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Effects of Fe(CO)$_5$ intra- and intermolecular phase transitions on the macroscopic dielectric constant (*)

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Résumé. — Des mesures de constante diélectrique ont été réalisées sur du fer pentacarbonyle, Fe(CO)$_5$. Plusieurs transitions de phase sont observées dont certaines ont pu être identifiées par comparaison avec des résultats de diffraction de neutrons et de spectrométrie Mössbauer : fusion à 252 K et transitions de rotation à ~ 115 K, 155 K et 205 K.

Abstract. — Dielectric constant measurements on bulk iron pentacarbonyl, Fe(CO)$_5$ display several phase transitions, some of them could be identified by comparison with neutron diffraction and Mössbauer results as melting (252 K), rotational transitions of the molecules at ~ 205 K, 155 K and a microrotational transition at ~ 115 K.

Among the molecules known for the richness of their intramolecular activities is the trigonal bipyramidal iron pentacarbonyl, Fe(CO)$_5$: the central Fe-atom forms five (almost) equivalent CO-bonds. Stretching and bendings of bonds, rotations and the effect of all these intramolecular activities on the molecular crystal bulk properties have been attracting considerable attention in the last two decades. Infrared vibrational spectra [1] assigned most of the fundamental modes for Fe(CO)$_5$, such as C-O and Fe-C stretchings, and C-Fe-C bendings. NMR studies of relaxation times were performed [2] to obtain information about the intramolecular dynamics as a function of temperature; their results suggest that a limited (slow) exchange among the CO-groups occurs at low temperatures (below ~ 100 K). The intramolecular motion was modelled as exchange between axial and equatorial CO-groups. The NMR results can also be interpreted as rotation of the equatorial CO-groups about the C$_3$ axis of the molecule. The exchange becomes very fast in the liquid state.

The net macroscopic electric properties of bulk Fe(CO)$_5$ are not well known at low temperatures. Although the molecule with its D$_{3h}$ symmetry cannot have a permanent electric dipole moment, the existence of such a quantity has been reported [3]. The effective electric dipole moment in Fe(CO)$_5$ originates directly in a special type of rotations which are known to exist in bipyramidal molecules. Such rotations are a result of interconversion between a bipyramidal and square pyramidal states. The relaxation between these two states results in a contribution

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to a static polarization of 0.2 Debye at 293 K [3]. The intramolecular re-arrangement which results in an induced electric dipole is inherently associated with the Berry [4] pseudorotation mechanism. The Berry pathway is associated with change of polarity; the exchanging non-polar ground state form passes through a slightly polar $C_4v$ configuration on the way to the pseudorotated conformer ($D_{3h} \rightleftharpoons C_4v \rightleftharpoons D_{3h}$). The geometries are traversed via small angle deformations. Dielectric losses in the microwave region suggest that the material behaves like being composed of rotating permanent dipoles.

The motivation for studying the dielectric constant of $\text{Fe(CO)}_5$ at low temperatures originates in recent reports on the results of neutron-diffraction and Mössbauer studies on the structure and dynamics of $\text{Fe(CO)}_5$ molecules in the form of adsorbed submonolayers [5] and of bulk matter. The measurements featured a few phase transitions which were believed to involve intra- and intermolecular rotational activities. The NMR studies suggest that when an energy barrier of $\sim 1 \text{ kcal/mole}$ is crossed the rotational diffusion increases and the relaxation time decreases. It is known that rotational transitions can occur in such systems [6] and indeed some discussions on rotational transitions in molecules with $D_{3h}$ symmetry have been reported [7]. It is therefore interesting to measure the T-dependence of the dielectric constant of bulk $\text{Fe(CO)}_5$ and see if the Berry-DiCarlo electric dipole moments of the molecule play any role in the cooperative nature of the rotational transitions we observe by the Mössbauer and elastic neutron techniques.

The measurements of the dielectric constant utilized a capacitor cell and an automatic AC bridge (General Radio, LC16). The experiment could measure small capacitance of $10^{-3} \text{ pF}$ with the accuracy of $\sim 5 \%$. A frequency of 10 kHz was used which is believed to be below all the relaxation frequencies. The cell was filled with the $\text{Fe(CO)}_5$ liquid and mounted on a cryostat which was cooled by LN$_2$ vapour to the desired temperature. The temperature was regulated by a gold-iron thermocouple and a differential amplifier which controlled the gas flow. Figure 1 shows the dielectric constant $\varepsilon(T)$ below the Mössbauer spectral intensity. Small cusps are observed in $\varepsilon(T)$, one at $\sim 115 \text{ K}$ the second at $\sim 160 \text{ K}$ in the slowly increasing $\varepsilon$ with $T$.

![Fig. 1.](image-url) - (a) Mössbauer spectral area of bulk (B) iron pentacarbonyl, and of two layers of $\text{Fe(CO)}_5$ adsorbed on graphite basal plane (2.0 L); Insert : the intensity ratio of the two components $\sigma$ and $\pi$ of the quadrupole Mössbauer doublet. The « V-shaped » $T$-dependence of the spectral area is a result of a soft mode (see Ref. [12]). The effective change in the MSD through the 115 K transition is from $\theta_D \approx 80 \text{ K} (T < 100 \text{ K})$ into $\theta_D \approx 65 \text{ K} (T > 120 \text{ K})$. (b) The dielectric constant of bulk iron pentacarbonyl vs. temperature. The approximate temperatures of the various transitions are marked by arrows.
At \( \sim 205 \) K the dielectric constant drops considerably and recovers at 252 K. We could associate part of these anomalies with the Mössbauer and neutron diffraction observations. Some ideas about the dynamical changes were obtained from the behaviour of Mössbauer spectra (see for example Fig. 2). The \( T \)-dependent spectral area is shown in figure 1. We display here only the results for bulk Fe(CO)\(_5\) and of 2-layer film adsorbed on graphite. The spectral area reflects the dynamical state of the Fe-atom in the molecule. One can see several deviations from the simple exponential (Debye-Waller \( T \)-dependence of the spectra are \( \sigma(T) \)). The comparison between \( \sigma(T) \) and \( \varepsilon(T) \) suggests a possible association between the small local dynamical changes and the macroscopic behaviour of the entire bulk.

At 252 K the Fe(CO)\(_5\) bulk solidifies (freezes) and a sharp drop is observed in the dielectric constant. This drop is expected for polar liquids when they solidify and the dipole motion is hindered. It was suggested [3] this non-polar molecule can have an instantaneous dipole moment which may be larger than the mean apparent value of 0.2 Debye. We can use the Onsager formula [8]

\[
\varepsilon - \varepsilon_\infty = \frac{3 \varepsilon}{3 \varepsilon + \varepsilon_\infty} \cdot \frac{4 \pi \mu^2 N}{3 kT}
\]

(where \( \varepsilon_\infty \) is the dielectric constant in the infrared region, \( \mu \) is the molecular dipole, \( N \)-the number of molecules in a unit volume and \( k \) is the Boltzmann factor) to estimate the mean molecular dipole. With the assumption \( \varepsilon_{\text{solid}} = \varepsilon_\infty \) [8], this approximation results in a dipole moment \( \mu \approx 0.2 \) D, in good agreement with the value reported in reference [3].

At \( T \) above 225 K we could record neither Mössbauer nor neutron signals due to the high degree of molecular unrest. The slight increase of \( \varepsilon \) between 252 K and 205 K may be some precursor indication of the dipole motion which appears again at the 205 K-transition. The reason for the large increase in the dielectric constant at \( \sim 205 \) K is not entirely clear yet, but it is possible that the pseudorotation replaces the free motion of the molecules when they were in their liquid state. Then \( \varepsilon \) diminishes gradually as \( T \) is lowered. From analysis of \( \varepsilon(T) \) it turns out that when \( \varepsilon \) decreases as \( T \) is lowered, it can mean either the increasing tendency toward antiparallel orientation between the dipoles of neighbouring molecules [8], or a decrease of the dipole moment of the single molecule due to intermolecular hindrance. Antiferroelectric correlations which are known to be responsible for a gradual decrease of the dielectric constant with \( T \) are probably weak, since not all the molecules have a net dipole moment at a given instant. It seems therefore more likely that the latter mechanism is responsible for the decrease of \( \varepsilon \) with lowered temperature.

Fig. 2. — A typical Mössbauer spectrum of Fe(CO)\(_5\) on graphite surface. The film thickness is 2.0 monolayers. The solid line through the points describes a fit of two Lorentzian lineshapes. The fit yields the spectral area, linewidths and position of the lines. It is possible that the spectrum is a superposition of more than one set of indistinguishable doublets (see text).
The first anomaly in the Mössbauer spectral area $\sigma(T)$ when $T$ is lowered, is seen at $\sim 205$ K: no structural changes could be detected at this temperature by our neutron experiments. We have found that the onresonance line depth does not change much through the 205 K transition, but the $\sigma$-line narrows more than the $\pi$-line, resulting in an abnormal drop of the spectral intensity ratio $I_\sigma/I_\pi$ of the two quadrupole components (see insert of Fig. 1). This effect can be observed in spectra composed of two or more superimposed doublets having different centre shifts ("concentrational broadening") — and small differences in $QS$ as well. When the transition temperature is approached, the increasing anisotropic diffusional motions (ADM) about the iron even the QS and shift differences. The effect of ADM on line shifts and shapes when hyperfine interaction (magnetic or electric) is present has been discussed in detail in the literature [9]. It is however worth mentioning the high sensitivity of Fe(CO)$_5$ to its immediate surroundings: Fe(CO)$_5$ as bulk shows a QS of 2.57 mm/s; when dissolved in aceton $\approx 2.44$ mm/s and in cyclohexane $\approx 2.52$ mm/s, and when adsorbed on graphite $\sim 2.54$-2.55 mm/s [10].

As $T$ approaches $\sim 200$ K the Mössbauer intensity ratio recovers. The neutron diffraction results suggest that the transition at $\sim 205$ K leaves the dimensions of the cell unchanged but rotational changes could explain the disappearance of some of the diffraction peaks. We therefore believe that this transition possibly involve some changes in the molecular orientation, which results in a smaller value for the dielectric constant. No irregular QS systematic changes could be detected through this transition. Thus the changes involved are slow in the Mössbauer scale ($\sim 10^{-7}$ s) and fast in the scale of the $\varepsilon(T)$ experiment ($\sim 10^{-4}$).

From the variation of $\varepsilon$ below $\sim 205$ K the energy difference between the two states of the molecule can be estimated. We obtain $\sim 2 \times 10^{-3}$ eV (about 0.5 kcal/mole) as the energy which can activate rotations in the molecule, including pseudorotation [3].

As the temperature is further lowered toward $\sim 167$ K, the neutron diffraction results indicate an orientational ordering. Toward $\sim 155$ K an anomaly in $\varepsilon(T)$ is observed and an inflection point is seen in $\sigma(T)$. Around this temperature there is a sharp instability in the QS [11]. When $T$ reaches $\sim 115$ K the smallest irregularity in $\varepsilon(T)$ is observed. The sharp increase in the spectral area $\sigma(T)$ is accompanied by a sharp increase [11] in the QS. The QS(T) displays a hysteresis [5] as an evidence for the first-order character of the transition. A narrowing of both « $\sigma$ » and « $\pi$ » lines is observed when the $\sim 115$ K is approached. Nevertheless, we could not detect structural changes or even changes in the general direction of the molecule by our neutron diffraction measurements. Thus the transition can be associated with the CO exchange within the molecules as suggested by the NMR experiments described in reference [2].

We could demonstrate the cooperative nature of the intramolecular rotational transitions by its manifestation on a macroscopic property. In particular it was interesting to find that the first-order microtransition at $\sim 115$ K, which probably involves merely a small fraction of the molecule, has such an extended long range observable effect on the dielectric constant.

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SHECHTER, H., TAUB, H., WANG, R., BRENER, R., HANSEN, F. Y., SUZANNE, J., to be published.
[11] At ~ 155 K the QS of the bulk drops from 2.54 mm/s, reaches 2.52 ± 0.01 mm/s at ~ 150 K and the previous value of 2.54 ± 0.01 is restored at ~ 140 K. At ~ 115 K the QS increases from (2.540 ± 0.005) mm/s to (2.555 ± 0.005) mm/s.