

The Ultimate Liquid Transmission Limit?

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which link up to form rings. Furthermore, Tanford¹⁰ has computed a hydrogen bond energy of 6.3 kcal./mole for the one hydrogen bond in the dimer structure based on the zig-zag model given by electron diffraction, from which the entropy of the dimer is calculated. He uses Briegleb's equilibrium constant k for $2\text{HF} \rightleftharpoons (\text{HF})_2$, the large error in which introduces but a small error into the bond energy calculation because $\log K$ is used. Thus, the zig-zag model, deduced from electron diffraction experiments and having the polarity necessary to explain the polarization measurements, also leads to a reasonable value for the energy of the hydrogen bond.

The semi-empirical quantum-mechanical treatment also accorded by Evans and Glockler⁵ to the hydrogen fluoride dimer indicates a linear configuration, and hence is in qualitative agreement with polarization data. However, the crudeness of the approximations necessary in evaluating the London equation leads to an admittedly unreliable result.

* This research was carried out with the support of the Office of Naval Research.

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¹⁰ C. Tanford, unpublished calculations.

The Ultimate Liquid Transmission Limit?

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September 30, 1948*

IN a recent paper,¹ the far ultraviolet transmission limits of n -heptane and of two perfluorocarbons were determined as shown in rows 1-3 of Table I. The markedly poorer transmission of the fluorocarbons was surprising, for the extremely low refractive indices of perfluoro compounds had indicated that their transmission limits might lie at shorter wave-lengths than those of the corresponding hydrocarbons. Moreover, the $M \rightarrow V$ transition in perfluorotoluene is at 1780Å,² compared with its location in toluene at 1885Å.³ Recently, a carefully fractionated n -perfluorooctane was made available.⁴ It transmits to 1592Å in an 0.5-mm cell, to 1565Å in an 0.03-cm cell, and to 1780-1830Å in a 1-cm cell. The cut-offs are very sharp, as indicated by the change of only 30Å with a 20-fold change in cell thickness.

The energy at the extreme transmission limit of the perfluorooctane is about $64,000 \text{ cm}^{-1}$. This extends the region of the ultraviolet available for solution studies some 5000 cm^{-1} from the previous hydrocarbon limit of $58,500 \text{ cm}^{-1}$, which is itself some $10,000 \text{ cm}^{-1}$ above the usual quartz spectrograph ultraviolet limit. This extension from the quartz region is one and one-half times the total frequency spread in the visible between 4000-7000Å, and

TABLE I. Transmission limits.

Compound	Source	Purification	Cell thickness	Limit
1. $n\text{-C}_7\text{H}_{16}$	Westvaco	sulf. acid and/or silica gel	0.13 mm	1700Å*
2. $n\text{-C}_7\text{F}_{16}$	du Pont	no treatment	0.5	1800*
3. $n\text{-C}_8\text{F}_{20}$	du Pont	no treatment	0.5	1830*
4. $n\text{-C}_8\text{F}_{18}$	see reference 4	repeated fractionation b.p. 104.5°C ; $n_D^{20} = 1.268$	0.03 0.5	1565 1592
5. $\text{CF}_3\text{-cycloC}_6\text{F}_{11}$	du Pont	no treatment	0.5	1860
6. $(\text{CF}_3)_2\text{-cycloC}_6\text{F}_{11}$	du Pont	sulf. acid	0.5	1850
		no treatment	0.5	1960

* See reference 1.

offers correspondingly large opportunities for characterization of complex molecules and studies of their electronic behavior.

We may consider whether this limit of 1565Å will be the ultimate transmission limit for practical solvents in absorption spectrophotometry. Fluorides transmit better than corresponding hydrides or other compounds because of the high ionization potential of fluorine, higher than that of any other combining element. Similarly, molecules made from second-row elements will transmit better than their heavier analogs. Price⁵ and others have pointed out these relations between ionization potentials and spectra. Now second-row fluorides with one central atom, BeF_2 , BF_3 , CF_4 , etc., are either solids or gases. They can be used as solvents only at low temperatures (with decreased solubility) and/or high pressures, or at high temperatures, with possible decomposition of complex solute molecules. Evidently, for a solvent, we need a larger fluoride molecule, with a skeleton of several other atoms such as $-\text{C}-\text{C}-\text{C}-$, $-\text{B}-\text{B}-\text{B}-$, $-\text{B}-\text{N}-\text{B}-$, forming a long enough chain to be liquid at room temperatures. Chains containing O, Si, or S would not be feasible because of their known absorption about 2000Å.

The transmission properties of the liquid 8-carbon fluoride chain we have seen here. As for boron chains, BF_3 is formed instead of B_2F_6 , and pure fluoroboron chains are probably not possible. If they could exist, or if mixed hydride-fluoride-boron chains existed, they would probably not be transparent below 1700Å because of their unsaturation characteristics (conjugated?) as shown by the recently reported maximum of about 1350Å for the bridge-like diborane,⁶ and as indicated by the absorption of B_3H_9 near 2000Å.⁷

As for $-\text{B}-\text{N}-\text{B}-$ chains, we may reason from the unsaturated rings of this type to the little-studied saturated chains. The $\text{N} \rightarrow \text{V}$ transition of benzene is at 1835Å, of borazole at 1720Å, and of perfluorobenzene at 1740Å (estimated from perfluorotoluene⁸). For perfluoroborazole, this transition might lie as low as 1625Å. Then a saturated $-\text{B}-\text{N}-\text{B}-$ hydride chain might transmit to about 1600Å and the fluoride analog to about 1475Å. A polymer of BH_2NH_2 is known which is a solid.⁹ Its ultraviolet transmission is not known. A similar polymer $(\text{BF}_2\text{NF}_2)_x$, with $x = 3$ or 4, might be a suitable solvent to extend the transmission limit if such a compound could be prepared.

It seems, therefore, that the liquids promising to be more transparent than fluorocarbons are at present largely hypo-

thetical. Even if one were found and prepared in suitable quantity and purity, there would still remain questions of its stability, reaction with window materials, and potency as a solvent (especially of complex organic compounds). The *n*-perfluoroparaffins promise to be satisfactory on all these counts.

¹ H. B. Klevens and J. R. Platt, *J. Am. Chem. Soc.* **69**, 3055 (1947).

² Unpublished results of the authors.

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⁴ Through the courtesy of Drs. H. M. Scholberg and W. H. Pearlson, Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.

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The Average Boundaries of Statistical Chains

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September 17, 1948

THIS is to acknowledge my discovery that a problem which I solved as an example in a recent paper¹ had already been solved by W. Kuhn and H. Kuhn.² These authors give a result that differs from mine by only 5 percent. They also give values of various other parameters of branched as well as unbranched chains.

¹ C. A. Hollingsworth, *J. Chem. Phys.* **16**, 544 (1948).

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On the Classification of Symmetry Coordinates*

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October 6, 1948

THE symmetry type or irreducible representations of the $3n-6$ vibrations of an *n*-atomic symmetrical molecule may be found by group theoretical methods which will be restated briefly. The atoms may be divided into sets equivalent under the point group of the molecule; the permutation matrices for any given set of equivalent atoms then form a reducible representation of the group, which may be reduced to a "sum" of irreducible representations by the standard orthogonality relation for group characters. The direct product of this sum by the sum of irreducible representations for translation yields the total contribution of this set of equivalent atoms. Summing the representations thus obtained over all sets of equivalent atoms in the molecule, and subtracting finally the representations for translation and rotation, yields the representations for the vibrations (with the sum of the dimensions equal to $3n-6$).

A similar procedure may be used to find *separately* the irreducible representations of the symmetry coordinates formed from equivalent internal coordinates, which are commonly taken as a starting point for normal coordinate analyses. It is a considerable advantage to be able to enumerate the irreducible representations of the symmetry

coordinates without, or before, actually setting up the analytical expressions for these coordinates. Comparison of the representations for the sets of symmetry coordinates taken separately with the sum of representations for the $3n-6$ vibrations is usually sufficient to identify the redundant coordinates. In making frequency assignments, even when a normal coordinate analysis is not contemplated, a knowledge of the representations of the symmetry coordinates is useful in indicating the physical nature of the vibrations allowed in the spectra, and therefore in estimating probable frequencies. As is well known, each normal mode is formed only from symmetry coordinates belonging to the same representation.

In this communication the general principles of the method for symmetry coordinates are described. A paper now in preparation will give a fuller account and will contain tables by means of which the irreducible representations of most sets of equivalent internal coordinates may be obtained by inspection.

A set of equivalent internal coordinates may be divided into (equal) subsets such that each subset is associated with one point of an equivalent set of points, in the sense that the subsets permute among themselves in the same way as the points under the operations of the point group. The permutation matrices for this set of equivalent points form a reducible representation of the group, which may be reduced as discussed in the first paragraph. Those operations of the point group which do not permute a particular point of the set form a subgroup of the group. The operations of this subgroup will transform in some manner the members of the subset associated with this point; the introduction of subsets is necessary because, in general, the transformations of a subset under the subgroup cannot be represented by the permutations of a set of points. The case of most interest is that in which the coordinates of the subset belong to a single irreducible representation of the subgroup, the number of coordinates in the subset being equal to the dimension of the representation. In the case of the cyclic and dihedral groups the subgroup can contain only non-degenerate or one-dimensional representations, and each subset only one coordinate, unless the point lies on the principal symmetry axis and the latter is threefold or higher. In the latter case, and also in the case of tetrahedral and octahedral groups, when the point lies on a three- or fourfold axis, the subgroup will contain one or more two-dimensional representations, and the subset may contain one or two equivalent internal coordinates. There is also the relatively unimportant case in which the single point of the set lies at the origin, in which case three-dimensional representations occur for the tetrahedral and octahedral groups. There are, in addition, some cases of interest in which the subset lies in more than one representation of the subgroup. It should be noted that when the representation of the subset in the subgroup is one-dimensional, it may still not be totally symmetric.

The representation of the subset in the subgroup (the same for all subsets) may be obtained by inspection by considering the transformations under the subgroup of the *s*-vectors associated with the coordinates of the subset