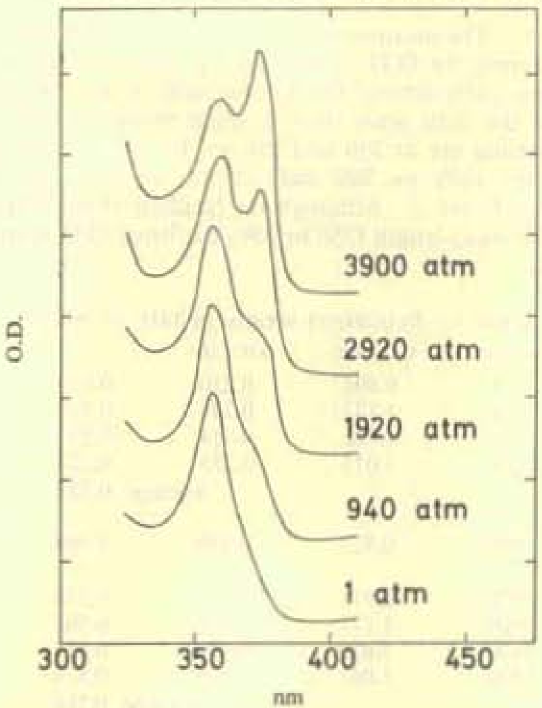

FIG. 2.—The spectra of sodium fluorenyl in THF at ~22°C at various pressures. The absorption curves are progressively shifted upwards to avoid overlapping.

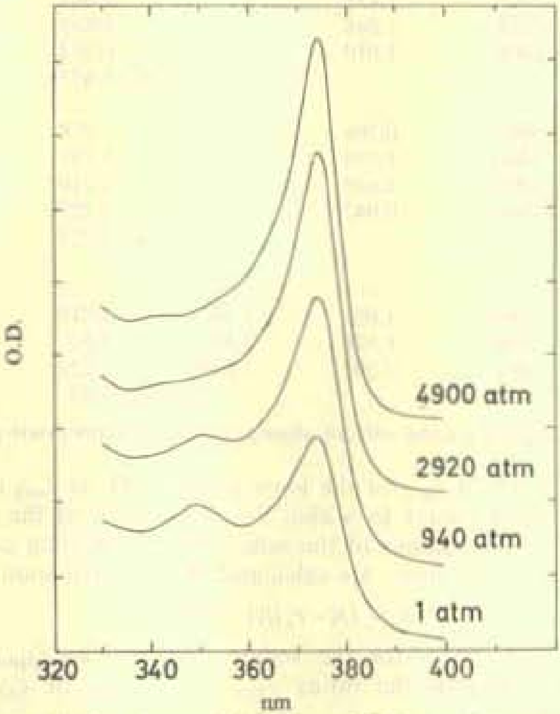

FIG. 3.—The spectra of lithium fluorenyl in THF at ~22°C at various pressures. The absorption curves are progressively shifted upwards to avoid overlapping.

shown in fig. 2 and 3. The maxima of absorption were carefully determined in each experiment by measuring the O.D. in the vicinity of each peak at 1.0 nm intervals. The $\lambda_{max}$ of the loose pairs derived from either salt are at 374 nm at all pressures, whereas the $\lambda_{max}$ of the tight pairs show a slight pressure dependence. At 1 atm their absorption maxima are at 356 and 350 nm for the sodium and lithium salts, respectively, but they shift to 360 and 353 nm at 4900 atm. The results are summarized in tables 1 and 2. Although the heading of the third column of each table refers to a fixed wave-length (356 or 350) the listed O.D. were measured at the appropriate maxima.

TABLE 1.—FLUORENYL SODIUM IN THF AT ~22°C

| expt. | pressure atm | O.D. (356) | O.D. (374) | *R* | *K* |
|---|---|---|---|---|---|
| 1 | 1 | 0.895 | 0.220 | 0.246 | — |
| 2 | 1 | 1.133 | 0.246 | 0.233 | — |
| 3 | 1 | 1.762 | 0.414 | 0.235 | — |
| 4 | 1 | 1.073 | 0.255 | 0.238 | — |
| | | | average | 0.238 | |
| 1 | 940 | 0.922 | 0.340 | 0.369 | 0.15 |
| 1 | 1920 | 0.911 | 0.525 | 0.576 | 0.42 |
| 2 | 1920 | 1.177 | 0.661 | 0.562 | 0.40 |
| 3 | 1920 | 1.639 | 0.920 | 0.561 | 0.40 |
| 4 | 1920 | 1.061 | 0.609 | 0.574 | 0.42 |
| | | | average | 0.568 | 0.41 |
| 1 | 2920 | 0.836 | 0.743 | 0.889 | 0.94 |
| 2 | 2920 | 1.131 | 0.974 | 0.862 | 0.89 |
| 3 | 2920 | 1.548 | 1.340 | 0.865 | 0.90 |
| 4 | 2920 | 1.010 | 0.893 | 0.884 | 0.93 |
| | | | average | 0.875 | 0.915 |
| 1 | 3900 | 0.768 | 0.982 | 1.278 | 1.88 |
| 2 | 3900 | 1.074 | 1.279 | 1.191 | 1.63 |
| 3 | 3900 | 1.445 | 1.748 | 1.210 | 1.68 |
| 4 | 3900 | 0.943 | 1.157 | 1.227 | 1.73 |
| | | | average | 1.227 | 1.73 |
| 1 | — | — | — | — | — |
| 2 | 4900 | 1.028 | 1.563 | 1.519 | 2.73 |
| 3 | 4900 | 1.378 | 2.10 | 1.52 | 2.74 |
| 4 | 4900 | 0.893 | 1.358 | 1.521 | 2.74 |
| | | | average | 1.52 | 2.74 |

O.D. corrected for the solvent absorption at the appropriate pressure.

The ratios *R* (O.D. at $\lambda_{max}$ of the loose pairs)/(O.D. at $\lambda_{max}$ of the tight pairs) at each pressure are constant to within 2-3 %, in spite of the substantial variations in the total concentrations of the salts. The equilibrium constants *K* of the process, tight pairs$\rightleftharpoons$loose pairs, are calculated from the equation,

$$K = (R - r_1)/(1 - r_2 R),$$

where $r_1 = \varepsilon_{374,\text{tight}}/\varepsilon_{356,\text{tight}}$ for the sodium salt and $\varepsilon_{374,\text{tight}}/\varepsilon_{350,\text{tight}}$ for the lithium salt, and $r_2$ denotes the ratios $\varepsilon_{356,\text{loose}}/\varepsilon_{374,\text{loose}}$ or $\varepsilon_{350,\text{loose}}/\varepsilon_{374,\text{loose}}$ of the respective salts.