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LIBRONS IN ORGANIC CONDUCTORS

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We will review a variety of effects in organic conductors, which arise from the existence of low-lying rotational lattice modes in these materials. A distinction will be made between unambiguous and ambiguous consequences of librational modes. An example of the former is the specific heat, whose value necessarily implies the excitation of low-lying Einstein modes far in excess of the number of existing translational modes. For the latter category of effect, we mention the much debated origin of the temperature dependence of the conductivity. We will also present recent progress in the lattice-dynamical calculation of the entire lattice mode spectrum of segregated stack systems such as TTF-TCNQ and single stack systems such as $(TMTSF)_2PF_6$ with emphasis on the mixing of rotational and translational components in the first Brillouin zone by the dynamical matrix. We will also discuss the implications of the phonon-libron hybridization and the specific phase relations between these components for the analysis of the structure factor observed in diffuse x-ray and neutron scattering.

I. INTRODUCTION

To understand the rich manifold of physical effects occurring in quasi one-dimensional conductors (1) consisting of planar, conjugated molecules arranged in stacks, it is desirable to have detailed information on the lattice modes of these compounds. This paper reviews various aspects of the hindered rotational modes, also called librations, which arise in molecular solids due to the orientational degrees of freedom in

addition to standard center-of-mass or positional degrees of freedom leading to acoustic and optical phonons. We will, in this paper, reserve the term "phonon" for center-of-mass modes only and use the term "libron" for the rotational branches. We have, of course, to keep in mind that this distinction is not meaningful at general points of the Brillouin zone as the steric arrangement of molecular crystals necessarily leads to coupling of forces and torques, and consequently to a nondiagonal dynamical matrix, whose solutions are hybridized phonon-libron modes (2,3).

The intent of this paper is to deal with two questions:

(1) Do librons exist in one dimensional organic conductors?

(2) Is the π-electron-libron interaction crucial for the understanding of the metal-insulator (4,5) and possibly metal-superconductor transitions?

As for the first question, it is answered affirmatively in Section II. In Section III, we review a selection of experimental and theoretical results germane to the second question. In Section IV, we present recent progress in our computational efforts to determine the lattice dynamics of organic conductors (6), with emphasis on the librational mode frequencies and the mixing of translational, rotational and intramolecular vibrational motions. Section V summarizes the discussion and gives some perspectives on needed work to fully answer the second question.

II. UNAMBIGUOUS ASPECTS OF LIBRONS

The very fact of geometrical structure of organic molecules adds a new and interesting aspect to their lattice dynamics: In addition to their positional coordinates within the unit cell their Euler angles, a set of three orientational parameters for each molecule have to be specified leading to 3N additional orientational degrees of freedom when the N molecules are arranged in a crystal (2).

In contrast to center-of-mass motion, however, which due to the translational invariance of the crystal always leads to three acoustic branches, the rotational invariance of the crystal does not lead to acoustic librons. The local hindered rotational displacements in the typical herringbone molecular crystals leads to in-phase and out-of-phase modes of finite frequencies split by a few cm^{-1} (see Fig. 1).

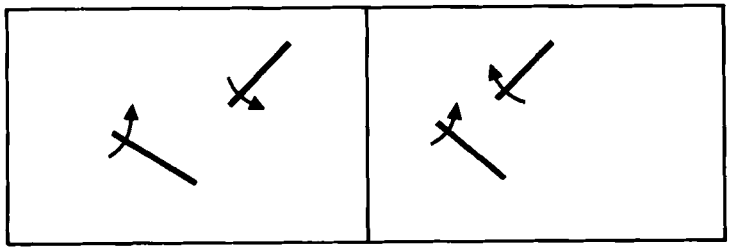

FIGURE 1 In-phase and out-of-phase rotational motion for k=0 librations in naphthalene.

As the intermolecular potentials determining the force constants for rotational motion are of the Van der Waals type in molecular crystals, the librational mode frequencies are low, typically between 30 cm^{-1} to 150 cm^{-1} (7). Due to their dynamical character as rotations (at least at k=0) librational modes are Raman-active and I.R. inactive and have been studied by Raman scattering for 40 years (8). The subtle chemical and physical phenomena leading to organic metals due to partial charge transfer, stacking and enhanced-electron delocalization in the stack direction may be expected to introduce some additional forces due to Coulomb and polarization interactions. Nevertheless, it seems that these additional forces do not substantially alter the potential energy distribution for local hindered rotational motion. We note that recent Raman studies of the neutral crystals TCNQ and TTF (9) and of TTF-TCNQ (10,11) give a range of values for the k=0 librational modes not very different from mixed stack donor-acceptor systems such as PMDA-anthracene (12), supporting our view that the general forces determining librational frequencies in molecular crystals are not very different in these three classes of materials.

The first and clearest early evidence for the presence of low frequency librations in organic conductors was found in specific heat measurements (13). Although these experiments were intended to confirm the existence and type of metal-insulator transition found, it is immediately clear from the absolute value of the specific heat (see Fig. 2) that a considerable number of low frequency modes far in excess of those arising from acoustic and optical phonons must be contributing at temperatures as low as 50K.

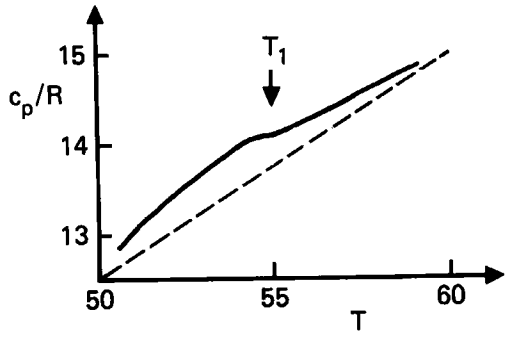

FIGURE 2 Specific heat of TTF-TCNQ near the metal insulator transition (from Ref. 13).

The second early indication that librations play a role in the lattice dynamics of partial charge transfer segregated stack compounds was found in the x-ray structural work (14) performed to detect the nature of the metal-insulator transition. Rigid body analysis (15) - a procedure probably not fully justified as we shall see in Section IV - of the thermal ellipsoids provides values of the mean square angular displacements combined with estimates of the corresponding moments of inertia leads to reasonably accurate librational frequencies at temperatures somewhat larger than the appropriate libron frequency. Typical values of the angular displacements from the equilibrium orientation are of order 2-4° (14), corresponding to mode frequencies between 30 cm^{-1} to 150 cm^{-1}.

The third and final unambiguous confirmation of librations in conducting organics is their observation in Raman scattering (11) and far I.R. absorption experiments (16). The Raman experiments were complicated considerably by a variety of experimental problems caused by sample absorption and laser power induced photodissociation of the TTF molecule. Nevertheless several modes were clearly seen in the Raman experiment corresponding to librational modes (11) although not so assigned in the original papers. Ironically the assignment of some of the observed modes comes from a systematic I.R. absorption study of selectively deuterated TTF and TCNQ molecules in TTF-TCNQ (16), which allowed the identification of the appropriate modes by following their frequency shifts as a function of the relevant inertial parameter, namely the total mass or the moment of inertia about one of the three principal axes. The technique used is not expected to supply information on the librational modes due to their evenness under reflection and it is

only because of the coupling to the electronic distortion at low temperatures that some of the librations acquire considerable oscillator strength. Similar effects for even intramolecular vibrational modes acquiring I.R. intensity by coupling to electronic charge transfer states have been known for some time (17).

III. AMBIGUOUS ASPECTS

In this section, we will discuss aspects of librational modes, which are controversial. These are the contribution of librations to the temperature dependence of the resistivity (18) and the presence of an orientational contribution in the observed phase transition(s) and their fluctuation induced precursors (19,20).

The origin of the temperature dependence of the conductivity has engaged the attention of theorists from the beginning of intense work in this field (21). A wide variety of mechanisms has been proposed to lead to the roughly T^2 dependence of the resistivity between room temperature and the onset of the metal-insulator transition. Due to the low dimensionality of the segregated stack organic conductors, the usually effective scattering channels for electrons are closed. The list includes electron-electron, electron-intramolecular vibration, electron-acoustic phonon, electron-two-libron scattering (18,22-24). These explanations were further complicated by the fact that all theoretical attempts up to 1979 attempted to account for the experimentally observed $T^{2.3}$ by a single mechanism. It was, however, pointed out by Cooper (25) that the experiments were performed at constant pressure, and taking into account the anisotropic, strong temperature dependence of the expansion coefficients, he finds that the resistivity at constant volume is superlinear. The most recent and detailed model for the resistivity of TTF-TCNQ was given by Conwell (26). She considers, at least in a schematic fashion, electron scattering from all external and internal vibrational modes of the system. The major part of the controversy still centers on the relative importance of electron-one phonon and electron-two libron (phonon) scattering processes. For inversion symmetric systems the different symmetry properties of center-of-mass displacements (phonons) and rotational displacements (librons) lead to the lowest nonvanishing electron-phonon (libron) matrix elements proportional to a first or second derivative of the electronic hopping integral with respect to the appropriate displacement. It is very likely, however, that most of the arguments whether one phonon processes dominate two libron processes or vice versa are academic. This is due to two reasons: (1) The spatial arrangement of the molecules in TTF-TCNQ is such that both molecules

are tilted with respect to the stack (conducting) axis (2). The principal axes for the rotational motion are not along the symmetry (inertial) axes of the molecules. The modulation of the π-electronic transfer integral by some of the rotational motions is such that a nonzero first derivative exists leading to linear electron-libron coupling even at k=0. We would like to point out that the bulk of the controversies and the motivation for the calculations reported here and earlier arose from emphasis on the electronic part of the metal-insulator transitions. The lattice modes were at best treated peremptorily with emphasis on aspects known from inorganic materials. It is therefore not surprising that the original emphasis was on considering only electron-acoustic phonon coupling in analogy with Peierls original considerations (27). It was pointed out, however, fairly early that the metal-insulator transition could be equally well induced by internal degrees of freedom, e.g., an orientational Peierls transition, spin-Peierls or intra-molecular Peierls transition(4,28-31). The symmetry arguments arose originally arose from considerations of pure modes only, i.e., either translational or rotational. As we have pointed out repeatedly in the past years (32,33), it is clear from lattice dynamical arguments in molecular crystals that such a separation breaks down almost everywhere in the Brillouin zone; even more surprisingly modes which at k=0 (where the separation into translational and rotational motion is exact) are purely translational may change their character to predominantly rotational and vice versa (3). This is particularly true for optical phonon modes and librations lying close in frequency (Fig. 3).

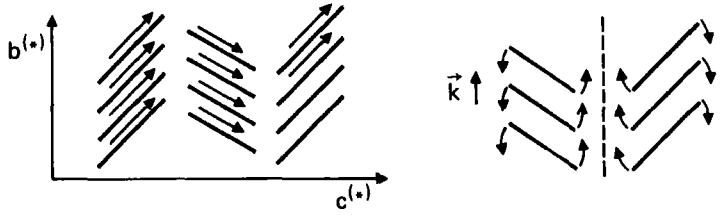

FIGURE 3 Superposition of translational (with both longitudinal and transverse components) and rotational motion (about as axis perpendicular to the paper) for nonzero $k_b(0,x,0)$.

In any case, this coupling of the dynamical matrix in the Brillouin zone makes the linear versas quadratic coupling controversy moot. Both

types of modes couple linearly and quadratically and it seems plausible that except for special points in reciprocal space, the strength of the linear coupling dominates higher order derivatives. Nevertheless, for locally flat pieces of the phonon or libron dispersion relations (i.e., in the vicinity of Van Hove singularities of the density of states) strong contributions from second order terms may be expected. We conclude, therefore, that the resistivity in quasi-one dimensional charge transfer crystals cannot be explained in terms of a single channel or single type of coupling (linear or quadratic) but contains comparable contributions from many of the translational and librational modes as well as intra-molecular vibrations.

The second controversial topic we want to address in this section is the nature of the lattice distortions responsible for the observed metal-insulator transitions. Ideally, neutron scattering experiments scanning in energy and wave-vector space on a sufficiently large single crystal coupled with knowledge of the form-factor for the different eigen-modes allows the determination of the dispersion relations for all lattice modes, phonons, librons and intra-molecular vibrations. Such work even on the simplest molecular crystals, such as deuterated napthalene, has only recently been reported (34). Although considerable efforts were made at Oak Ridge as well as Brookhaven to use neutron scattering to determine the character of the softening mode in TTF-TCNQ, the small size of sample crystals presented great difficulties, which caused some initial disagreements (20,35). The final verdict from the neutron-scattering experiments is that the softening mode has transverse acoustic character (36). It is also very likely that some hybridization with low-lying optical or librational modes occurs leading to an unusual steepening of the slope (36). No systematic effort was made to search for the librational modes in the absence of structure factor predictions (37).

The evidence of the diffuse x-ray scattering experiments (19), which were the first clear-cut indication that one-dimensional fluctuation effects at $2k_F$ and $4k_F$ occurred has helped considerably in the detailed clarification of the interplay of the electronic instabilities (38). In the most recent and careful analysis of the microdensitometer traces of the various satellite patterns, Yamaji, Pouget, and Comes (39) conclude that the displacement pattern of the $2k_F$ instability is, in fact, a transverse displacement along the long axis of the molecules (herringbone mode). The same authors also conclude in contrast to the much earlier and preliminary work by Weyl et al. (40) that they find no indication of a rotational contribution. It should be noted, however, that in the

particular symmetry direction studied, namely modes propagating along the k_b direction, transverse displacements of the type deduced must necessarily be coupled to rotations about an axis parallel to the a* direction (see Fig. 3).

The remaining symmetry element for this direction, namely the screw axis parallel to b, requires that the rotational displacement pattern is phase-shifted by $\pi/2$ with respect to the translational displacement pattern (3). We expect, therefore, that the manner in which the contribution of the rotational motion was considered in (39) is inadequate and does not disprove the presence of an orientational component in the actual displacement pattern (41).

IV. LATTICE-DYNAMICAL UPDATE

In this section, we want to present progress on direct calculations of the total vibrational spectra of segregated stack charge transfer crystals and give some preliminary results on the k=0 modes of the single stack conductors of type $(TMTSF)_2PF_6$.

We have used an approach and programs developed for organic crystals by Warshel (42), which is semi-empirical in nature relying on analytic potentials for the σ-skeleton and using a Pariser-Pople-Parr (PPP) description for the π-system. We restate the key assumptions of this approach and refer the reader interested in more detail to a recent review (42). The key assumptions made are:

(1) Separability with values for the various (nonlinear) potentials adjusted by fitting to experiment.
(2) Treatment of the π-electrons by the PPP approximation with some configuration interactions allowed for.
(3) Use of Cartesian coordinates for all atoms and thus avoiding the rigid molecule approximation.
(4) Use of atom-atom potentials for inter-molecular interactions.

The total energy is then minimized in a 3N+6 dimensional parameter space, with N the number of atoms in the asymmetric unit cell. Finding the minimum in the total potential energy it is straight-forward to find the matrix of second derivatives with respect to the Euclidean coordinates. The diagonalization of this matrix - the dynamical matrix then gives eigenvectors and eigenvalues for the normal vibrational modes. To find the dispersion relations for the 6M "external" modes, 3 of which are acoustic phonon like while the rest are optical phonon and libron-like, the diagonal matrix has to be expanded by the appropriate phase-factors relating the corresponding k-vector to the dynamical matrix element. M is the number of inequivalent

molecules in the unit cell. The modification of the dynamical matrix for finite values of k is given by

$$[\vec{F(k)}]_{st,s't'} \equiv \sum_{l'} \frac{\partial^2 V}{\partial r\binom{s}{t}\,\partial r^{l'}\binom{s'}{t'}} \exp\{i\vec{k}\cdot\vec{R}_{l'}\} \qquad (1)$$

where V is the total potential energy, a function of 3N+6 variables, $r\binom{s}{t}$ a radius vector between atoms s and t and l' is a unit cell index. The relevant dynamical matrix F(k) is then used to solve the determinental equation

$$\| \vec{F(k)} - \omega^2 M \| = 0$$

where M is a diagonal matrix containing the inertial parameters namely masses and moments of inertia. We have performed calculations with this approach for the neutral molecular crystals TTF and TCNQ making modifications in the potential parameters to account for the C-N groups and the sulphur heteroatoms, respectively. We have continued our calculations reported at Helsingor (6) to find all "external" and "internal" modes for the TTF-TCNQ crystal and also attempted to do calculations for the $(TMTSF)_2X$ class of materials. Recently we have also obtained results on PMDA-anthracene, a mixed stack molecular crystal (43). We found, however, that the computational approach fails using the full set of Cartesian coordinates corresponding to the TTF-TCNQ unit cell. We have, therefore, performed calculations on a simplified crystal structure consisting of a single TTF-TCNQ supermolecule occupying half the unit cell (Fig. 4).

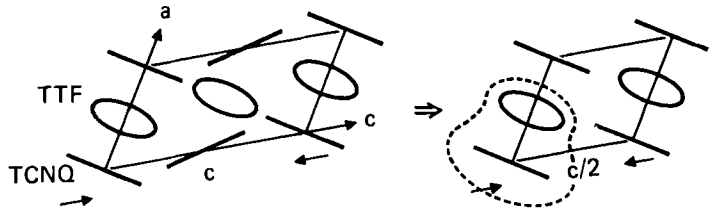

FIGURE 4 Simplified unit cell for TTF-TCNQ neglecting the screw axis symmetry and showing the TTF-TCNQ supermolecule (dotted shape) used for calculations.

We obtained all 102 vibrational modes and their eigenvectors and show the resulting librational frequencies in Table I.

Table I. Librational and optical mode frequencies in TTF-TCNQ with unit cell (a, b, c/2) (see Fig. 4) at k=0.

Librational (with some intramolecular character) (cm^{-1})	Optical
25	15
35	
46	
60	63
118	
157	203

The TTF-TCNQ supermolecule is specified as a neutral complex consisting of one TTF and one TCNQ molecule with relative position and orientation corresponding to the crystal structure with no charge transfer and only nonbonded interactions between any atom pair of the respective molecules.

For the case of $(TMTSF)_2PF_6$ we again find that the four additional methyl groups per molecule lead to size problems in the minimization routines (the dimensionality of the parameter space is 183-too large for the program). We construct an (over)simplified unit cell and supermolecule occupying it, namely (TMTSF) CH_4, i.e., neglecting the transverse dimerisation along the a axis and the charge aspects of the counterion. We obtain all 93 modes for our hypothetical crystal and the k=0 librational frequencies and three optical phonon frequencies are listed in Table II.

Table II. Librational and optical mode frequencies in (TMTSF)CH_4 with unit cell (a/2, b, c) at k=0.

Librational (with some intramolecular character) (cm^{-1})	Optical (cm^{-1})
10 (?)*	
43	
57	66
128	100
154	138

*Because of round-off error, the very lowest frequency calculated is not reliable.

We finally turn to the calculation of $k \neq 0$ modes. As we have seen above, the number of atoms in the molecules studied and the size of the unit cell strain the capacity of the programs used. For finite k the dynamical correlations between different atoms in the unit cell are more complicated due to the additional sum over l' (Eq. 1) and complex phase factor. As a first step to get insight into the dispersion of various modes, we consider the modes at the zone boundary for a particular crystal axis (see Figure 5) in a well-studied case (napthalene) (2,3). It is intuitively obvious that the dynamics of zone boundary modes can be calculated with a k=0 program by doubling the cell constant in that direction.

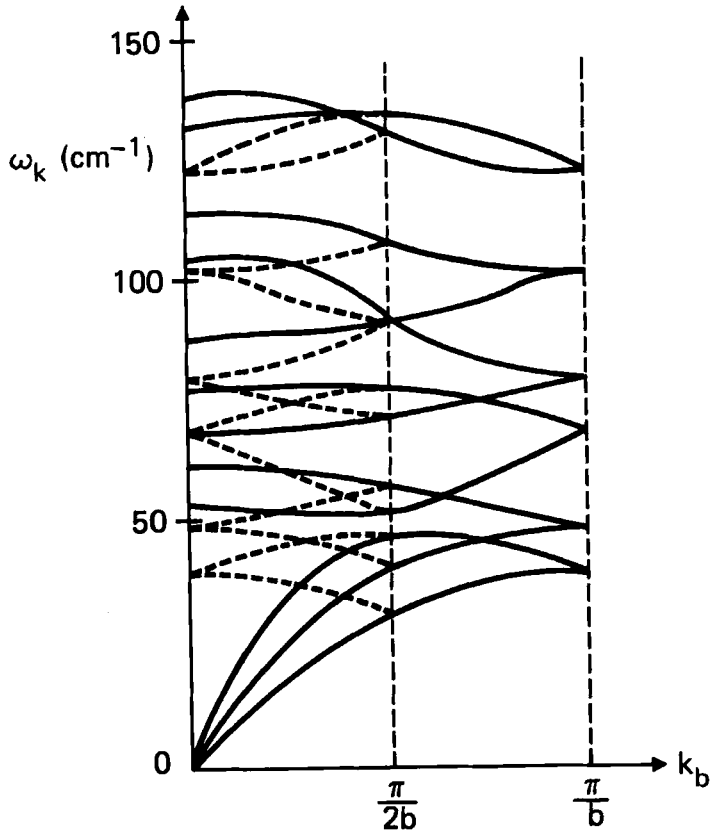

FIGURE 5 External modes in naphthalene (Ref. 3) and folding back of branches for the doubled unit cell in the b direction.

This operation halves the Brillouin zone size in the corresponding reciprocal space direction and folds the branches back to k=0. We had hoped, therefore, by increasing the unit cell constants in the three crystal axis directions to find the appropriate zone boundary mode frequencies and hence get information on the dispersion of the librational and optical phonon branches. Unfortunately, even for the simplest case - napthalene - the computational procedure fails and gives large imaginary eigenvalues.

V. SUMMARY AND OUTLOOK

The purpose of this paper has been to present an assessment of the current evidence for and agreement on the importance of hindered rotational modes (librations) in conducting organics. We have shown that these lattice modes certainly play a role in the thermal properties of the organic metals and probably contribute to the metal-insulator transition(s). We have also shown by calculation that some of these modes have very low frequencies (<40 cm^{-1}) and that they easily mix with low frequency intramolecular vibrational modes leading to a breakdown of the rigid molecule picture.

Some additional work remains to be done to work out the full dispersion of the various modes throughout the first Brillouin zone. For some of the larger systems such as TTF-TCNQ with 36 atoms/per formula unit and 4 molecules/unit cell, we are encountering size limitations for nonzero k values. We have given some preliminary results for simplified unit-cells (e.g., omitting the screw axis symmetry and hence c axis doubling for TTF-TCNQ, and simplifying the structure of $TMTSF_2X$ to TMTSF CH_4) to get some feeling for librational mode frequencies. The open shell nature of both TCNQ and TTF has not yet been included in the calculation nor have Coulomb interactions due to their presence. We hope these modifications will be completed soon to allow a more complete picture of the lattice dynamics of organic metals and the interplay of π-electron delocalization and hindered rotational motion, particularly in view of recent interest in strong coupling effects such as bipolaronic superconductors (44).

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