, this also shows that the assumption made concerning the friction factor f is really not too bad.

II. THE FRICTION FACTOR

If one considers a particular molecule of the solid, it is possible to imagine that a sedimenting force F could be applied to that molecule alone. As a result of this force the molecule will move with a velocity v just such that the viscous force will equal the sedimenting force, i.e.,

$$F = Nfv. \tag{4}$$

The above relation gives the same meaning to f which was used above. In order to find out what the physical basis for f really is, it will be necessary to calculate the viscous force by a more detailed method.

When the sedimenting molecule moves, it is restrained by two types of forces. The first of these is the ordinary friction experienced by each chain segment as it slides past the other surrounding segments. This force per segment may be represented by the product of a sliding friction constant f_0 and the velocity of the segment.

A second restraining force must be considered when the "solvent" is polymeric. It arises as a result of the fact that from time to time a "solvent" molecule will be hooked into the moving molecule in such a way that the two molecules must move more or less together. Mathematically, this may be described by assuming that a chain of molecular weight M will have KM molecules coupled to it. One would expect the coupling constant K to vary from polymer to polymer but to be independent of molecular weight. For polystyrene one would have K equal to 0.0001 if there were one coupled chain for every 200 chain atoms.

It would be wrong to think that each coupled chain moves with the same velocity v as the sedimenting chain. In fact, it may be shown from a consideration of the simple problem of ropes sliding over each other in a viscous medium that the coupled chain will move with an average velocity equal to $(4/9)v$. If the chains may not be considered smooth, this factor may be somewhat larger. It is possible to express this behavior by a slippage factor s, defined by the fact that on the average a coupled molecule will move with a velocity sv. It is expected that s will be a constant for any one polymer and should have a value of about 0.1 to 0.5.

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[4] P. J. Flory, J. Chem. Phys. **17**, 303 (1949).

With the above definitions in mind it is possible to calculate F, the force needed to pull a molecule through the polymeric solvent with a velocity v. It will be

$$F = vNf_0 + C_1Nf_0sv + C_2Nf_0s^2v + \cdots,$$

where C_1 is the number of first-order coupled chains (i.e., number of chains coupled to the primary molecule), C_2 is the number of second-order coupled chains, etc.

A crude approximation would be to set $C_1 = KM$, $C_2 = (KM)^2$, etc. This cannot be correct since it would predict that at a value of M such that $KMs = 1$, the force will become infinite. The reason that such is not actually the case is that not all couples can be effective. There are two reasons why a coupling may be ineffective. The coupling may be made to a chain which has been previously coupled and so would be moving with a velocity larger than the required velocity; or two couplings of the same order may be made to the same molecule, in which case each would exert only one-half its normal force.

Therefore,

$$F = vNf_0\{1 + C_1s + C_2s^2 + \cdots\}. \tag{5}$$

It is apparent that the only remaining obstacle to the calculation of F is the evaluation of the C_n.

Qualitatively it is possible to see quite readily what the values of the C_n will be. One would expect the first-order couplings to be nearly all effective and so C_1 will be KM. However, if we represent the sedimenting molecule as a sphere, the number of effective second-order couplings will be decreased within that sphere, because there is a possibility that some of the couplings will be made to chains already coupled as first-order chains. From this, C_2 should be less than $(KM)^2$ and similarly for $C_3 \cdots C_m$. In fact, it will eventually be true at some critical coupling order, say the mth order, that essentially no uncoupled molecules will exist inside the sphere available for couplings. At this value of $m = g$, the C_n will decrease fairly rapidly since effective couplings may only be made at the surface of the coupling sphere.

The calculation of the C_n may be carried out reasonably rigorously, as is shown in the appendix. When this is done, one arrives at the result that

$$F = vf_0N^* \quad \text{or} \quad Nf = N^*f_0, \tag{6}$$

where N^* is an effective number of chain links. The behavior of N^* is shown in Fig. 1 where $\log N^* \sim \log \eta$ is plotted against $\log N \sim \log M$. It will be seen that N is proportional to N^* for small values of N. However, when N becomes large enough so that on the average one chain is coupled to one other chain, i.e., $KM \cong 1$, the effective number of segments N^* varies as some higher power of N. The exact power is chiefly dependent upon the value of the slippage factor s, as shown in Fig. 1. At very large values of N, the quantity $N^* \sim N^{2\cdot5}$.
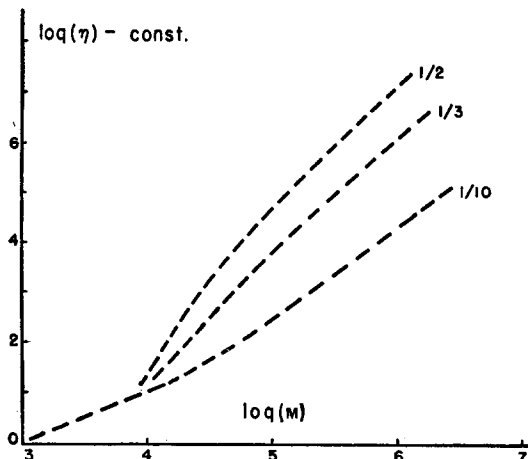
In order to compare this theoretical viscosity with that found by experiment, the values for R^2 and ρ have been chosen to approximate those known for polystyrene.

The value used is that for a very poor solvent $(R^2/M = 0.50 \times 10^{-16})$ since Flory[4] has shown this to be the proper value to use in concentrated polymer systems.[5] Using this value, the family of curves plotted in Fig. 1 were obtained. The quantity K was chosen as 10^{-4}. Choice of other values of K merely shifts the break in the curve along the axis since the break always occurs at the place where $KM \cong 1$.

Since Fox and Flory[6] have found experimentally that the data exhibit a break much like the one shown by theory at $M = 50,000$, one would estimate that K must have a value of about 2×10^{-5}. This would mean that a couple exists for each 500 chain units, which is not at all unreasonable.

Also, since experiment shows that the high molecular weight portion has a slope of about 1.5 units higher than the low molecular weight region, it is apparent that s must be about 0.3. This again is about the expected value. However, this value is uncertain due to the following fact.

The agreement between experiment and theory is not very good below $M = 50,000$. Whereas it is found here that the slope should be unity, experiment leads to a rather complex curve with slope near two. Such a discrepancy is to be expected since we have not considered the important fact that the presence of chain ends acts to "loosen" the structure. This is treated a little more fully in a later section where it is shown that the discrepancy is most likely due to a change in segmental jumping frequency when the number of chain ends becomes large. Unfortunately, this fact ceases to become

[5] Outer, Carr, and Zimm, J. Chem. Phys. **18**, 830 (1950).
[6] T. G. Fox and P. J. Flory, J. Phys. Colloid Chem. **55**, 221 (1950).

important at $M = 50,000$ (as shown by transition temperature and density data), and so a decrease in slope is superposed due to this effect. Therefore, a good value for s is not easily obtained until the chain end effect is better known. It is reasonable to assume that this chain end effect is largely responsible for the molecular weight dependence of Flory's data[7] on the viscosity of low molecular weight polyesters.

III. SEGMENTAL MOBILITY

It is possible to calculate the diffusion constant in another way which gives us direct information concerning segmental mobility. In addition, this second method leads to a more easily visualized picture of the actual diffusion process.

As a first approximation, consider the polymer molecule to be composed of N freely jointed segments. Further, suppose each chain link to have a probability P of jumping in either the positive or negative x direction in unit time. Call the average length of each jump a. One then knows that the number of links of a given chain jumping in the x direction in time Δt is $NP\Delta t$.

Now if Δt is taken short enough so that the number of jumps is small compared to N, each of these will be essentially independent, and so one has $n = NP\Delta t$ steps in a random walk.

From the theory of the random walk one may obtain a distribution function for the excess number of steps taken in the positive x direction. Call it $D(pa)$ where p is the number of excess steps and a is the length of each step. For a particular p the center of mass of the molecule will move a distance $pa/N = X$. To get $\langle X^2 \rangle_{Av}$ one must evaluate

$$\int_0^n X^2 D(pa) dp.$$

This then gives

$$\langle X^2 \rangle = na^2/N^2.$$

Now if the value of $\langle X^2 \rangle$ in the next instant Δt is independent of its previous value, one may show that[8]

$$D = \langle X^2 \rangle / 2\Delta t. \tag{7}$$

The required independence of $\langle X^2 \rangle$ may be shown to be approximately true for particular types of chains, and if one assumes it to hold closely enough for present purposes in all practical cases, one obtains

$$D = a^2 P / 2N. \tag{8}$$

But it was found above that

$$D = kT/f_0 N^*.$$

To bring these two relations into agreement one must replace N by the effective number of chain segments N^*.

After that is done one obtains the interesting result

$$f_0 = 2kT/a^2 P. \tag{9}$$

This equation relates the friction coefficient to the easily estimated quantities P, the jumping frequency, and a, the average x component length of each jump. Using this fact it is now possible to express the previous equations for D and η in terms of either f_0 or Pa^2.

Before leaving this section it should be pointed out that it is easy to derive the above equations without recourse to Einstein's relation. This is accomplished by calculating the sedimentation velocity for both ways of considering the process—a viscous drag and a directed walk—and comparing results.[9]

Since it is now possible to relate the bulk viscosity of a polymer directly to the segmental jumping frequency, it would be of interest to calculate the jumping frequency at the volume expansion transition temperature. Fortunately, Fox and Flory[10] list the approximate values of the bulk viscosity which one would find experimentally at the transition temperature in the case of polystyrene. They list the values of η at T_g for several molecular weights between 3000 and 300,000. To avoid the errors involved in the estimation of N we shall use the data for $M = 30,000$ where $N^* \cong N$. There one has $\eta = 10^{11}$.

Upon combining Eqs. (1), (6), and (9) it is found that

$$\eta = \frac{R^2}{M} \frac{\rho A}{16} \frac{kT}{a^2 P} N^*. \tag{10}$$

Taking $R^2/M = 0.50 \times 10^{-16}$, $a^2 = 10^{-15}$, and $N^* = 300$, one finds that P should be about 0.3 sec^{-1}.

According to this, if a sample of polystyrene of molecular weight = 30,000 is held at its transition temperature, each chain segment makes one jump every 3 seconds on the average. Such a frequency is about what one would expect if the transition temperature represents the temperature at which the chain segments are just able to adjust to the most favored position in a reasonable length of time.

Fortunately, another check is available on this point. The volume expansion and 3000-cycle dielectric properties of a single sample of polyvinyl chloride have been measured in this laboratory. The volume expansion transition temperature was found to be 83°C. The dielectric properties were essentially the same as for a sample studied extensively by Fuoss,[11] so his much more complete data were used. By extrapolation of his data one is able to show that the dielectric resonance frequency for this polymer is about 0.05 cycle when the sample is held at 83°C.

Since the dipoles of polyvinyl chloride are attached

[7] P. J. Flory, J. Am. Chem. Soc. 62, 3036 (1940).

[8] G. Joos, *Theoretical Physics* (Hafner Publishing Company, Inc., New York, 1934), p. 565.

[9] Originally the calculation was made in just that way. I am indebted to Professor P. Debye for pointing out this simpler approach.

[10] T. Fox and P. J. Flory, J. Appl. Phys. 21, 581 (1950).

[11] R. M. Fuoss, J. Am. Chem. Soc. 63, 378, 369, 2410 (1941).

directly to the chain, the average rotation frequency of the dipoles should be about equal to P, the jumping frequency. Moreover, the dielectric resonance frequency should be approximately equal to the average dipole rotation frequency. From dielectric measurements one would conclude that P should be about 0.05 at the transition temperature for polyvinyl chloride. This is to be compared with the value of 0.3 found for polystyrene at its transition temperature. Considering the inaccuracies of the extrapolations, the leeway in assuming values for the calculations, and the fact that the two polymers are much different, the agreement is quite acceptable. In fact, if one remembers that N is the number of freely orienting chain segments instead of actual segments as assumed here, the agreement can be made perfect. However, the author feels that the actual uncertainty in P is too large to justify perfect agreement.

It is also interesting to notice that the data for the molecular-weight dependence of Tg as given by Fox and Flory[10] seems to support the statement made previously concerning the molecular-weight dependence of η at low molecular weights. For if one calculates P for each molecular weight they have used, one finds

FIG. 2. Diagram illustrating the quantities used in the text.
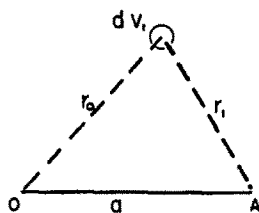
that P is essentially constant at the transition temperature. Therefore, it would seem that the transition temperature represents a state of constant segmental jumping frequency. This, of course, fits in very well with Fox and Flory's[10] supposition that Tg is an iso free volume state.

APPENDIX

It is shown in the text that in order to calculate the force needed to pull a molecule through the solid with a given velocity one must know the value of C_n. This quantity is defined as the number of the nth-order couples which are effective. In order to calculate it, one must know the spatial distribution of coupling points for any coupling order. This may be found as follows.

The distribution of segments of a molecule may be taken as[4]

$$\sim \exp[-\beta_0 r_0{}^2] r_0{}^2 dr_0,$$

where β_0 is $9/R^2$ and r_0 is measured from the center of mass of the molecule.

Since this is also the distribution function for the coupling points, the probability that a second molecule having its center at a distance a from the first will have a couple in the volume element dV (see Fig. 2) is
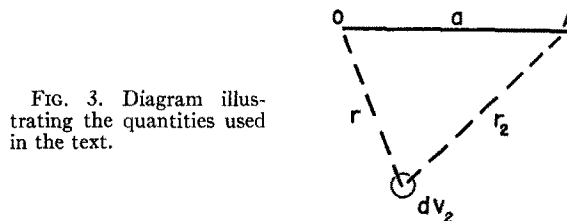

FIG. 3. Diagram illustrating the quantities used in the text.

given by

$$\sim \exp[-\beta_0 r_0{}^2 - \beta_1 r_1{}^2] dV_1.$$

Integrating this over all elements of volume gives the probability that a molecule with center at A is coupled to the original molecule:

$$\text{(constant)} \exp(-a^2[\beta_0\beta_1/(\beta_0+\beta_1)]).$$

Since the molecule with center at A has the probability given above of being first-order coupled, the above expression may be used to represent the density of centers of first-order coupled molecules as a function of a.

The density of segments from first-order coupled molecules in a volume dV_2 is found by summing the contributions of all such molecules as A.

The density of segments in dV_2 due to first-order coupled molecules at A will be proportional to (see Fig. 3)

$$\exp\left[-a^2\left(\frac{\beta_0\beta_1}{\beta_0+\beta_1}\right)-\beta r_2{}^2\right].$$

Integrating over all positions of A one obtains for the distribution of segments of first-order coupled molecules and therefore of second-order coupling points

$$D \sim \exp\left\{\frac{\beta[(\beta_0\beta_1/\beta_0+\beta_1)]}{\beta+(\beta_0\beta_1/\beta_0+\beta_1)}\right\} r^2.$$

But $\beta_1=\beta_0=\beta_n=\alpha$, and so the distribution of nth-order coupling points is

$$D_n = \text{(constant)} \exp[-r^2\alpha\gamma_n]$$

where $\gamma_1=1$, $\gamma_2=\frac{1}{3}$, $\cdots$, $\gamma_n=1/(2n-1)$.
But one also knows that

$$\int D_n dV = 1.$$

This gives the normalization constant, and one then knows that the distribution of nth-order coupling points is given by

$$D_n = \left(\frac{\gamma_n\alpha}{\pi}\right)^{\frac{3}{2}} \exp[-r^2\alpha\gamma_n],$$

where $\alpha=9/R^2$, $\gamma_n=1/(2n-1)$, and r is the distance from the center of mass of the original molecule. A similar expression applies for the distribution of centers of nth-order coupled molecules. It is obtained

by replacing γ_n by a new constant λ_n, which is equal to $1/2n$.

Now from the definition of K, each primary chain has KM primary (or first-order) couples. This essentially divides the chain into KM coupling segments. There will be Q such segments per cc. Such a definition does not appear reasonable at KM values less than unity, but this is of no consequence for the present purposes.

It is necessary now to consider what happens as M becomes very large. In that event only a small number of coupling segments of the secondary molecule will be effectively pulled along by the primary couple. Call this number ξ_0. For $KM < \xi_0$ we shall have $\xi = KM$.

Therefore the density of nth-order couples will be approximately

$$\rho_n = 3\alpha_n KM \xi^{n-1} \exp[-\alpha_n r^3] r^2 dr,$$

where $\alpha_n = 12.6\gamma_n^{\frac{3}{2}}/R^3$. In writing this expression the Gaussian previously used has been replaced by an exponential to r^3 having the same average of r^2. This is done to facilitate later computation and is probably not a serious limitation.

The effective number of couples may be obtained to good approximation by multiplying ρ by $e^{-\rho/Q}$ and integrating. One then finds

$$C_n = \frac{KM \xi^{n-1}}{A_n}(1-e^{-An}),$$

where

$$A_n = (3\alpha_n KM \xi^{n-1})/(4\pi Q).$$

Now the total force is given by

$$F = vN f_0 \{1 + C_1 s + C_2 s^2 + \cdots\}$$

or

$$F = vN f_0 \left\{ 1 + KM \sum_1^\infty \frac{s^n \xi^{n-1}}{A_n}(1-e^{-An}) \right\}.$$

This may be simplified in special cases. But in general one has $F = vf_0 N^*$ where N^* is defined as $N\{\ \}$.

For the calculations of the text, $\xi_0 = 5$ and $K = 10^{-4}$. The function is not very sensitive to ξ_0, and a change to a value of $\xi_0 = 10$ does nothing but increase N^* slightly above the break.

The Complete Symmetry Group for Internal Rotation in CH₃CF₃ and Like Molecules

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The symmetry for the wave functions of molecules like CH₃CF₃ is analyzed, and a new group, C₉ is proposed. The irreducible representations in C₉ are derived in the general case for the nuclear spin and internal rotation factors of the wave function. The procedure is described for determining the symmetry and statistical weight of any given internal rotation, vibration energy level.

PAST treatments of the symmetry for internal rotation in molecules like CH₃CF₃ have utilized the group of threefold rotations of one top alone.[1,2] This has led to the introduction of an artificial asymmetry into the problem, which gives rise to certain problems in assigning symmetry characteristics to the various wave functions, and statistical weights to the corresponding energy levels.[2] Actually the combined rotations of both tops comprise a group, called here C₉, which must be used in considering the symmetry of the wave functions.

If R_1 is a rotation of the CH₃ top by 120° and R_2 the corresponding rotation of the CF₃ top, the complete set of operations is

$E;\ R_1;\ R_1^2;\ R_2;\ R_2^2;\ R_1R_2;\ R_1R_2^2;\ R_1^2R_2;\ R_1^2R_2^2,$

where E is the identity element. The subgroup $E;\ R_1R_2;\ R_1^2R_2^2$ is the well-known three-fold external

rotation group of the molecule, while $E;\ R_1;\ R_1^2$ and $E;\ R_2;\ R_2^2$ are the rotational subgroups for the CH₃ and the CF₃ tops, respectively. Each of the latter has the representations

	E	R	R^2
A	1	1	1
E	1	ω	ω^2
	1	ω^2	ω

where $\omega = \exp(2\pi i/3)$.

In constructing the representation of the total group, one can assign the characters to the rotations as follows:

$$E_1 \begin{cases} R_1 \sim \omega & R_2 \sim 1 \\ R_1 \sim \omega^2 & R_2 \sim 1 \end{cases} \qquad E_2 \begin{cases} R_1 \sim 1 & R_2 \sim \omega \\ R_1 \sim 1 & R_2 \sim \omega^2 \end{cases}$$

$$E_3 \begin{cases} R_1 \sim \omega & R_2 \sim \omega \\ R_1 \sim \omega^2 & R_2 \sim \omega \end{cases} \qquad E_4 \begin{cases} R_1 \sim \omega & R_2 \sim \omega^2 \\ R_1 \sim \omega^2 & R_2 \sim \omega^2. \end{cases}$$

[1] J. S. Koehler and D. M. Dennison, Phys. Rev. **57**, 1006 (1940).
[2] J. O. Halford, J. Chem. Phys. **18**, 444 (1950).