

## Decomposition of Benzoyl Peroxide in a Magnetic Field

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TABLE I. The Raman spectrum of vinylidene fluoride.

Line	Intensity*	$\rho$ **	Assignment
1. 439 $\text{cm}^{-1}$	<i>M</i>	<i>D</i>	$B_1$ ; $\text{CF}_2$ rocking
2. 549	<i>M</i>	<i>P?</i>	$A_1$ ; $\text{CF}_2$ deformation
3. 603	<i>S</i>	<i>D</i>	$B_2$ ; $\text{CF}_2$ wagging
4. 714	<i>VW</i>		$A_2$ ; torsion?
5. 810	<i>M</i>	<i>D</i>	$B_2$ ; $\text{CH}$ wagging
6. 915	<i>VS</i>	<i>P</i>	$A_1$ ; C—F stretching
7. 949	<i>W</i>	<i>D</i>	$B_1$ ; $\text{CH}_2$ rocking
8. 1212	<i>VW</i>		$2 \times 603$
9. 1280	<i>W</i>		$B_1$ ; C—F stretching
10. 1359	<i>M</i>	<i>P?</i>	$A_1$ ; $\text{CH}_2$ deformation
11. 1389	<i>VW</i>		$439 + 949$
12. 1433	<i>VW</i>		$2 \times 714?; 2 \times 439 + 549$
13. 1472	<i>VW</i>		$549 + 915$
14. 1619	<i>VW</i>		$2 \times 810$
15. 1718	<i>W</i>	<i>P</i>	$A_1$ ; $\text{C}^{13} = \text{C}$ stretching
16. 1728	<i>VS</i>	<i>P</i>	$A_1$ ; C=C stretching
17. 1790	<i>VW</i>		$439 + 1359$
18. 1893	<i>VW</i>		$2 \times 949$
19. 3101	<i>VW</i>	<i>P</i>	$A_1$ ; C—H stretching
20. 3171	<i>VW</i>	<i>D</i>	$B_1$ ; C—H stretching

\* *VS*=very strong; *S*=strong; *M*=medium; *W*=weak, *VW*=very weak.  
 \*\* *P*=polarized; *D*=depolarized.

which can form a sound basis for the treatment of the latter type of molecule. Consequently, a study of the rotational and vibrational spectrum of vinylidene fluoride has been undertaken in this laboratory. This note is a preliminary report on the Raman effect and related work; the microwave studies are reported separately.<sup>1</sup>

The Raman effect was studied in the liquid state at  $-100$  to  $-125^\circ\text{C}$  with a Lane-Wells spectrograph having a camera aperture of  $F/3$ . Filters were used to reduce general scattering and to eliminate Raman excitation from the mercury lines of the 4046A group. Qualitative polarization runs were made with Polaroid cylinders. The results are listed in Table I together with the assignment. The line at  $714\text{ cm}^{-1}$  was observed only on the best films. Besides those listed, weak lines appeared shifted 857 and  $1667\text{ cm}^{-1}$  from 4358A. These are believed to be the fundamentals 915 and  $1728\text{ cm}^{-1}$  excited by 4348A.

Dr. George Evans of this laboratory made preliminary observations of the infra-red spectrum with a Perkin-Elmer spectrograph. For the most part the experimental results were essentially in agreement with the earlier work of Torkington and Thompson.<sup>2</sup>

The assignment of Table I was made on the basis of the polarization data, the expected magnitude of the fundamentals, and the infra-red data for this and the related olefins studied by Torkington and Thompson.<sup>2</sup> The torsional frequency is uncertain. One is led to expect it between 600 and  $900\text{ cm}^{-1}$ . A much less satisfactory way would be to assign the line at  $857\text{ cm}^{-1}$  to it; then 1667 becomes  $857+810$ .

A normal coordinate treatment has been carried out using a simple valency force field (no interaction terms) as a basis and with one additional term  $-kR^2$ . Here  $R$  is the change in the distance between fluorine atoms. This latter term is an attempt to approximate the combined effect of the repulsions between the two fluorine atoms and between each fluorine atom and the  $\pi$ -electrons of the double bond. Force constants pertaining to the motion of the  $\text{CH}_2$  group and the stretching of the C=C bond were given values essentially the same as in ethylene and those pertaining to the motions of the  $\text{CF}_2$  group were evaluated from the experimental results. This procedure resulted in good quantitative agreement between the calculated and the experimental values for all frequencies and provided a substantial number of independent checks. It is worth while noting that the value obtained for the C—F bond stretching constant,  $3.8 \times 10^5$  dynes/cm, seems more satisfactory for a single bond than the extremely high ("double bond") value of  $9.15 \times 10^5$  dynes/cm obtained for several fluorocarbons using another type of potential function.<sup>3</sup>

The considerable importance of the repulsions in these molecules is indicated by the value for  $k$  of  $1.17 \times 10^6$  dynes/cm—nearly one-third as large as the C—F stretching constant. And this one

constant adequately replaces several valency type interaction constants otherwise required.

A full report on this work will be published soon.

One of us (W. F. E.) wishes to express his gratitude to the Research Corporation for a grant which made the purchase of the Lane-Wells spectrograph possible. Thanks are also due to Dr. George Evans for making his infra-red data available.

<sup>1</sup> A. Roberts and Walter F. Edgell, *J. Chem. Phys.* (to be published).

<sup>2</sup> P. Torkington and H. W. Thompson, *Trans. Faraday Soc.* **41**, 236 (1945).

<sup>3</sup> E. L. Pace, *J. Chem. Phys.* **16**, 74 (1948).

## Decomposition of Benzoyl Peroxide in a Magnetic Field

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 June 13, 1949

THE decomposition of benzoyl peroxide is analogous to the polymerization of styrene in that both are radical chain reactions. In view of the reported effect of an external magnetic field on the rate of styrene polymerization,<sup>1</sup> it was decided to look for a similar effect on the rate of decomposition of benzoyl peroxide. The reaction was carried out in benzene under a nitrogen atmosphere and the peroxide content of the solutions determined by the method of Nozaki.<sup>2</sup> In each run one ampoule was between the poles of a 7518 gauss Alnico magnet and the control ampoule was in a remote part of the same thermostat, at  $35.00 \pm 0.01^\circ$ .

Run I, 102 hours		Run II, 766 hours	
Magnet	Control	Magnet	Control
20.53 cc*	20.28 cc	17.04 cc	16.88 cc
20.52	20.30	17.05	17.12
20.66	20.27	17.02	17.20
Av. 20.57	20.28	17.04	17.07

\* Cc. of 0.00544 N sodium thiosulfate solution for each 1 cc aliquot. The initial titer was 20.72 cc.

There appears to be no significant difference between the magnetic and the control reaction rates. The author has received a private communication from Dr. J. W. Breitenbach reporting similarly negative results in an attempt to repeat the observation of Schmid on styrene polymerization.<sup>3</sup>

\* du Pont Post-Doctoral Fellow, 1948–1949.

<sup>1</sup> Schmid, Muhr, and Marek, *Zeits. f. Elektrochemie* **51**, 37 (1945). For a theoretical discussion of such phenomena see J. E. Leffler and M. J. Sienko, *J. Chem. Phys.* **17**, 215 (1949).

<sup>2</sup> K. Nozaki, *Anal. Chem.* **18**, 583 (1946).

<sup>3</sup> To appear in *Monatshette*.

## Spectral Resemblances of Cata-Condensed Hydrocarbons

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 June 14, 1949

IN 1936 I introduced for the first time the comparative method in the study of the absorption spectra of polynuclear aromatic hydrocarbons and called it the anellation method,<sup>1</sup> which attributes bands of similar intensity and general character to similar origin. This method was applied systematically in numerous papers and reviewed in my book.<sup>2</sup> In this way I obtained three classes of bands:

(1) Para-bands, which shift most strongly with linear anellation to the red, and less strongly on angular anellation to the violet. These are, e.g., the long wave bands in anthracene and in the higher acenes and the second group of bands in benzene and naphthalene

(2)  $\alpha$ -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.<sup>3</sup>

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

Recently H. B. Klevens and J. R. Platt,<sup>4</sup> 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.<sup>1,2</sup> 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 benzanthracene 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.

<sup>1</sup> 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).

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

<sup>3</sup> See reference 2, p. 26.

<sup>4</sup> 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 letter<sup>1</sup> Clar has criticized statements made in our earlier papers<sup>2</sup> which did not do adequate justice to his priority on the idea of spectral resemblances in condensed-ring systems.<sup>3</sup>

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  $\alpha$ -bands<sup>1</sup> (our  $L_b$  bands) to bands of ethane and ethylene,<sup>4</sup> which seemed unreasonable.

(2) The  $\alpha$ -bands were identified in only 3 out of the 15 3-ring, 4-ring, and 5-ring spectra.<sup>4</sup>

(3) The  $\beta$ -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.<sup>5</sup>

(4) Even after he had revised his numerical parameters completely from the integers and half-integers with which he started, there remained four cases<sup>6</sup> 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,<sup>5</sup> to the Moseley and Rydberg laws,<sup>7</sup> and to the existence of Kékulé and Dewar structures in benzene;<sup>4</sup> 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,<sup>8</sup> 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  $\beta$ - and para-bands in most of the compounds and of the  $\alpha$ -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 benzanthracene 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.

<sup>1</sup> E. Clar, J. Chem. Phys. 17, 741 (1949).

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

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

<sup>4</sup> See reference 3, p. 24.

<sup>5</sup> See reference 3, p. 26.

<sup>6</sup> See reference 3, pp. 26, 33.

<sup>7</sup> 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.<sup>1</sup> 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-