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N,N′-dicyanoquinonediimines as a molecular constituent of organic conductors: Vibrational behavior and electron–molecular vibration coupling

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The results of a vibrational analysis of neutral *N,N′*-dicyanoquinonediimine (DCNQI) and of 2,5-X,Y-DCNQI (X═Y═Cl; X═Cl, Y═CH_3; X═Y═CH_3 or CD_3) are presented. A sound assignment of the in-plane fundamental vibrational modes is discussed also in terms of a normal coordinate analysis (NCA) based on a modified valence force field. For light and deuterated 2,5-dimethyl-dicyanoquinonediimine (DMDCNQI) the vibrational analysis is extended to the corresponding radical anion. The comparison of the vibrational assignment of neutral and fully ionized species, together with the results of the NCA, leads to the identification of a strong Duschinsky effect, as well as of the frequency shifts relative to the ionization process. The $b_u \nu_{47}$ fundamental mode (quinoid C═N stretch) is recognized as diagnostic of the degree of charge transfer (CT) for DMDCNQI component units of CT systems. The relative values of the linear electron–molecular vibration (*e–mv*) coupling constants for the neutral and ionized DMDCNQI molecular structure, evaluated by a spectroscopic version of the complete neglect of differential overlap (CNDO/S) calculation associated with the eigenvectors coming from the NCA, are also reported. The infrared vibronic features of the $Ba(DMDCNQI)_2$ salt are sorted out by exploiting their intensity evolution with the temperature and are interpreted by applying Rice's model for a dimerized linear chain together with the calculated *e–mv* coupling constants. Furthermore, the visible absorption spectrum of the DMDCNQI radical anion is analyzed and its vibronic structure is attributed to a coupling with the three vibrational modes $a_g \nu'_5$, 1585; ν'_8, 1290; and ν'_{18}, 395 cm^{-1}. The dependence of the vibrational frequencies on ionicity and the vibronic features of the optical spectra are discussed with a view to their application in the investigation of the physical properties and the temperature and/or pressure-dependent phase transitions of conductors based on the DCNQI structure, particularly in the case of the open questions raised by the physical properties of the highly conducting Cu $(DMDCNQI)_2$ salt.

I. INTRODUCTION

Since the discovery of the first synthesized organic metal tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ),[1] attention has been focused on strong electron donor or acceptor molecules as potential basic structures to produce synthetic organic conductors and even superconductors.[2]

In the field of strong electron donors, a leading role is held by TTF which has generated many families of organic metals through the success obtained with substituted TTF structures and/or by exchanging sulphur with selenium or tellurium [e.g., tetramethyl-tetraselenafulvalene (TMTSF) and bis-ethylenedithio–tetrathiafulvalene (BEDT–TTF) structures].[2,3]

In the field of strong electron acceptors, the quinoid molecular structure takes a central position, mainly through the key case of TCNQ.[2,4] Some difficulties have been encountered in exploiting the production of new organic metals with this basic structure, first because the rigidity of the functional group C═C—$(CN)_2$ can introduce a loss of planarity of the quinoid ring with substitution,[5] preventing the formation of charge transfer (CT) stacked systems. Second, substituted TCNQs are only obtainable via tedious multistep synthesis.

A new class of electron acceptors based on the quinoid structure with the functional group C═N—CN (*N,N′*-dicyanoquinonediimine, henceforth DCNQI) has recently been synthesized.[6,7] DCNQI and its derivatives present the great advantage of a simple one-pot synthesis from the corresponding *p* quinones and show an electron affinity comparable to that of the TCNQ analogs.[8] Since with the DCNQI acceptors the planarity is preserved even on tetrasubstitution,[7] the large number of CT complexes obtainable favors a wide investigation of substituent-effect tuning of the molecular and solid state properties.

Attention has mainly been focused up to now on the radical anion salts,[9,10] $M(2,5\text{-X,Y-DCNQI})_2$ [M = alkali metals, Cu^+ (Refs. 11 and 12) and Ag^+] which display a high single crystal conductivity ($\sigma_{RT} = 100\text{–}1000\ S\ cm^{-1}$). Most of these compounds undergo low temperature metal–semiconductor transitions related to the strong 1D character. In contrast, some copper salts retain a stable metallic state down to 0.3 K.[13] Among them the copper salt with 2,5-dimethyl-DCNQI (DMDCNQI) has attracted and still attracts most attention. It displays an extraordinarily high low temperature conductivity ($\sigma_{3.5\ K} = 5 \times 10^5\ S\ cm^{-1}$) (Ref. 14) and is unique being the only presently known case of an organic conductor in which the insulating form is the high pressure phase, whereas in all other known cases, the pressure leads to a transition in the opposite direction.[15] Moreover, this copper salt is of special interest in view of its analogies to both the (quasi-2D) CuO_2 based high temperature superconductors and the (quasi-1D) halogen bridged metallic chains.[16] It is worthwhile to note that all the abovementioned DCNQI salts possess an architecture where the conducting organic stacks are bridged through the metal cation.[17,18] This structural situation makes it possible (e.g., in the case of the Cu cation) to get a new type of molecular conductor, which is a combination of an anion radical salt and a metal complex in which the transition metal atom interacts with the $p\pi$ conduction band of organic molecules. The relevance of this admixture in the copper salts and consequently the dimensionality of their conductivity system is an open problem[11,19] together with the univocal determination of the metal charge and of its temperature and/or pressure dependence.

Optical spectroscopy can contribute significantly to investigation of the physical properties of organic conductors and semiconductors.[20] Their structure based on molecular units makes the study of the role of molecular vibrations essential and very informative. In fact, due to the presence of low-lying CT electronic transitions, the interaction between CT electrons and molecular vibrations (*e–mv* coupling) is crucial in determining the physical properties and the characteristic phase transitions of these low-dimensional solids. Therefore optical spectroscopy in the region of intramolecular vibrations and CT transitions is a rich source of information on important physical parameters such as electron–phonon coupling constants, degree of ionicity, CT integrals, and on-site interelectronic correlation energy. Moreover, one can throw light on the temperature- and pressure-induced phase transitions.

Section II of the present paper describes the preparation of the materials studied, the procedures followed in the sampling, and the instrumentation employed. Section III reports the vibrational analysis of the in-plane fundamental modes for DCNQI and for some of its representative derivatives of the type 2,5-X,Y-DCNQI [X=Y=Cl; X=Cl, Y=CH_3; X=Y=CH_3 or CD_3; henceforth we will use the acronyms DClDCNQI (dichloro-DCNQI), ClMDCNQI (chloromethyl-DCNQI), DMDCNQI, and DMDCNQI-d_8, respectively]. The infrared and Raman spectra are presented and discussed together with the results of a normal coordinate analysis (NCA) based on a modified valence force field (MVFF). In Sec. IV, the vibrational analysis of light and deuterated DMDCNQI is extended to the corresponding radical anions. In the spectra of the solid Ba$(DMDCNQI)_2$ salt, the infrared vibronic effects due to the *e–mv* interaction are interpreted by applying Rice's model for a dimerized linear chain of stacked ion radicals.[21] Furthermore, the visible absorption spectrum of the DMDCNQI radical anion and its vibronic structure is analyzed.

II. EXPERIMENT

A. Materials

DCNQI, DClDCNQI, DMDCNQI, and ClMDCNQI were synthesized and purified as previously reported.[6,7] DMDCNQI-d_8 was synthesized as follows: Mononitration of *p*-xylene-d_{10} (Aldrich 99 at. % D) was carried out according to a known procedure[22] by using deuterated mixed acid (nitric acid-d_1 68 wt. % solution in D_2O 99.5 at. % D; Janssen Chimica). Mononitro-*p*-xylene-d_9 was catalytically reduced to *p*-xylidine-d_{11} by using deuterium gas (>99.4 at. % D) and palladium on activated carbon (10% Pd, Janssen Chimica). *p*-xylidine-d_{11} was directly oxidized to 2,5-dimethyl–*p*-benzoquinone-d_8 by $K_2Cr_2O_7$ according to a known procedure[23] and using sulphuric acid-d_2 in D_2O (99.8 at. % D, Janssen Chimica). From 2,5-dimethyl–*p*-benzoquinone-d_8 we obtained 2,5-dimethyl-dicyanoquinonediimine-d_8 by reaction with *bis*-trimethylsilyl–carbodiimide and titanium tetrachloride.[7] By mass spectral and magnetic resonance analysis, the deuterium content of the final product resulted better than 98 at. % D. The 1:2 Ba salts of light and deuterated DMDCNQI were obtained from almost boiling CH_3CN slowly pouring a DMDCNQI solution ($\simeq 0.017$ mol dm^{-3}) into an equimolar solution of BaI_2. Violet–black powder separated almost immediately, and after half an hour at room temperature, the product was collected and washed on the filter with CH_3CN. The stoichiometry was verified by elemental analysis. Li$(DMDCNQI)_2$ was prepared electrochemically as black needles by a reported method.[18] Spectroscopic grade acetonitrile and Fluka puriss grade dimethylsulfoxide (DMSO) and its deuterated analog dried by molecular sieves (4A) were used. 2-methyl-tetrahydrofuran (MTHF) was purified as previously reported.[24]

B. Sampling and instrumentation

A single crystal of DCNQI, obtained by sublimation, and crystals of light and deuterated DMDCNQI, grown by recrystallization from CH_3CN, were oriented along their optical extinction directions in order to measure polarized infrared absorption spectra. Powder infrared spectra were recorded from Nujol or perfluorocarbon mulls, whereas KBr window cells with Teflon spacers were used for the solutions of neutral compounds changing to BaF_2 windows in the case of DMDCNQI radical anion solution. Liquid cells of the latter type were used also for the spectra in the visible region. Raman spectra were measured for solutions at room temperature using the rotating cell technique[25] and for powders at low temperature by pressing the powders onto a KBr disk which was mounted on the cold finger of a cryogenic apparatus in a back scattering geometry. The glassy solutions at 77 K in MTHF of the DMDCNQI radical anion were prepared as previously reported,[24] except for the initial addition of one drop of dimethylsulfoxide (DMSO) to increase the low solubility of the Ba salt.

Infrared measurements were performed by a Perkin–Elmer (model 580B) and a Bruker Fourier transform infrared (FTIR) (model FS 113v) spectrometer. The instrumentation for Raman measurements consisted of a Spectra Physics krypton laser (model 171), a Spex double monochromator (model 1403), a thermoelectrically cooled RCA 31034A photomultiplier and a photon-counting system. The scanning of the spectra and the data acquisition were controlled by a microcomputer. The visible absorption spectra were recorded by a Cary 14 spectrometer. All low temperature measurements were performed in a closed-cycle refrigerator (CTI Cryodine model 21).

III. *N,N'*-DICYANOQUINONEDIIMINE (DCNQI) NEUTRAL MOLECULES

A. Vibrational spectra and assignment

The DCNQI crystal structure is monoclinic, space group $P2_1/c$, with two molecules on C_i sites.[6] In the crystal, the DCNQI molecule exhibits an *anti*-configuration and only a slight nonplanarity of the cyano groups with respect to the quinoid ring. Although the crystal structure of the neutral DClDCNQI, ClMDCNQI, DMDCNQI, and its fully deuterated analog is not available, that of some 1:2 metal salts[17,18] has been reported. The latter supports the assumption that the molecular structure of the neutral precursors has a nearly planar *anti*-configuration. Disregarding, as a reasonable approximation, the slight deviation from an ideal molecular C_{2h} symmetry, and considering the methyl groups in DMDCNQI as point masses, the distribution of the vibrational normal modes among the various symmetry species of unsubstituted and symmetrically 2,5-disubstituted DCNQIs is as follows:

$$\Gamma_{C_{2h}} = 15(20)a_g + 6(10)b_g + 7(11)a_u + 14(19)b_u.$$

The numbers in parentheses refer to the normal mode distribution for DMDCNQI including the internal vibrations (C—H stretching and H—C—H and C—C—H deformations) of the methyl groups frozen in a configuration which preserves the C_{2h} symmetry. The g modes are only Raman active and the in-plane a_g ones are polarized in solution spectra, whereas the out-of-plane b_g modes are depolarized. The u modes are only infrared active, the b_u being polarized in the molecular plane and the a_u out of the plane. Adopting analogous criteria as above, we have assumed C_s molecular symmetry for ClMDCNQI so that the distribution of the vibrational normal modes is

$$\Gamma_{C_s} = 34a' + 17a''.$$

All the modes are both Raman and infrared active, the in-plane a' ones being polarized in solution Raman spectra.

Tables I–V give the assignments of the in-plane vibrational modes for DCNQI and for 2,5-X,Y-DCNQI (X=Y=Cl; X=Cl, Y=CH_3; X=Y=CH_3 or CD_3).[26] The assignment is supported by the Raman depolarization ratios for the attribution of the totally symmetric modes, by the polarization of single crystal infrared absorptions for disentangling in-plane and out-of-plane modes in the case of DCNQI and of light and deuterated 2,5-dimethyl derivative, and for the latter compound also by isotopic shifts. Further support for the assignments came from a normal coordinate analysis reported in the following section.

TABLE I. Vibrational assignment[a] of DCNQI: in-plane normal modes.

	$\tilde{\nu}/\mathrm{cm}^{-1}$			
	Obs.[b]	Calc.	PED(%)[d]	
$a_g\nu_1$		3048	$K_7(54)$,	$K_6(45)$
$a_g\nu_2$		3045	$K_6(54)$,	$K_7(45)$
$a_g\nu_3$	2177	2176	$K_5(82)$,	$K_4(18)$
$a_g\nu_4$	1626	1626	$K_1(50)$,	$K_3(24)$
$a_g\nu_5$	1501	1487	$K_3(66)$,	$K_1(28)$
$a_g\nu_6$	1430	1437	$K'_2(35)$,	$K''_2(32)$,
			$H_4(20)$,	$H_5(17)$
$a_g\nu_7$	1285	1288	$H_5(34)$,	$H_4(30)$
$\alpha_g\nu_8$	1184	1171	$H_5(41)$,	$H_4(39)$
$a_g\nu_9$	1016	1032	$K_4(61)$	
$a_g\nu_{10}$	803	823	$K''_2(38)$,	$K'_2(28)$
$a_g\nu_{11}$	662	658	$H_8(57)$	
$a_g\nu_{12}$	594	592	$H_1(35)$,	$H_2(26)$
$a_g\nu_{13}$	432	455	$H_6(45)$,	$H_8(24)$
$a_g\nu_{14}$	371	360	$H_6(34)$,	$H_3(21)$
$a_g\nu_{15}$	101?	105	$H_7(77)$	
	Obs.[c]	Calc.		
$b_u\nu_{29}$	3071	3048	$K_7(56)$,	$K_6(43)$
$b_u\nu_{30}$	3057	3046	$K_6(56)$,	$K_7(43)$
$b_u\nu_{31}$	2171	2176	$K_5(82)$,	$K_4(18)$
$b_u\nu_{32}$	1571	1575	$K_1(71)$,	$K''_2(16)$
$b_u\nu_{33}$	1555	1553	$K_3(72)$	
$b_u\nu_{34}$	1391	1373	$H_4(40)$,	$H_5(37)$
$b_u\nu_{35}$	1340	1335	$K'_2(32)$,	$K''_2(29)$
$b_u\nu_{36}$	1118	1135	$H_4(30)$,	$H_5(29)$
$b_u\nu_{37}$	1048	1030	$K_4(57)$	
$b_u\nu_{38}$	955	939	$K'_2(25)$,	$K''_2(18)$
$b_u\nu_{39}$	791	779	$H_8(25)$,	$K''_2(18)$
$b_u\nu_{40}$	572	569	$H_8(60)$	
$b_u\nu_{41}$	360?	323	$H_6(46)$,	$H_7(22)$
$b_u\nu_{42}$		81	$H_7(63)$,	$H_6(32)$

[a] A tentative proposal for the assignment of the out-of-plane a_u (ν_{16}–ν_{22}) modes is the following: 872, 768, 572, 499, 374?, 146?, and 118? cm^{-1}. The $a_u\nu_{18}$ mode is assumed to be overlapped by $b_u\nu_{40}$.

[b] Observed frequencies from powder spectrum.

[c] Observed frequencies from crystal spectrum.

[d] Potential energy distribution. Only contributions greater than 15% are included.

B. Normal coordinate analysis of the in-plane vibrations

The nomenclature of the internal coordinates and the choice of the molecular axes are shown in Fig. 1. The values of the bond lengths and angles used in building the inverse kinetic energy matrix **G** were taken from the reported x-ray structure of the DCNQI (Ref. 6) for the *N,N'*-dicyanoquinonediimine skeleton, whereas those of the C—H and C—Cl bonds were transferred from chlorinated *p*-benzoquinones[27] and those of the C—CH_3 groups from tetramethyl–tetrathiafulvalene (TMTTF).[28] The overall MVFF for the quinoid skeleton was derived from the one tested for TCNQ,[29] whereas the stretching force constants for the C—N bonds were determined by using an empirical relation between bond length and force constant.[30] Concerning the chloro and methyl substituents, the force field was completed by transferring the corresponding constants from the chlorinated *p*-benzoquinones[27] and from TMTTF.[28] The agreement of the zeroth-order calculated frequencies with the experimental ones was satisfactory. The values of the force constants were subsequently adjusted by hand, according to the indications of the Jacobian matrix and the procedure of the overlay tech-

TABLE II. Vibrational assignment[a] of DClDCNQI: in-plane normal modes.

	$\tilde{\nu}/\mathrm{cm}^{-1}$		
	Obs.[b]	Calc.	PED(%)[d]
$a_g\nu_1$		3047	$K_7(99)$
$a_g\nu_2$	2180	2176	$K_5(82)$, $K_4(18)$
$a_g\nu_3$	1600	1604	$K_1(48)$, $K_3(25)$, $K_2''(21)$
$a_g\nu_4$	1513	1497	$K_3(63)$, $K_1(25)$
$a_g\nu_5$	1378	1384	$K_2'(53)$, $K_2''(28)$
$a_g\nu_6$	1236	1246	$H_5(78)$
$a_g\nu_7$	1049	1055	$K_4(50)$
$a_g\nu_8$	947	954	$K_6(33)$, $K_2''(29)$
$a_g\nu_9$	715	714	$H_8(23)$, $K_6(18)$
$a_g\nu_{10}$	652	640	$H_8(41)$, $H_1(17)$
$a_g\nu_{11}$		553	$H_4(44)$, $H_6(34)$
$a_g\nu_{12}$	415	418	$H_8(19)$, $H_3(18)$
$a_g\nu_{13}$	315	323	$K_6(29)$, $H_2(16)$
$a_g\nu_{14}$	237	210	$H_4(39)$, $H_6(21)$, $H_7(17)$
$a_g\nu_{15}$	96	83	$H_7(62)$, $H_6(27)$
	Obs.[c]	Calc.	
$b_u\nu_{29}$	3037	3047	$K_7(99)$
$b_u\nu_{30}$	2184	2176	$K_5(82)$, $K_4(18)$
$b_u\nu_{31}$	1571	1574	$K_1(42)$, $K_3(33)$, $K_2''(21)$, $H_5(16)$
$b_u\nu_{32}$	1553	1525	$K_3(52)$, $K_1(36)$
$b_u\nu_{33}$	1365	1352	$K_2'(47)$, $K_2''(22)$, $H_5(22)$
$b_u\nu_{34}$	1254	1265	$H_5(42)$, $K_2''(21)$, $K_1(16)$
$b_u\nu_{35}$	1050	1058	$K_6(23)$, $H_1(16)$
$b_u\nu_{36}$	1040	1028	$K_4(54)$
$b_u\nu_{37}$	822	824	$H_8(16)$
$b_u\nu_{38}$	586	604	$H_8(60)$, $K_6(20)$
$b_u\nu_{39}$	558	528	$K_6(35)$
$b_u\nu_{40}$	336	312	$H_6(29)$, $H_7(21)$
$b_u\nu_{41}$		197	$H_4(70)$
$b_u\nu_{42}$	69?	75	$H_7(61)$, $H_6(33)$

[a] A tentative proposal for the assignment of most of the out-of-plane a_u modes is the following: 916, 663, 558, 416, 137, and 69 cm^{-1}. The 558 and 69 cm^{-1} modes are assumed to be overlapped by the $b_u\nu_{39}$ and $b_u\nu_{42}$ modes, respectively.

[b] Observed frequencies from solution spectrum, except for the 2180 and 96 cm^{-1} observed from powder spectrum.

[c] Observed frequencies from powder spectrum.

[d] See footnote d to Table I.

nique.[31] The force constants are assumed to be transferable from one molecule to another, except when they refer specifically to chloro or methyl substituents, in order to increase the ratio of frequencies to parameters. Several least-squares refinement cycles yielded the final values of the force constants reported in Table VI. The calculated frequencies are compared with the observed ones in Tables I–V, where the approximate description of the normal modes in terms of the distribution of the potential energy (PED) among the internal coordinates is also reported.

IV. DMDCNQI RADICAL ANION

The spectroscopic analysis of the DMDCNQI radical anion can be based on the C_{2h} molecular symmetry already assumed above for the neutral molecule.

π-radical ions display a strong tendency toward CT intermolecular interaction so that spectroscopic data directly

TABLE III. Vibrational assignment[a] of DMDCNQI: in-plane normal modes.

	$\tilde{\nu}/\mathrm{cm}^{-1}$		
	Obs.[b]	Calc.	PED(%)[d]
$a_g\nu_1$		3047	$K_7(99)$
$a_g\nu_2$	2951	2960	$K_8(99)$
$a_g\nu_3$	n.e.	2843	$K_8(100)$
$a_g\nu_4$	2188	2176	$K_5(82)$, $K_4(18)$
$a_g\nu_5$	1641	1625	$K_1(51)$, $K_2''(19)$, $K_3(19)$
$a_g\nu_6$	1502	1503	$K_3(69)$, $K_1(17)$
$a_g\nu_7$	1439	1450	$H_{10}(66)$
$a_g\nu_8$	1410	1408	$H_{10}(31)$, $K_2'(29)$
$a_g\nu_9$	1370	1393	$H_9(48)$, $H_{10}(40)$
$a_g\nu_{10}$	1279	1259	$H_5(78)$
$a_g\nu_{11}$		1141	$K_6(47)$, $K_2''(30)$
$a_g\nu_{12}$	1025	1021	$K_4(40)$
$a_g\nu_{13}$	1012	1006	$H_9(66)$
$a_g\nu_{14}$	739	759	$K_2'(25)$
$a_g\nu_{15}$	634	644	$H_8(51)$
$a_g\nu_{16}$		562	$H_4(49)$, $H_6(27)$
$a_g\nu_{17}$	472	469	$H_1(18)$, $K_2''(16)$
$a_g\nu_{18}$	390	405	$H_3(21)$
$a_g\nu_{19}$	282?	249	$H_4(33)$, $H_6(31)$
$a_g\nu_{20}$	109?	93	$H_7(70)$, $H_6(22)$
	Obs.[c]	Calc.	
$b_u\nu_{42}$	3039	3047	$K_7(99)$
$b_u\nu_{43}$	2955	2960	$K_8(99)$
$b_u\nu_{44}$	2854	2843	$K_8(99)$
$b_u\nu_{45}$	2180	2176	$K_5(82)$, $K_4(18)$
$b_u\nu_{46}$	1591	1581	$K_1(64)$, $K_2'(18)$, $H_5(17)$
$b_u\nu_{47}$	1537	1549	$K_3(71)$
$b_u\nu_{48}$	1441	1443	$H_{10}(84)$
$b_u\nu_{49}$	1401?	1398	$H_9(54)$, $H_{10}(44)$
$b_u\nu_{50}$	1372	1376	$K_2'(47)$, $K_6(16)$
$b_u\nu_{51}$	1282	1285	$H_5(34)$, $K_2''(26)$
$b_u\nu_{52}$	1182	1174	$K_6(32)$, $H_5(25)$
$b_u\nu_{53}$	1052	1031	$K_4(53)$
$b_u\nu_{54}$	1002	1004	$H_9(64)$
$b_u\nu_{55}$	838	843	$K_2'(28)$, $K_2''(16)$
$b_u\nu_{56}$	686	695	$K_6(26)$, $H_8(26)$
$b_u\nu_{57}$	580	568	$H_8(49)$
$b_u\nu_{58}$	352	339	$H_4(30)$, $H_6(22)$
$b_u\nu_{59}$	294	267	$H_4(46)$, $H_6(22)$
$b_u\nu_{60}$		78	$H_7(62)$, $H_6(33)$

[a] A tentative proposal for the assignment of most of the out-of-plane a_u modes is the following: 2955, 1424, 1037, 907, 643, 566?, 423, 124, 119, and 111? cm^{-1}. The values of the calculated frequencies for the out-of-plane normal modes of the methyl group $a_u\nu_{21}$–ν_{23} are 2957, 1441, and 1020 cm^{-1}.

[b] Observed frequencies from low temperature powder spectrum, except for the 2188 cm^{-1} observed from a CH_3CN solution. The spectral region 2250–2900 cm^{-1} was not examined (n.e.).

[c] Frequencies from crystal or Nujol mull spectrum: the 2180 cm^{-1} was observed from a $CHCl_3$ solution.

[d] See footnote d to Table I.

TABLE IV. Vibrational assignment[a] of DMDCNQI-d_8: in-plane normal modes.

	$\tilde{\nu}$/cm^{-1}			
	Obs.[b]	Calc.	PED(%)[d]	
$a_g\nu_1$	2261	2264	$K_7(95)$	
$a_g\nu_2$	2208	2211	$K_8(97)$	
$a_g\nu_3$	2178	2176	$K_5(82)$,	$K_4(18)$
$a_g\nu_4$	2049	2050	$K_8(98)$	
$a_g\nu_5$	1615	1609	$K_1(49)$,	$K_3(24)$,
			$K_2''(21)$	
$a_g\nu_6$	1500	1499	$K_3(64)$,	$K_1(21)$
$a_g\nu_7$	1392	1395	$K_2'(54)$,	$K_2''(20)$
$a_g\nu_8$	1156	1163	$K_6(59)$,	$K_2''(19)$,
			$H_9(18)$	
$a_g\nu_9$	1043	1059	$K_4(37)$	
$a_g\nu_{10}$	1029	1038	$H_{10}(92)$	
$a_g\nu_{11}$	1007	1018	$H_9(24)$,	$H_{10}(21)$,
			$H_5(20)$	
$a_g\nu_{12}$	973	955	$H_5(41)$,	$K_4(20)$
$a_g\nu_{13}$	813	783	$H_9(67)$	
$a_g\nu_{14}$	707	732	$H_8(23)$,	$K_2'(19)$
$a_g\nu_{15}$	611	634	$H_8(44)$	
$a_g\nu_{16}$		501	$H_4(34)$,	$H_6(30)$
$a_g\nu_{17}$	450	447	$H_1(17)$	
$a_g\nu_{18}$	379	393	$H_2(19)$,	$H_3(19)$,
			$H_4(16)$	
$a_g\nu_{19}$	266	233	$H_4(37)$,	$H_6(26)$
$a_g\nu_{20}$		91	$H_7(68)$,	$H_6(23)$
	Obs.[c]	Calc.		
$b_u\nu_{42}$	2257	2264	$K_7(95)$	
$b_u\nu_{43}$		2211	$K_8(97)$	
$b_u\nu_{44}$	2165	2176	$K_5(82)$,	$K_4(18)$
$b_u\nu_{45}$		2050	$K_8(98)$	
$b_u\nu_{46}$	1571	1560	$K_1(59)$,	$K_2''(23)$,
			$K_3(21)$	
$b_u\nu_{47}$	1529	1547	$K_3(62)$,	$K_1(21)$
$b_u\nu_{48}$	1342	1355	$K_2'(54)$,	$K_6(21)$,
			$K_2''(18)$	
$b_u\nu_{49}$	1208	1203	$K_2''(30)$,	$H_4(18)$
$b_u\nu_{50}$	1137	1110	$H_9(34)$,	$H_{10}(26)$,
			$K_6(25)$	
$b_u\nu_{51}$	1038	1041	$K_4(31)$,	$H_{10}(23)$
$b_u\nu_{52}$	1030	1036	$H_{10}(82)$	
$b_u\nu_{53}$	963	973	$H_5(21)$,	$K_4(20)$
$b_u\nu_{54}$	768	795	$H_9(41)$,	$H_5(32)$
$b_u\nu_{55}$	742	728	$H_9(37)$,	$H_8(18)$
$b_u\nu_{56}$	647	651	$K_6(24)$,	$H_8(21)$
$b_u\nu_{57}$	554	552	$H_8(40)$	
$b_u\nu_{58}$	381	323	$H_6(30)$,	$H_7(19)$,
			$H_4(16)$	
$b_u\nu_{59}$		241	$H_4(60)$	
$b_u\nu_{60}$	113?	77	$H_7(62)$,	$H_6(33)$

[a] A tentative proposal for the assignment of the out-of-plane a_u modes is the following: 1035, 768, 577, 554, 343, and 258 cm^{-1}. The normal modes $b_u\nu_{54}$ and $b_u\nu_{57}$ are overlapped by the a_u modes with frequencies 768 and 554 cm^{-1}, respectively. The values of the calculated frequencies for the out-of-plane normal modes of the methyl group $a_u\nu_{21}$–ν_{23} are 2205, 1035, and 789 cm^{-1}.

[b] Observed frequencies from low temperature powder spectrum, except for the 2178 cm^{-1} observed from a CH_3CN solution.

[c] Frequencies from powder spectra.

[d] See footnote d to Table I.

TABLE V. Vibrational assignment of ClMDCNQI: in-plane normal modes.

	$\tilde{\nu}$/cm^{-1}			
	Obs.[a]	Calc.	PED(%)[b]	
$a'\nu_1$	3030	3047	$K_7(99)$	
$a'\nu_2$		3047	$K_7(99)$	
$a'\nu_3$		2960	$K_8(99)$	
$a'\nu_4$	n.e.	2843	$K_8(99)$	
$a'\nu_5$	2177	2175	$K_5(82)$,	$K_4(18)$
$a'\nu_6$		2175	$K_5(82)$,	$K_4(18)$
$a'\nu_7$	1621	1607	$K_1(50)$,	$K_3(21)$,
			$K_2''(19)$	
$a'\nu_8$	1566	1572	$K_1(43)$,	$K_3(31)$,
			$K_2''(21)$,	$H_5(16)$
$a'\nu_9$	1545	1531	$K_3(56)$,	$K_1(29)$
$a'\nu_{10}$	1507	1499	$K_3(63)$,	$K_1(24)$
$a'\nu_{11}$	1442	1448	$H_{10}(69)$	
$a'\nu_{12}$	1398	1410	$K_2'(35)$,	$H_{10}(25)$
$a'\nu_{13}$		1395	$H_9(52)$,	$H_{10}(41)$
$a'\nu_{14}$	1369	1362	$K_2'(48)$,	$K_2''(21)$,
			$H_5(18)$	
$a'\nu_{15}$	1283	1282	$H_5(38)$,	$K_2''(23)$
$a'\nu_{16}$	1253	1250	$H_5(75)$	
$a'\nu_{17}$	1145	1164	$K_6^{\mathrm{M}}(38)$,	$H_5(17)$,
			$K_2''(16)$	
$a'\nu_{18}$	1049	1056	$K_4(40)$	
$a'\nu_{19}$		1030	$K_4(55)$	
$a'\nu_{20}$	1010	1010	$H_9(56)$	
$a'\nu_{21}$	973	983	$K_4(20)$,	$K_6^{\mathrm{Cl}}(18)$
$a'\nu_{22}$	829	832	$K_2'(22)$,	$K_2''(16)$
$a'\nu_{23}$	727	748	$H_8(18)$,	$K_2'(18)$
$a'\nu_{24}$	644	651	$H_8(49)$	
$a'\nu_{25}$	619	631	$H_8(34)$,	$K_6^{\mathrm{Cl}}(16)$
$a'\nu_{26}$		562	$H_8(30)$,	$H_4^{\mathrm{Cl}}(16)$
$a'\nu_{27}$		554	$H_4^{\mathrm{M}}(25)$,	$H_6(22)$
$a'\nu_{28}$	430	427	$H_8(17)$	
$a'\nu_{29}$	370	373	$H_2(17)$	
$a'\nu_{30}$	329	320	$H_6(21)$,	$H_7(16)$
$a'\nu_{31}$	229	257	$H_4^{\mathrm{M}}(39)$,	$H_6(25)$
$a'\nu_{32}$	208?	205	$H_4^{\mathrm{Cl}}(52)$,	$H_6(16)$
$a'\nu_{33}$	98?	87	$H_7(65)$,	$H_6(25)$
$a'\nu_{34}$	n.e.	34	$H_7(61)$,	$H_6(33)$

[a] Observed frequencies from powder Raman spectra, except for the 3030 cm^{-1} observed from infrared Nujol mull spectra. Below 50 and between 2300 and 2900 cm^{-1}, the spectrum was not examined (n.e.).

[b] See footnote d to Table I. The K_6 stretching and H_4 bending force constants for the chloro and methyl substituents are distinguishable by the superscripts Cl and M, respectively.

attributable to a monomeric species must be collected from dilute solutions. In such a way, the collection of data is limited by sampling problems and the extension of the vibrational analysis requires the study of systems in which the radical anion is no longer free from CT intermolecular interaction. When this interaction is active, peculiar spectroscopic features of vibronic origin appear in the spectra and must be disentangled from the spectroscopic features proper to the isolated radical ion.[20] A simulation of the abovementioned vibronic effects by a suitable theoretical model is then required and is well exemplified by the reported treatment of the simplest interacting unit, namely, the radical ion self-dimer.[32] Clearly, this type of simulation also gives an insight

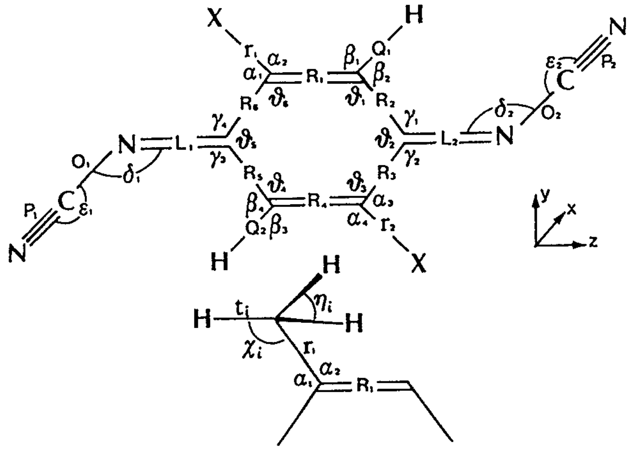

FIG. 1. Symbolic designation of the internal coordinates used in the normal coordinate calculations of DCNQI, DClDCNQI, DMDCNQI, and ClMDCNQI.

into microscopic physical parameters which characterize the CT systems allowing one to extract their experimental values when polarized optical reflectance can be measured. For the following considerations concerning a stack of planar ion radicals, the pertinent model is that of a dimerized linear chain, as developed first by Rice.[21]

Without entering into technical details, we directly recall here the final result obtained by such a model, which allows one to estimate the infrared conductivity along the direction joining the molecular centers in a dimer. For a system containing N_d dimers per unit volume,

$$\tilde{\sigma}(\omega) = -i\omega \frac{e^2 d^2}{4} N_d \frac{\chi(\omega)}{1-\tilde{\chi}(\omega)D(\omega)}, \tag{1}$$

where

$$\chi(\omega) = \frac{|\mu_{\mathrm{CT}}|^2 2\omega_{\mathrm{CT}}}{\omega_{\mathrm{CT}}^2 - \omega^2 - i\omega\gamma_{\mathrm{CT}}} \tag{2}$$

is the electronic susceptibility, $\tilde{\chi}(\omega) = \chi(\omega)/\chi(0)$ denotes its reduced form. In Eq. (2), we have assumed a single CT transition for simplicity.

$$D(\omega) = \sum_i \frac{\lambda_i \omega_i^2}{\omega_i^2 - \omega^2 - i\omega\gamma_i} \tag{3}$$

is the phonon propagator.

The symbols used in the above expressions refer to e, electronic charge; d, intradimer distance; μ_{CT}, dipolar moment of the CT transition, whose frequency and half-width are, respectively, ω_{CT} and γ_{CT}; $\lambda_i = g_i^2 \chi(0)/\hbar\omega_i$ are the dimensionless *e–mv* coupling constants for the *i*th unperturbed vibration of the radical ion with frequency ω_i and half-width γ_i. The dimensional linear *e–mv* coupling constants g_i are defined as $g_i = (1/2)^{1/2}(\partial\epsilon_{\mathrm{MO}}/\partial Q_i)_0$, where ϵ_{MO} is the energy of the molecular orbital of the radical ion in which the unpaired electron resides and Q_i is the dimensionless normal coordinate of the *i*th vibration which modulates the energy of the orbital. Simple symmetry arguments show that in the absence of degenerate electronic states the vibrational modes with $g_i \neq 0$ are the only totally symmetric ones.

Equation (1) simulates the optical conductivity spectrum of a dimerized linear chain of stacked ion radicals. It describes the spectral features due to the CT electronic transition as well as those due to the out-of-phase coupling of the originally infrared-inactive totally symmetric vibrational

TABLE VI. Valence force constants for DCNQI, DClDCNQI, DMDCNQI, and ClMDCNQI.

Symbol	Coordinate involved[a]	Force constant[b]
K_1	R_1R_1	7.80 (7.20)
K_2'	R_3R_3	5.23 (5.76)
K_2''	R_2R_2	5.31 (5.70)
K_3	L_1L_1	8.30 (7.20)
K_4	O_1O_1	6.43 (6.82)
K_5	P_1P_1	15.57 (14.36)
K_6	r_1r_1	5.047^{H}; 3.80^{Cl}; 4.77^{M}
K_7	Q_1Q_1	5.047
K_8	t_it_i	4.65^{M}
H_1	$\vartheta_1\vartheta_1$	0.898
H_2	$\vartheta_3\vartheta_3$	0.772
H_3	$\vartheta_2\vartheta_2$	0.960
H_4	$\alpha_1\alpha_1 = \alpha_2\alpha_2$	0.51^{H}; 1.014^{Cl}; 1.00^{M}
H_5	$\beta_1\beta_1 = \beta_2\beta_2$	0.510
H_6	$\gamma_1\gamma_1 = \gamma_2\gamma_2$	0.790
H_7	$\delta_1\delta_1$	0.485
H_8	$\epsilon_1\epsilon_1$	0.715
H_9	$\chi_i\chi_i$	0.680^{M}
H_{10}	$\eta_i\eta_i$	0.530^{M}
F_1	$R_1R_2 = R_3R_4$	0.436
F_2	R_2R_3	0.160
F_3	$R_1r_1 = R_6r_1$	0.037^{H}; 0.160^{Cl}; 0.300^{M}
F_4	$R_1Q_1 = R_2Q_1$	0.037
F_5	R_3L_2	0.669
F_6	R_2L_2	0.674
F_7	L_1O_1	0.180
F_8	O_1P_1	0.025
F_9	$R_1\vartheta_1 = R_1\vartheta_6$	0.101
F_{10}	$R_2\vartheta_1 = R_3\vartheta_3$	0.200
F_{11}	$R_2\vartheta_2 = R_3\vartheta_2$	0.283
F_{12}	$R_1(\beta_1\text{–}\beta_2)$	0.098
F_{13}	$R_1(\alpha_2\text{–}\alpha_1)$	0.098^{H}; 0.331^{Cl}; 0.350^{M}
F_{14}	$R_2(\beta_2\text{–}\beta_1)$	0.095
F_{15}	$R_3(\alpha_3\text{–}\alpha_4)$	0.095^{H}; 0.381^{Cl}; 0.310^{M}
F_{16}	$R_3(\gamma_2\text{–}\gamma_1)$	0.160
F_{17}	$R_2(\gamma_1\text{–}\gamma_2)$	0.132
F_{18}	$L_1\gamma_3$	0.400
F_{19}	$L_1\gamma_4$	0.259
F_{20}	$L_1\delta_1$	0.420
F_{21}	$O_1\delta_1$	0.015
F_{22}	$O_1\epsilon_1$	0.057
F_{23}	$P_1\epsilon_1$	0.200
F_{24}	$\vartheta_1\vartheta_6 = \vartheta_1\vartheta_2 = \vartheta_2\vartheta_3$	− 0.022
F_{25}	$r_1\alpha_1 = r_1\alpha_2$	0.000^{H}; 0.674^{Cl}; 0.283^{M}
F_{26}	$r_1\chi_i$	0.305^{M}

[a] $i = 1,2,3$.

[b] The values of the force constants used specifically for DCNQI, DClDCNQI, and DMDCNQI are marked with the superscripts H, Cl, and M, respectively. Stretch constants are in units of $\mathrm{Nm}^{-1} \times 10^{-2}$; stretch–bend, $\mathrm{Nrad}^{-1} \times 10^{-8}$; bend, $\mathrm{Nmrad}^{-2} \times 10^{18}$. The force constant values in parentheses are those used in the case of the DMDCNQI radical anion.

modes of the constituent radicals. The latter are characterized by a vibronic intensity borrowing from the CT transition.

The renormalized frequencies of the vibronic peaks are found as poles of $\tilde{\sigma}(\omega)$ or, equivalently, as solutions of the equation

$$\mathrm{Re}[\tilde{\chi}(\omega)D(\omega)] = 1. \quad (4)$$

For a totally symmetric mode far from the CT transition and from the other totally symmetric modes (isolated band), by resolving Eq. (4) one can easily evaluate the vibronic frequencies (Ω_i) with respect to the corresponding unperturbed vibrational modes (ω_i),

$$\Omega_i^2 = \omega_i^2(1 - \lambda_i). \quad (5)$$

The spectroscopic phenomena in the visible spectrum as well as in the infrared and Raman ones associated with the mentioned intermolecular interaction have been extensively investigated[20] particularly for the case of TCNQ (Ref. 33) and TTF (Ref. 34) radical ions.

A. Vibrational spectra and assignment

In the present study of the DMDCNQI radical ion, a procedure similar to that used for TCNQ or TTF (Refs. 33 and 34) has been adopted. First of all, the electronic absorption measurements have been used to check in what experimental conditions an appreciable amount of dimeric species is present.

Figure 2 shows the electronic spectrum of a very dilute solution of $\mathrm{Ba(DMDCNQI)_2}$ in $\mathrm{CH_3CN}$ with the corresponding spectrum of the DMDCNQI neutral molecule for comparison. By increasing the DMDCNQI radical anion concentration, a very weak additional absorption at about 840 nm rises at a concentration of about 10^{-1} mol dm^{-3}. This new feature becomes well evident (Fig. 2) for a saturated solution in (1:1) $\mathrm{DMSO{:}D_2O}$. Considering the main features in the electronic absorption spectra given in Fig. 2 in terms of a simple spectroscopic version of the complete neglect of differential overlap (CNDO/S) calculation, one finds that the absorptions at about 350 and 610 nm of the radical ion in a dilute solution are attributable to localized excitations of the monomeric species both of the ${}^2A_u \leftarrow {}^2B_g$ type [dipole moment along the long molecular axis z (see Fig. 1)], whereas in the same spectral region, only one transition of the ${}^1B_u \leftarrow {}^1A_g$ type (polarized along the z axis) is observed for the neutral species. The broad absorption at about 840 nm rising with increasing radical ion concentration is safely attributable to a CT transition and is the most distinctive indication of the intermolecular CT interaction between radicals in the dimer.

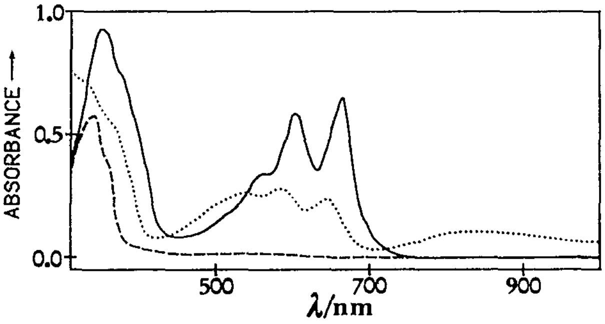

FIG. 2. Electronic absorption spectra of: (dashed line) 2.8×10^{-5} mol dm^{-3} solution of DMDCNQI in $\mathrm{CH_3CN}$, optical path 1 cm; (full line) 1.7×10^{-5} mol dm^{-3} solution of $\mathrm{Ba(DMDCNQI)_2}$ in $\mathrm{CH_3CN}$, optical path 2 cm; (dotted line) saturated solution of $\mathrm{Ba(DMDCNQI)_2}$ in $\mathrm{DMSO{:}D_2O}$(1:1).

The effect of concentration has been investigated for DMSO-d_6 solutions simultaneously in the above discussed visible spectral region and in the 1500–1700 cm^{-1} infrared one, keeping the product of the analytical concentration and of the optical path constant.[33,34] An additional absorption at 1594 cm^{-1} (1571 cm^{-1} for the deuterated radical ion) rises with increasing concentration ($>10^{-1}$ mol dm^{-3}) simultaneously with the appearance of the CT absorption at 840 nm. The 1594 cm^{-1} absorption clearly has a vibronic origin related to the CT interaction present in the radical self-dimer and is representative of the numerous vibronic features expected in the infrared spectra of the dimer.[20]

From the observations above, it follows that infrared and Raman data collected from dilute solutions ($<10^{-2}$ mol dm^{-3}) can be referred to the monomeric radical ion. However, also as a consequence of the limitations imposed by the solution sampling, one has to resort to crystalline samples. For this purpose, the $\mathrm{Ba(DMDCNQI)_2}$ salt containing the fully ionized DMDCNQI radical anion has been synthesized. The Ba salt was chosen because the alkaline salts of DMDCNQI display only a (1:2) stoichiometry.[18]

The visible spectrum of the powder salt shows a very broad absorption centered at about 1150 nm, an unmistakable sign of strong CT intermolecular interaction, accompanied by a remarkable infrared absorption at 1588 cm^{-1}. The presence of both these features can be safely assumed to be an indication of a structure made up of dimerized DMDCNQI anion stacks as observed, e.g., in the dimerized stack crystal phases of (1:1) alkaline salts of TCNQ.[35] As a consequence, the use of the infrared spectrum of crystalline $\mathrm{Ba(DMDCNQI)_2}$ for the assignment of the infrared active fundamental modes of the monomeric DMDCNQI radical anion requires the disentangling of the absorptions related with these modes from those of vibronic origin. For this purpose, one can take advantage of polarized absorption or reflection spectral data or explore the temperature dependence of the intensity of the vibronic infrared absorptions. The first possibility is prevented here by the difficulty of growing suitable single crystals, thus the infrared absorption spectrum of powder samples has been examined. We have noticed that the intensity of some absorptions, already present at room temperature, increases noticeably by lowering the temperature. This behavior is selective of the vibronic features and is a consequence of an increasing distortion of the organic stacks and/or of the depopulation of thermally accessible triplet states.[36] An analogous temperature dependence of vibronic absorptions, but with an abrupt intensity variation, has been observed in systems where a structural phase transition from regular to distorted (dimerized) stack occurs.[35] The assignment of the infrared vibronic absorptions of

TABLE VII. Vibrational assignment of DMDCNQI[a] radical anion: in-plane normal modes.

	$\tilde{\nu}/\mathrm{cm}^{-1}$		PED(%)[d]	
	Obs.[b]	Calc.		
$a_g\nu_1$	3030	3047	$K_7(99)$	
$a_g\nu_2$	2981	2960	$K_8(99)$	
$a_g\nu_3$		2843	$K_8(100)$	
$a_g\nu_4$	2121	2118	$K_5(78)$,	$K_4(21)$
$a_g\nu_5$	1619	1590	$K_1(47)$,	$K''_2(27)$
$a_g\nu_6$	1489	1476	$K''_2(51)$	
$a_g\nu_7$	1445	1440	$H_{10}(61)$,	$K_3(24)$
$a_g\nu_8$	1417	1403	$K_3(40)$,	$K_1(25)$,
			$H_{10}(17)$	
$a_g\nu_9$		1395	$H_9(57)$,	$H_{10}(45)$
$a_g\nu_{10}$	1268	1257	$H_5(77)$	
$a_g\nu_{11}$	1157	1156	$K_6(46)$,	$K''_2(28)$
$a_g\nu_{12}$	1018	1027	$K_4(46)$	
$a_g\nu_{13}$	1008?	1007	$H_9(76)$	
$a_g\nu_{14}$	748	768	$K'_2(23)$	
$a_g\nu_{15}$	657	647	$H_8(53)$	
$a_g\nu_{16}$		564	$H_4(49)$,	$H_6(28)$
$a_g\nu_{17}$	476	470	$H_1(18)$	
$a_g\nu_{18}$	406	402	$H_3(21)$	
$a_g\nu_{19}$	284?	250	$H_4(33)$,	$H_6(31)$
$a_g\nu_{20}$		93	$H_7(71)$,	$H_6(22)$
	Obs.[c]	Calc.		
$b_u\nu_{42}$		3047	$K_7(99)$	
$b_u\nu_{43}$	2961	2960	$K_8(99)$	
$b_u\nu_{44}$		2843	$K_8(100)$	
$b_u\nu_{45}$	2116	2118	$K_5(78)$,	$K_4(21)$
$b_u\nu_{46}$	1530	1547	$K_1(61)$,	$K''_2(25)$,
			$H_5(19)$	
$b_u\nu_{47}$	1478	1475	$K_3(68)$	
$b_u\nu_{48}$	1445?	1447	$H_{10}(59)$	
$b_u\nu_{49}$	1431	1418	$K'_2(39)$,	$H_{10}(31)$
$b_u\nu_{50}$	1382?	1395	$H_9(55)$,	$H_{10}(43)$
$b_u\nu_{51}$	1289	1286	$H_5(27)$,	$K''_2(19)$
$b_u\nu_{52}$	1175	1176	$K_6(30)$,	$H_5(30)$
$b_u\nu_{53}$	1032	1043	$K_4(52)$	
$b_u\nu_{54}$	995	1000	$H_9(66)$	
$b_u\nu_{55}$	851	855	$K'_2(23)$	
$b_u\nu_{56}$	692	693	$H_8(29)$,	$K_6(25)$
$b_u\nu_{57}$	580	566	$H_8(47)$	
$b_u\nu_{58}$	355	340	$H_4(30)$,	$H_6(22)$
$b_u\nu_{59}$	290	268	$H_4(47)$,	$H_6(22)$
$b_u\nu_{60}$		78	$H_7(63)$,	$H_6(33)$

[a] A tentative proposal for the assignment of most of the out-of-plane a_u modes is the following: 1420, 1032, 882, 634, 601?, and 447 cm^{-1}. The values of the calculated frequencies for the out-of-plane normal modes of the methyl group $a_u\nu_{21}$–ν_{23} are 2957, 1441, and 1020 cm^{-1}.

[b] Observed frequencies from a CH_3CN or CD_3CN solution of Ba(DMDCNQI)$_2$ except for the 1008 cm^{-1} observed from powder spectra.

[c] Frequencies from powder spectrum at about 10 K. The 2116 cm^{-1} was observed from DMSO solution.

[d] See footnote d to Table I.

Ba(DMDCNQI)$_2$ is discussed thoroughly in the next section.

The collected infrared and Raman data[26] for solutions of the monomeric DMDCNQI anion and for its crystalline Ba salt, as well as for the corresponding fully deuterated species, have been analyzed according to the above criteria and with some correlative ones based on the already available assignment of the neutral molecule (Tables III and IV). The assignment of the in-plane fundamental modes of the radical anions is given in Tables VII and VIII.

The normal coordinate analysis given in the following provides support for the assignments presented above and a

TABLE VIII. Vibrational assignment of the DMDCNQI-d_8[a] radical anion: in-plane normal modes.

	$\tilde{\nu}/\mathrm{cm}^{-1}$		PED(%)[d]	
	Obs.[b]	Calc.		
$a_g\nu_1$	2292	2263	$K_7(96)$	
$a_g\nu_2$	2204	2211	$K_8(97)$	
$a_g\nu_3$	2121	2118	$K_5(78)$,	$K_4(21)$
$a_g\nu_4$	2045	2050	$K_8(98)$	
$a_g\nu_5$	1594	1572	$K_1(48)$,	$K''_2(31)$
$a_g\nu_6$	1472	1458	$K'_2(57)$,	$K_3(28)$
$a_g\nu_7$	1414	1399	$K_3(44)$,	$K_1(31)$
$a_g\nu_8$	1175	1172	$K_6(59)$,	$K''_2(19)$
$a_g\nu_9$	1060	1067	$K_4(35)$,	$H_9(18)$
$a_g\nu_{10}$	1042	1038	$H_{10}(91)$	
$a_g\nu_{11}$	1002?	1021	$H_9(23)$,	$H_{10}(22)$,
			$H_5(17)$	
$a_g\nu_{12}$	982	959	$H_5(44)$,	$K_4(17)$
$a_g\nu_{13}$	806	782	$H_9(66)$,	$H_5(16)$
$a_g\nu_{14}$	722	739	$H_8(20)$,	$K'_2(18)$
$a_g\nu_{15}$	637	638	$H_8(47)$	
$a_g\nu_{16}$		502	$H_4(33)$,	$H_6(30)$
$a_g\nu_{17}$	456	447	$H_1(17)$	
$a_g\nu_{18}$	397	391	$H_3(19)$,	$H_2(18)$
			$H_4(16)$	
$a_g\nu_{19}$	261?	234	$H_4(37)$,	$H_6(26)$
$a_g\nu_{20}$		91	$H_7(69)$,	$H_6(23)$
	Obs.[c]	Calc.		
$b_u\nu_{42}$		2263	$K_7(96)$	
$b_u\nu_{43}$		2211	$K_8(97)$	
$b_u\nu_{44}$	2112	2118	$K_5(78)$,	$K_4(21)$
$b_u\nu_{45}$		2050	$K_8(98)$	
$b_u\nu_{46}$	1498	1527	$K_1(66)$,	$K''_2(31)$
$b_u\nu_{47}$	1457	1471	$K_3(70)$	
$b_u\nu_{48}$	1363?	1396	$K'_2(55)$	
$b_u\nu_{49}$	1229	1217	$K''_2(28)$,	$H_4(18)$
$b_u\nu_{50}$	1140	1113	$H_9(33)$,	$K_6(28)$,
			$H_{10}(25)$	
$b_u\nu_{51}$	1067?	1049	$K_4(35)$	
$b_u\nu_{52}$	1037	1037	$H_{10}(94)$	
$b_u\nu_{53}$	966	969	$H_5(23)$	
$b_u\nu_{54}$	800	795	$H_9(38)$,	$H_5(33)$
$b_u\nu_{55}$	741	734	$H_9(41)$	
$b_u\nu_{56}$	640	652	$H_8(25)$,	$K_6(24)$
$b_u\nu_{57}$	569	550	$H_8(38)$	
$b_u\nu_{58}$	382?	324	$H_6(30)$,	$H_7(19)$
$b_u\nu_{59}$	274?	242	$H_4(61)$	
$b_u\nu_{60}$		77	$H_7(62)$,	$H_6(33)$

[a] A tentative proposal for the assignment of some of the out-of-plane a_u modes is the following: 578, 349, and 255 cm^{-1}. The values of the calculated frequencies for the out-of-plane normal modes of the methyl group $a_u\nu_{21}$–ν_{23} are 2205, 1035, and 789 cm^{-1}.

[b] Observed frequencies from a CH_3CN solution of Ba(DMDCNQI-d_8)$_2$.

[c] Frequencies from powder spectrum at about 10 K. The 2112, 1229, and 1140 cm^{-1} were observed from a DMSO or DMSO-d_6 solution.

[d] See footnote d to Table I.

tool for gaining some insight into the nature of the normal modes of the radical ion. This analysis is analogous to the one which turned out useful in similar cases.[33,34]

In going from neutral to fully ionized species, the DCNQI skeleton is expected to change from a quinoid to a benzenoid structure, as confirmed by our results on bond order variations obtained from a CNDO/S calculation. Thus in the ionization process, the multiple bonds ($C{=}C$, $C{=}N$, and $C{\equiv}N$) are weakened and the single bonds ($C{-}C$ and $C{-}N$) are strengthened. In the normal coordinate calculation, the **G** matrix was kept the same as for the neutral molecule, owing to the lack of structural data for the ion and considering the slight influence that a small variation of the geometrical parameters has on the calculated frequencies.

The first step in the modification of the force field of the neutral molecule is the variation of the diagonal force constants of the multiple and single bonds mentioned above with a trend similar to that of the bond order. The force constant values were adjusted to the best fit following the indications of the Jacobian matrix and keeping their percentage variation of the order of that adopted in the case of TCNQ.[33] The calculated frequencies reported in Tables VII and VIII are obtained with the final values of modified diagonal force constants included in parentheses in Table VI. Tables III, IV, VII, and VIII allow the comparison of the vibrational behavior of neutral and fully ionized DMDCNQI molecules.

Mainly on the basis of the observed frequencies, it clearly results that besides the C—H stretchings, the ν_9–ν_{20} and the ν_{51}–ν_{60} normal modes are not appreciably affected by the ionization process. The $C{\equiv}N$ stretchings (ν_4 and ν_{45}) and the ring stretchings ν_5 and ν_{47} display a red frequency shift, whereas the NCA calculation indicates that their PED description is practically unchanged. On the other hand, the calculation shows that the PED description of the ν_6–ν_8, ν_{46}, and ν_{48}–ν_{50} modes changes strongly by ionization, a fact which underlines the presence of a strong Duschinsky effect.[37] Such a situation can be unequivocally tested considering the frequency values observed in the case of $M(DMDCNQI)_2$ salts (M = alkali metals), where by stoichiometry the average electron charge per molecule is 0.5. A detailed discussion of the optical spectra of these systems is beyond the scope of the present paper[38] and we limit ourselves here only to one clarifying example. For instance, for the $a_g\nu_6$ mode, the $M(DMDCNQI)_2$ salt spectra display a frequency of about 1470 cm^{-1}, a value which is not intermediate between that of the neutral DMDCNQI (1502 cm^{-1}, Table III) and that of the radical anion (1489 cm^{-1}, Table VII). The $a_g\nu_6$ mode is clearly affected in the ionization process by the Duschinsky effect in the absence of which there should be linearity in the frequency ionization shift. Namely, in the case of the (1:2) alkaline salts, one should observe a frequency value of about 1495 cm^{-1}.

The vibrational modes free from Duschinsky effect sorted out above are natural candidates as diagnostic probes of the average degree of electronic charge (ρ). The $a_g\nu_5$ mode is unsuitable because its frequency ionization shift is rather small ($\simeq 20$ cm^{-1}) to ensure sufficient accuracy in the measure of ρ. The use of the $a_g\nu_4$ and $b_u\nu_{45}$ ($C{\equiv}N$ stretchings) is prevented by the strong sensitivity to environment effects already evidenced for analogous vibrational modes in the case of TCNQ (Ref. 33) and $TCNQF_4$.[39] The infrared active $b_u\nu_{47}$ mode responds to all the basic requirements and is qualified as a probe for the measure of ρ in DMDCNQI systems. A definite test of this choice comes from the 1505 cm^{-1} frequency observed for this mode in the polarized infrared conductivity spectrum of $Li(DMDCNQI)_2$ single crystal.[38] In fact, this frequency value, intermediate between that of neutral (1537 cm^{-1}) and ionic (1478 cm^{-1}) DMDCNQI, is what one expects for a compound with $\rho \simeq 0.5$ in the case of a linear ionization shift.

B. Electron–molecular vibration interaction and vibronic effects

The vibronic features sorted out from the infrared spectra of light and deuterated $Ba(DMDCNQI)_2$ exploiting the temperature dependence of the absorption intensity are reported in the third and fifth columns of Table IX.

In proposing a connection between vibronic absorptions and the bare frequency of the totally symmetric modes observed in Raman (Table IX, second and fourth columns), one can take advantage of the knowledge of the relative values of the linear *e–mv* coupling constants (g_i) defined above. They have been calculated by a standard method[40] combining a CNDO/S electronic calculation with the vibrational eigenvectors from the normal coordinate analysis. The values for the highest occupied and the lowest empty orbital of neutral DMDCNQI as well as those for the highest occupied orbital of the corresponding radical anion are given in the last three columns of Table IX.

Rice's model[21] predicts that the strongest infrared vibronic bands with a large vibronic shift [Eq. (5)] correspond to isolated totally symmetric modes having the highest g_i value. This trend is what one substantially observes comparing columns two, three, and eight of Table IX and the experimental relative intensities,[26] except for the case of the $a_g\nu_6$, ν_7, and ν_8 modes characterized by rather near frequency and high g_i values. Only one very strong infrared vibronic absorption (1320 cm^{-1}) can be straightforwardly correlated with them, but the observed absorption pattern can still be understood by applying Rice's model. From Eq. (1), we have calculated the infrared conductivity considering three normal modes having the $a_g\nu_6$, ν_7, and ν_8 bare frequencies and the corresponding g_6, g_7, and g_8 calculated *e–mv* constants (Table IX, columns two and eight). The experimental values of γ_i ($\gamma_6 = 4.0$; $\gamma_7 = 5.0$; $\gamma_8 = 9.0$ cm^{-1}), $\omega_{CT} = 1150$ nm and $\gamma_{CT} \simeq 3500$ cm^{-1} have been used. Given the lack of crystal structure data, values of 2.5×10^{21} and 3.4×10^{-8} cm, taken from the well-studied case of KTCNQ,[41] have been assumed for the number density of dimers (N_d) and for the intermolecular intradimer distance (d), respectively. The best simulation of the strong vibronic feature at about 1320 cm^{-1} is obtained with a value of 0.40 for $|\mu_{CT}|^2$. The calculated spectroscopic pattern, shown in Fig. 3 (solid curve), displays a strong peak at about 1302 cm^{-1} and two weak peaks at about 1425 and 1473

TABLE IX. Vibronically activated infrared bands of Ba(DMDCNQI)$_2^a$ and Ba(DMDCNQI-d_8)$_2^a$; totally symmetric fundamental Raman lines of the radical ions ($\tilde{\nu}$/cm^{-1}); calculated linear *e–mv* coupling constants for DMDCNQI neutral and radical anion species.

Normal mode	DM$^-$ Raman[b]	Ba(DM)$_2$ infrared[c]	DM-d_8^- Raman[b]	Ba(DM-d_8)$_2$ infrared[c]	DM		DM$^-$
					g_i (meV)$^d_{34}$	g_i (meV)$^e_{35}$	g_i (meV)$^f_{35}$
$a_g\nu_1$	3030		2292		3.1	1.3	9.3
$a_g\nu_2$	2981		2204		3.5	1.2	6.2
$a_g\nu_3$			2121	2064	3.8	7.6	10.3
$a_g\nu_4$	2121	2072	2045		73.8	118.1	146.2
$a_g\nu_5$	1619	1588	1594	1565	182.1	222.5	187.7
$a_g\nu_6$	1489	(1478)?	1472	(1457)?	65.5	181.3	147.1
$a_g\nu_7$	1445		1414	1298	12.9	36.0	146.0
$a_g\nu_8$	1417	1320	1175	1180?	28.7	53.1	102.0
$a_g\nu_9$			1060		24.9	1.0	37.7
$a_g\nu_{10}$	1268	1243	1042		24.5	24.9	34.5
$a_g\nu_{11}$	1157	1143?	1002?	995?	3.5	77.6	76.2
$a_g\nu_{12}$	1018		982	977	48.8	27.4	4.8
$a_g\nu_{13}$	1008[b]?	1006	806	800	2.4	31.8	39.9
$a_g\nu_{14}$	748	745	722	719	31.0	24.4	5.1
$a_g\nu_{15}$	657	658	637	640	1.0	61.1	57.0
$a_g\nu_{16}$					21.2	21.0	12.3
$a_g\nu_{17}$	476	474	456	448	1.5	7.3	19.4
$a_g\nu_{18}$	406	392	397	382	0.0	68.8	73.5
$a_g\nu_{19}$	284?		261?		1.7	11.8	21.9
$a_g\nu_{20}$					3.9	16.5	9.1

[a] In the column headings DMDCNQI and DMDCNQI-d_8 are shortened as DM and DM-d_8.

[b] Frequencies from solution spectra; the value of 1008 refers to a band observed in the powder spectra only. For the meaning of the braces, see the text.

[c] Values in parentheses refer to cases in which overlapping with a b_u infrared active normal mode is quite strong.

[d] *e–mv* coupling constants calculated for the highest occupied orbital (34).

[e] *e–mv* coupling constants calculated for the lowest empty orbital (35).

[f] *e–mv* coupling constants for the highest occupied orbital (35).

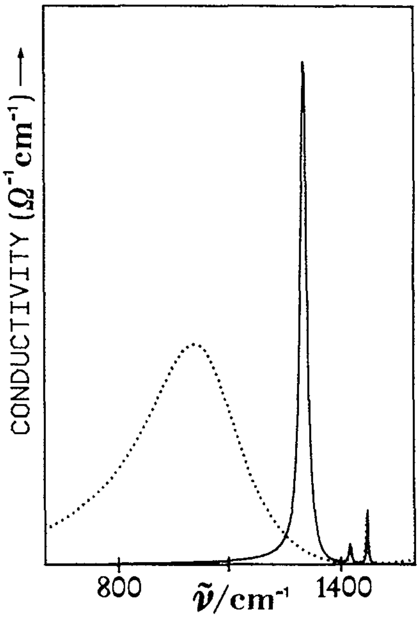

FIG. 3. Infrared conductivity of a dimerized linear chain of DMDCNQI anions calculated by Rice's model [Eq. (1)] in the region of the intramolecular vibrations. Only three normal modes with $\omega_6 = 1489$, $\omega_7 = 1445$, and $\omega_8 = 1417$ cm^{-1} are coupled with the CT transition. Parameters used in the calculation $|\mu_{\rm CT}|^2 = 0.4$; $\gamma_{\rm CT} = 3500$ cm^{-1}; $N_d = 2.5\times 10^{21}$ cm^{-3}; $d = 3.4\times 10^{-8}$ cm; $\gamma_6 = 4.0$; $\gamma_7 = 5.0$, and $\gamma_8 = 9.0$ cm^{-1}; $g_6 = 147$, $g_7 = 146$, and $g_8 = 102$ meV. Solid curve refers to the $\omega_{\rm CT} = 1150$ nm case; dotted curve is the simulation with $\omega_{\rm CT} = 3300$ nm.

cm^{-1}, respectively. By changing the $|\mu_{\rm CT}|^2$ value within a wide range (0.4–1.4), the qualitative spectroscopic pattern remains the same except for the shift to lower frequency of the strong vibronic feature originally at about 1302 cm^{-1}. A quantitative simulation of the complete conductivity spectrum would require the availability of absolute conductivity data from single crystal samples. However, lacking such data, it is still advantageous to compare the limited and qualitative simulation of Fig. 3 with the observed vibronic absorptions from powder samples[26] assuming that *for thin* samples the conductivity spectrum is proportional to that of absorbance.[42] Actually, the pattern of Fig. 3 (solid curve) accounts for the experimentally observed strong vibronic absorption at 1320 cm^{-1} (Table IX, column three), whereas the two weak vibronic absorptions predicted at about 1425 and 1473 cm^{-1} are not found in the spectrum and the latter could well be overlapped by the $b_u\nu_{47}$ infrared active mode. Braces in Table IX remind us that one cannot rely too much on the pairing between Raman and vibronic frequencies because the description of the braced normal modes can be modified in the vibronic activation process through coupling with the CT electronic excitation.

The strong coupling effect considered above resembles what has been observed and successfully simulated by a cluster model in the case of the 1:1 CT complex of TTF with tetracyanoethylene (TCNE).[43] In this case, the C=C stretch normal modes of the two component molecules have near frequency values and high *e–mv* coupling constants so that they strongly interact through the CT excitation producing one strong infrared absorption accompanied by a second weak and elusive one.

The analysis of the vibrational data of $Ba(DMDCNQI)_2$ (Ref. 26) guided by Rice's model for a dimerized linear chain leads to an extensive and satisfactory interpretation of most of the vibronic infrared features of the light as well as of the deuterated Ba salt as reported in Table IX.

From the above discussion, one may note that the weak vibronic absorption underlying absorption related to the $b_u \nu_{47}$ mode does not appear to interfere with the diagnostic character of this mode for identifying the degree of charge transfer in systems containing ionic DMDCNQI ($\rho = 1$). However, for lower ρ values, the situation may become less favorable. With a dimer model[21] we can simulate the vibronic spectral pattern in the case of $\rho = 0.5$ (quarter-filled system). The result of such a simulation with $\omega_{CT} \cong 3300$ nm is given in Fig. 3 (dotted line). It appears that the vibronic band predicted again at about 1473 cm^{-1} remains of weak intensity with respect to the strongest vibronic absorption at lower frequency, so that its interference with the diagnostic absorption due to the $b_u \nu_{47}$ mode should remain small. However, an unambiguous identification of the $b_u \nu_{47}$ frequency requires spectra of single crystals polarized parallel and perpendicular to the stack direction. Vibronic absorptions are absent in the latter having their dipole moment directed along the stack.

We can now focus our attention on the complex structure of the electronic absorption centered at about 610 nm of the DMDCNQI radical ion already observed for a dilute CH_3CN solution in Fig. 2. In Fig. 4, the same visible absorption for a MTHF solution at room temperature is compared with that of a glassy solution at 77 K which displays a better resolved vibronic structure. The frequency of the absorption peaks are given in Table X together with the frequency shifts relative to the 0–0 band (14 780 cm^{-1} at 77 K). The vibronic structure of the $^2A_u \leftarrow {}^2B_g$ electronic transition is represented by

$$\tilde{\nu} = \tilde{\nu}_{00} + v_a \tilde{\nu}'_a + v_b \tilde{\nu}'_b + v_c \tilde{\nu}'_c, \qquad (5)$$

where $\tilde{\nu}'_a = 1585$ cm^{-1}, $\tilde{\nu}'_b = 1290$ cm^{-1}, and $\tilde{\nu}'_c = 395$ cm^{-1} and v_a, v_b, and v_c assume the values given in Table X. In the resonance Raman spectrum of DMDCNQI anion solution[26] obtained with the 647.1 nm exciting line, the bands at 1619, 1417, and 406 cm^{-1} display the strongest intensities. Thus the corresponding $a_g \nu_5$, ν_8, and ν_{18} modes are the ones most strongly coupled with the electronic transition because the resonance Raman intensity is directly related to the degree of coupling.[44] It follows that the most reasonable assignment of the vibrational frequencies of the excited ($\tilde{\nu}'$) electronic state (Table X) with respect to that of the ground state ($\tilde{\nu}$) is $\tilde{\nu}'_5$, 1585–1619 cm^{-1} (ring C=C stretch); $\tilde{\nu}'_8$, 1290–1417 cm^{-1} (C=N stretch); and $\tilde{\nu}'_{18}$, 395–406 cm^{-1} (skeletal bending). It is worthwhile to note that the above spectroscopic features resemble those observed in the visible spectrum for the $^2B_{3u} \leftarrow {}^2B_{2g}$ electronic transition of the similar structure of the TCNQ anion.[24] In that case, one finds that the frequencies $\tilde{\nu}'_3 = 1597$ cm^{-1}, $\tilde{\nu}'_4 = 1257$ cm^{-1}, and $\tilde{\nu}'_9 = 330$ cm^{-1} play a dominant role in the vibronic coupling of the excited state and are related with the ring C=C stretch, external C=C stretch, and skeletal bending fundamental vibrations of the electronic ground state ($\tilde{\nu}_3 = 1615$ cm^{-1}; $\tilde{\nu}_4 = 1391$ cm^{-1}; and $\tilde{\nu}_9 = 337$ cm^{-1}). In both TCNQ and DMDCNQI radical anions, the vibronic coupling involves analogous normal modes of the semiquinoid structure.

Moreover, in the visible spectrum of the TCNQ anion (see Fig. 1 in Ref. 24), the 0–0 band displays a relatively greater intensity with respect to that of the vibronic structures, whereas in the case of the DMDCNQI anion the relative intensities are more comparable. This fact clearly indicates for the latter radical structure a stronger coupling of the vibrational modes with the electronic transition.[45]

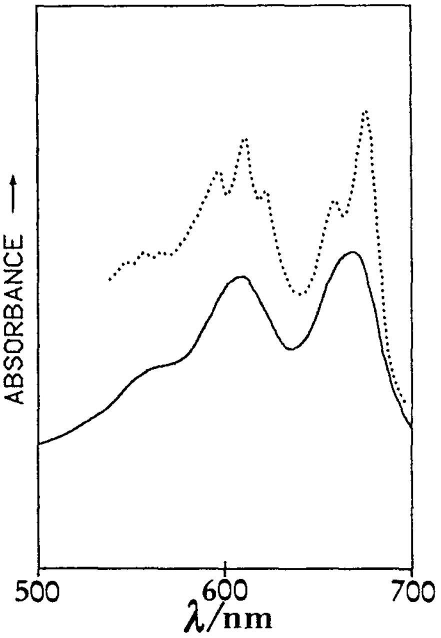

FIG. 4. Visible absorption spectra of $Ba(DMDCNQI)_2$ salt in MTHF: (full line) solution at 300 K; (dotted line) glassy solution at 77 K.

TABLE X. Visible absorption system of the DMDCNQI anion in MTHF glassy solution at 77 K: vibronic frequencies ($\tilde{\nu}$/cm^{-1}) and assignment.

		Assignment[b]		
$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}$[a]	v_a	v_b	v_c
14 780		0	0	0
15 175	395	0	0	1
16 070	1290	0	1	0
16 365	1585	1	0	0
16 765	1985	1	0	1
17 645	2865	1	1	0
17 950	3170	2	0	0
18 340	3560	2	0	1

[a] Frequency shift relative to the 0–0 band (14 780 cm^{-1}).

[b] v_a, v_b, and v_c are the quantum numbers by which one can represent the vibronic frequencies by Eq. (5) (see the text).

V. CONCLUSION

Knowledge of the vibrational behavior of the quinoid structure has been extended to the dicyanoquinonediimine family making available basic information for the exploitation of the optical properties of case organic conductors and semiconductors built up of strong electron acceptor moieties. A sound vibrational assignment of the in-plane modes has been achieved for neutral DCNQI and for some of its 2,5-disubstituted derivatives with particular regard to the DMDCNQI. A useful description of the vibrational behavior in terms of a normal coordinate analysis has been obtained by a simple empirical MVFF transferred from the one working for other key quinoid structures [TCNQ (Ref. 29) and *p*-benzoquinones (Ref. 27)] and able to describe satisfactorily all the studied members of the DCNQI family.

Since in conducting or semiconducting molecular systems the basic donor or acceptor unit plays its role as fully or partially ionic moiety, a sound vibrational assignment of the in-plane modes has been performed for the DMDCNQI radical anion. From this analysis, it turns out that some normal modes strongly vary their description in terms of PED in going from neutral to ionized structure (Duschinsky effect). As a consequence, the use of Raman fundamental frequencies in trying to determine the formal charge on a molecular site is ruled out. On the other hand, the Duschinsky effect appears weaker for infrared active modes and the $b_u \nu_{47}$ (C=N stretch) mode has been successfully identified as diagnostic for the degree of charge transfer.

The analysis of the spectroscopic data of the Ba(DMDCNQI)$_2$ salt, which can be considered a system built up of segregated DMDCNQI radical anion stacks, has offered the opportunity to clear up some peculiarities in the spectroscopic vibronic effects developed by a distorted stack of DMDCNQI anions. This case gives rise to the problem of recognizing a vibronic feature generated by three totally symmetric vibrational modes ($a_g \nu_6$, ν_7, and ν_8) strongly coupled with a CT electronic transition and characterized by bare frequency values fairly near to each other. This paper shows that the application of Rice's model for a linear chain[21] together with the use of calculated *e–mv* coupling constants leads to a satisfactory qualitative rationalization of the experimental vibronic effects. A quantitative simulation by Rice's model or by a more sophisticated cluster model[46] and its comparison with absolute spectroscopic data has been hampered so far by the lack of structural information on half-filled systems containing DMDCNQI anion stacks and by the difficulty of collecting single crystal polarized reflectance spectra.

The analysis of the optical data for the monomeric DMDCNQI anion extended to the absorption in the visible has led to an interpretation of the vibronic structure displayed by the lowest energy electronic transition. The consideration of this analysis, with the parallel one already reported for the monomeric TCNQ radical anion,[24] provides a useful hint on the excitation process in semiquinoid structures. It appears that for the radical anion structure, modified from the quinoid one of the neutral molecule toward the benzenoid one, only three totally symmetric vibrational modes play a dominant role in the vibronic coupling, namely those related with the C=C ring stretch, the external quinoid double bond stretch, and a skeletal deformation, respectively.

In conclusion, the collected experimental data and the findings reported here on representative members of the DCNQI family, and especially on the DMDCNQI radical anion, open the way to a detailed analysis of the optical spectra of various types of structures containing fully or partially ionized *N,N'*-dicyanoquinonediimine molecular units. A first application has been recently reported in a preliminary communication on the infrared spectrum of Ag(DMDCNQI)$_2$ and its temperature dependence. The ability of infrared spectra to selectively probe the temperature evolution of a $4\mathbf{k}_F$ modulation (dimerization) and a $2\mathbf{k}_F$ modulation (tetramerization) of the structure of quarter-filled organic conductors has been demonstrated for the first time for the abovementioned silver compound.[47]

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