

TABLE 3. *Isomer shift versus pressure at 295°K.**

| Pressure (kb) | Acetyl Acetate | | Oxalate | | Strontium Oxalate | |
|------------------|----------------|--------|---------|--------|-------------------|--------|
| | Fe(III) | Fe(II) | Fe(III) | Fe(II) | Fe(III) | Fe(II) |
| 0 | 0.35 | — | 0.45 | — | 0.41 | — |
| 25 | 0.38 | 1.28 | 0.44 | 1.24 | 0.40 | 1.27 |
| 50 | 0.40 | 1.20 | 0.43 | 1.26 | 0.39 | 1.29 |
| 75 | 0.39 | 1.16 | 0.43 | 1.29 | 0.385 | 1.31 |
| 100 | 0.38 | 1.14 | 0.42 | 1.31 | 0.38 | 1.33 |
| 125 | 0.36 | 1.12 | 0.41 | 1.34 | 0.375 | 1.36 |
| 150 | 0.33 | 1.11 | 0.40 | 1.36 | 0.37 | 1.38 |
| 175 | 0.33 | 1.10 | 0.39 | 1.38 | 0.365 | 1.40 |

* Mm/sec relative to iron metal at 1 atmosphere.

TABLE 4. *Quadrupole splittings (mm/sec).*

| Pressure (kb) | (A) Ferric Ion | | | | | | | |
|------------------|----------------|-------|----------------|-------|---------|-------|-------------------|-------|
| | Basic Acetate | | Acetyl Acetate | | Oxalate | | Strontium Oxalate | |
| | 378°K | 418°K | 295°K | 375°K | 295°K | 335°K | 295°K | 382°K |
| 0 | — | — | 0.46 | 0.70 | 0.59 | 0.54 | 0.50 | 0.72 |
| 25 | — | — | 0.76 | 1.00 | 0.82 | 0.77 | 0.68 | 0.88 |
| 50 | — | 0.85 | 0.80 | 1.10 | 0.95 | 0.92 | 0.78 | 1.00 |
| 75 | 0.82 | 0.90 | 0.92 | 1.15 | 1.02 | 1.00 | 0.90 | 1.10 |
| 100 | 0.90 | 0.95 | 1.03 | 1.17 | 1.08 | 1.07 | 1.02 | 1.18 |
| 125 | 0.96 | 1.02 | 1.14 | 1.20 | 1.13 | 1.12 | 1.12 | 1.25 |
| 150 | 1.02 | 1.06 | 1.22 | 1.23 | 1.20 | 1.16 | 1.16 | 1.32 |
| 175 | 1.08 | 1.10 | 1.28 | 1.26 | 1.26 | 1.20 | 1.20 | 1.38 |

| Pressure (kb) | (B) Ferrous Ion | | | | | | | |
|------------------|-----------------|-------|----------------|-------|---------|-------|-------------------|-------|
| | Basic Acetate | | Acetyl Acetate | | Oxalate | | Strontium Oxalate | |
| | 378°K | 418°K | 295°K | 375°K | 295°K | 335°K | 295°K | 383°K |
| 0 | — | — | — | — | — | — | — | — |
| 25 | — | — | 2.20 | 2.10 | 1.90 | 1.90 | 2.00 | 2.00 |
| 50 | — | 1.80 | 2.15 | 2.05 | 2.00 | 2.00 | 2.08 | 2.08 |
| 75 | 2.20 | 1.84 | 2.12 | 2.00 | 2.10 | 2.08 | 2.14 | 2.14 |
| 100 | 2.16 | 1.86 | 2.00 | 2.00 | 2.18 | 2.16 | 2.20 | 2.20 |
| 125 | 2.14 | 1.88 | 2.00 | 1.98 | 2.23 | 2.21 | 2.26 | 2.26 |
| 150 | 2.12 | 1.90 | 2.00 | 1.96 | 2.28 | 2.23 | 2.30 | 2.30 |
| 175 | 2.10 | 1.90 | 2.00 | 1.95 | 2.30 | 2.25 | 2.35 | 2.35 |

In both oxalates the isomer shift of the ferrous ion formed increased with pressure, i.e., the electron density at the iron nucleus decreased. This is in contrast to the behavior of all but a few other systems, and indeed to that of ordinary ferrous oxalate.¹ The bonding must be very strained and changes in occupation of the bonding orbitals with pressure apparently overwhelm the shielding and orbital compression effects.⁵

In the acetyl acetate, there is a maximum in the isomer shift at about 40–50 kb, as shown in Figure 3. The apparent isomer shift at 102°C is plotted in the same figure to show that it also exhibits the maximum. In this case the changes in orbital occupation dominate in the low-pressure region, whereas the usual orbital distortion effects govern at high pressure. Figure 4 shows the quadrupole splitting for acetyl acetate as a function of pressure. At room temperature there is a distinct leveling in the region of the isomer shift maximum, then a second rise at higher pressures. It is clear that the change in orbital occupation of the bonding orbitals affects the local asymmetry. At 102°C the change in quadrupole splitting with pressure is too small to determine whether the irregularity is

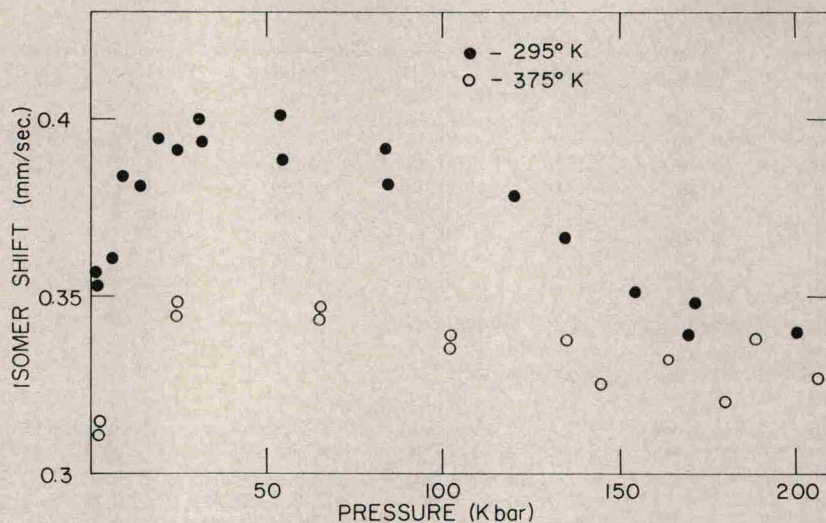


FIG. 3.—Isomer shift vs. pressure—ferric acetyl acetonate (Fe(III)).

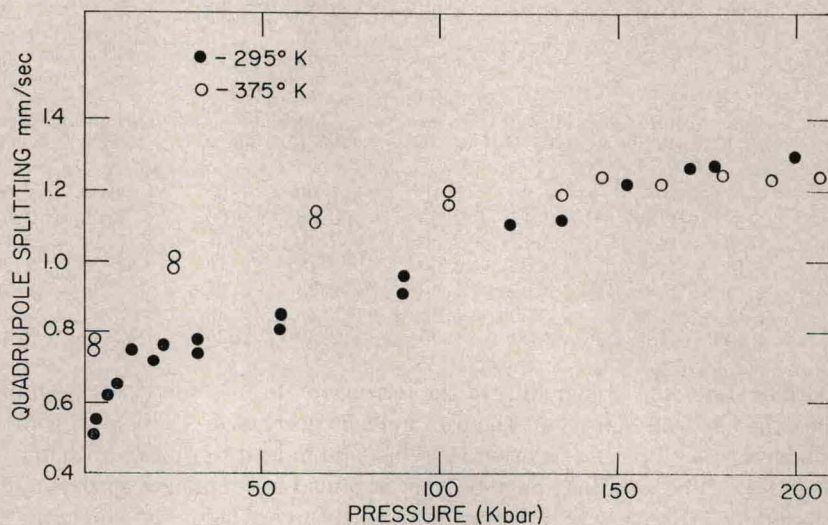


FIG. 4.—Quadrupole splitting vs. pressure—ferric acetyl acetonate (Fe(III)).

present. The increase in quadrupole splitting with increasing temperature in the low-pressure region is unusual. The anomalies in isomer shift and quadrupole splitting are not reflected in the conversion, which shows no irregularities with increasing pressure or temperature. This is not surprising as the conversion involves only nonbonding and antibonding orbitals.

Summary.—The effect of pressure on the oxidation state of ferric ion, in a site of essentially octahedral symmetry with six oxygen ligands, has been measured. Four compounds have been studied: basic ferric acetate, ferric acetyl acetonate, ferric oxalate, and strontium ferric oxalate. For all these