observation, then the intensities of l-light and r-light, I_l and I_r, in the luminescence excited by l-light or r-light depend on the excited state populations according to

$$I_l \sim \{en_L{}^* + (1 - e)n_R{}^*\} \qquad (5a)$$

and

$$I_r \sim \{(1 - e)n_L{}^* + en_R{}^*\} \qquad (5b)$$

As a measure for the magnitude of optical activity in emission, g_{lum}[10] has been introduced.[2,3] For our mixture of enantiomers we define χ analogous to g_{lum}

$$\chi = (I_l - I_r)/{}^1/_2(I_l + I_r) \qquad (6)$$

For an optically impure compound, χ must be dependent on the ellipticity of the exciting light. This follows from symmetry arguments. Thus χ for excitation with l-light (χ_l) will be unequal to χ for excitation with r-light (χ_r). The method proposed in this paper is based on this property. One derives

$$\chi_l = 2(2e - 1)\frac{a_1 n_L - a_2 n_R}{a_1 n_L + a_2 n_R} = g_{lum}\frac{p + {}^1/_2 g}{1 + {}^1/_2 pg} \qquad (7)[11]$$

and

$$\chi_r = g_{lum}\frac{p - {}^1/_2 g}{1 - {}^1/_2 pg} \qquad (8)[12]$$

Numerical values for χ_l and χ_r follow from CPL measurements.

There are three unknown quantities in (7) and (8). Thus in order to determine p we need a third equation. This equation is obtained by measuring CD and absorption of the mixture at the same wavelength as used for excitation. It is obvious that the ratio $\equiv \Phi$ of these effects is equal to pg

$$\Phi = pg \qquad (9)$$

Combining (7), (8), and (9) yields an equation from which p can be solved

$$p^2 = {}^1/_2\Phi\frac{\chi_l + \chi_r + {}^1/_2\Phi(\chi_l - \chi_r)}{\chi_l - \chi_r + {}^1/_2\Phi(\chi_l + \chi_r)} \qquad (10)$$

Once p is known it is also possible, of course, to determine the anisotropy factors g and g_{lum} which characterize the optical activity of a molecule in its ground state and in its excited state.

It must be emphasized that the measuring light in the determination of absorbance and CD should have the same band width and intensity distribution as the excitation light in the two luminescence experiments. This condition can be rather influential because in order to get a measurable signal-to-noise ratio in an actual CPL measurement, the slit width of the excitation monochromator is made much larger than in a usual absorption measurement.

The maximum accuracy in the determination of CPL, and thus in the determination of optical purity using the method presented in this paper, is obtained when the compound studied has both a large value of g_{lum} and a

(10) $g_{lum}(\lambda')$, the effect in CPL of the *optically pure* compound, has been defined as $g_{lum}(\lambda') = (I_l(\lambda') - I_r(\lambda'))/{}^1/_2(I_l(\lambda') + I_r(\lambda'))$, where $I_l(\lambda')$ is the intensity of the left circularly polarized component of the emitted light of wavelength λ'.
(11) To see the simple relation between $2(2e - 1)$ and g_{lum} one might consider the case of optical purity ($p = 1$: 100% L).
(12) Note that $100|(p + {}^1/_2 g)/(1 + {}^1/_2 pg)|$ and $100|(p - {}^1/_2 g)/(1 - {}^1/_2 pg)|$ have the meaning of optical purity in the excited state (in %).

high quantum yield in the luminescence. We suggest an application of this method to transition metal complexes where these requirements can be expected to be frequently met.

W. C. M. C. Kokke

*Department of Theoretical Organic Chemistry, University of Leiden
Leiden, The Netherlands*

Synthesis of "Superstoichiometric" Poly(carbon monofluoride)

Sir:

Poly(carbon monofluoride), $(CF_x)_n$, has been known since 1934 when Ruff and coworkers[1] prepared a gray compound of composition $CF_{0.92}$. In 1947 W. and G. Rudorff[2] reported a series of compositions $CF_{0.68}$ to $CF_{0.99}$, varying in color from black in the case of $CF_{0.68}$ through gray to white in the case of $CF_{0.99}$. Reviews of this chemistry have been published by Rudorff[3] and Hennig,[4] and it is perhaps due to the widespread review of these syntheses that the difficulty of preparing samples of stoichiometry higher than $CF_{0.8}$ is not generally appreciated even by fluorine chemists.

Poly(carbon monofluoride) (Figure 1) is a white compound, often reported to be explosive and unstable but found in this work to be stable in air to temperatures up to at least 600°. In fact, poly(carbon monofluoride) is the most thermally stable fluorocarbon polymer known. It decomposes upon heating at 800° or under a high vacuum at 580° to form a series of polyolefinic–fluorocarbons.[5] The compounds with compositions in the range of $CF_{0.68}$ to $CF_{0.8}$ are nearly black. The $CF_{0.8}$ to $CF_{0.95}$ compounds become gray and the $CF_{0.95}$ to $CF_{1.12}$ develop into a snow white solid. The earlier syntheses[1,2] report that poly(carbon monofluoride) may be prepared by passing fluorine over graphite at 450–600° for several hours. In some cases hydrogen fluoride is used as a catalyst.[2] Using these methods, a gray material of stoichiometry $CF_{0.68}$ to $CF_{0.8}$ is normally obtained.

Careful control of the reaction temperature at higher temperatures than previously reported was necessary to reproducibly obtain a completely fluorinated pure white material. One to one and a half grams of graphite were spread uniformly over the bottom of a 6-in. boat. The boat was placed in a 1-in. nickel tube heated by a resistance furnace and the furnace was allowed to warm to 200° for about 1 hr while helium was passed over the sample at a rate of 4 cm³/min to drive oxygen and moisture from the sample and reaction chamber. At the end of this period the furnace was

(1) O. Ruff, D. Bretschneider, and F. Elert, *Z. Anorg. Allg. Chem.*, 217, 1 (1934).
(2) W. Rudorff and G. Rudorff, *Z. Anorg. Allg. Chem.*, 253, 281 (1947); *Chem. Ber.*, 80, 417 (1947).
(3) W. Rudorff, *Advan. Inorg. Chem. Radiochem.*, 1, 125 (1959).
(4) G. R. Hennig, *Progr. Inorg. Chem.* 1, 125 (1959).
(5) A. K. Kuriakase and J. L. Margrave, *Inorg. Chem.*, 4, 1639 (1965).

raised to a temperature of 627 ± 3° and fluorine passed over the sample at a flow rate of 3–4 cm³/min. The flow was continued at that temperature for at least 12 hr. Then the furnace was cooled and the fluorine shut off while helium was again passed over the chamber to drive the fluorine out of the chamber. A snow white product (~3 g) was then removed from the nickel boat. *Anal.* Calcd C, 35.98; F, 61.11. Found: C, 36.01; F, 63.57. Calculated empirical formula, $CF_{1.12\pm0.03}$.

A high resolution infrared spectrum revealed a strong band at 1217 cm⁻¹ which may be assigned to the C–F stretching vibrations for tertiary carbon atoms. Previously Rudorff and Brodersen[6] had reported only a single band at 1215 cm⁻¹. Two medium bands were observed at 1342 and 1072 cm⁻¹, presumably due to asymmetric and symmetric stretching vibrations, respectively, of the peripheral CF_2 groups. A 332-cm⁻¹ far-infrared band was observed and is probably due to bending in CF_2 groups.

X-Ray powder pattern analysis with copper radiation yielded interplanar "d" spacings of 5.80 (s), 2.89 (m), 2.22 (s), and 1.29 (s) Å. Interplanar spacings of 6.0, 2.23, and 1.30 have been previously reported by Palin and Wadsworth.[7]

To produce $(CF_x)_n$ of the highest fluorine content and whitest color, it was necessary to maintain a temperature of 627 ± 3°. This six-degree range was very critical. In the previous work this was not recognized and consequently the process for production of $(CF_x)_n$ gained a reputation for being very irreproducible. $(CF_x)_n$ is formed from about 540 to 630° at atmospheric fluorine pressure. It has been found that at higher pressures the critical reaction temperatures decrease.[8] At the 540° temperature the empirical formula is $CF_{0.68}$ and the product is black. One may observe this effect experimentally in the reaction boat. If the furnace has a "hot" zone within this 6° range smaller than the length of the boat, only the central region of the boat produces white $(CF_x)_n$ and on either side the color ranges from gray to black. At temperatures over 630° the compound is unstable in fluorine and burns to produce CF_4 and a black soot. $(CF_x)_{1.1}$ is therefore a solid subfluoride of carbon which should be considered metastable with respect to CF_4. These observations of reaction variations with temperature can be explained by consequent changes in fluorine atom concentrations and subsequent kinetics.

As a result of the discovery of the critical nature of the temperature control, the limiting stoichiometry of $(CF_x)_n$ has been found to be $CF_{1.12\pm0.03}$. Other maximum values have been reported previously in the $CF_{0.98}$ region, *i.e.*, the x in $(CF_x)_n$ approaches one. The stoichiometry $CF_{1.12\pm0.03}$, implies extra fluorine atoms and these fluorines occur as CF_2 groups around the edge of the ring. Rudorff's $CF_{0.95}$ empirical formula does not provide evidence for these peripheral CF_2 groups and even indicates some fluorine deficiencies on the tertiary carbon atoms in the graphite plane. It is also possible that Rudorff's particle size may have been large enough to make this excess negligible stoichiometrically. The peripheral CF_2 groups would have fluorine atoms in

(6) W. Rudorff and K. Brodersen, *Z. Naturforsch.*, 126, 595 (1957).
(7) D. E. Palin and K. D. Wadsworth, *Nature (London)*, 162, 925 (1958).
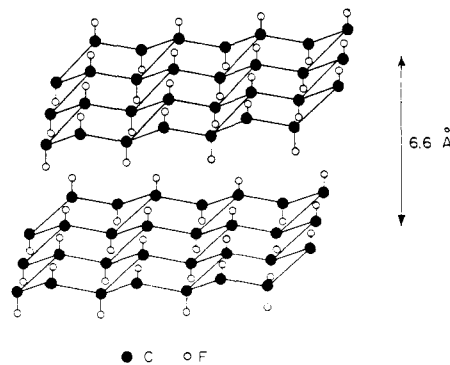(8) R. J. Lagow, R. B. Badachhape, J. L. Wood, and J. L. Margrave, *J. Chem. Soc.*, in press.

Figure 1. Rudorff $(CF_x)_n$ structure.

axial and equatorial positions. The side bands at 1342 and 1072 cm⁻¹ are due to the asymmetric and symmetric stretching of these groups and provide evidence of their presence. The CF_2 bending at 332 cm⁻¹ also supports this conclusion.

Recently, studies by the Lewis Research Center of the National Aeronautics and Space Administration[9] and by the Frankford Arsenal of the U. S. Army[10] have shown that poly(carbon monofluoride) is a superior solid lubricant under heavy loads, high temperatures, in oxidizing atmospheres, and under other such extreme conditions. Workers at the U. S. Army Electronics Command at Ft. Monmouth, N. J.[11] and industrial workers in Japan have concurrently demonstrated a high potential for carbon monofluoride for use as a cathode material in high energy batteries.

(9) R. L. Fusaro and H. E. Sliney, NASA Technical Memorandum NASA TMX 5262Y (1969).
(10) N. Gisser, M. Petronio, and A. Shapiro, *J. Amer. Soc. Lubric. Eng.*, 61, May (1970).
(11) K. Brauer, Technical Report ECOM-3322, U. S. Army Electronics Command, Fort Monmouth, N. J.; H. F. Hunger, G. J. Heymark, Technical Report ECOM 4047 U. S. Army Electronics Command, Fort Monmouth, N. J. (1972).
(12) Address correspondence to this author at Massachusetts Institute of Technology, Cambridge, Mass. 02139.

R. J. Lagow,*[12] R. B. Badachhape
J. L. Wood, J. L. Margrave*
Department of Chemistry, Rice University
Houston, Texas 77001

A Paramagnetic Dioxygen Complex of Iron(II) Derived from a "Picket Fence" Porphyrin. Further Models for Hemoproteins

Sir:

Recently attention has been given to models for the dioxygen binding hemoproteins, myoglobin (Mb), and hemoglobin (Hb).[1–4] We have demonstrated that iron(II) complexes constructed from "picket fence" porphyrins,[1] having steric shielding on one side of the

(1) J. P. Collman, R. R. Gagne, T. R. Halbert, J.-C. Marchon, and C. A. Reed, *J. Amer. Chem. Soc.*, 95, 7868 (1973).
(2) J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Nat. Acad. Sci. U. S.*, in press.
(3) J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, 95, 5757 (1973).
(4) (a) C. K. Chang and T. G. Traylor, *Proc. Nat. Acad. Sci. U. S.*, 70, 2647 (1973); (b) *J. Amer. Chem. Soc.*, 95, 5810 (1973); (c) *ibid.*, 95, 8475 (1973); (d) *ibid.*, 95, 8477 (1973).