takes $E_0^H = 4000$ cm^{-1} and $E_0^D = 5500$ cm^{-1} for $C_{1-\eta}H_\eta$ and $C_{1-\eta}D_\eta$, respectively (it can be shown theoretically[2] that $E_0^D > E_0^H$). Considerable scattering is observed in Fig. 1 for $\tau_0 \gtrsim 15$ sec, presumably on account of variations in the true radiative lifetime.

Applying the isotope rule [Eq. (3)] to Fig. 1, one obtains $\mu_i/\mu = 1.8$, which value is almost independent of the choice of E_0^H and E_0^D. Since $\mu^{CD}/\mu^{CH} = 1.855$ for the CD and CH molecule, it follows that nonradiative triplet decay in aromatic hydrocarbons is governed by CH and CD vibrations, in agreement with the conclusions of Ref. 1. More detailed considerations[2] indicate that CH and CD stretching modes are primarily responsible for this behavior.

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On the Off-Center Dipole Model for Polar Gases*

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THE off-center dipole model has recently[1,2] been used to calculate the ordinary (B) and the dielectric ($\mathcal{B}$) second virial coefficients for dipolar gases. In this model a rigid point dipole (μ) is presumed to be displaced a distance a from the center of the repulsive and dispersion forces, which are represented by a modified Lennard-Jones (12–6) potential. The rather extensive numerical integrations required in the calculations of the virial coefficients have been performed and the results applied to a few dipolar gases.[2]

An off-center dipole is equivalent to an infinite number of linear multipoles centered on the origin, the nth multipole being given by[3]

$$M^{(n)} = na^{n-1}\mu. \tag{1}$$

TABLE I. Comparison of calculations of the ordinary second virial coefficient B (cm³/mole) and the dielectric second virial coefficient $\mathcal{B}$ (10^3 cm⁶/mole²) for fluoroform.

Temp 60°C	B(OCD)	$B(\mu, \Theta)$	B(polarizability)	B(steric)	Exptl error
	-137.5	-139	-3.8	-1	± 5
80.5°C	$\mathcal{B}$(OCD)	$\mathcal{B}(\mu, \Theta)$	$\mathcal{B}$(polarizability)	$\mathcal{B}$(steric)	
	-0.3	-0.28	$+1$	-0.3	± 1.4

It is of interest to know how significant a contribution to the virial coefficients is made by the third (octopole) and higher multipoles. For if the first and second (dipole and quadrupole) moments only are sufficient, then the virial coefficients can be calculated more conveniently with the well-known series expansions.[4–6] Furthermore, other contributions to the potential, such as that due to the molecular polarizability, can be included with much simpler numerical work in the central multipole formulation than in the off-center dipole formulation.

Both the ordinary and dielectric second virial coefficients of fluoroform (CHF₃) have been calculated by Dymond and Smith[2] for the off-center dipole model with the parameters $\sigma = 4.16$ A, $\epsilon/k = 206.4°$K, $a = 0.946$ A, and $\mu = 1.645$ D (where σ is the zero of the modified 12–6 potential and ϵ its potential well depth). These values of a and μ correspond to a linear quadrupole moment[4] of $\Theta = 3.115 \times 10^{-26}$ esu (origin at the center of mass). We have calculated B and $\mathcal{B}$ at 60° and 80.5°C, respectively, using the above values of σ, ϵ/k, μ, and Θ with the series-expansion method,[4,5] to an accuracy of about 1 in 1000. The difference between the values calculated for the off-center dipole model (OCD) and our values (μ, Θ) correspond to the contributions of the octopole and higher moments, and to the effect of the rigid core used by Dymond and Smith[2] to prevent the off-center dipoles from ever coinciding. It can be seen (Table I) that for the representative substance chosen, these contributions are within the errors of the experimental measurements.

A good estimate of the contributions to the virial coefficients of the polarizability of the molecule and of the anisotropy of its repulsive forces is given by their leading terms in the series expansions for the virial coefficients. We have added such terms to the potential model and calculated their leading contributions to B and $\mathcal{B}$, using a mean polarizability[7] of $\bar{\alpha} = 3.28 \times 10^{-25}$ cm³ and a repulsion anisotropy parameter[4] of $D = 0.1$. Results are shown in Table I, as calculated from Eq. (3.9) of Ref. 4 and Eq. (6.5) of Ref. 6 for B(polarizability), Eq. (3.14) of Ref. 4 for B(steric), and Eqs. (3.3) and (3.5) of Ref. 5 for $\mathcal{B}$(polarizability) and $\mathcal{B}$(steric), respectively. It can be seen that the contribution to B from the octopole and higher moments

is comparable to that from the polarizability and steric anisotropy, but that for ⑤ the octopole and higher-moment contributions are much less than either of the latter two.

We conclude that the off-center dipole model can often be replaced by an equivalent central dipole-quadrupole model, for which calculations are easier.

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Intersystem Crossing in Pyrene

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EXPONENTIAL molecular fluorescence decay curves of pyrene ($2 \times 10^{-6} M$) in outgassed ethanol have been recorded as a function of temperature in the range $77°$–$415°$K using the pulsed-flash technique[1]; the temperature dependence of the corresponding lifetime τ is shown in Fig. 1.

In the absence of photoassociation and diffusional quenching under these conditions, the processes competing with fluorescence emission (F) are limited to internal conversion (IC) and intersystem crossing (IS) whence

$$1/\tau = k_F + k_{IC} + k_{IS}.$$

At room temperature, where the quantum yield of molecular fluorescence γ_F is 0.65,[2] internal conversion is negligible,[3,4] i.e.,

$$k_{IC} \ll k_F + k_{IS} = k_F/0.65,$$

although this may become significant at higher temperatures if it requires an activation energy. Accordingly at lower temperatures

$$1/\tau = k_F + k_{IS} = k_F + k_{IS}{}^0 \exp(-E_{IS}/RT) \qquad (1)$$

(E_{IS} in calories per mole) and the solid curve in Fig. 1 is drawn with

$$1/\tau = 1.33 \times 10^6 + 3.3 \times 10^7 \exp(-2270/RT) \ \sec^{-1}, \qquad (2)$$

which provides a value for the quantum yield of

fluorescence

$$\gamma_F = k_F/(k_F + k_{IS}) = 0.65$$

at $23°$C, identical with the value obtained spectrophotometrically at the same temperature[4]; the assumption that $\gamma_F = 1$ at $77°$K, used to evaluate $k_{IS}{}^0$ and E_{IS} from Eq. (1) is vindicated and the validity of Eq. (2) over the whole temperature range eliminates internal conversion as a significant competing process.

Since E_{IS} is close to the activation energy for viscous flow ($E_\eta \sim 3$ kcal mole^{-1}) of this solvent, similar measurements were made with pyrene ($10^{-4} M$) in liquid paraffin ($E_\eta \sim 12$ kcal mole^{-1}) to eliminate the possibility that k_{IS} describes diffusional quenching by an unspeci-
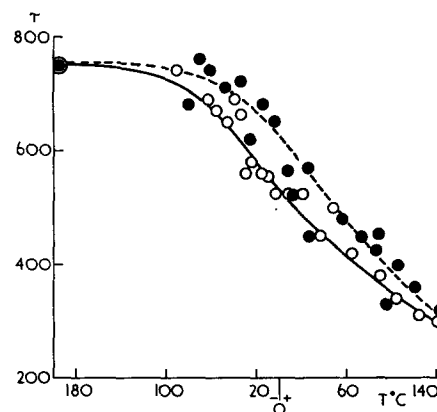
Fig. 1. Temperature dependence of fluorescence lifetime τ (nanosecond) of pyrene, O, in ethanol ($2 \times 10^{-6} M$); ●, in liquid paraffin ($10^{-4} M$).

fied quenching species; the data are also shown in Fig. 1 where the dashed curve is drawn according to

$$1/\tau = 1.33 \times 10^6 + 7.95 \times 10^7 \exp(-3100/RT) \ \sec^{-1}.$$

These results are similar to those reported for 9-methyl- and 9,10-dichloroanthracene by Bennett and McCartin[5] who conclude that a significant temperature dependence of fluorescence quantum yield (or lifetime) is diagnostic of an intersystem crossing to a virtually degenerate triplet state; on this basis intersystem crossing from the ^1L_b state of pyrene at 27 000 cm^{-1} most probably involves the ^3L_b or ^3B_b states which are estimated[6] to lie at 27 100 and 24 400 cm^{-1}, respectively, above the ground state. Although the selection rules are at present not completely defined it is of interest to note that $k_{IS}{}^0$ is some two orders of magnitude less than the corresponding values obtained[5] for the anthracene derivatives but is almost equal to that obtained for radiationless relaxation (ID) of the pyrene excimer $^1A_2*$ expressed as[7]

$$k_{ID} = 2.9 \times 10^7 \exp(-1150/RT) \ \sec^{-1}.$$

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