

The Microwave Spectrum of CF₂=CH₂

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(2) α -bands, less intense, shifting to the red on linear and angular anellation and hidden or partly hidden in the more intense para-bands in the higher acenes beginning with anthracene.³

(3) β -bands, the most intense, showing the same anellation effect and in a fixed ratio to the α -bands, lying more in the ultra-violet.

Recently H. B. Klevens and J. R. Platt,⁴ in a paper of the above title described the same classes of bands and regularities calling them, however, (1) L_a -, (2) L_b - and (3) B_b -bands respectively. Although the authors take the details of 8 absorption spectra out of my book and quote them as such, no reference is made to the fact that these spectral regularities are already described quantitatively in my papers and my book.^{1,2} Thus they claim in Section III:

"The preceding discussion has imputed properties to levels of a given type, which they retain from compound to compound and which make possible unambiguous identification according to the type. That states in compounds so diverse as benzene and benzantracene should have so much in common seems to be a *novel idea*. To date, theory has offered no prediction of such result and indeed has sometimes denied the likelihood of it. We should therefore state this doctrine of types explicitly and summarize the evidence for it.

(1) Levels of a given type have unambiguous identifying characteristics, which do not change from compound to compound.

(2) Levels of a given type move in a systematic way from compound to compound."

As can be seen from the references given these results do not represent at all a novel idea, but have been worked out quantitatively in detail in my publications. The theoretical implications of these empirical regularities need not to be discussed here.

¹ E. Clar, Ber. 69, 607, 1671 (1936); Atti d.X. Congresso Intern. d. Chimica, Roma II, 213 (1938); Ber. 72, 1819 (1939); Ber. 73, 81, 104, 596 (1940); Ber. 76, 149, 257, 328, 458, 609 (1943); Chem. Ber. 81, 52, 63, 163 (1948).

² E. Clar, *Aromatische Kohlenwasserstoffe* (Springer-Verlag, Berlin, 1941), p. 20.

³ See reference 2, p. 26.

⁴ H. B. Klevens and J. R. Platt, J. Chem. Phys. 17, 470 (1949); J. R. Platt, J. Chem. Phys. 17, 484 (1949).

Spectral Resemblances of Cata-Condensed Hydrocarbons

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June 30, 1949

IN a recent letter¹ Clar has criticized statements made in our earlier papers² which did not do adequate justice to his priority on the idea of spectral resemblances in condensed-ring systems.³

We made these statements because we had found the following difficulties in his scheme of resemblances and numerical relations as developed in his articles and book:

(1) He related the α -bands¹ (our L_b bands) to bands of ethane and ethylene,⁴ which seemed unreasonable.

(2) The α -bands were identified in only 3 out of the 15 3-ring, 4-ring, and 5-ring spectra.⁴

(3) The β -bands (our B_b bands) were derived from an admittedly non-existent strong allowed band in benzene which he predicted should be at about 2000Å.⁵

(4) Even after he had revised his numerical parameters completely from the integers and half-integers with which he started, there remained four cases⁶ of serious disagreement with experiment in his plotted comparisons.

(5) He made no comparisons at all for two of the five 4-ring spectra (3,4-benzphenanthrene and triphenylene).

(6) His resemblances were, in various contexts, related to the Balmer series,⁵ to the Moseley and Rydberg laws,⁷ and to the existence of Kékulé and Dewar structures in benzene;⁴ and indeed particular types of bands were assigned to particular types of resonance structures; and so on with several relations so difficult to fit into a rational quantum-theoretical account of the spectra that one is inclined to regard them as accidental.

As a result, since we sought a quantum-mechanical explanation of these spectra, we dismissed Clar's general correlations along with his unsatisfactory numerical formulae. We were not alone in this error. For instance, the longest wave-length bands of naphthalene have only within the past year been generally accepted as belonging to *two* electronic transitions,⁸ although Clar clearly postulated this as long ago as 1939. We therefore began a fresh search in the original spectra for more acceptable and comprehensive relations which would omit no observed bands. The results were given in reference 2. Until Clar's letter was brought to our attention we overlooked the fact that we had come back to some of Clar's original correlations.

On reading his book and articles it is clear that he indeed must be credited with the idea of the resemblances and with the correlation of the β - and para-bands in most of the compounds and of the α -bands in several of them. Our new contribution was to eliminate the discrepancies of points 1 and 3 above; to extend his correlation to the bands he omitted, as mentioned in points 2 and 5; to make new correlations for the triplet bands and for the shorter wave-length bands which he did not know; and to make an interpretation of these levels and regularities on a quantum-mechanical basis, relating it to other theoretical work. Our statement quoted by Clar would perhaps be correct if it were amended to read, "That states in compounds so diverse as benzene and benzantracene should have so much in common seems to be a novel idea *in the quantum-mechanical treatment of these molecules*."

Our objections concerning Clar's numerical relations do not diminish our admiration for his labors in obtaining and organizing the data on these compounds.

¹ E. Clar, J. Chem. Phys. 17, 741 (1949).

² H. B. Klevens and J. R. Platt, J. Chem. Phys. 17, 470, 484 (1949).

³ E. Clar, *Aromatische Kohlenwasserstoffe* (Verlag, Julius Springer, Berlin, 1941) and articles.

⁴ See reference 3, p. 24.

⁵ See reference 3, p. 26.

⁶ See reference 3, pp. 26, 33.

⁷ See reference 3, p. 23.

The Microwave Spectrum of $\text{CF}_2=\text{CH}_2$

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June 8, 1949

THE microwave spectrum of $\text{CF}_2=\text{CH}_2$ has been studied in the region between 22,000 and 29,000 mc using a Stark effect sweep spectrometer of the Hughes-Wilson type.¹ Over eighty lines were observed with an intensity of ten times noise or greater; lines of lesser intensity were not recorded at this time since it was not likely that they would enter critically into the analysis.

All strong and moderately strong lines were examined to see whether their Stark patterns could be resolved. For most weak lines (10 to 20 times noise), and for many stronger ones, no definite Stark pattern could be seen; there were too many com-

TABLE I. The Lines of the Q_{01}^* band-head.

Initial state	Final state	Calc.	Obs.
3-2	3-1	26,648 mc	26,649 mc
4-1	4-0	26,328	26,329
5-0	5-1	25,729	25,729
6-1	6-2	24,770	24,770
7-2	7-3	23,434	23,433
8-3	8-4	21,735	21,734

TABLE II. Molecular constants of $CF_2=CH_2$.

$$\begin{aligned}
 \kappa &= 0.7973 \\
 (a-c) &= 5,656.2 \text{ mc} \\
 (a+c) &= 16,347.4 \text{ mc} \\
 I_a &= 76.257 \times 10^{-40} \text{ g cm}^2 \\
 I_b &= 80.450 \times 10^{-40} \text{ g cm}^2 \\
 I_c &= 156.946 \times 10^{-40} \text{ g cm}^2 \\
 \mu &= 1.366 \pm 0.02 \text{ debye}
 \end{aligned}$$

ponents, identifying the line with high J values. For some lines resolution of Stark components was incomplete even at the highest fields available, about 3000 volts per cm. Well-resolved Stark components were found for about fifteen lines, and the transitions giving rise to them were eventually identified.

On the basis of reasonable structural parameters, this molecule would approximate an oblate symmetric top. The figure axis might be either the axis of least moment of inertia or the axis of intermediate moment of inertia, only small changes in the parameters separating the two cases. Qualitatively the main features of the spectrum would be the same in either case, and consist of two Q sub-branches ($J \geq 3$) having their band-heads at about 26,700 mc, one extending to lower and the other to higher frequencies. In addition one $R(J=1 \rightarrow J=2)$ transition should be found in the region of each Q sub-branch near the band-head. Moreover, the general region would be covered with transitions involving high J values and belonging to other Q sub-branches having their band-heads outside the region of observation. The experimental results are in agreement with these expectations.

So far it has been impossible to obtain quantitative agreement between the calculated and observed spectrum on the assumption that the figure axis is the axis of intermediate moment of inertia. On the other hand if one assumes the figure axis to be that of least moment of inertia, all lines with resolvable Stark patterns are quantitatively accounted for. Table I gives a comparison between the observed frequencies of the Q_{01}^* (i.e. band-head at $J=3$) sub-band and those calculated by interpolation in the tables of King, Hainer and Cross.² Two parameters, $(a-c)$ and κ^* are required for the calculation, which gives excellent results for all six lines.

Equally good agreement was found for 5 lines of the Q_{21}^* sub-branch expected in this region, as well as for two lines of the Q_{21}^* sub-branch and three R_{01} lines of the $J=1$ to $J=2$ transition.

The dipole moment was measured from the Stark effect of the $1_0 \rightarrow 2_{-1}$ and $1_{-1} \rightarrow 2_{-2}$ transition.

The values of the spectroscopic parameters and the moments of inertia obtained from them are found in Table II. While it is not possible to determine uniquely the five structural parameters from these data, it is interesting to note that with $C-F=1.32\text{\AA}$, $C=C=1.31\text{\AA}$, $C-H=1.07\text{\AA}$ and $LHCH=110^\circ$,

$$\begin{aligned}
 I_a &= 76.34 \times 10^{-40} \\
 I_b &= 80.60 \times 10^{-40} \\
 I_c &= 156.94 \times 10^{-40} \text{ g cm}^2
 \end{aligned}$$

The presence of transitions due to isotopic modifications is now being investigated. A more detailed report on this work will appear shortly.

This research was supported in part by ONR under contract N8ori-79400.

¹ R. H. Hughes and E. B. Wilson, Jr., Phys. Rev. **71**, 562 (1947).

² King, Hainer, and Cross, J. Chem. Phys. **11**, 27 (1943).

* The nomenclature is that of reference 2.

Light Scattering from Solutions of Charged Macromolecules

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June 27, 1949

IN the conventional theory of light scattering from dilute solutions the basic assumption is made that the fluctuations in solute concentration in neighboring volume elements are independent.¹ However, in view of the long range repulsive forces that are operative between similarly charged proteins or polymeric electrolytes in solutions of very low ionic strength it would appear that such an assumption is invalid. We have therefore considered the theory for such solutions from the point of view of the diminution of scattering per molecule as a result of intermolecular interference. In this approach the form of the radial distribution function must be selected. The Debye-Huckel approximation is not generally applicable because the potential energy is greater than the thermal energy. Of the several other choices available the simplest is that of characterizing the molecular interactions by a distance of closest approach thereupon imposing the hard sphere approximation. A general expression is then readily derived, the calculation being analogous to the solution of the problem of x-ray diffraction in monoatomic gases.² For the intensity of light scattered per unit volume of illuminated solution viewed, as a function of the angle of observation, in excess of that scattered by the solvent, when the incident light is vertically polarized and the scattered light is observed in the plane perpendicular to the electric vector, we obtain:

$$i = KMcP\{1 - (\psi/V)\Phi(\kappa sd)\}.$$

The constant, $K = 2n_0^2 I_0 (dn/dc)^2 / (N_0 \lambda^4 r^2)$, where n_0 is the refractive index of the solvent; I_0 , the intensity of the incident light of wave-length λ ; dn/dc , the refractive index increment based on the weight concentration c ; N_0 , Avogadro's number; r , the distance from the scattering solution to the detector. The molecular weight of the solute is represented by M and the internal interference function, which is unity when the solute molecules are small relative to the wave-length, by P . The ratio ψ/V denotes the ratio of the excluded volume to the volume of the solution, its value has the limits of zero and unity. The function $\Phi(x) = 3x^{-3}(\sin x - x \cos x)$. In the argument, $x = \kappa sd$, κ is the phase difference, $2\pi/\lambda$, $s = 2 \sin(\theta/2)$ where θ is the angle of observation and d is the distance of closest approach.

This equation predicts that when d is of the order of hundreds of angstroms i/c will fall rapidly from its infinite dilution value and become approximately constant at concentrations of the order of 1 g/liter. At higher concentrations the value of d must diminish for the excluded volume has attained its maximum value. Furthermore, if P is unity or if the data are corrected to this basis, the intensity of light scattered in backward directions will exceed that scattered in the corresponding forward directions; this would be a new experimental effect. Moreover, the ratio of the intensities of the forward and backward scattered light should with increasing concentration diminish from unity at infinite dilution, pass through a minimum and finally return to a value of unity as d diminishes to negligible values.

We have observed this behavior in solutions of several macromolecular electrolytes, data obtained for salt-free solutions of bovine serum albumin are summarized in the following table. These molecules are so small that the value of P may be taken as unity. Titration data indicate that under these conditions the albumin molecules carry net charges of about fifty protons. The consequence of intermolecular interference is clearly evident both in the absolute intensity of scattering per molecule and in the reduction of the dissymmetry, i_{45}/i_{135} . A value of d can be calculated from either effect. For the former we can set $(1 - i/KMc)$ equal to ψ/V and proceed to solve the relation $\psi = 4\pi d^3 V N_0 c / 3M$ for d . This result is only approximate for it assumes that there is no interpenetration of the excluded volume spheres of radius d .