[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 841]

The Internuclear Distance in the Fluorine Molecule

BY MAX T. ROGERS, VERNER SCHOMAKER AND D. P. STEVENSON[1]

Introduction

Neither the internuclear distance nor the fundamental vibration frequency of the ground state of the fluorine molecule has been determined spectroscopically. Gale and Monk[2] photographed the band spectrum obtained from a discharge tube through which fluorine gas was flowing. They analyzed two bands at $\nu_0 = 16{,}378.8$ cm.$^{-1}$ and $\nu_0 = 17{,}439.5$ cm.$^{-1}$, and reported the values $r_0' = 1.48$ Å. and $r_0'' = 1.28$ Å. for the initial and final states of a transition $^1\Sigma \rightarrow {}^1\Pi$. Since these bands are not observed in the absorption spectrum of fluorine gas (the continuous absorption is not strong in this region), the transition does not involve the ground state of the F_2 molecule. Although it has not been verified by magnetic measurements, Mulliken[3] has shown that the ground state of F_2 is probably $^1\Sigma$. The values $r_0'' = 1.28$ Å. and $\omega_0 = 1130$ cm.$^{-1}$ must accordingly refer to an excited state. Attempts to observe the Raman spectrum and so determine ω_0 directly have been unsuccessful.[4]

For the internuclear distance in the normal fluorine molecule Brockway[5] reported the value 1.45 ± 0.05 Å., obtained by electron diffraction. Because the photographs were somewhat unsatisfactory and the interatomic distance values obtained from the several rings showed an unusually great deviation from each other, Brockway preferred to regard his result as only provisional. We here report a reinvestigation of fluorine vapor by the electron diffraction method which confirms Brockway's value. We find $r_{F-F} = 1.435 \pm 0.010$ Å.

We have already discussed[6] this value with respect to the additivity rule for interatomic distances and the covalent radius table.[7] With Badger's rule,[8] for rows and for columns of the periodic table, it leads to values for the vibrational frequency $\omega_e = 892$ cm.$^{-1}$ and $\omega_e = 1060$ cm.$^{-1}$, respectively.

Experimental

Fluorine was prepared by the high temperature method. A mixture of potassium acid fluoride and hydrogen fluoride in a Monel can with a graphite electrode was electrolyzed at 200°. The gas produced was passed over potassium fluoride to remove hydrogen fluoride and through a copper trap immersed in dry-ice to remove easily condensable impurities. Several volumes of fluorine were allowed to pass through a brass container fitted with an all-metal valve which was then closed off and attached to the nozzle of the electron diffraction apparatus by way of the all-metal valve and tapered brass joints. The system in which the fluorine was handled was entirely of metal. Care had to be taken to eliminate all organic matter. Indeed, some of the photographs from the first run clearly showed a superposition of the carbon tetrafluoride diffraction pattern; the carbon tetrafluoride, a strong scatterer relative to fluorine (or hydrogen fluoride), was undoubtedly formed by the action of fluorine on any grease or oil which had not been removed from the system. The chief impurities in the final samples were probably carbon tetrafluoride from the action of fluorine on the graphite anode, and oxygen from the electrolysis of any water which may have remained in the electrolyte. The rate at which the anode was attacked during the electrolysis indicates that the fluorine probably contained less than 3% carbon tetrafluoride, while the amount of oxygen was probably much less since the samples were collected after 20 to 30 hours of continuous electrolysis. Samples of fluorine were also collected by condensing the gas in a Pyrex trap and evaporating into the evacuated metal container.

The electron diffraction pictures were made and interpreted using the apparatus and general technique described by Brockway.[9] The electron wave length, about 0.06 Å., was determined in the usual way from gold-foil ($a_0 = 4.070$ Å.) calibration photographs, and corrections, amounting to a few tenths of 1%, were made for the observed differences in the expansion of the films used for the fluorine and for the calibration photographs. The camera distance was about 11 cm.

The photographs from the first runs were unsatisfactory in another, curious way which probably had nothing to do with the purity of the samples of fluorine used. The emulsion of about a half of each film, that half which in the camera stood nearest the axis of the film holder,[9] remained unblackened after development and dissolved only extremely slowly in the fixing solution. It seemed that this effect disappeared at about the same time that the last traces of oil from the film-holder bearing had been removed by the continual action of fluorine. Throughout the work with fluorine we noticed that fingerprints on the emulsion

---

[1] Present address: Westinghouse Research Laboratories, East Pittsburgh, Pa.

[2] Gale and Monk, *Astrophys. J.*, **69**, 77 (1929).

[3] R. S. Mulliken, *Phys. Rev.*, **36**, 699 (1930).

[4] C. S. Garner and D. M. Yost, THIS JOURNAL, **59**, 2738 (1937).

[5] L. O. Brockway, *ibid.*, **60**, 1348 (1938).

[6] V. Schomaker and D. P. Stevenson, *ibid.*, **63**, 37 (1941).

[7] L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[8] R. M. Badger, *J. Chem. Phys.*, **3**, 710 (1935); *Phys. Rev.*, **48**, 284 (1935).

[9] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

side of the films were preserved in a similar way as a light pattern on a dark background which fixed-out only with difficulty.

Finally, four different samples of fluorine gave 25 photographs identical in appearance except for density, and showing altogether six clearly resolved maxima and minima (12 features) of a simple diatomic pattern extending to $s \approx 30$. The heavier pictures were taken with gas pressures ranging up to 1000 mm., nearly the most intense electron beam we could get, and only one or two tenth-second exposures. Because fluorine could not rapidly be removed from the apparatus by condensation in the liquid air traps, each exposure was followed by a high-pressure discharge of the electron tube. Neither this nor the rapid spread of the gas through the diffraction chamber seems to affect adversely the diffraction pattern obtained; excellent photographs of nitrogen and oxygen, which gave the correct interatomic distances (as known from band spectra) to within 0.01 Å. have been obtained[10] under similar circumstances. Our fluorine photographs are not as clean as those of, say, oxygen, but we feel that they are nevertheless entirely satisfactory.

Presentation of Measurements

Each of us has made two or more sets of measurements of the ring diameters on different groups of photographs made from the last four samples of fluorine. The corresponding values of $s_0 = (4\pi/\lambda)\sin(\varphi/2)$ were calculated and compared with the positions of the maxima and minima of $(\sin rs)/rs$, the simplified intensity function for a diatomic molecule. The resulting values are given in Table I where we have foregone a presentation of the observed s_0 values in order to give separately the results of the various sets of measurements. Each value of r given is obtained from a consecutive series of features, the measurements from the innermost and outermost rings only being rejected from the average. In the column headed "Average deviation" there is given for each set of measurements the average deviation from the value "Average r" of the values obtained from the individual features included in "Average r." The consistency of the values given in Table I is such that we believe our result to be as accurate as those obtained for other diatomic molecules by the electron-diffraction method.[10] We accordingly report for the normal state of the fluorine molecule $r_{\text{F-F}} = 1.435 \pm 0.010$ Å.

TABLE I

Observer	Features in av.	Readings on each	Features incl. in av.	Av. r, Å.	Av. dev., Å.
V.S.	7	6	2nd max.–5th max.	1.428	0.008
V.S.	7	5	2nd max.–5th max.	1.430	.004
M.T.R.	6	10	2nd max.–5th min.	1.437	.004
V.S.	8	5	2nd min.–5th max.	1.431	.004
V.S.	8	10	2nd min.–5th max.	1.436	.007
D.P.S.	7	10	2nd min.–5th max.	1.441	.008
D.P.S.	6	5	4th min.–6th max.	1.430	.004
M.T.R.	9	8	2nd max.–6th max.	1.435	.008
			Final average	1.434	
			Average deviation	0.004	

Summary

An electron diffraction reinvestigation of the internuclear distance in the fluorine molecule leads to the value 1.435 ± 0.010 Å., substantiating the provisional value found by Brockway.[5]

PASADENA, CALIFORNIA RECEIVED JULY 7, 1941

---

[10] V. Schomaker and D. P. Stevenson, unpublished results.

[CONTRIBUTION FROM RESEARCH LABORATORIES, SHAWINIGAN CHEMICALS LTD.]

The Viscosity Function. III. Complete Viscosity Range*

BY ERNEST P. IRANY

It has been shown in the first paper of this series[1] that the viscosity functions of all *ideal mixtures*[2] follow one common law which, deduced by graphical means, is represented by the "ϕ scale" of viscosity. The observation that the temperature–viscosity functions of most pure liquids appear to obey the same or a closely related scale-law indicates its fundamental significance. The combined evidence very amply supports the conclusion that an *ideal* law governing the additivity of liquid viscosity is definable and that its expression by the ϕ scale is unique.

Thanks to abundant and very accurate viscosity data on pure liquids and their mixtures, the construction of the ϕ scale between about 0.25 and 50 centipoises encountered no great difficul-

---

* Original manuscript received July 5, 1940.

[1] Irany, THIS JOURNAL, **60**, 2106 (1938).

[2] "A system is *ideal* if there are no changes of molecular state, *i. e.*, no association, dissociation or combination, on admixture of its components" (Findlay, "Osmotic Pressure," p. 30). These conditions may be considered fulfilled if admixture produces no calorimetric, gravimetric or cryoscopic effects. Many such systems are known and have been carefully studied; they provided the original data for the construction of the ϕ scale as well as proof of its validity. The terms *ideal* and *ideality* as used in the present work have no connection with the concept of an "ideal liquid" composed of spherical or perfectly symmetrical molecules.