A new type of neutral-ionic interface in mixed stack organic charge transfer crystals:
Temperature induced ionicity change in ClMePD-DMeDCNQI

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Raman and polarized infrared spectra of the mixed stack charge transfer crystal 2-chloro-5-methyl-p-phenylenediamine–2,5-dimethyl-dicyanoquinonediimine (ClMePD-DMeDCNQI) are reported as a function of temperature. A detailed spectral interpretation allows us to gain new insight into the temperature induced neutral-ionic transition in this compound. In particular, the crossing of the neutral-ionic borderline appears to be quite different from that of the few known temperature induced neutral-ionic phase transitions. First of all, the ionicity change is continuous. Furthermore, the onset of stack dimerization precedes, rather than accompanies, the neutral-ionic crossing. The (second order) phase transition is then driven by the dimerization, but the extent of dimerization is in turn affected by the ionicity change.
I. INTRODUCTION

Pressure or temperature induced neutral to ionic phase transitions (PINIT and TINIT, respectively) in mixed stack organic charge transfer (CT) complexes were experimentally discovered about twenty years ago. The discovery, which followed earlier theoretical predictions, triggered intense experimental and theoretical investigations. However, the experiments were slowed down by the difficulties connected with high pressure studies, since for a long time tetrathiafulvalene-chloranil (TTF-CA) was the only complex undergoing TINIT. On the other hand, theoretical interest declined after a satisfactory and rather complete interpretation of the then available experimental data was reached.

Renewed interest on NIT has been recently prompted by the discovery that the transition can also be photoinduced, thus shifting both the experimental and theoretical focus to the dynamical aspects of the phase transition and of its precursor regimes. Furthermore, it has been pointed out that since at the NIT the ionicity jump is accompanied by a dimerization of the mixed stack, the transition is at least potentially of ferroelectric type. This connection puts NIT into a new and interesting perspective.

As mentioned above, very few compounds exhibit TINIT in addition to (room temperature) PINIT, thus allowing more detailed experimental studies. Apart from TTF-CA and its variants, like dimethyltetrafulvalene–chloranil or tetracelenofulvalene–chloranil, only two other CT complexes have been reported to undergo TINIT, namely tetramethylbenzidine–TCNQ, and more recently 2-chloro-5-methyl-p-phenylenediamine–2,5-dimethyl-dicyanoquinodimine, ClMePD-DMeDCNQI.

Aim of the present paper is to obtain a more detailed characterization of the TINIT in ClMePD-DMeDCNQI, through micro-Raman and polarized single crystals infrared (IR) studies. As shown below, in ClMePD-DMeDCNQI the crossing of the neutral-ionic borderline is different from the other known cases. First of all, there is no appreciable jump of ionicity at the phase transition. Furthermore, the onset of stack dimerization appears well before the neutral-ionic crossing.

II. EXPERIMENTAL

ClMePD-DMeDCNQI crystals have been prepared by mixing saturated solutions in dichloromethane followed by slow evaporation of the solvent. The IR spectra have been obtained with a FT-IR spectrometer equipped with a microscope (Bruker IFS66 with A590 microscope). The MCT detector employed in this arrangement limit the low frequency side of the IR spectra to 600 cm\(^{-1}\). The Raman spectra were recorded with a Renishaw System 1000 Microscope with excitation from an Ar ion laser (\(\lambda = 514.5\) nm). For both low (down to 80 K) and high temperature measurements we have employed a Linkam HFS91 cold stage.

III. RESULTS

A. Spectral Predictions

ClMePD-DMeDCNQI crystallizes in the triclinic system, space group P1, with \(a=7.463\)Å, \(b=7.504\)Å, \(c=7.191\)Å, \(\alpha=91.23^\circ\), \(\beta=112.19^\circ\), \(\gamma=96.91^\circ\), and \(Z=1\). The crystal structure is characterized by the presence of mixed stack columns along the \(b\) axis, where the electron-donor (D) ClMePD and the electron acceptor (A) DMeDCNQI alternate along the stack. The details of the crystal structure are not available, but it appears that at room temperature the stack is regular, that is, each molecule has equal distance (CT integral) with its two nearest neighbors along the chain. Moreover, the stack structure presents disorder in the relative orientation of the two molecules: the 2- and 5- substitutional sites of ClMePD are considered to be occupied by chlorine and methyl group with equal probability along the stack.

Vibrational spectroscopy is an important tool to study the ground state structural properties of CT compounds and of NIT in particular, since the normal modes of vibration are probes of the local electronic environment. Vibrational frequencies can respond to molecular charge variations, therefore detecting the change of ionicity (\(\rho\)) implied in the NIT. Generally, \(\rho\) is estimated by assuming a linear frequency dependence upon the molecular charge, \(\omega(\rho) = \omega_0 - \rho \Delta\), where \(\omega_0\) is the frequency of the neutral molecule, and \(\Delta\) the ionization frequency shift. A shift of at least 25 cm\(^{-1}\) can give reasonably accurate \(\rho\) values. Vibrational spectroscopy has been also the first investigative tool able to show that the NIT is associated with a distortion (dimerization) of the mixed stack. The possibility of discriminating between regular and dimerized stacks through vibrational spectroscopy is due to the effect of the interaction between CT electron and the molecular vibrations (\(e-m\) coupling). We summarize here the simple symmetry arguments which are the basis for this discrimination.

If the frontier molecular orbitals are non-degenerate, the only molecular vibrations which can couple to the electronic excitations are the ones belonging to the totally symmetric (\(ts\)) representation of the molecular symmetry group. Therefore, for a regular mixed stack made up of centrosymmetric molecules, no vibronic effects due to \(e-m\) coupling can be observed in the IR spectra, since the molecules lie on inversion centers along the stack and the \(ts\) vibrations are forbidden. On the other hand, \(ts\) modes are Raman active, so that perturbation effects due to the \(e-m\) interaction are observed in Raman, with a frequency shift of \(ts\) bands towards lower wavenumbers. In dimerized mixed stack systems the inversion center is
lost, and the $ts$ modes coupled to CT are both Raman and IR active. In IR, they borrow intensity from the nearby CT electronic transition, and are therefore polarized along the stack, with an intensity proportional to the extent of stack dimerization.

In the case of ClMePD-DMeDCNQI the situation is more complicated, and we deal separately with the A and D vibrations. If one disregards as reasonable approximation the slight deviation from planarity of the ring with its substituents in DMeDCNQI, and considers the methyl groups as point masses, then the centrosymmetric $C_{2h}$ group can be used to classify the normal modes. The distribution of the vibrational modes is as follows:

$$\Gamma_{\text{DMeDCNQI}} = 15a_g + 6b_g + 7a_u + 14b_u$$

In the isolated molecule, the ungerade modes are IR active, the $b_u$ being polarized in the molecular plane, and the $a_u$ out-of-plane, whereas the gerade modes are Raman active. To the above modes, we have to add the 18 vibrations of the methyl group, which can be both IR and Raman active, and polarized both in the molecular plane and normal to it. Since at this level of approximation DMeDCNQI is centrosymmetric, the above considerations about the effect of $e$-$mv$ coupling apply. We note, however, that the room temperature ClMePD-DMeDCNQI space group is non-centrosymmetric (actually, it has no symmetry elements), so that in the crystals DMeDCNQI molecules do not reside on inversion center, and there is no actual symmetry restriction on the IR activity of the modes.

Adopting the same criteria as in in the case of DMeDCNQI, we assume $C_s$ molecular symmetry for ClMePD, so that the distribution of the vibrational modes is:

$$\Gamma_{\text{ClMePD}} = 29a' + 13a''$$

and all modes are Raman and IR active. Totallysymmetric $a'$ vibrational modes are polarized in the molecular plane (perpendicular to the stack direction), and their frequency is affected by $e$-$mv$ coupling both in regular and dimerized mixed stack. On the other hand strong vibronically activated $a'$ IR absorptions polarized along the stack are expected only when the stack is dimerized. Again, the 9 vibrations due to the methyl group can be both Raman and IR active, with unpredictable polarization.

In view of the above, the ClMePD-DMeDCNQI degree of ionicity $\rho$ can only be estimated on the basis of the DMeDCNQI $b_u$ modes, since all the other in-plane modes are perturbed by $e$-$mv$ coupling, and the out-of-plane ones generally do not display a linear frequency shift with ionization. The onset of dimerization is marked by the appearance of IR bands polarized along the stack, at the same frequency of the Raman counterpart. The analysis of the spectral region 1350-1500 cm$^{-1}$ is made difficult due to presence of the many methyl group bending vibrations, whose intensity may also change with temperature due to rearrangements in the methyl groups orientation.

**B. Room Temperature Vibrational Spectra**

The room temperature Raman and polarized IR absorption spectra of ClMePD-DMeDCNQI are shown in Fig. 1. For the sake of clarity, the polarized IR spectra in Fig. 1 refer to two different crystals, the one relevant to the polarization perpendicular to the stack (⊥, bottom panel) being obtained on a thicker crystal. The corresponding parallel (||) spectrum in fact saturates completely in the 1200-1400 cm$^{-1}$. The IR frequencies, relative intensities and polarizations reported in Table 1 obviously refer to the thinner crystal. The micro-Raman data do not give polarization information. Since we shall not be concerned with the CH and NH stretching modes, data above 2300 cm$^{-1}$ are not reported. The interpretation of the spectra takes advantage of the available assignments of neutral and fully ionized DMeDCNQI molecules. For ClMePD a detailed vibrational assignment is not available, and the interpretation is based on the comparison with the frequencies of neutral ClMePD and with the normal mode analysis of $p$-phenylenediamine. The resulting assignment of ClMePD-DMeDCNQI spectra is reported in the rightmost column of Table 1.

Since the Raman exciting line is in pre-resonance with an intramolecular electronic excitation of DMeDCNQI, we expect (and find) that the Raman bands are for the most part due to DMeDCNQI $a_g$ modes. We remark again that the frequencies of these modes are perturbed (lowered) by $e$-$mv$ interaction, so that they cannot be used to estimate $\rho$.

**FIG. 1.** Room temperature Raman and polarized IR spectra of ClMePD-DMeDCNQI. The IR spectra polarized parallel and perpendicular to the stack axis are labeled with the symbols $||$ and $\perp$, respectively. The $e$-$mv$ induced band in the $||$ IR spectrum are marked by an asterisk (see text)
In the IR spectrum polarized parallel to the stack direction (Fig. 1, middle panel) we notice a couple of strong bands below 900 cm$^{-1}$, attributable to out-of-plane modes of DMeDCNQI and ClMePD. In the spectral region 1200-1600 cm$^{-1}$ one sees the clustering of many bands, also due to the presence of the methyl group vibrations. Despite the difficulty in interpreting this complex spectral region, one can notice several peaks (the main ones are marked by an asterisk in Fig. 1) whose frequency coincides with the Raman modes of DMeDCNQI and ClMePD. In the spectral region 1250-1700 cm$^{-1}$, attributable to out-of-plane modes of DMeDCNQI and ClMePD, the $b_u\nu_{47}$ mode should be preferred to the $\nu_{46}$ since it is not subject to Duschinsky effects and its frequency has a nice linear dependence on $\rho$. On the other hand, as already pointed out by Ref. 1 in the present case we have the interference of a very strong $a'$ band of ClMePD at 1504 cm$^{-1}$ (see Fig. 1 bottom panel), so that it is difficult to assess the frequency of the overlapping $b_u\nu_{47}$. We exclude the assignment to this band at 1522 cm$^{-1}$, since this band is rather weak, whereas the $b_u\nu_{47}$ has generally remarkable intensity. The $b_u\nu_{46}$ mode, on the other hand, occurs in a spectral region free from other vibrational modes, and has a reasonably good linear dependence on $\rho$. We therefore use this mode as a primary reference for the $\rho$ estimate, and check for compatibility with the spectral region where the $\nu_{47}$ should occur. On this basis we conclude that at room temperature the degree of ionicity of ClMePD-DMeDCNQI is between 0.35 and 0.44 (see below for a more detailed discussion). We do not discuss in detail the interpretation of the remaining parts of the IR perpendicular spectrum, whose assignment is reported in the rightmost column of Table 1.

C. Temperature Evolution of the Spectra

We first discuss the change in ionicity with temperature, and for this purpose we report in Fig. 2 the perpendicular IR spectrum at different temperatures in the spectral region 1250-1700 cm$^{-1}$. We immediately notice that the nearly isolated band at 1570 cm$^{-1}$, due to DMeDCNQI $b_u\nu_{46}$ mode, shows a remarkable frequency shift towards lower wavenumbers, opposite to the usual thermal hardening presented by the other vibrational bands. We therefore use this frequency to estimate $\rho$, as made in Ref. 2 and discussed in the previous Section, the red shift indicates a change in ionicity from $\sim$ 0.34 at 298 K to $\sim$ 0.57 at 80 K. We have also increased the temperature up to 400 K (sample sublimation starts already above 320 K), and $\rho\sim 0.30$ at this temperature. Since the spectral region of the $b_u\nu_{46}$ mode is free from overlapping with other modes, the temperature evolution of the corresponding frequency allows us to follow the change in $\rho$, as reported in the top panel of Fig. 2. The Figure clearly shows that $\rho$ changes smoothly with temperature. We have not observed hysteresis. Furthermore, the simultaneous presence of neutral and ionic domains can be excluded, since we always observe a single band throughout all the temperature range.

We now look for the other $\rho$ diagnostic mode, DMeDCNQI $b_u\nu_{47}$, whose presence is obscured by the strong band due to ClMePD $a'\nu_{10}$ mode, located at 1508 cm$^{-1}$ in the neutral molecule. At room temperature one sees...
FIG. 3. Top panel: Temperature evolution of the degree of ionicity, $\rho$, estimated from the frequency of the DMeDNCNI $b_u\nu_{46}$ mode. Bottom panel: the corresponding change in the intensity of the $e$-$mv$ induced bands, normalized to the low-temperature value. The square, circle and diamond correspond to the DMeDNCNI $a_g\nu_5$, $\nu_7$, and $\nu_{13}$ modes, respectively.

A last observation on the perpendicular spectra of Fig. 2 is the considerable hardening of the band at 1351 cm$^{-1}$, assigned to the DMeDNCNI $a'\nu_{12}$, which below 170 K melts into the nearby intense doublet, with an estimated frequency shift of 15-20 cm$^{-1}$. The hardening is probably associated with the ionicity variation, in this case towards higher frequencies, but in any case we do not use this mode to estimate the ionicity since, as discussed in Section 3.1, the ClMePD $a'$ are perturbed by $e$-$mv$ interaction.

Upon dimerization of the stack, the $e$-$mv$ coupling yields the intensity enhancement of the D and A $ts$ modes in the IR spectra polarized parallel to the stack axis. In Fig. 4 we report the temperature evolution of the parallel IR absorption spectra in the 800-1200 and 1380-1800 cm$^{-1}$ (the absorbance of the frequency region in between saturates completely by lowering temperature). The $e$-$mv$ induced (vibronic) bands due to $ts$ modes are immediately recognized since they gain IR intensity by lowering the temperature. They also have their counterpart at the same frequency in the Raman spectra (see Table 1). The detailed evolution of the intensity enhancement of the vibronic bands is better followed through the DMeDNCNI $a_g\nu_{13}$ mode (1006 cm$^{-1}$ at room temperature), since its intensity is easily compared with that of the nearby band at 873 cm$^{-1}$ assigned to an ungerade out of plane ($a''$) IR active vibration of ClMePD, which does not show any spectral variation with temperature. In Fig. 4 bottom panel, we have reported the intensity (normalized to the 80 K value) of this mode, together with that of the bands at 1417 and 1587 cm$^{-1}$, assigned to the DMeDNCNI $a_g\nu_7$ and $\nu_5$ modes, respectively. From the bottom panel of Fig. 4 we again notice that at room temperature the $e$-$mv$ bands are already developed. This residual residual IR intensity (about 10% of the low temperature value) of the $ts$ modes puts in evidence that there is some degree
of stack distortion at 298K, that is, the structural phase transition has already started. We have also verified that the residual IR intensity decreases further by increasing the temperature up to \( \sim 320 \) K, but we could not go further since sample sublimation prevents the collection of reliable relative intensity data.

From Fig. 5 we also observe the onset of two weaker bands in the low temperature parallel IR spectra. The first feature, which is still present in the room temperature spectrum as a weak band at \( 1138 \) cm\(^{-1} \), can be assigned to the weakly coupled \( \nu_1 \) \( \rho \)\( \text{e-mv} \) mode, since it exhibits a frequency coincident Raman counterpart. The second spectral feature appears in the low temperature spectrum as a doublet around \( 1535 \) cm\(^{-1} \), in a region where no fundamental modes are expected. Therefore, overtones and combinations are likely involved in the doublet observed in this region.

The C≡N stretching region deserves a separate discussion. In Fig. 5 we present the temperature evolution of the Raman spectra in the corresponding frequency range. We have already remarked that at room temperature Raman and IR spectra present more bands than expected. As shown in Fig. 5, the room temperature Raman spectra shows two bands. By lowering temperature, the high frequency band at \( 2168 \) cm\(^{-1} \) decreases in intensity, but remains present also at \( 80 \) K, hardening to \( 2175 \) cm\(^{-1} \), whereas the low frequency band grows. Moreover, we observe the onset of a third band at still lower frequency. We also find a counterpart of the above three low temperature Raman bands in the parallel IR spectrum, indicating that they correspond to \( \rho \text{e-mv} \) coupled modes. At present, we are unable to interpret this spectral region, where, as mentioned above, disorder effects may be important.

We finally remark that several other minor features and intensity changes appearing below about 200 K both in IR and Raman spectra are not interpreted. They might be due to some molecular rearrangements following the ionicity change, but at the moment this remains a speculative hypothesis.

### IV. Discussion

As we have seen in the previous Section, the ClMePD-DMeDCNQI vibrational spectra are rather complex, and their assignment is not obvious. The parallel use of Raman and polarized IR spectra as function of temperature helps us to reach a satisfactory spectral interpretation. Our data essentially confirm the previously given analysis of ClMePD-DMeDCNQI TINIT, but the detailed study presented here offers a more extensive picture and puts in evidence new and interesting features of the N-I interface in this compound.

As it is immediately evident from the top panel of Fig. 5, the ClMePD-DMeDCNQI ionicity changes continuously with lowering \( T \). The ionicity change from high to low temperature turns out to be about 0.3, of the same order of magnitude as in TTF-CA in TTF-CA, on the other hand, the temperature evolution of \( \rho \) is different: by lowering \( T \) at ambient pressure, \( \rho \) increases continuously from about 0.22 to about 0.30, and at \( T_c = 82 \) K there is a first order transition to \( \rho \sim 0.64 \). The first order nature of the phase transition is confirmed by several evidences, among which we cite the small hysteresis and the sometimes observed simultaneous presence of N and I domains in proximity of the phase transition. The latter fact is evidenced by the presence of IR and Raman bands due to both neutral and ionic species. On the opposite, in ClMePD-DMeDCNQI the passage from neutral to ionic side is smooth, and we do not find spectral signatures of different domains.

We remark that all the so far known TINIT’s exhibit a discontinuous \( \rho \) jump at \( T_c \), albeit in some cases the jump is rather small. Another feature common to all ambient pressure TINIT’s is sudden dimerization of the stack at \( T_c \). Also in this respect the behavior of ClMePD-DMeDCNQI is remarkably different. As shown in Fig. 1 and discussed in the previous Section, the ClMePD-DMeDCNQI stack is already dimerized to some extent at room temperature. The intensity of the \( \rho \text{e-mv} \) induced IR bands, which is related to stack distortion, has the same S-shape as the \( \rho \) variation (see Fig. 5). The point of maximum slope occurs in both cases around 220 K. Given the already mentioned uncertainty in the absolute \( \rho \) value, we cannot say whether or not the crossing from N to I side also occurs around 220 K. On the other hand, \( \rho \) can be considered an order parameter only in the case of first order, discontinuous phase transitions. Furthermore, if \( \rho \) changes continuously, the N-I borderline is ill-defined: From a theoretical point of view, the borderline...
is at $\rho = 0.5$ in the limit of an isolated DA pair, and at $\rho = 0.64$ for a regular stack. In any case, it is clear that for ClMePD-DMeDCNQI the dimerization phase transition is already started when the compound is still well into the N phase.

The crystal contraction induced by lowering the N phase.

The commonly reported picture of TINIT is as follows. The crystal contraction induced by lowering $T$ increases the crystal’s Madelung energy, up to the point of inducing a first order NI phase transition. On the ionic side, the system is considered to be intrinsically unstable towards dimerization due to spin-Peierls mechanism, so that the NI transition is accompanied by stack dimerization. Although the above picture explains the salient features of the so far known TINIT’s, it represents a simplified view, since it considers only the small CT integral ($\epsilon_{lph}$ coupling). Certainly, the ClMePD-DMeDCNQI phase limit, and disregards the role of electron-lattice phonon $e$-$lph$ coupling.

diagonalization methods, corroborated by experimental observations on several mixed stack CT complexes, provide a more complete and detailed picture and allow us to rationalize the ClMePD-DMeDCNQI phase transition.

First of all, the dimerization transition is attributable to the spin-Peierls mechanism only in the case of fully ionic ($\rho \equiv 1$) CT complexes like TTF-BA, namely in the large $\delta/t$ limit ($\delta$ is the difference between D and A site energies). By decreasing the ionicity, the charge modulation acquires importance, and the dimerization is better classified as an ordinary Peierls transition. The top panel of Fig. 6 shows the calculated energy gain upon dimerization. The gain is maximum for intermediate ionicity, corresponding to a pure Peierls mechanism, and progressively decreases as $\rho \to 1$, corresponding to pure spin-Peierls. We can then understand why the temperature of the dimerization transition increases with decreasing $\rho$ from 1 to intermediate values: it is 220 K for TMPD-TCNQ ($\rho \sim 0.9$) and TMPD-CA ($\rho \sim 0.6$) is already dimerized at room temperature.

Finally, if the $e$-$lph$ coupling is strong enough, the dimerization transition may occur also on the neutral side, as in the case of DBTTF-TCNQ under pressure. Whereas the dimerization transition is induced by $e$-$lph$ coupling, the $\rho$ variation is driven by the Madelung energy, and is affected by the interplay of $\delta$, the electron- molecular vibration $e$-$mv$ coupling, and the CT integral. Since the $\rho$ variation does not imply a symmetry change, we can assimilate the NI interface to the gas-liquid one, where we have a critical point beyond which there is no phase boundary.

We then propose the following scenario for the ClMePD-DMeDCNQI phase transition. As pointed out in Ref. 3, the CT integral in this compound is higher than in TTF-CA. Since the position of the critical point for the passage from a discontinuous to a continuous NI interface depends on the ratio of the Madelung potential to the CT integral, we might be beyond the critical point, so that the interface is continuous and $\rho$ is not a proper order parameter. In any case, at room temperature $\rho \geq 0.35$ (in TTF-CA $\rho \equiv 0.3$ when the NIT occurs), and for such high $\rho$ the gain in energy upon dimerization is such that the dimerization transition already starts around 320 K. The dimerization phase transition is very broad, about 200 K, and is in many aspects similar to that of TMPD-TCNQ. TMPD-TCNQ, on the other hand, is already ionic, and the $\rho$ change during the dimerization transition, if any, is very small.

For ClMePD-DMeDCNQI the dimerization transition starts on the neutral side, and in such a case we expect that the extent of dimerization increases with $\rho$. Fig. 6, bottom panel, shows the $\rho$ dependence of the asymmetry parameter, $\phi \propto (t_i - t_{i+1})/(t_i + t_{i+1})$, as obtained by VB calculation for a set of parameters relevant to systems exhibiting continuous ionicity change. It is seen that $\phi$, which is clearly related to the extent of dimerization, increases as the ionicity increase, reaching the maximum for $\rho$ between 0.6 and 0.7. Thus the dimerization represents the order parameter of the phase transition, but it is driven by the degree of ionicity (assuming constant the strength of $e$-$lph$ coupling).

The above picture is highly reminiscent of what may occur in Langmuir monolayers, where one has the coupling between a first-order phase transition (order parameter: the area per molecule) and a second order, orientational phase transition. An analysis in terms of Ginzburg-Landau theory of coupled phase transitions...
is beyond the aim of the present paper, but represents one of the most interesting developments in the study of CIMEPD-DMeDCNQI phase transition. Further experiments, including high pressure measurements, are in progress to confirm and extend the present results.

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| Infrared | Raman | Assignment |
|---|---|---|
| $\tilde{\nu}/\text{cm}^{-1}$ (298 K) | $\tilde{\nu}/\text{cm}^{-1}$ (80 K) | Polariz. | $\tilde{\nu}/\text{cm}^{-1}$ (298 K) | $\tilde{\nu}/\text{cm}^{-1}$ (80 K) |
| 589m | 595w | $\perp$ | 279w | 279 |
| 623s | || | 361m | 363 |
| 629s | 628m | $\parallel$ | 631w | 644w |
| 693w | 694w | $\perp$ | 637w | 644w |
| 729w | 729w | $\perp$ | 729w | 746w |
| 824w | 828w | $\perp$ | 806m | 806w |
| 900m | 9005w | $\perp$ | 1006m | 1006w |
| 1017w | 1016w | $\parallel$ | 1018w | 1025w |
| 1035w | || | 1036w | 1036w |
| 1056w | 1064w | $\parallel$ | 1073m | 1073m |
| 1059w | 1068w | $\perp$ | 1073w | 1073w |
| 1138w | 1144s | $\parallel$ | 1144m | 1144m |
| 1154w | 1176m | $\perp$ | 1176m | 1176m |
| 1181m | 1186w | $\perp$ | 1200m | 1200m |
| 1230s | || | 1245s | 1245s |
| 1263m | || | 1263m | 1263m |
| 1266s | 1269sh | $\perp$ | 1269s | 1269s |
| 1285s | 1286m | $\perp$, $\parallel$ | 1286m | 1286m |
| 1329m | 1325ys | $\parallel$ | 1325ys | 1325ys |
| 1335s | 1350s | $\perp$ | 1328s | 1328s |
| 1351m | 1368m | $\perp$ | 1350s | 1350s |
| 1368m | 1379w | $\perp$ | 1418w | 1418w |
| 1417m | 1412w | $\parallel$ | 1425w | 1425w |
| 1425m | 1424s | $\perp$ | 1448s | 1448s |
| 1441w | 1448w | $\perp$ | 1457w | 1457w |
| 1468w | 1477w | $\parallel$ | 1480s | 1480s |
| 1480s | 1490sh | $\perp$ | 1496s | 1496s |
| 1504s | 1506s | $\perp$, $\parallel$ | 1506s | 1506s |
| 1507w | || | 1507w | 1507w |
| 1511s | || | 1522w | 1522w |
| 1522w | || | 1522w | 1522w |
| 1532w | || | 1532w | 1532w |
| 1536w || || | 1536w | 1536w |
| 1570m | 1556m | $\perp$ | 1570m | 1570m |
| 1587m | 1582w | $\parallel$ | 1587m | 1587m |
| 1621br | 1622w | $\parallel$ | 1621br | 1621br |
|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| 1640w | 1649m | ⊥     | 1637s | 1640s | A, $a_y\nu_5$ |
| 1721br|       | ⊥     |       |       | $D, a'\nu_5$  |
|       | 2085w | ⊥     | 2124m |       | A, $a_y\nu_4$  |
|       | 2124w | ⊥     |       | 2124w |       |
| 2138w |       | ⊥     |       | 2124w | A, $a_y\nu_4$  |
| 2150sh| 2153vs| ⊥     | 2148w | 2153s | A, $a_y\nu_4$  |
| 2167s | 2175s |       | 2168s | 2175m | A, $a_y\nu_4$  |
| 2171vs| 2171s | ⊥     |       | 2175m | A, $b_u\nu_{45}$ |
| 2197w | 2213w | ⊥, || |       |       |       |