of α-particles sufficiently energetic to produce the (α, n) reaction is relatively very much lower in the monazite sample. The monazite also contains a much higher relative content of contaminants of high neutron-capture cross-sections than does pitchblende. Consequently, in a qualitative fashion, the fact that monazite has a much lower Th^{229} to Th^{232} ratio than does pitchblende is satisfactorily explained, even on the assumption that nearly all of the Th^{229} is present as the result of the Th^{232}(n, γ) reaction.

CHICAGO 80, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

An Electron Diffraction Investigation of the Molecular Structures of Ketene, Carbonyl Fluoride and Tetrafluoroethylene[1]

BY T. TAYLOR BROUN AND R. L. LIVINGSTON

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The interatomic distances in ketene, carbonyl fluoride and tetrafluoroethylene have been determined by electron diffraction, using the visual correlation procedure. The following results were obtained: ketene, C=C = 1.30 ± 0.02 Å., C=O = 1.16 ± 0.02 Å. with ∠HCH and C–H assumed to be 117.5 ± 12.5° and 1.07 ± 0.02 Å., respectively; carbonyl fluoride, C–F = 1.32 ± 0.02 Å., C=O = 1.17 ± 0.02 Å. and ∠FCF = 112.5 ± 6°; tetrafluoroethylene, C–F = 1.30 ± 0.02 Å., C=C = 1.33 ± 0.06 Å. and ∠FCF = 114 ± 3°. The results for ketene are compared with an earlier electron diffraction investigation and with infrared and microwave results. The interatomic distances in C_2F_4 compare favorably with those obtained in a recent electron diffraction investigation in which the rotating sector was employed.

The interatomic distances in ketene have been determined both by electron diffraction and by spectroscopy. The electron diffraction results[2] gave C–C = 1.35 Å. and C–O = 1.17 Å. and were compatible with a linear arrangement of the carbon and oxygen atoms. A study of the infrared spectrum[3] of this compound did not yield sufficient data to fix all of the parameters, but a model with C–C = 1.300 Å. and C–O = 1.154 Å. was found to be in agreement with the infrared data. It was because of the disagreement between the electron diffraction and infrared results that the present reinvestigation of ketene was undertaken. It was felt possible to improve upon the early electron diffraction study since the results of that investigation were based upon measurements of only six features and gave an average deviation of 0.033 from the mean $s_{\text{calcd}}/s_{\text{obsd}}$ ratio. After the present investigation was started, the results of two microwave studies of ketene were published. The first of these[4] led to a preferred model with C–C = 1.333 Å. and C–O = 1.150 Å., while the second[5] gave the long C–O distance as 2.62 Å.; these results will be discussed later.

The interest in tetrafluoroethylene stems from the rather large differences which have been observed in the length of C–F bonds in various fluorine compounds. In methyl fluoride, this distance is 1.39 Å.[6]; in methylene fluoride, it is 1.36 Å.[7]; in fluoroform, it is still shorter.[8] It seemed interesting to be able to compare with the above distances the C–F distances in C_2F_4 and in F_2CO where the double bond on the same carbon atom might cause additional shortening. Such a shortening has been observed in the corresponding chlorine compounds.[9]

A comparison of the C–C bond distances in ketene and in ethylene with that in C_2F_4 should indicate whether or not the presence of the fluorine atoms has any effect on this bond length. Further, a comparison of the C–O distances in H_2CO and in F_2CO should permit one to determine if the fluorine atoms have any effect on this bond length.

Experimental

Ketene was prepared in this Laboratory by the thermal cracking of acetone.[10] After removal of acetone from the ketene by simple distillations, the product was subjected to rectification in a Podbielniak Hyd-Robot distillation column. The ketene distilled at a temperature of −73.8 ± 0.5° at 187 mm. and the sample used for the diffraction photographs was taken from the middle of this fraction. The sample was judged to be well above 99% in purity.

The carbonyl fluoride sample was provided by the Carbide and Carbon Chemicals Co. (Oak Ridge) operating under a contract with the U. S. Atomic Energy Commission. Infrared examination of the compound carried out at Oak Ridge indicated that the sample contained much less than 1% of impurities.

Two samples of tetrafluoroethylene were employed. One of these was obtained in this Laboratory by distillation of a commercial sample in the Podbielniak Hyd-Robot distillation column; a middle portion of the constant-boiling mixture was collected for photographing. The second was a specially purified sample supplied by Dr. C. F. Hammer of the Research Division, Polychemicals Department of the du Pont Company.

The electron diffraction photographs were prepared using an apparatus constructed by Professor H. J. Yearian of the Purdue Department of Physics. The wave lengths of the electrons were determined from transmission patterns of zinc oxide and were about 0.055 Å.; the camera distances were about 11 cm.

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(1) Contains material from the Ph.D. thesis of T. Taylor Broun, Purdue Research Foundation Fellow in Chemistry, 1949–1951.

(2) D. P. Stevenson and J. Y. Beach, *J. Chem. Phys.*, **6**, 75 (1938).

(3) G. Herzberg, Symposium on Molecular Structure and Spectra, The Ohio State University, June, 1947.

(4) B. Bak, S. Knudsen, E. Madsen and J. Rastrup-Andersen, *Phys. Rev.*, **79**, 190 (1950).

(5) H. R. Johnson, J. G. Ingersoll and M. W. Strandberg, *ibid.*, **82**, 327 (1951).

(6) V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

(7) R. L. Livingston and C. R. Rice, to be published.

(8) See references 20–22.

(9) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(10) (a) Fieser and Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944; (b) R. O. Rice, J. Greenberg, C. E. Waters and R. E. Vollrath, THIS JOURNAL, **56**, 1760 (1934).

Interpretation of the Patterns

The visual correlation procedure was used throughout, with some guidance from calculated radial distribution curves. The latter were calculated from the equation[11]

$$rD(r) = \sum_{q=1,2,\ldots q_{\max}} I(q) \exp(-bq^2) \sin \frac{(\pi q r)}{10}$$

with $e^{-bq^2} = 0.1$ at $q = q_{\max}$. The terms for the range $q = 1$ to $q = 15$ or 20 were obtained from one of the acceptable theoretical intensity curves. The latter curves were calculated on IBM machines using the equation[11]

$$I(q) = \sum_i \sum_j{}' \frac{Z_i Z_j}{r_{ij}} \exp(-b_{ij}q^2) \sin \frac{(\pi q r)}{10} \quad (1)$$

In all cases, measurements and intensity estimates were made by two or more independent observers.

Ketene.—Measurements of the pattern are summarized in Table I and the visual curve is shown in Fig. 1; the numbers used to identify the features are the same as those used by Stevenson and Beach.[2] Theoretical intensity curves were calculated from rigid models of ketene for which the symmetry of the point group C_{2v} was assumed. In all models the C–C distance was kept at 1.30 Å. and the labels on the curves in Fig. 1 refer to the C–O distances used.

TABLE I

QUANTITATIVE DATA FOR KETENE

Max.	Min.	q_{obsd}	1.17	1.16	1.16A	1.16B	1.15	Wts.
	1	14.83	0.897	0.897	0.903	0.890	0.897	0
1		19.35	1.034	1.034	1.028	1.044	1.039	0
	3	30.18	0.987	0.991	0.984	0.991	0.994	1
3		34.66	1.018	1.021	1.030	1.018	1.030	1
	5	46.98	0.981	0.990	0.990	0.990	0.994	2
5		50.87	1.010	1.012	1.010	1.016	1.016	2
	6	54.81	1.005	1.007	1.000	1.011	1.007	2
6		58.51	0.991	1.000	0.996	0.984	1.005	2
	7	63.06	0.994	1.002	1.001	1.002	1.007	2
7		66.81	1.006	1.009	1.010	1.009	1.010	2
	8	71.33	0.994	0.994	0.994	0.992	0.995	2
8		75.41	.990	0.997	0.998	0.997	1.005	2
	9	79.29	.999	1.006	1.006	1.008	1.016	1
9		83.43	.992	0.995	0.996	0.995	0.995	1
	10	87.38	.991	0.993	0.992	0.994	0.997	1
10		91.23	1.001	1.006	1.007	1.007	1.013	1
Average quoted wt.			0.997	1.002	1.001	1.001	1.006	
Mean deviation			0.008_1	0.006_9	0.007_3	0.009_3	0.007_0	

On comparison with the visual curve it is seen that model 1.18 can be excluded from the acceptable ones because in the curve for this model, the heights of maxima 7 and 8 relative to each other and the depths of minima 9 and 10 relative to each other are not as observed. In curve 1.17, these same minima occur with about equal depths, but the other relations are correct; model 1.17 is thus a borderline case. The theoretical curve for model 1.16 is acceptable in every detail. Maximum 9 does not appear as prominent in 1.15 as the observers feel it should; also in this curve, the relative depths of minima 8 and 9 do not agree with experiment. Model 1.15 is considered a borderline case. The curve for 1.14 must be rejected because of the exaggerated height of maximum 6, the relative depths of minima 7 and 8, and 8 and 9, as well as the virtual absence of maximum 9.

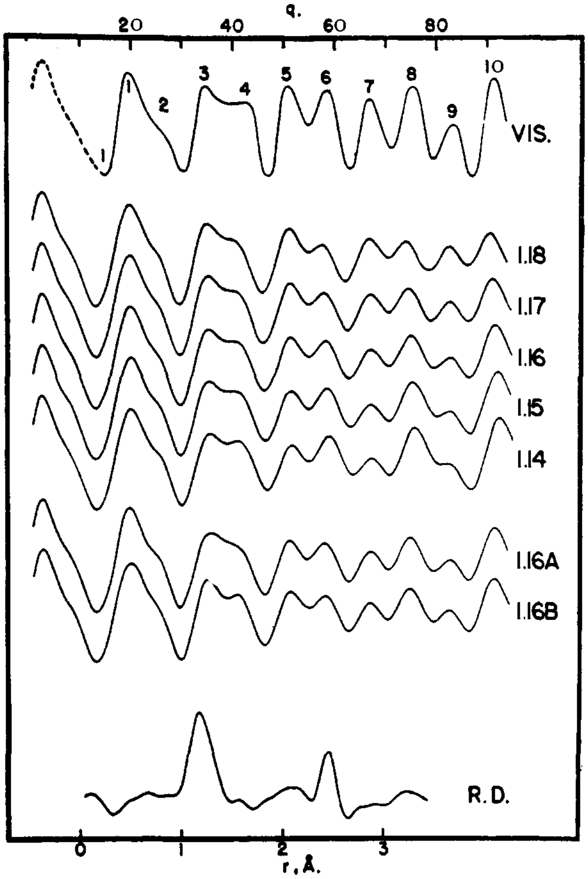

Fig. 1.—Intensity and radial distribution curves for ketene.

In the five models considered above, the hydrogen atoms were located by the parameters C–H = 1.07 Å. and ∠HCH = 117.5°. The effect of changing this angle may be seen by comparing curves for models 1.16, 1.16A and 1.16B. In 1.16A, this angle was 105° and in 1.16B, it was 130°. The changes in the qualitative appearance of the curve with changes in hydrogen parameters are seen to be very small and it was shown that reasonable variations of these angles and of the C–H distances would not produce a fit among any of the rejected models.

Calculations were then made to determine the nature of the dependency of the choice of distance ratio on the magnitudes assigned to the damping factors for the various interatomic distances. Table II summarizes the values of b_{ij} used in equation 1. The values of b_{ij} for distances involving only the heavy atoms were zero. The variations of the damping factors as outlined in Table II produce only very small changes in the theoretical intensity curves; this leads one to conclude that the heavy

TABLE II

VALUES OF b_{ij} USED FOR KETENE

Group	C–H	C···H	O···H	H···H
1	0	0	0	Infinity
2	0.00018	0.00035	0	Infinity
3	.00018	.00035	0.00055	Infinity
4	.00018	.00035	Infinity	Infinity

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[11] P. A. Shaffer, Jr., V. Shomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

TABLE III

$q_{\text{calcd}}/q_{\text{obsd}}$ RATIOS FOR CARBONYL FLUORIDE MODELS

Max.	Min.	$q_{\text{obsd.}}$	G	H	I	L	M	N	Q	R	S	Wt.
1		20.72	0.951	0.956	0.951	0.951	0.951	0.946	0.946	0.946	0.941	0
	2	25.90	.965	.961	.958	.958	.958	.958	0.961	.954	.954	0
2		29.79	.997	.994	.990	.987	.990	.990	1.000	.994	.990	1
	3	34.27	.957	.954	.954	.954	.954	.951	0.945	.942	.940	1
3		38.31	.968	.963	.960	.963	.963	.958	.958	.958	.953	2
	4	43.79	.959	.957	.952	.954	.954	.954	.957	.952	.952	2
4		47.93	.978	.976	.974	.976	.976	.974	.983	.980	.974	3
	5	52.71	.977	.971	.971	.971	.973	.971	.986	.977	.971	3
5		56.61	.975	.972	.966	.975	.972	.968	.977	.968	.957	3
	6	61.82	.961	.959	.954	.958	.959	.954	.954	.951	.950	3
6		65.63	.975	.972	.972	.972	.974	.970	.977	.972	.970	3
	7	70.75	.972	.971	.970	.970	.971	.968	.982	.978	.974	3
7		75.54	.974	.972	.969	.972	.970	.966	.997	.992	.982	3
	8	79.54	.978	.976	.970	.976	.974	.970	1.021			1
8		83.35	.978	.974	.972	.974	.974	.972				1
	9	87.27	.984	.981	.978	.981	.981	.980		.995	.977	1
9		91.55	.992	.991	.987	.990	.990	.986	1.007	1.005	.999	1
		[a]	.973	.971	.968	.970	.970	.967	0.975	0.971	.966	
			.0089	.0085	.0091	.0092	.0092	.0095	.0180	.0167	.0149	
		[b]	.973	.971	.968	.970	.970	.967	.978	.973	.967	
			.0064	.0059	.0069	.0066	.0066	.0070	.0136	.0127	.0117	

[a] An average in which all features were given equal weight. The number below the average is the mean of the deviations from the average. [b] An average in which the features were given the weights quoted.

atom distance ratio is essentially independent of reasonable variations in the vibration factors and that it is not possible to determine accurate values for these factors from the visual data. The values of b_{ij} used for the curves shown in Fig. 1 are those of group 3 in Table II.

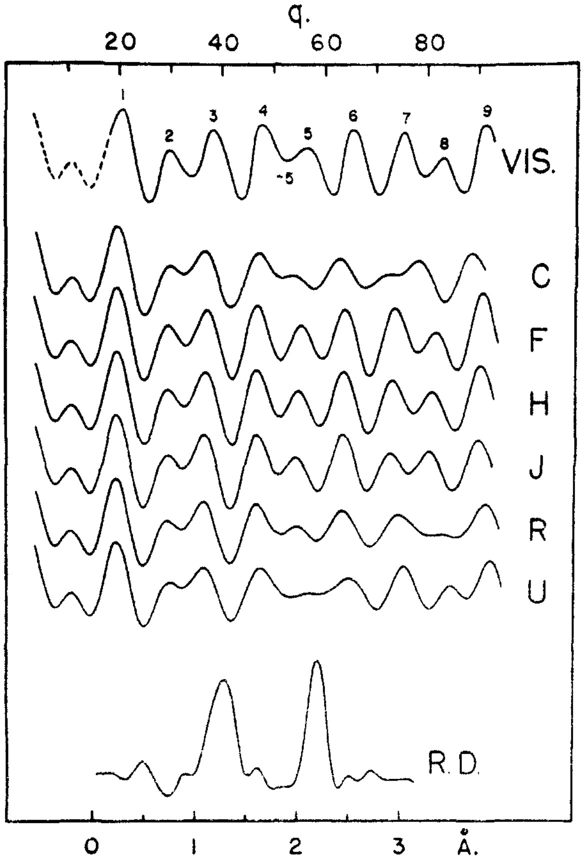


Fig. 2.—Intensity and radial distribution curves for carbonyl fluoride.

The $q_{\text{calcd}}/q_{\text{obsd}}$ ratios are given in Table I. The averages given at the bottom have been taken with the weights indicated in the right-hand column. The average deviations from the means of these ratios are seen to be satisfactory for all these models.

The final results are C–C = 1.30 ± 0.02 Å. and C–O = 1.16 ± 0.02 Å., assuming C–H = 1.07 ± 0.02 Å. and ∠HCH = 117.5 ± 12.5°. These distances are in agreement with the two strong peaks on the radial distribution curve (Fig. 1); the peak at 2.46 Å. is interpreted as the sum of the C–C and C–O distances and agrees perfectly with the final results.

Carbonyl Fluoride.—The visual curve for COF_2 is shown in Fig. 2 and Table 3 gives the measurements of feature diameters.

Preliminary calculations were made on the basis of rigid models of symmetry C_{2v} in which the C–F distance was kept fixed at 1.36 Å. while the ∠FCF and the C–O distance were varied. The values assumed for the parameters are given in Fig. 3. Many more models were actually tried, but these need not be discussed because of similarities to the representative ones shown.

The region of acceptable parameter ratios is shown by the closed curved line in Fig. 3; this region was established in the following way: Of the group of curves, B, C, D and E, curve C comes closest to being acceptable and is shown in Fig. 2. All of these were rejected because of the lack of the strong 7th maximum and because the 8th maximum is much too strong. Curves A, F, K and P are very similar; of these, only F is shown. These four were rejected because minimum 5 is at least as deep as minimum 6. Curves J and O are unacceptable because the relative heights of maxima 7 and 8 are not as observed; curve J is shown in Fig. 2.

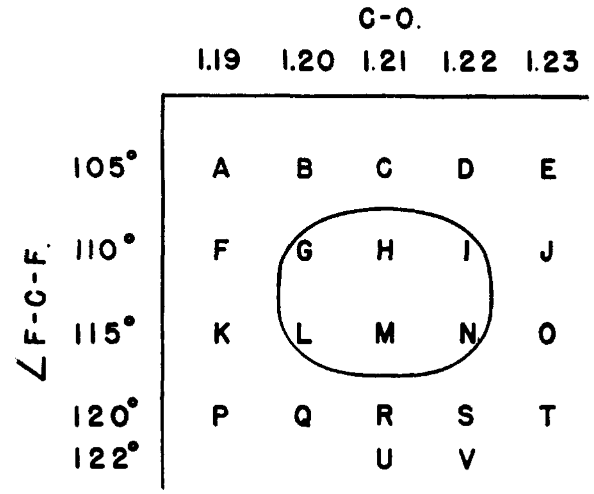


Fig. 3.—Parameters of calculated models of carbonyl fluoride. C–F = 1.36 Å in all models.

Models G, H, I, L, M and N are accepted as giving theoretical intensity curves that agree sufficiently well with the visual curve. All members of this group are very similar and are represented in Fig. 2 by H. By a comparison of the curves J, H and F, it is seen that there is a trend in which maximum 8 decreases in height relative to 7, if the comparison is made in the order given. For this feature alone, H and F are acceptable, while J is not. One also notes, however, that while in J and H the relative depths of minima 5, 6 and 7 are essentially correct, in F minimum 6 is not as deep as 5 or 7 and hence F may be rejected. On the basis of these arguments, the limits of acceptability have been placed just outside of G and I. Minimum 6 is only very slightly deeper than 5 in G while in I, maximum 7 is only slightly higher than 8.

The same remarks apply to the curves calculated from models having ∠FCF = 115°. When this angle is increased to 120°, maximum 8 practically disappears as may be seen by curve R, Fig. 2.

The qualitative comparisons place the 120° models on the borderline and the quantitative comparisons clearly eliminate them. Models with the ∠FCF at 122° were qualitatively unacceptable as illustrated by curve U in which maximum 5 is extremely weak and in which the relative depths of minima 5 and 6 are opposite to that observed.

Calculations have been made to demonstrate the nature of the dependency of the limits of the area of compatibility upon reasonable values for the vibrational damping factors. The values of b_{ij} were chosen as 0.0001 for the non-bonded distances. Curves calculated by use of these factors showed a general damping, but the intensity relationships of adjacent features were the same as in the original undamped curves. For factors of this magnitude, the area of acceptable parameter ratios is unchanged. If one assumes that the damping factors for the non-bonded distances have b_{ij} values no greater than 0.0001 larger than those for the bonded distances, then the area of acceptability remains that which is shown in Fig. 3. The q_{calcd}/q_{obsd} ratios are given in Table III. It will be noted that models Q, R and S give rise to average deviations from the mean q ratios which are sufficiently large to justify rejection of these models. In Table IV are listed the interatomic distances obtained by multiplying the assumed values for each acceptable model by its average q_{calcd}/q_{obsd} ratio. The final results are taken as C–F = 1.32 ± 0.02 Å., C=O = 1.17 ± 0.02 Å. and ∠FCF = 112.5 ± 6°. These distances lead to a value of 2.20 Å. for both the F–O and F–F distances; exactly this value is given by the stronger peak on the radial distribution curve (Fig. 2).

TABLE IV

CARBONYL FLUORIDE DISTANCES (IN ÅNGSTRÖM UNITS)

Model	G	H	I	L	M	N
F–C	1.32_3	1.32_1	1.31_6	1.31_9	1.31_9	1.31_5
C–O	1.16_8	1.17_5	1.18_1	1.16_4	1.17_4	1.18_0
F···O	2.20_9	2.21_4	2.21_7	2.18_2	2.18_2	2.18_5
F···F	2.16_9	2.16_5	2.15_9	2.22_1	2.22_1	2.21_4

Tetrafluoroethylene.—The visual curve for this compound is reproduced in Fig. 4 and is a result of examination of photographs of both samples mentioned earlier. There were no significant differences between the intensity estimates or measurements made on photographs of the two samples.

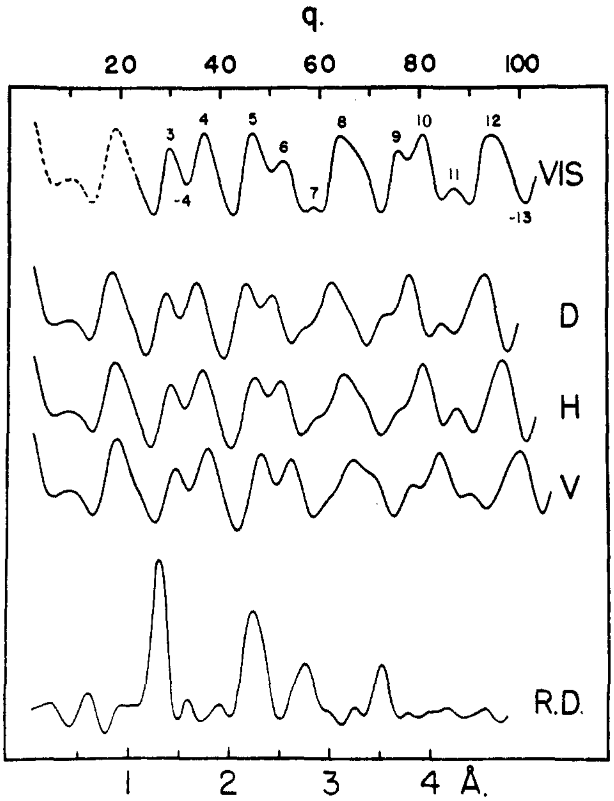


Fig. 4.—Intensity and radial distribution curves for tetrafluoroethylene.

A discussion of some of the critical features of the visual curve follows: Maximum 7 was drawn as a very small symmetrical peak although by the nature of this feature it was realized that it would be necessary to be liberal in its interpretation. The hump on the outside of the 8th maximum is judged to be less pronounced than are the similar features which occur on diffraction photographs of CO_2.

Maximum 9 is shown as it impresses most observers, but the only requirements which one can justifiably place upon this feature are that it must be asymmetric to the inside, that this asymmetry must be more obvious than the hump on the outside of the 8th maximum, and that this maximum be better resolved than is maximum 7.

The establishment of parameter limits was first done tentatively by comparing the visual curve with theoretical intensity curves calculated by rigid planar models having D_{2h} symmetry. The values of parameters chosen are indicated in Fig. 6. Curves were calculated for both the labeled and unlabeled points, but a discussion of curves corresponding to the unlabeled points is not necessary for the present purpose. The enclosed area on this chart indicates the limits of models compatible with the visual curve while the extended line is a boundary of the shapes of particular features considered alone.

The solid line extension on the lower side of the compatible area excludes the models below it because of the absence of maximum 11 and the unresolved doublet appearance of the 12th maximum. Of the models so eliminated, curve K shown in Fig. 5 is the most nearly acceptable. Models close to this line, but on the upper side, such as O and L, are in satisfactory agreement with observations.

Curves A, E, H, Q, X and Y are eliminated by failing to meet the asymmetry and resolution requirements placed on maximum 9 and V is on the borderline. Each of these is rejected or, at best, considered as a borderline case, because of other features.

Curve A is to be compared as an end member to the series L, G and D, in which a tapering of acceptability of the maximum 9 relations and the convex character of the 8th maximum is evident. Curves D and A are shown in the figures; D is considered to meet only the minimum requirements. It is because of the slow pace of this trend that the limit of compatibility has been placed half-way between D and A.

Curves E, H and Q are on a line which goes below B and Y that excludes from acceptability all models which are above it because they have their 6th maxima at least as high or higher than their 5th ones. Among the cases close to and on the boundary, the best in this respect is H, which is shown in Fig. 4. Curves F, J and R were quite clearly rejected on this basis.

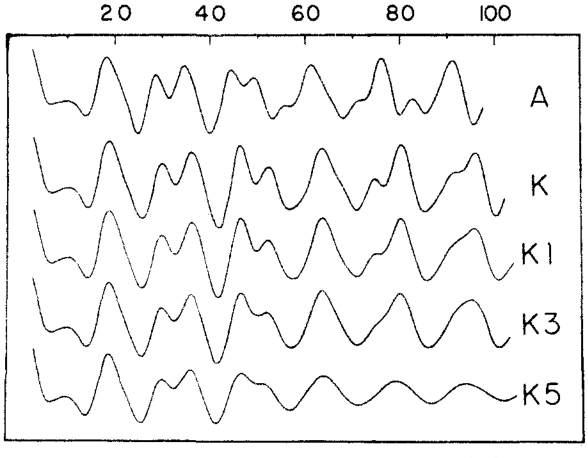


Fig. 5.—Intensity curves for tetrafluoroethylene.

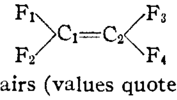
The series of models M, P, S, U, V and X exhibits trends that are responsible for the rejection of X and the reserved acceptance of V; the latter curve has been reproduced in Fig. 4. In each of these curves, the 6th maximum approaches the 5th in height, but does not get as bad as in H, the example borderline case for this test. The 7th maximum becomes barely perceptible in V and X, while the hump on the outside of the 8th maximum gets so pronounced in comparison to the 9th maximum that V is accepted only because of the desire to be as liberal as possible. Also in this curve, the 11th minimum and maximum seem to climb up the side of the 10th peak.

On the basis of the curves for the rigid models, the conclusion is that the C–F/C–C ratio is 0.987 ± 0.046 with an FCF angle of 114 ± 3.0°.

The effects of the inclusion of vibrational damping factors in the calculation of theoretical intensity curves is well illustrated by curves K, K1, K3 and K5 of Fig. 5, where the numerals in the labels indicate which factor set of Table V was applied. The results were very consistent; the amount of smoothing of the major features and suppression of the minor ones is regular from curve to curve, being proportional to the original intensities of the individual features in the curves for the rigid models and to the amount of damping (that is, the number and magnitude of the factors greater than zero). Thus we see that the asymmetry of the minimum in which the 7th maximum should appear is completely lost in going from K to K1; the well resolved 9th maximum of K is progressively reduced to a very slight asymmetry in K3. In every case tried of the representative group inside and outside the area of compatibility, the individuality of each feature is reduced step by step as the damping on the long distance terms is increased until as in K5 all the features look alike beyond what is left of the 6th maximum.

TABLE V

DAMPING FACTORS TESTED FOR TETRAFLUOROETHYLENE



Scattering pairs (values quoted are for b_{ij})

Set no.	$C_1–F_1$	$C_1–C_2$	$C_1\cdots F_1$	$F_1\cdots F_2$	$F_1\cdots F_3$	$F_1\cdots F_4$
1	0	0	0	0	0.0001	0.0001
2	0	0	0	0	.0002	.0002
3	0	0	0.0001	0.0001	.0002	.0002
4	0	0	.0001	.0001	.0002	.00035
5	0.00016	0	.00038	.00044	.00040	.00064

A note should be made here of an exception to the proportional action of the factors that is not demonstrated by the damped curves shown. The convex character of the 8th maximum withstands the smoothing effect of the factors more than any of the other minor features. Thus damping of the type tried would not make a curve such as V more

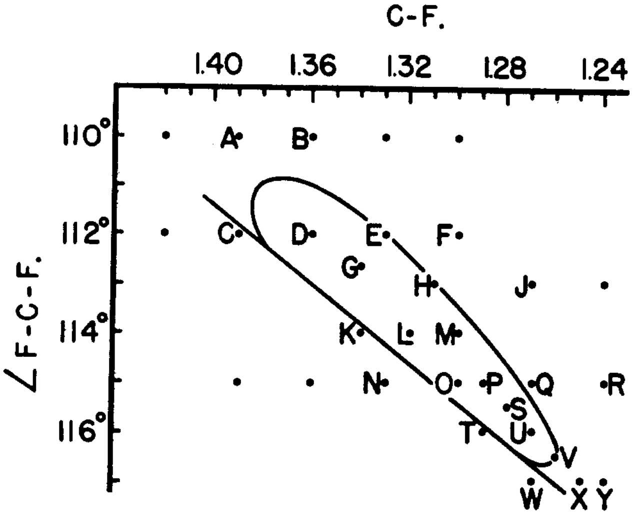


Fig. 6.—Parameters of calculated models of tetrafluoroethylene. C–C = 1.34 Å. in all models.

acceptable, even though the prominence of this hump is one of its objectionable features.

The general conclusion is the following: In no case was a curve seen to be improved by the inclusion of vibrational damping factors in its calculation. The rigidity of the requirements placed on the shapes of the features in the intensity curves would have to be considerably relaxed to allow acceptance of factor set K1, while it would be impossible to correlate curves calculated with sets 4 or 5.

TABLE VI

$q_{\text{calcd}}/q_{\text{obsd}}$ RATIOS FOR TETRAFLUOROETHYLENE

Max.	Min.	$q_{\text{obsd.}}$	D	G	L	M	O	P
	3	26.55	0.949	0.964	0.976	0.987	0.990	0.994
3		29.92	.979	.986	1.003	1.013	1.006	1.016
	4	33.42	.958	.969	0.978	0.987	0.993	0.993
4		36.76	.960	.971	.987	.996	.996	1.001
	5	42.65	.957	.966	.980	.989	.994	0.996
5		46.44	.975	.988	.999	1.012	1.012	1.016
	6	50.20	.960	.974	.986	0.992	0.998	1.000
6		52.81	.956	.968	.985	.992	1.000	1.002
8		64.01	.976	.987	1.001	1.012	1.009	1.015
	9	72.45	.959	.969	.984	0.998	0.995	1.005
10		80.72	.966	.979	0.992	1.001	1.006	1.011
	11	84.48	.971	.985	1.000	1.006	1.016	1.014
11		87.06	.970	.982	0.997	1.003	1.010	1.008
	12	90.08	.967	.974	.986	1.004	0.994	1.005
	13	101.19	.964	.975	.988	0.996	1.000	1.003
Average			0.964	0.976	0.989	0.999	1.001	1.005
Mean deviation			0.007_0	0.006_7	0.007_3	0.007_5	0.006_8	0.006_4

Max.	Min.	S	U	V
	3	0.998	1.006	1.017
3		1.023	1.033	1.039
	4	0.999	1.005	1.008
4		1.009	1.015	1.020
	5	1.006	1.008	1.018
5		1.023	1.029	1.038
	6	1.006	1.012	1.020
6		1.009	1.017	1.024
8		1.023	1.031	1.037
	9	1.009	1.020	1.027
10		1.017	1.026	1.033
	11	1.022	1.029	1.038
11		1.014	1.022	1.026
	12	1.012	1.021	1.027
	13	1.010	1.018	1.024
Average		1.012	1.019	1.026
Mean deviation		0.006_7	0.007_4	0.007_2

The tentative conclusions on the values and limits of the distance ratio and the F–C–F angle obtained from rigid models are thus accepted as final results. The $q_{\text{calcd}}/q_{\text{obsd}}$ ratios, together with the mean deviations from these values, are listed in Table VI. The interatomic distances as determined by these ratios for each model are given in Table VII, together with the final preferred values.

The radial distribution curve, Fig. 4, shows four peaks. The first and strongest is very narrow and is due to the bonded C–F and C–C distances; since the C–F contribution to this peak is so much greater than that of the C–C bond, the former distance is seen to be very near the 1.30–1.31 Å. indicated. The second peak, occurring at 2.24 Å., is due to the long C · · · F and the shortest F · · · F distances. Each of the last two peaks is caused by two pairs of equivalent distances. The intermediate F · · · F distance is responsible for the peak at 2.76 Å., while the long (diagonal) F · · · F has produced the one at 3.52 Å. Both these values are within 0.02 Å. of all values listed for these two distances in Table VII.

TABLE VII

INTERATOMIC DISTANCES IN TETRAFLUOROETHYLENE (IN ÅNGSTROM UNITS) AS DETERMINED BY THE ACCEPTABLE MODELS

Distance	Range of values obtained	Final value	Radial distribution result
C_1–C_2	1.29_2–1.37_5	1.33 ± 0.06	(1.31)[a]
C_1–F_1	1.29_3–1.31_1	1.30 ± .02	1.31
$C_1 \cdots F_3$	2.30_3–2.32_9	2.31 ± .03	(2.31)[a]
$F_1 \cdots F_2$	2.16_9–2.19_6	2.18 ± .03	(2.18)[a]
$F_1 \cdots F_3$	2.73_9–2.76_2	2.75 ± .02	2.76
$F_1 \cdots F_4$	3.50_5–3.51_4	3.51 ± .02	3.52

[a] These values were calculated from the other radial distribution results assuming a planar model.

It should finally be pointed out that the above interpretation is based entirely on planar models and that it would undoubtedly be quite impossible to eliminate models in which the planes containing the two CF_2 groups were rotated by about 10° from the planar configuration.

Comparison of Results

The results obtained for ketene in the present investigation are believed to be considerably more

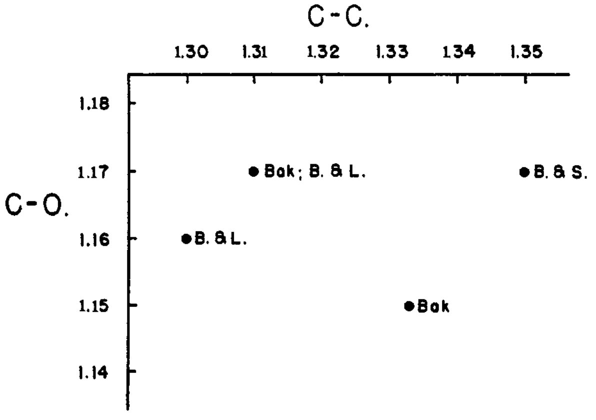


Fig. 7.—Parameters of ketene models (see text).

accurate than those of the previous electron diffraction study[2] since the former are based on diffraction patterns extending to much larger scattering angles. The present results are compatible with the infrared results[3] quoted in the introduction. The early electron diffraction results (B and S) are indicated in Fig. 7 together with the results of the present investigation (B and L).

The microwave results of Bak, *et al.*, are also indicated in Fig. 7 (Bak). These distances were obtained from absorption frequencies for H_2CCO, HDCCO and D_2CCO assuming the rigid rotator approximation and that ∠HCH = 122.5°. Since their three experimental data are not sufficient to define a unique solution to the problem, it seemed possible that another solution might be found which would give better agreement with the electron diffraction data. By successive approximations the model indicated in Table VIII was found; this model is not only compatible with the microwave data but also agrees fairly well with the new electron diffraction values. It is indicated in Fig. 7 by the label (Bak, B and L).

TABLE VIII

MICROWAVE SPECTRA INFORMATION AND COMPARISONS FOR KETENE

	Bak, Knudsen, Madsen, Rastrup-Anderson	Johnson, Ingersoll, Strandberg	
		(Corrected values)	
Molecular species	$0_0 \rightarrow 1_{-1}$ transition, mc.	$(b + c)$, mc.	$(b - c)$, mc.
H_2CCO	20,200	20,209.14 ± 0.05	377.41 ± 0.02
D_2CCO	17,690	17,673.42 ± .05	568.138 ± .005
HDCCO	18,825	18,821.67 ± .05	472.422 ± .005
Orig. investig.	C–C = 1.333	C····O = 2.62	
preferred model	C–O = 1.150	C–H = 1.19	
(rigid rotator	C–H = 1.06	∠HCH = 106°	
approxn.)	∠HCH = 122.5°		
Model obtd. by	C–C = 1.310	C–C = 1.309	
present invest.	C–O = 1.170	C–O = 1.168	
(rigid rotator	C–H = 1.072	C–H = 1.092	
approxns.)	∠HCH = 123°	∠HCH = 123°	
	C–C/C–O = 1.120	C–C/C–O = 1.121	

Also indicated in Table VIII is a model which agrees well with both the new electron diffraction data and with the microwave data of Johnson, *et al.*[5] This model does not agree with the value of 2.62 Å. which the latter authors have given for the C · · · O distance; it would be surprising if such a distance were really in agreement with the microwave results.

Preliminary values of the moments of inertia of COF_2 (as obtained from microwave data) have been given in a recent article[12] as 69.98×10^{-40} g. cm.^{2}, 71.70×10^{-40} g. cm.^{2} and 141.68×10^{-40} g. cm.^{2}, where the smallest moment is about the C_2 axis. These data are not sufficient to fix the structure of this molecule but do lead to a value of 2.106 Å. for the F–F distance which is much smaller than the value of 2.20 Å. given by the electron diffraction data. A model which is in good agreement with the electron diffraction results except for the FCF angle will lead to moments of inertia very close to those given above; thus with C–F = 1.31, C=O = 1.17 and ∠FCF = 107°, $I_a = 69.94$, $I_b = 71.80$ and $I_c = 141.75 \times 10^{-40}$ g. cm.^{2}. While a model with such an angle is within the estimated uncertainties of the electron diffraction results, the agreement cannot be considered as good.

After the present investigation had been started, an electron diffraction study of C_2F_4 was published by I. Karle and J. Karle.[13] Making use of a rotating sector and methods of analysis which should be quite accurate, they arrive at C–C = 1.313 ± 0.035 Å. and C–F = 1.313 ± 0.010 Å. with ∠FCF = 114 ± 2°. They have also determined the magnitudes of the vibration factors as those labeled set 5 in Table V. The agreement between the interatomic distances obtained in the two investigations is good, but application of the damping factors, set 5, results in a curve (K5 of Fig. 5) which cannot account for the pattern observed in the present investigation.

Discussion

It is interesting to compare the C–F distances obtained in the current investigation (1.30 ± 0.02 Å. in C_2F_4 and 1.32 ± 0.02 Å. in COF_2) with the C–F distances in other molecules containing the CF_2 group. In CF_2CH_2, this distance is 1.321 ± 0.015 Å.[14] while in CH_2F_2 it is appreciably larger at 1.36 ± 0.02 Å.[15] Three cyclic compounds containing the CF_2 group have been studied by electron diffraction. In C_4F_8 the C–F distance is 1.33 ± 0.02 Å.[16] For both C_5F_{10} and C_6F_{12} the radial distribution curves were interpreted by setting C–F = 1.38 Å. with C–C assumed as 1.54 Å. but no systematic variation of parameters was made in an effort to put limits on these values.[17]

Comparisons of the C–F distances may also be made with those in CH_3F and CHF_3. In CH_3F, the C–F distance has been determined as 1.39 Å. by electron diffraction[6] and 1.385 Å. by microwave and infrared spectroscopy.[18] One electron diffraction investigation[19] of CHF_3 gave C–F = 1.35 ± 0.03 Å. with ∠FCF = 108 ± 1.5° while another[20] gave C–F = 1.34 ± 0.02 and ∠FCF = 109 ± 2°. Spectroscopic results[21] give C–F between 1.32 and 1.33 Å. assuming an FCF angle of 110°; if the angle is reduced to 108°, the C–F distance is increased to 1.335 Å. which is in fairly good agreement with the electron diffraction results. It seems, then, quite definite that the C–F distance decreases as one replaces H atoms by F in the series CH_3F,

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(14) See reference 13 (electron diffraction). This result is also compatible with the moments of inertia obtained from the microwave spectrum by A. Roberts and W. F. Edgell, *Phys. Rev.*, **76**, 178 (1949).

(15) L. O. Brockway, *J. Chem. Phys.*, **41**, 185 (1937) (electron diffraction). A study of the infrared spectrum of this compound (H. B. Stewart and H. H. Nielsen, *Phys. Rev.*, **75**, 640 (1949)) gave C–F = 1.32 Å. A recent investigation of this compound in this Laboratory by electron diffraction has, however, confirmed the earlier electron diffraction investigation.

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(19) L. O. Brockway, J. H. Secrist and C. Lucht, paper presented at the Meeting of the American Chemical Society, Buffalo, N. Y., 1942.

(20) S. H. Bauer and J. Y. Beach, quoted by P. W. Allen and L. S. Sutton, *Acta Cryst.*, **3**, 46 (1950).

(21) H. J. Bernstein and G. Herzberg, *J. Chem. Phys.*, **16**, 30 (1948) (infrared) and reference 18 (microwave).

CH_2F_2, CH_3. In CF_4, however, the electron diffraction value for the C–F distance is 1.36 ± 0.02 Å. (Brockway, reference 15).

The C=O distances in H_2CCO and F_2CO (1.16 ± 0.02 Å. and 1.17 ± 0.02 Å.) are shorter than that in H_2CO[22] (1.21 ± 0.01 Å.). The data do not, unfortunately, permit any valid comparison of the C=C distance in C_2F_4 with this distance in other compounds. The rather short C=C distance found in ketene (1.30 ± 0.02 Å.) indicates that this bond distance is appreciably shorter than that in ethylene[23] (1.35 ± 0.01 Å.).

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LAFAYETTE, INDIANA

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

An Analysis of the General Mathematical Formulations for the Calculation of Association Constants of Complex Ion Systems

BY J. C. SULLIVAN AND J. C. HINDMAN

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Three general mathematical methods for the calculation of the association constants of a complex ion system have been examined. The three methods have been shown to yield unique values for the constants of a given system. The transformations in the general case have been developed. Evaluation of the constants of a system by both graphical methods and the solution of simultaneous linear equations have been discussed. The limitations of the methods have been considered. The methods have been applied to the calculation of the constants for the uranium(IV) sulfate complex ion system investigated by Betts. Within the manipulative uncertainties in treating the data, identical values of the constants of the system are obtained by the three methods.

In recent years an increasing amount of interest has been shown in the problems associated with the formation of complex ions in aqueous solution. In a review Bjerrum[1,2] has pointed out that the formation of complexes always appears to occur in stepwise fashion, with the stabilities of the various species MA_j characterized by a series of mass action constants, $k_1, \ldots k_j$. He also shows that if corrections for the statistical effect are made, a certain number of the ligands initially bound to the central atom, M, are attached with about the same affinity and suggests that a mean complexity constant $k = \sqrt[j]{k_1k_2 \ldots k_j}$ can be used as a convenient measure of the tendency to complex formation. From an examination of the relationships of the successive constants he has made deductions about the existence of characteristic coördination numbers, statistical effects, electrostatic effects, as well as certain anomalies—such as might be caused by change in coördination number—that may exist.

In order to correlate the free energy data on various complex systems, particularly if quantitative comparisons are to be made, not only are precise experimental data obtained from demonstrably valid experimental techniques necessary but the data must be treated in as mathematically rigorous and physically significant a manner as possible.

There are available only a limited number of general mathematical methods for the calculation of successive complexity constants although a variety of slight modifications and specific applications of these general formulations have been made by a number of investigators. The three general treatments are those proposed by Leden,[3] Bjerrum[2] and Fronaeus.[4] In the present communication we have undertaken to restate the general mathematical formulation for the calculation of successive complexity constants, examine the foundations in each case, analyze the physical significance of the treatment, apply the various methods to a particular set of data and then critically compare the results obtained, pointing out the aspects of each treatment that might be expected to introduce uncertainties.

I. Calculation of the Successive Constants of Mononuclear Complexes

General equations and definitions:

M = central ion or molecule
[M] = concentration of uncomplexed central ion or molecule
A = ligand
[A] = concentration of unbound ligand
$MA, MA_2 \ldots MA_j$ series of complexes formed
$[MA_j]$ = concentration of jth complex

$$M + A = MA,\ M + 2A = MA_2 \ldots M + jA = MA_j \quad (1)$$

For the jth complex the equilibrium constant

$$\beta_j = \frac{[MA_j]}{[M][A]^j} = \prod_{i=1}^{j} k_i \quad (2)$$

where the k's are constants for the formation of the individual complexes formed in stepwise manner.

Now the total central ion concentration, C_m, is

$$C_m = [M] + \sum_{i=1}^{j} [MA_i] \quad (3)$$

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