The Vibrational Frequencies of CF2=CH2

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Differential Diffusion Coefficients of Sodium Ion in Sodium Chloride Solutions

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A SERIES of investigations are being carried out in this laboratory on the determination of differential or self-diffusion coefficients of radioactive ions in aqueous solutions. Previous results published by one of us[1] on the differential diffusion coefficients of Na^+ in NaI solutions disagreed with the limiting value given by the Nernst equation, and the present work was undertaken to determine whether similar deviations occurred for Na^+ in NaCl solutions.

The limiting law equations for self diffusion are:[1]

$$D(\text{cm}^2/\text{day}) = 7.75 \times 10^{-5}\lambda + T(1 + c(\partial \ln r/\partial c)), \quad (1)$$

or, for Na^+ in aqueous solutions,

at 25°C: $D = D^0(1 - 1.41c^{\frac{1}{3}})$, where $D^0 = 1.15$ cm²/day, (2)

at 35°C: $D = D^0(1 - 1.43c^{\frac{1}{3}})$, where $D^0 = 1.47$ cm²/day. (3)

The McBain-Northrop[2] technique has been used in obtaining the diffusion constants. (The apparatus employed consisted of a double ended glass diaphragm cell which could be suspended horizontally in a thermostat and rotated about its central axis. By means of an automatic reversing mechanism, the direction of rotation was changed every half-minute, and the eddy currents produced inside the compartments were sufficient to keep the solutions adequately stirred during the run. This method avoided the undesirable practice of introducing glass spheres, rods, etc., inside the compartments.)
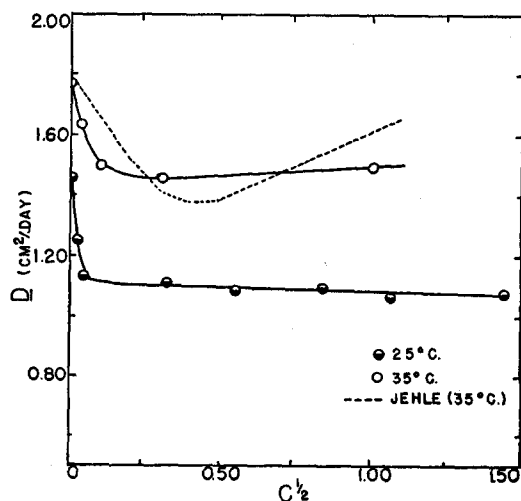

FIG. 1.

The cells were calibrated by using the standard calibration procedure recommended by Gordon,[3] using 0.1N KCl diffusing into water, and a mean diffusion coefficient of 1.58 cm²/day. The radioactive isotopes[4] employed were Na^{22} (3-yr.) and Na^{24} (14.8-hr.). No differences in diffusion behavior due to isotopic mass effects were observed. The change in concentration of the radio-isotope in each compartment was determined by means of a solution counter and scaling circuit, and from this the diffusion constants were calculated by means of the standard equation.[2] The diffusion times were such as to allow approximately 25 percent changes in concentration, and the calculated D values were precise to about 1 percent.

The experimental results obtained at both 25°C and 35°C are plotted in the figure, and the limiting behavior is approximated by the equations below:

at 25°C: $D = D^0(1 - 6.64c^{\frac{1}{3}})$, where $D^0 = 1.46$ cm²/day, (4)

at 35°C: $D = D^0(1 - 3.00c^{\frac{1}{3}})$, where $D^0 = 1.80$ cm²/day. (5)

Comparison of Eqs. (2)–(5) shows that our results, although reproducible and consistent in themselves, do not agree with the limiting law demanded by present theory. On the other hand, Harned and Nuttall[5] have recently published values for the mean diffusion coefficients of KCl which are in excellent agreement with the Onsager-Fuoss limiting law. If this can be considered to be a general confirmation of present theory, then, clearly, the glass diaphragm technique must give spurious results, at least in dilute solutions. This conclusion is strengthened by comparing our results at 35°C with those of Jehle[6] (see Fig. 1) which were obtained by means of free diffusion studies.

We are now examining in some detail the ability of the diaphragm cell technique to give accurate diffusion data, and find that an important systematic error arises from surface diffusion of ions adsorbed on the walls of the diaphragm pores. These surface effects were reported by Mysels and McBain,[7] who observed that the glass membranes show an anomalously high conductance in dilute solution, as would be expected if surface transport were involved. The diffusion coefficients should be similarly affected. The conductance effect has been confirmed in our laboratories for sodium sulfate solutions more dilute than 0.01M and this study will be extended to NaCl solutions. Since an effective cell constant can be calculated from such conductance measurements, a subsequent correction of our diffusion data for surface conduction may bring them into agreement with theory.

The need for such corrections throws doubt on the validity of diffusion coefficient values in the literature obtained for dilute solutions by means of the glass diaphragm method, and in general can be expected to limit the advantages which this method has so far appeared to enjoy.

The authors wish to acknowledge the support of these studies by a grant-in-aid from the Research Corporation.

[1] A. W. Adamson, J. Chem. Phys. 15, 762 (1947).
[2] J. W. McBain and T. H. Liu, J. Am. Chem. Soc. 53, 59 (1931).
[3] A. R. Gordon, Ann. N. Y. Acad. Sci. 46, 285 (1945).
[4] The Na^{22} was supplied by the Carnegie Institute of Terrestial Magnetism; the Na^{24} by the Atomic Energy Commission.
[5] H. S. Harned and R. L. Nuttall, J. Am. Chem. Soc. 71, 1460 (1949).
[6] L. P. Jehle, Ph.D. Thesis (Univ. of California at Berkeley, 1938).
[7] K. J. Mysels and J. W. McBain, J. Coll. Sci. 3, 45 (1948); we are indebted to Professor Mysels for calling our attention to this effect as a possible source of error.

The Vibrational Frequencies of $CF_2 = CH_2$

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T HE nature of the intramolecular forces, molecular structure and dimensions in fluorine containing molecules is of much interest. In particular, molecules which are intermediate between hydrocarbons and fluorocarbons should yield much information

TABLE I. The Raman spectrum of vinylidene fluoride.

Line		Intensity*	ρ**	Assignment
1.	439 cm⁻¹	M	D	B_1; CF₂ rocking
2.	549	M	P?	A_1; CF₂ deformation
3.	603	S	D	B_2; CF₂ wagging
4.	714	VW		A_2; torsion?
5.	810	M	D	B_2; CH wagging
6.	915	VS	P	A_1; C—F stretching
7.	949	W	D	B_1; CH₂ rocking
8.	1212	VW		2×603
9.	1280	W		B_1; C—F stretching
10.	1359	M	P?	A; CH₂ deformation
11.	1389	VW		439+949
12.	1433	VW		2×714?; 2×439+549
13.	1472	VW		549+915
14.	1619	VW		2×810
15.	1718	W	P	A_1; C¹³=C stretching
16.	1728	VS	P	A_1; C=C stretching
17.	1790	VW		439+1359
18.	1893	VW		2×949
19.	3101	VW	P	A_1; C—H stretching
20.	3171	VW	D	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.[1]

The Raman effect was studied in the liquid state at −100 to −125°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 cm⁻¹ was observed only on the best films. Besides those listed, weak lines appeared shifted 857 and 1667 cm⁻¹ from 4358A. These are believed to be the fundamentals 915 and 1728 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.[2]

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.[2] The torsional frequency is uncertain. One is led to expect it between 600 and 900 cm⁻¹. A much less satisfactory way would be to assign the line at 857 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 π-electrons of the double bond. Force constants pertaining to the motion of the CH₂ 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 CF₂ 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, 3.8×10⁵ dynes/cm, seems more satisfactory for a single bond than the extremely high ("double bond") value of 9.15×10⁵ dynes/cm obtained for several fluorocarbons using another type of potential function.[3]

The considerable importance of the repulsions in these molecules is indicated by the value for k of 1.17×10⁵ 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.

[1] A. Roberts and Walter F. Edgell, J. Chem. Phys. (to be published).
[2] P. Torkington and H. W. Thompson, Trans. Faraday Soc. 41, 236 (1945).
[3] E. L. Pace, J. Chem. Phys. 16, 74 (1948).

Decomposition of Benzoyl Peroxide in a Magnetic Field

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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,[1] 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.[2] 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 ±0.01°.

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.[3]

* du Pont Post-Doctoral Fellow, 1948–1949.
[1] 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).
[2] K. Nozaki, Anal. Chem. 18, 583 (1946).
[3] To appear in Monatshefte.

Spectral Resemblances of Cata-Condensed Hydrocarbons

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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,[1] 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.[2] 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