

Study of the Phase Transitions of $(\text{DI-DCNQI})_2M$ ($M=\text{Ag, Li, Cu}$) through the Analysis of the Temperature-Dependent Vibronic and Vibrational Infrared Absorptions

M. Meneghetti,^{*,1} C. Pecile,^{*} K. Yakushi,[†] K. Yamamoto,[†] K. Kanoda,[†] and K. Hiraki[§]

^{*}Department of Physical Chemistry, University of Padova, 2 Via Loredan, I-35131 Padova, Italy; [†]Institute for Molecular Science, Myodaiji, Okazaki, Aichi, 444-8585 Japan; [‡]Department of Applied Physics, University of Tokyo, Hongo, Bunkyo-ku, 113-8656, Japan; and [§]Department of Physics, Gakushuin University, Mejiro, Toshima-ku, 171-8588, Japan

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The temperature-dependent phase transitions of 2,5 diiodo-dicyanoquinondiimine (2,5-DI-DCNQI) title compounds are analyzed by looking at the bond order wave (BOW) and at the charge density wave (CDW) which characterizes the transitions. The analysis is done by studying the temperature-dependent powder infrared spectra which allow one to have a separate evaluation of both types of contribution to the phase transition of these molecular metals. A model for the spectroscopic infrared features related to the transitions is reported and used for the analysis. It is found that all the title compounds develop a BOW structure at low temperatures with characteristics which recall an instability toward a tetramerized $2k_F$ periodicity particularly for the Ag and Li compounds. An appreciable CDW amplitude contribution to the transitions is not found in the spectra. © 2002

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INTRODUCTION

The interplay of electron–electron and electron–phonon interactions determines the ground states of organic conductors which display many types of phase transitions as a function of temperature and pressure. The transitions are characterized by changes in the electronic charge and/or spin degrees of freedom together with inter- and intramolecular structural variations since inter- and intramolecular phonons are coupled to the electronic structure.

Electronic correlations were found to be very important in determining inhomogeneous charge and spin structures in low-dimensional systems like high- T_C superconductors (1). In organic metals, not only structural transitions have been found in many compounds but also charge ordering,

described as Wigner crystals, which was recently deduced to be present in prototype compounds like $(\text{TMTTF})_2\text{X}$ (2). The interpretation of temperature-dependent NMR data allowed to deduce that also in a diiodo-dicyanoquinondiimine DI-DCNQI compound, namely $(\text{DI-DCNQI})_2\text{Ag}$, a charge ordering was present (3) with a disproportionation of charges.

A theoretical study of phase transitions of low-dimensional solids has recently found that off-site Coulomb interactions can stabilize, in one-dimensional quarter-filled compounds, charge disproportionation with $4k_F$ periodicity (alternation of site charges: $4k_F$ charge density wave (CDW) (4), but others showed that $2k_F$ (tetramerization) structures ($2k_F$ bond and charge density waves (BCDW) are more appropriate to describe the ground state of these systems (5). On this basis it was proposed that the charge ordering of the $(\text{DI-DCNQI})_2\text{Ag}$ compound was a dimerized $4k_F$ CDW (3) or a tetramerized $2k_F$ BCDW structure (6). Further experimental investigations were considered important to conclude about the phase transition of this compound.

A direct experimental description of a structural phase transition is usually obtained by diffuse X-ray scattering which allows one to have a direct view of the periodic distortion of the low-dimensional structures characteristic of organic metals (7). The interpretation of the satellite reflections and diffuse streaks makes possible to find the intra- or inter-molecular nature of the structural distortion. In the case of $(\text{DI-DCNQI})_2\text{Ag}$, satellite reflections give indications of a low-temperature $4k_F$ structure and their relatively great intensity was first interpreted as due to a bond order wave (BOW) structure (8) although the consideration of a charge dependence of the molecular structure makes possible to find that a $4k_F$ CDW also can be a good candidate for describing the low-temperature $(\text{DI-DCNQI})_2\text{Ag}$ (9).

¹To whom correspondence should be addressed. Fax: +39-049-8275135. E-mail: moreno.meneghetti@unipd.it.

Other techniques which can give a direct description of a phase transition are the infrared and Raman vibrational spectroscopies (10). The normal mode of vibrations are local probes of the electronic situation and they can be used to reveal both the local charge on the molecules and the local interaction of a molecule with its neighbors. In this case, therefore, there is a direct view of the origin of the phase transition if it involves a variation of the average charge of the molecules or a structural transition. However, the periodicity of the structural change can only be deduced by a detailed analysis of the spectra.

The vibrational technique, on which will be based the present study of the phase transition of DI-DCNQI compounds, is particularly useful for the interpretation of the properties of molecular conductors since the molecules present in these compounds have many intra-molecular modes, coupled to the electronic structure, which can be used for the analysis. Usually, the molecules present in organic conductors have at least an inversion center which makes possible to distinguish between totally symmetric modes, which are only Raman active for the isolated molecules and can couple to the charge transfer excitations, and the other type of vibrations. This is an important starting point of the analysis since it allows the use of totally symmetric modes for describing structural variations and the use of other type of vibrations for determining the charges on the molecules (see the model below). The first type of vibrations is therefore useful for revealing BOW (bond order waves), whereas the second one for describing CDWs. Moreover, one must remember that, since vibrations are local probes, the spectra also reveal fluctuations and not only well-developed transitions.

Below we will analyze the infrared spectra of (DI-DCNQI)₂M (*M* = Ag, Li, Cu) and find that BOWs develop in all these compounds at low temperatures, whereas there is no clear evidence of strongly associated CDW.

EXPERIMENTAL

The crystals of (DI-DCNQI)₂M (*M* = Ag, Li, Cu) were obtained by electrochemical reduction of DI-DCNQI in acetonitrile solution in the presence of AgBF₄, LiClO₄, and [Cu(CH₃CN)₄]ClO₄ for the Ag, Li and Cu compounds, respectively, following already reported experimental procedures (11, 12).

The sample powders were dispersed in a 10 mm diameter KBr pellet. Infrared spectra were recorded with the vacuum-type FT-IR JASCO VM7. For the low-temperature measurements, the KBr pellet was pressed to a copper sample holder using screws and indium washer. The sample holder, with a 5 mm hole, was fixed to the cold head of a cryostat (Oxford CF1104). The temperature of the sample was measured using a silicon diode sensor fixed near the KBr pellet in the sample holder.

MODEL FOR THE VIBRATIONAL AND VIBRONIC INFRARED ABSORPTIONS

The normal modes of vibrations of a molecule with an inversion center, as the DI-DCNQI molecule, can be classified as gerade and ungerade. The first ones are observed, for the isolated molecule, in the Raman spectrum whereas the second ones in the infrared spectrum. The totally symmetric modes are gerade modes and are the only ones which can couple to the charge transfer electronic excitations, namely to the excitations at low-energy characteristic of low-dimensional metals. The mechanism which allows the coupling for this type of vibrations is the Holstein one, namely the modulation of the molecular energy by the vibrational motion. The hopping of the electrons along the molecular stacks, which determine the conductivity of the organic metals, are charge transfer excitations that can be observed in the infrared spectra and as a consequence also the totally symmetric modes, coupled to these excitations, can appear in the infrared spectra when, for the isolated molecule, they can be observed only in the Raman ones. The totally symmetric modes activated in the infrared spectra are called vibronic absorptions. They can be easily identified in the single crystal spectra since they are polarized out of the molecular plane. It is noteworthy that the appearance in the infrared spectra of the vibronic bands is governed by selection rules which show that only for a distorted stack, namely for molecules in a stack with unequal interaction with its neighbors, their infrared intensity is different from zero. Models for the simplest situations, like a dimerization, show that their intensity is proportional to the square of the difference between the hopping integrals of a molecule with its neighbors (13). The low energy of the charge transfer excitations makes possible to observe very intense vibronic bands, sometimes more intense than the normally infrared active modes. For the same reason, their frequency is usually strongly renormalized toward lower energies with respect to what is expected for an isolated molecule (also several hundred cm⁻¹). The intensity of these modes in the infrared spectra is, therefore, an important tool for describing a BOW structural transition, which is characterized by unequal interaction of the molecules along a stack.

All the other vibrations, which are not totally symmetric modes, do not couple to the charge transfer excitations through the Holstein mechanism and can be used for determining the charge on the molecules since their frequency is usually found to be linearly dependent on the charge itself. For vibrations, which involve bonds where there is a large electronic density of the molecular orbitals occupied by the unpaired electrons (HOMO for donor molecules and LUMO for acceptor molecules), the charge-dependent frequency shift may be very large, of the

order of $50\text{--}100\text{ cm}^{-1}$ and therefore easily determined. One should also note that vibrations are very fast probes and that localization of charges could be detected on the time scale of femto- to pico-seconds in time resolved experiments.

The problem of the interpretation of the infrared spectra is that electronic, vibronic and vibrational spectral features overlap in the same spectral region and it is usually not easy to interpret the experimental data. Nonetheless, temperature-dependent infrared spectra of powders are easily accessible data and can be used, as it will be shown below, for describing transitions which are not easily characterized by other techniques.

The problem of the interpretation of the vibronic and vibrational features of the infrared spectrum needs the help of a scheme which allows one to have some fixed points to refer to. It is therefore useful to start thinking of a regular stack where all the molecules are equal and all the contact of the molecules with their neighbors are equal. This case can be described with stacks of molecular sites with an inversion center on the molecules *and* on the bonds (see Fig. 1 (a)). In this regular situation, no vibronic bands (activated totally symmetric modes) are present in the

infrared spectra and only one vibrational frequency is found for each infrared active normal mode.

From the regular situation, one can obtain a stack with lower symmetry by losing some symmetry elements. The first situation can be found by losing the inversion center on the molecules (see Fig. 1 (b)). Now all the molecules are still equal because of the inversion centers on the bonds, but the bonds are now unequal: the system is a dimerized BOW (a $4k_F$ BOW for a quarter-filled system). In this situation, one finds in the infrared spectra one vibronic band for each totally symmetric mode and, all the molecules being equal, one vibrational band for each infrared active mode.

A further loss of another symmetry element, namely an inversion center present on the long *or* on the short bonds can be considered (see Fig. 1 (c)). The structure now becomes that of a tetramerized BCDW (a $2k_F$ BCDW1 for a quarter-filled system). In this situation, one finds two vibronic bands for each totally symmetric mode and two vibrational bands for each infrared active mode. Intensity and frequency of all these modes depend on the peculiarities of the structure.

A second situation, which can be generated from the regular structure with all the inversion centers, is that obtained by losing the inversion center on the bonds (see Fig. 1 (d)). All the bonds are now still equal the inversion centers on the molecules being present, but the molecules are now different. This structure is a dimerized CDW (a $4k_F$ CDW for a quarter-filled system) which can be recognized as a Wigner crystal, a structure without a BOW but with charge disproportionation. In this situation, one does *not* find vibronic bands but two vibrational bands for each infrared active normal mode. This situation can be clearly recognized with respect to the pure BOW for which vibronic bands are present.

The evolution of this situation can be obtained by losing the inversion centers on alternate molecules (see for example Fig. 1 (e)). This situation originates another tetramerized BCDW ($2k_F$ BCDW2 for a quarter-filled system) which can be characterized by one vibronic absorption for each totally symmetric mode and two vibrational absorptions for each infrared active mode.

Both types of BCDW (BCDW1 and BCDW2), losing the remaining inversion center, remain without symmetry elements (see Fig. 1 (f)) and the vibronic and vibrational spectra depend on the details of the structure.

Other symmetry arrangements can be thought for the one-dimensional stacks, and among them it could be important that of a trimerized BCDW which can be obtained by losing two consecutive inversion centers of the regular stack, leaving, therefore, one symmetry element on the bonds and one on the molecules alternatively. For this structure, one can predict one vibronic band for each totally symmetric mode and two vibrations for each

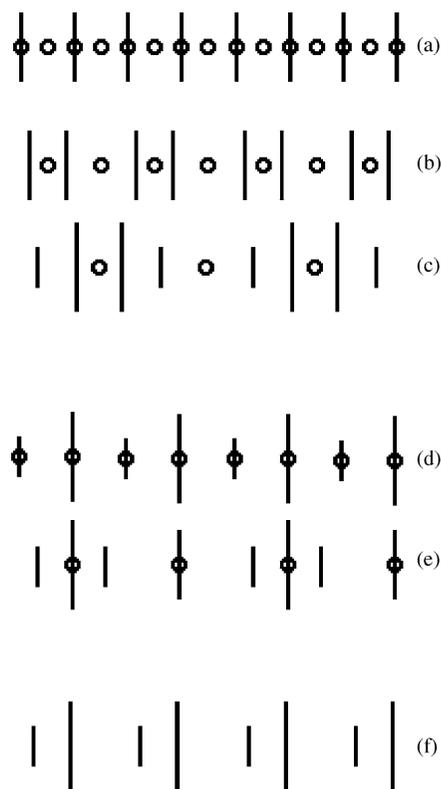


FIG. 1. Schemes for a one-dimensional stack where the long and short bars indicate molecules with different charges and the circles indicate inversion centers: (a) regular stack; (b) BDW; (c) BCDW1; (d) CDW; (e) BCDW2; (f) stack without inversion centers.

infrared active mode. The situation is similar to that of a BCDW2 and only quantitative details can distinguish the two structures.

The above scheme is therefore useful to describe a phase transition in which a structural and/or charge degrees of freedom are involved. As recalled above, however, the interpretation of the infrared spectra must be careful due to the presence of many electronic, vibronic and vibrational features. Furthermore, one has to pay attention to factor group splittings which can be activated when more than one molecule is present in the crystallographic unit cell (14). The size of these splittings is usually much less relevant than that related to the vibronic effects, described above, which can also be considered as factor group effects arising from the charge transfer interaction present in a stack.

RESULTS AND DISCUSSION

(DI-DCNQI)₂Ag

Figure 2 shows the temperature-dependent infrared spectra of powders of (DI-DCNQI)₂Ag from room temperature down to 5.5 K. One can see broadbands like that at about 1200 cm⁻¹ and more sharp absorptions. Among the more sharp bands, some have an intensity which do not depend strongly on temperature like that at 795 cm⁻¹ and other like that at 622 cm⁻¹ which strongly increases in intensity at low temperatures. The broadbands can be interpreted as renormalized vibronic bands due to totally symmetric modes strongly coupled to the electronic transitions which are present as a background in the whole spectrum. The sharp absorptions, whose intensity is not strongly temperature dependent, can be recognized as due to infrared active modes whereas those with a strong

temperature dependence as vibronic band with a small coupling to the electronic excitations.

An accurate identification of all the features is possible on the basis of the detailed knowledge of the vibrational behavior of the neutral and fully ionized molecules whose spectra are usually simpler to analyze than that of quarter-filled systems like the present Ag compound. This analysis is not available, however, for the DI-DCNQI molecule although it was published for a similar molecule like (dimethyl-DCNQI) (DM-DCNQI) (15). On the basis of this and on that of the neutral molecule of DCI-DCNQI (dichloro-DCNQI) (15), one can qualitatively identify the normal modes related to some absorptions which can be used for the description of the phase transition, the aim of the present analysis.

The broadband observed above at about 1200 cm⁻¹ can be identified as a vibronic band related to a totally symmetric mode which involves stretching of the C=N and C=C bonds. As a vibronic band, it can be used for the description of a structural phase transition. However, its overlap with other spectral features does not make it suitable for a quantitative analysis. More appropriate for such an analysis are the temperature-dependent sharp features which can be easily identified and do not show strong interference with other spectral features. Looking at the spectra, one finds that the vibronic band at 622 cm⁻¹, which can be associated to the totally symmetric N-C≡N bending, is apt for the analysis of the temperature dependent transition as previously found in a preliminary report (16). Figure 3 shows the integrated intensity of this band as a function of temperature normalized to its maximum value. One can see that the band is already present at room temperature and that its intensity increases smoothly by lowering the temperature. The intensity of this band does not seem to saturate suggesting that the

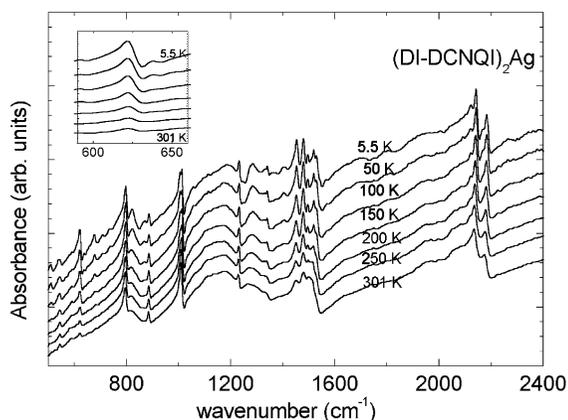


FIG. 2. Infrared powder spectra of (DI-DCNQI)₂Ag in KBr as a function of temperature (reported on the spectra). The inset shows in more detail the region around 600 cm⁻¹.

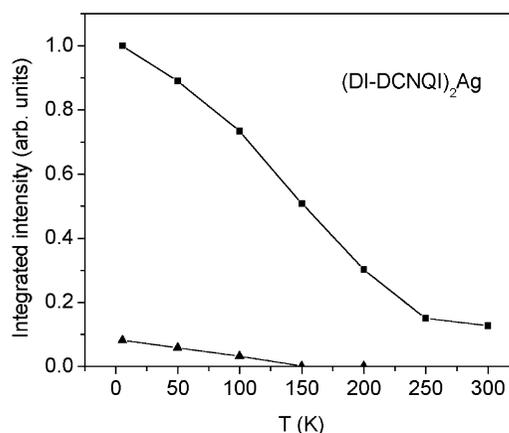


FIG. 3. Temperature-dependent integrated intensity of the absorptions at 622 cm⁻¹ (■) and at 637 cm⁻¹ (▲) of (DI-DCNQI)₂Ag.

structural transition is not completed at the lowest temperature explored here.

On the basis of the above model for the vibronic bands, the presence and the temperature evolution of the 622 cm^{-1} absorption shows that a dimerization (a $4k_F$ BOW) is already present at room temperature and that its amplitude increases by lowering the temperature. Recalling that the theoretical interpretation suggests for such a compound a possible tetramerization (5), one can look whether a second vibronic feature related to the 622 cm^{-1} absorption is present in the spectra. This is what was clearly observed, below 100 K, for the case of $(\text{DM-DCNQI})_2\text{Ag}$ (17) which is known to undergo a $2k_F$ BOW. In the present case one sees, in the spectrum at 5.5 K, only the presence of a side band with a small intensity at about 637 cm^{-1} whose integrated intensity is also reported in Fig. 3. Its temperature dependence shows that it can be found only below 150 K.

The experimental data suggest, therefore, that $(\text{DI-DCNQI})_2\text{Ag}$ has a structural instability which drives the system toward a tetramerization. The possibility of a $4k_F$ CDW with the presence of a bond alternation, which was previously suggested as a possible alternative to the tetramerized structure (16), is not appropriate on the basis of the comparison between the infrared and recent Raman spectra (unpublished data by K. Yakushi) which shows that an inversion center, not present in the $4k_F$ CDW with bond alternation, is found in the low-temperature structure.

The analysis of the infrared active modes can show, as recalled above with the model for the vibronic and vibrational modes, the presence of CDW in the low-symmetry structures. One can therefore look at the temperature-independent features of the spectra to find signs of such a structure. In a previous paper (17), it was noted that the band at 1010 cm^{-1} , which derives from a C–N stretching, shows a splitting below 150 K which was related to the observation of the charge disproportionation deduced from the NMR data (3) below 200 K. By looking at the analysis of the normal modes of the DM-DCNQI molecule one can see that large ionization shifts (of the order of 60 cm^{-1}) are found for the modes related to the stretching of the $\text{C}\equiv\text{N}$, $\text{C}=\text{C}$ and $\text{C}=\text{N}$ bonds which are observed at 2180 , 1591 and 1537 cm^{-1} , respectively, for the neutral molecule. The present infrared spectra of $(\text{DI-DCNQI})_2\text{Ag}$ show that in these spectral regions more than one band for each normal mode can be observed also at room temperature where the X-ray structure shows that all the molecules are equivalent in the unit cell. The reason can be found in the factor group splitting since eight equal molecules are present in the unit cell (14). Although in the presence of this complication in the analysis of the spectra one does not observe strong frequency variation of these bands from room temperature down to the lowest one.

Only some infrared modes with a temperature-dependent intensity, to be recognized as vibronic bands, can be found. A more detailed analysis of these spectra regions is not the aim of the present paper; however, the spectral patterns are clearly in favor of a tetramerized $2k_F$ low-temperature structure, which in principle (see above) is a BCDW1, has a CDW component that, if present, has a very-small-amplitude variation across the transition. The reason of the splitting of the 1010 cm^{-1} band must have therefore another origin and at present one can ascribe it to the tetramerization and therefore to selection rules governing the infrared activity of the larger unit cell due to the structural distortion.

$(\text{DI-DCNQI})_2M$ ($M = \text{Li and Cu}$)

The analysis of the temperature-dependent infrared spectra of the $(\text{DI-DCNQI})_2\text{Ag}$ compound can also be used to analyze the spectra of the Li and Cu compounds.

Figure 4 shows the temperature-dependent spectra of $(\text{DI-DCNQI})_2\text{Li}$. One finds a situation similar to that of the Ag compound although the vibronic features are more intense already at room temperature as can be seen by comparison with the infrared active modes. Figure 5 reports the temperature-dependent integrated intensity of the 623 cm^{-1} band. A comparison with Fig. 3 shows that in this case the BOW is far from being fully developed at the lowest temperature. For this reason the component at 638 cm^{-1} is barely visible below 10 K. Also, in this case, one does not find frequency shifts denoting a CDW development. The interpretation of the phase transition is therefore that a $2k_F$ BOW instability is developing by lowering temperature although the transition is not fully completed and the system shows a dominant dimerization.

Figure 6 reports the temperature-dependent infrared spectra of $(\text{DI-DCNQI})_2\text{Cu}$. The spectra show features

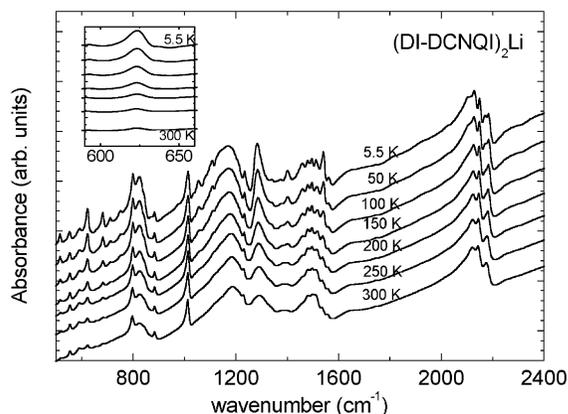


FIG. 4. Infrared powder spectra of $(\text{DI-DCNQI})_2\text{Li}$ in KBr as a function of temperature (reported on the spectra). The inset shows in more detail the region around 600 cm^{-1} .

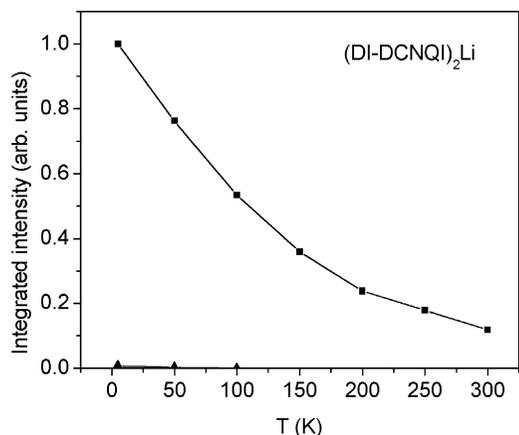


FIG. 5. Temperature-dependent integrated intensity of the absorptions at 623 cm^{-1} (■) and at 638 cm^{-1} (▲) of $(\text{DI-DCNQI})_2\text{Li}$.

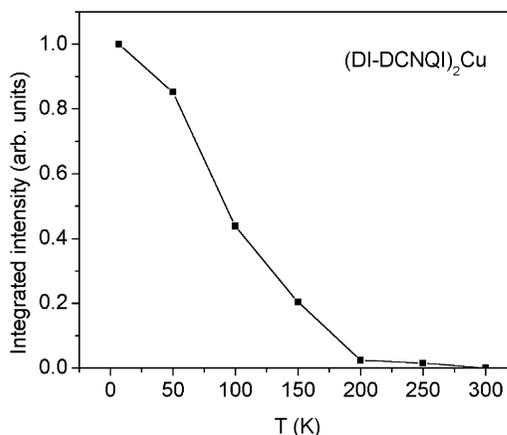


FIG. 7. Temperature dependent integrated intensity of the absorption at 625 cm^{-1} of $(\text{DI-DCNQI})_2\text{Cu}$.

which are different from those of the Ag and Li compounds. The first reason is that the compound is a conductor down to the lowest temperature and the absorption spectrum has electronic transitions in the background. These transitions also influence the vibronic features making them broader and with a Fano-type structure, which is similar to a derivative of the usual band structure. The temperature-dependent integrated intensity of the 625 cm^{-1} band is shown in Fig. 7. It is now difficult to find clear signs of the vibronic activity at room temperature although broad-bands suggest that some BOW fluctuations must be present. What is clear from Fig. 7 is that below 200 K a structural instability is present since the vibronic activity of the 625 cm^{-1} band develops. In this case, however, one does not find a high-frequency counterpart of this band also below 10 K suggesting that the transition is different from that of the Ag and Li compounds. As in the other cases, however, no signs of a

CDW development can be found in the spectra. Remembering that the compound shows a metallic behavior to the lowest temperatures (11), one should ask therefore how a structural phase transition is possible which is usually related to a charge localization. One can suggest that in this case, the electronic gap related to the structural transition is not at the Fermi level. This is possible in particular in the case, of the Cu compound since the d orbitals of the copper atom mix with those of the DI-DCNQI molecules and the degree of charge transfer is not that of the Ag and Li compounds. It is possible therefore that the structural instability is not driven by an electronic gain in energy, like in the Peierls mechanism, but by an external potential like that of the counterions.

CONCLUSIONS

Temperature-dependent infrared absorption spectra of powders of low-dimensional compounds show features which can be related to phase transitions due to structural transitions and modifications of the average charge of the molecules, namely to BOWs and to CDWs. A qualitative model, based on the symmetry elements of a low-dimensional structure, makes it possible to describe the transitions and also to characterize their periodicity, although in these cases the help of the temperature-dependent Raman spectrum is required. It is particularly important the possibility of deciding about the presence of a BOW by looking at the presence of vibronic bands in the infrared spectra recalling also that fluctuations which precede the formation of a BOW can be revealed. The analysis of the spectra must be careful because of the presence of many resonances of electronic, vibronic or vibrational nature which overlap in the same spectral region. Although single-crystal spectra help the analysis,

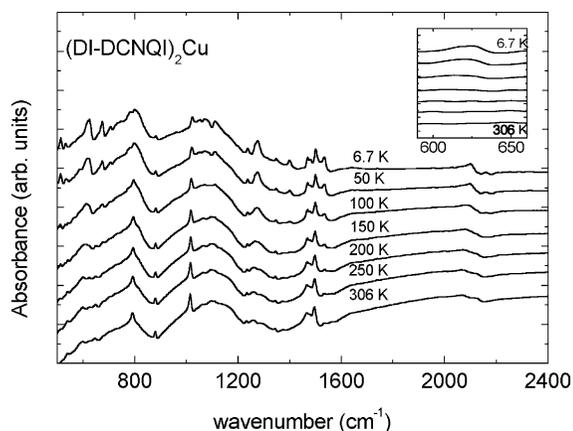


FIG. 6. Infrared powder spectra of $(\text{DI-DCNQI})_2\text{Cu}$ in KBr as a function of temperature (reported on the spectra). The inset shows in more detail the region around 600 cm^{-1} .

the knowledge of the vibrational behavior of the molecular units allows one to profitably use also the powder spectra.

The analysis of the temperature-dependent infrared spectra of (DI-DCNQI)₂Ag shows that a $4k_F$ BOW (alternation of short and long contacts between molecules in the stacks) begins from room temperature and that below 150–200 K there are signs characteristic of a $2k_F$ transition which in principle may be a BCDW1 although the amplitude of the associated CDW, if present, is not found to vary during the transition. A different situation is found for (DI-DCNQI)₂Li since in this case the $4k_F$ BOW is well present already at room temperature, but it does not saturate at the lowest explored temperature (5.5 K) and only below 50 K some signs of a $2k_F$ modulation can be hardly found. On the other hand, no charge variations are found in the whole temperature range. Another situation is observed for (DI-DCNQI)₂Cu. In this case, there are strong electronic transitions in the infrared region and signs of a structural distortion are very small at room temperature and probably due to fluctuations. Below 150 K, however, one finds that a structural transition begins to develop and continues down to the lowest explored temperature (6.7 K).

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