

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U.S. Patent Office. © Copyright, 1976, by the American Chemical Society

VOLUME 98, NUMBER 14

JULY 7, 1976

## Resonance Raman Spectroelectrochemistry. 2. Scattering Spectroscopy Accompanying Excitation of the Lowest ${}^2B_{1u}$ Excited State of the Tetracyanoquinodimethane Anion Radical

David L. Jeanmaire and Richard P. Van Duyne\*<sup>1</sup>

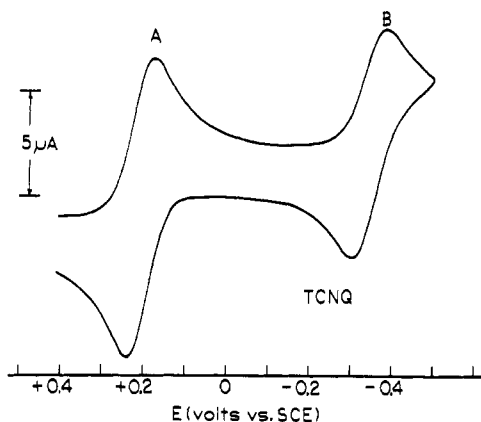
*Contribution from the Department of Chemistry, Northwestern University,  
Evanston, Illinois 60201. Received September 8, 1975*

**Abstract:** Resonance Raman scattering spectra have been obtained for the electrogenerated monoanion radical of tetracyanoquinodimethane (TCNQ) upon excitation of its lowest  ${}^2B_{1u}$  excited state with  $Ar^+$ ,  $Kr^+$ , and  $Ar^+$  pumped CW dye lasers. In addition we report the preresonance Raman spectrum of neutral TCNQ excited with the 4579 Å  $Ar^+$  laser line. The utility of resonance Raman spectroscopy as a molecularly specific monitor for electrochemical processes is discussed along with an interpretation of the measured frequency shifts between TCNQ and  $TCNQ^{\cdot-}$  based on the  $\pi$  bond order changes determined from SCF-LCAO-MO calculations.

In aprotic polar solvents (such as acetonitrile or dimethyl formamide), the primary one-electron oxidation or reduction products of molecules with conjugated  $\pi$ -electron systems are radical ions (cations or anions, respectively). The comprehensive study of radical ions involves the development of methods for generation, identification, elucidation of decay reaction pathways, and determination of electronic structure. Radical ions can be generated in chemically, electrochemically, photochemically, and radiolytically initiated redox reactions. Identification, elucidation of decay reactions, and determination of electronic structure are most typically performed using the techniques of electronic absorption spectroscopy and electron spin resonance (ESR) spectroscopy, since radical ions have open-shell ground states resulting in intense absorption of light (near ultraviolet, visible, and near infrared) as well as paramagnetism. The determination of spin densities in the ground electronic state of radical ions by ESR and the concomitant testing of molecular orbital theory has been well documented.<sup>2</sup> Infrared spectroscopy has been successfully applied to the study of radical ions in solid state environments<sup>3-12</sup> and to a somewhat more limited extent in solution.<sup>12-19</sup> Recently it has been recognized that radical ions can be studied by resonance Raman (RR) spectroscopy because of their intense electronic absorption spectra and the fact that radical ions do not strongly luminesce following optical excitation presumably due to the dominance of fast nonradiative processes such as internal conversion in the doublet manifold and doublet quartet intersystems crossing. To date RR spectra have been reported for the chemically prepared radical anions of anthracene,<sup>9,20</sup> tetracyanoethylene (TCNE),<sup>10</sup> biphenyl,<sup>21</sup>

*cis*- and *trans*-stilbene,<sup>22</sup> and tetracyanoquinodimethane (TCNQ),<sup>12,23,24</sup> as well as the radical cation of *p*-phenylenediamine.<sup>25</sup> In a recent paper we reported the successful interfacing of electrochemical radical ion generation with resonance Raman spectroscopic observation to form the hybrid technique of resonance Raman spectroelectrochemistry (RRSE).<sup>26</sup> Using  $TCNE^{\cdot-}$  as a test system we demonstrated that spectra with high S/N ratios could be obtained either in bulk solution via controlled potential electrolysis or in the electrochemical diffusion layer by cyclic potential step electrolysis from solutions initially ca.  $10^{-3}$  M in TCNE. The vibrational frequencies of  $TCNE^{\cdot-}$  obtained by RRSE were more amenable to comparison with those of neutral TCNE than the  $TCNE^{\cdot-}$  vibrational data previously available<sup>10</sup> due to the absence of solid state effects. It is anticipated that RRSE will greatly facilitate both the study of electrode reaction mechanisms and radical ion electronic structure in a manner analogous to that resulting from the coupling of electrochemical generation with ESR detection.

In this paper we will report on the resonance Raman scattering spectrum of electrochemically generated  $TCNQ^{\cdot-}$  obtained by excitation of its lowest  ${}^2B_{1u}$  excited state ( ${}^2B_{1u}^{(1)}$ ). An assignment of the observed vibrational bands of  $TCNQ^{\cdot-}$  in acetonitrile solution will be given based on the normal coordinate analysis and polarized single crystal spectra of TCNQ and  $TCNQ-d_4$  reported by Girlando and Pecile.<sup>27</sup> In addition to the fact that a normal coordinate analysis has been carried out on TCNQ, which greatly simplified our interpretational task, the TCNQ radical anion was selected as a particularly suitable candidate for RRSE investigation for a series



**Figure 1.** First-scan cyclic voltammogram of 0.66 mM TCNQ in acetonitrile containing 0.10 M TBAP at a platinum disk microelectrode. The scan rate =  $0.100 \text{ V s}^{-1}$ .

of practical as well as fundamental reasons. From the practical standpoint TCNQ $^{\cdot-}$  was chosen because it is chemically stable (i.e., not extremely  $\text{O}_2$  sensitive), the polarographic data in the literature suggested nearly ideal behavior<sup>28–30</sup> (i.e., fast heterogeneous electron transfer rate and no follow-up chemical reactions), and the red absorption band in the TCNQ $^{\cdot-}$  optical spectrum is well situated for excitation by our “jet-stream”  $\text{Ar}^+$  pumped CW dye laser. From a more fundamental point of view, TCNQ $^{\cdot-}$  is an attractive RRSE system since there is intense interest at the present time in the one-dimensional conductivity properties of TCNQ containing radical ion salts.<sup>31</sup> The most interesting of these systems is TCNQ-TTF (tetrathiofulvene) which may exhibit a Peierls metal-insulator transition and Fröhlich-type superconductivity. This possibility has touched off a flurry of calculational activity on the electronic structure and properties of TCNQ, TCNQ $^{\cdot-}$ , and TCNQ $^{2-}$ .<sup>33–36</sup> The  $\pi$  bond order changes for the TCNQ  $\rightarrow$  TCNQ $^{\cdot-}$  transformation that result from these calculations will be useful in interpreting the corresponding frequency changes in the totally symmetric normal modes of TCNQ and TCNQ $^{\cdot-}$  that result from the RRSE experiments. In turn the frequency changes which accompany redox processes, as measured by the RRSE technique, will be useful in providing experimental data in addition to optical and ESR spectroscopy for evaluating the validity of various SCF-LCAO-MO calculations.<sup>10</sup> Another fundamental reason for studying the TCNQ/TCNQ $^{\cdot-}$  system is the fact that it can serve as a conceptual model for investigating the role of intramolecular vibrational energy dissipation processes in electron transfer reactions.<sup>37–39</sup>

## Experimental Section

The TCNQ used in this work was either purchased from Aldrich Chemical Co. or prepared by Method A of Acker and Hertler.<sup>29</sup> All TCNQ samples were purified by at least two high vacuum ( $10^{-5}$  Torr) sublimations at  $140^\circ\text{C}$  followed by recrystallization from acetonitrile. TCNQ purified in this manner gave an acceptably low fluorescence background for Raman work. Both purchased and prepared TCNQ gave identical results in all experiments. The TCNQ anion radical was prepared by exhaustive electroreduction at  $+0.10 \text{ V}$  vs. SCE in thoroughly deoxygenated ( $\text{N}_2$  bubbling technique) acetonitrile solutions containing  $1 \times 10^{-4}$  to  $3 \times 10^{-3} \text{ M}$  TCNQ and  $0.10 \text{ M}$  tetrabutylammonium perchlorate (TBAP). Resultant TCNQ $^{\cdot-}$  concentrations were determined coulometrically. The acetonitrile and TBAP purification procedures have been described along with the apparatus and techniques for conducting cyclic voltammetry and controlled potential reversal coulometry experiments.<sup>26</sup>

All resonance Raman spectroelectrochemistry experiments were carried out in the controlled potential coulometry electrogeneration mode. The RRSE coulometry cell and backscattering sampling optics have been described elsewhere.<sup>26</sup> Resonance Raman spectra of elec-

trogenated TCNQ $^{\cdot-}$  were collected using either a 0.85 m Spex Model 1401 or a 0.75 m Spex Model 1400-II double monochromator equipped with cooled RCA C31034 photomultiplier tubes and standard low-level threshold photon counting detection. Raman spectra were recorded on magnetic tape, processed on a CDC-6400 computer, and plotted on a Calcomp plotter. The excitation sources used in this work included Spectra Physics Model 164  $\text{Ar}^+$  and  $\text{Kr}^+$  lasers, a Coherent Radiation Model CR-8  $\text{Ar}^+$  laser, and a Coherent Radiation Model 490 jet-stream dye laser pumped all-lines by the CR-8. Due to the large amount of moderately well collimated superradiant background fluorescence emission from the dye laser, it was found necessary to direct the dye laser output beam through a premonochromator (quartz prism, Littrow mount) in order to obtain high-quality Raman spectra when operating in the backscattering geometry. All of the ion lasers were operated in the light regulated mode for intensity stability. Laser power measurements were made with a Coherent Radiation Model 210 power meter. The spectrometers were wavelength calibrated using the emission lines from a neon lamp. Reported frequencies are accurate to  $\pm 2 \text{ cm}^{-1}$ . Depolarization ratios were measured by passing the scattered radiation through a polaroid analyzer followed by a scrambler in front of the spectrometer entrance slit.

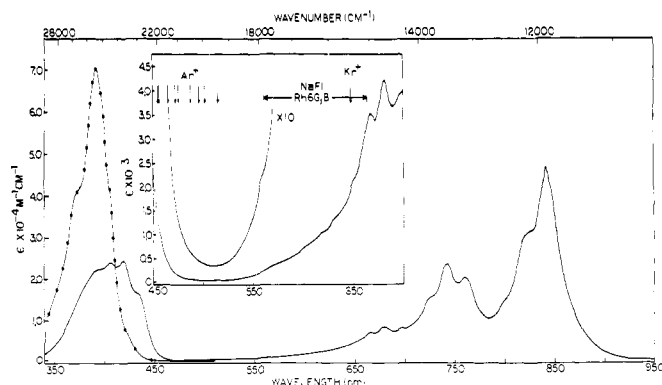
Electronic absorption spectra were determined on a Cary Model 14 spectrophotometer fitted with a Dumont Model 7664 photomultiplier tube for extended red response.

## Results and Discussion

**Electrochemistry and Electronic Absorption Spectroscopy of TCNQ $^{\cdot-}$ .** The cyclic voltammetry of TCNQ in acetonitrile solution is shown in Figure 1. Scanning in the cathodic direction, peaks due to the generation of TCNQ $^{\cdot-}$  (peak A,  $E_{pc} = +0.172 \text{ V}$  vs. SCE at a scan rate,  $V$ , of  $100 \text{ mV s}^{-1}$ ) and TCNQ $^{2-}$  (peak B,  $E_{pc} = -0.362 \text{ V}$  vs. SCE at  $100 \text{ mV s}^{-1}$ ) are observed. For both reductions  $(i_{pc}V^{-1/2}C^0)^{-1} = \text{constant}$  and  $i_{pa}/i_{pc} = 1.00 \pm 0.03$  as a function of  $V$  and bulk concentration,  $C^0$ , indicating that the anion radical and dianion of TCNQ are chemically stable on the cyclic voltammetric time scale. In addition both reductions are electrochemically reversible (fast heterogeneous rate constant) since  $\Delta E_p = 0.060 \text{ V}$  for  $V \leq 100 \text{ mV s}^{-1}$ . Larger  $\Delta E_p$  are observed at faster scan rates due to uncompensated  $iR$  drop.

The long-term stability of TCNQ $^{\cdot-}$  was evaluated by controlled potential reversal coulometry in bulk solution. At an applied potential of  $+0.10 \text{ V}$  vs. SCE, where only TCNQ $^{\cdot-}$  is generated, the number of Faradays consumed per mole of neutral substrate,  $n_{app}$ , was  $1.00 \pm 0.01$  for the forward electrolysis. On stepping the applied potential back to  $+0.50 \text{ V}$  vs. SCE, where TCNQ is not electroactive and TCNQ $^{\cdot-}$  is converted back to starting material, the reversal coulometry ratio,  $Q_b/Q_f$ , was found to be 1.00 within experimental error. Both  $n_{app}$  and  $Q_b/Q_f$  were independent of  $C^0$  and the forward generation period from 15 min to 1.5 h. These results indicate that electrogenerated TCNQ $^{\cdot-}$  is completely stable for at least 3 h (forward plus reverse generation periods). It should be pointed out that TCNQ $^{\cdot-}$  is vastly more stable (less  $\text{O}_2$  sensitive) than is TCNE $^{\cdot-}$ .<sup>26</sup> None of the RRSE experiments reported here exceed 3 h in duration so that it can be confidently assumed that the only species observed by resonance Raman spectroscopy that is generated at  $+0.10 \text{ V}$  vs. SCE is TCNQ $^{\cdot-}$  associated weakly with a tetrabutylammonium counterion.

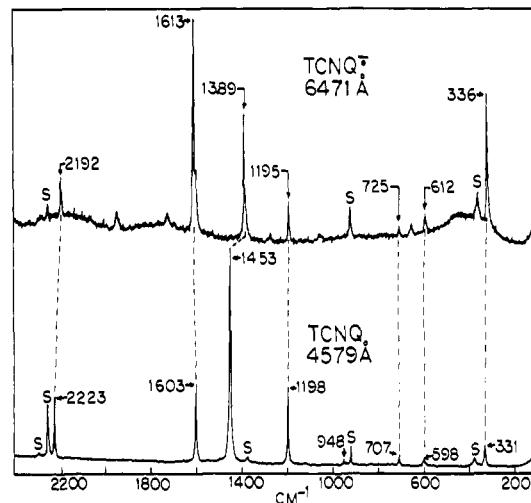
The electronic absorption spectrum of electrogenerated TCNQ $^{\cdot-}$  is shown in Figure 2 along with the absorption spectrum of the neutral. These spectra agree well with those previously reported.<sup>40,41</sup> The inset in Figure 2 presents the TCNQ $^{\cdot-}$  absorption spectrum with an expanded extinction coefficient scale in the region of overlap with the fixed frequency ion laser lines ( $\text{Ar}^+$  and  $\text{Kr}^+$ ) and the dye laser tuning range. With three dye solutions, sodium fluorescein (NaFl), rhodamine 6G (R6G), and rhodamine B (RB), the range of dye laser excitation wavelengths with useful power output ( $\geq 50$



**Figure 2.** Electronic absorption spectra of TCNQ and TCNQ $\cdot^-$  from 350–950 nm. (●) TCNQ in acetonitrile. (—) TCNQ $\cdot^-$  electrogenerated at +0.00 vs. SCE in acetonitrile containing 0.10 M TBAP. [TCNQ $\cdot^-$ ] =  $1.40 \times 10^{-4}$  M; cell pathlength = 0.10 cm. The inset figures show the TCNQ $\cdot^-$  absorption spectrum from 450 to 700 nm with two different expanded extinction coefficient scales in the region of spectral overlap with the fixed frequency ion laser lines (Ar $^+$  and Kr $^+$ ) and the CW dye laser tuning range for sodium fluorescein (NaFl), rhodamine 6G (R6G), and rhodamine B (RB) dye solutions.

mW) is ca. 5450 to 6600 Å. The TCNQ $\cdot^-$  absorption spectrum in the range 350–900 nm consists of two main bands. In earlier work<sup>42</sup> it was suggested that the absorption maxima located at 841 (1.47 eV) and 760 nm (1.63 eV) in the red-band system (550–900 nm) might represent separate electronic transitions to the first two doublet excited states of TCNQ $\cdot^-$  even though Pople type SCF-LCAO-MO calculations with limited configuration interaction (CI) located only one doublet excited state near 1.48 eV. Subsequent SCF-MO calculations<sup>34</sup> which studied the effects of: (1) ground state geometry variation; (2) the Pariser-Parr (PP) vs. the Mataga-Nishimoto (MN) methods for calculating the two-center coulomb integrals; and (3) extended CI on the TCNQ $\cdot^-$  energy levels also fail to locate a second low-energy doublet excited state. Only one level, excited  ${}^2B_{1u}^{(1)}$ , has been found in the 1.3 to 1.8 eV range at 1.57 (PP) or 1.39 eV (MN). Consequently the red-band system may be assigned as the  ${}^2B_{3g} \rightarrow {}^2B_{1u}^{(1)}$  transition (long-axis polarized) with the fine structure representing partially resolved vibronic transitions. The blue-band system in TCNQ $\cdot^-$ , which extends from ca. 350 to 480 nm, is then assigned to contributions from both the  ${}^2B_{3g} \rightarrow {}^2B_{1u}^{(2)}$  (long-axis polarized) and the  ${}^2B_{3g} \rightarrow {}^2A_u$  (short-axis polarized) transitions. Partially resolved vibronic transitions are also evident in this band system. This assignment is based on the SCF-MO calculations of Bieber et al. who locate the  ${}^2B_{1u}^{(2)}$  state at 2.92 (PP) or 2.63 eV (MN) and the  ${}^2A_u$  state at 3.34 (PP) or 2.99 eV (MN). The symmetry designations of the TCNQ $\cdot^-$  ( $D_{2h}$ ) ground and excited states are based on a Cartesian coordinate system with the Y axis parallel to the long  $C_2$  axis and the X axis parallel to the short  $C_2$  axis.

**Resonance Raman Scattering Spectroscopy of TCNQ $\cdot^-$  ( ${}^2B_{3g} \rightarrow {}^2B_{1u}^{(1)}$  Excitation) and TCNQ.** The resonance Raman scattering spectrum of electrogenerated TCNQ $\cdot^-$  (2.24 mM) obtained by excitation into the region of its  ${}^2B_{3g} \rightarrow {}^2B_{1u}^{(1)}$  transition with the 6471 Å Kr $^+$  laser line is presented in Figure 3. Also shown is the corresponding preresonance Raman spectrum of 10.9 mM TCNQ neutral excited near its transition to the  ${}^1B_{2u}$  excited state with the 4579-Å line of the Ar $^+$  laser. The depolarization ratios were measured for all strong and medium intensity bands in these spectra and were found to be  $1/3$  showing that only one diagonal element of the Raman scattering tensor is resonance enhanced (i.e., these bands are assignable to totally symmetric normal modes<sup>43</sup>). Assuming that the normal modes of the TCNQ anion radical are approximately the same as those for the neutral, one can make



**Figure 3.** Resonance Raman spectra of TCNQ and electrogenerated TCNQ $\cdot^-$ . [TCNQ] = 10.9 mM, laser power = 20 mW, bandpass =  $1.2 \text{ cm}^{-1}$ ; [TCNQ $\cdot^-$ ] = 2.24 mM, laser power = 74 mW, bandpass =  $2.2 \text{ cm}^{-1}$ . TCNQ $\cdot^-$  was electrogenerated by controlled potential coulometry at -0.10 V vs. SCE in 0.1 M TBAP/CH $_3$ CN. All spectra were scanned at  $50 \text{ cm}^{-1} \text{ min}^{-1}$  using a 1.00 s counting interval. Plasma lines were removed at 4579 Å with an interference filter and at 6471 Å with a Claassen filter. S denotes a normal Raman band of the solvent (acetonitrile). No normal Raman bands are observed for the supporting electrolyte (TBAP).

assignments for all of the observed Raman bands in Figure 3 by analogy with those made by Girlando and Pecile<sup>27</sup> and Takenaka.<sup>44</sup> These assignments for the observed resonance enhanced totally symmetric fundamentals are summarized in Table I. Overtones and combination bands were also observed in the TCNQ $\cdot^-$  spectrum and are listed along with probable assignments in Table II. No overtones or combination bands could be observed in the TCNQ neutral spectrum in accord with its designation as preresonance Raman.<sup>45</sup> Discussion of these resonance Raman scattering spectra will focus on three issues: (1) the utility of RRS as a molecularly specific monitor of an electrochemical process; (2) a comparison of the spectral features of electrogenerated TCNQ $\cdot^-$  weakly associated with a tetrabutylammonium cation in solution vs. chemically prepared TCNQ $\cdot^-$  strongly associated with alkali metal cations in the solid state; and (3) a qualitative interpretation of the vibrational frequency shifts which accompany the electron transfer reaction  $\text{TCNQ} + e^- \rightarrow \text{TCNQ}\cdot^-$  in terms of  $\pi$  bond order changes.

The TCNQ system, studied here by RRSE in the controlled potential electrolysis mode, serves well to illustrate two important features of this hybrid technique for application to electrochemical problems:

(i) High quality ( $S/N \geq 10$ ) spectra with sharp, distinguishable features can readily be observed by RRSE for both the electroactive substrate (TCNQ) and the electrode product (TCNQ $\cdot^-$ ). Useful TCNQ spectra can only be obtained with the 4545 and 4579 Å Ar $^+$  laser lines. All strong and medium intensity TCNQ fundamentals are observable under 4579 Å excitation at concentration levels down to ca. 1 mM. In the case of TCNQ $\cdot^-$  all the fundamentals listed in Table I are observable with excitation in the 6000 to 6600 Å range for 0.9 mM  $\leq [\text{TCNQ}\cdot^-] \leq 3.0 \text{ mM}$  and  $700 \text{ M}^{-1} \text{ cm}^{-1} \leq \epsilon_{\text{TCNQ}\cdot^-} \leq 3500 \text{ M}^{-1} \text{ cm}^{-1}$ .

(ii) Minimal solvent interference is encountered even though TCNQ and TCNQ $\cdot^-$  are present at low concentrations (a few mM) and possess a functional group in common with the solvent (19 M CH $_3$ CN). This is due primarily to the narrow line widths of Raman bands as well as the fact that normal Raman photons scattered from the solvent are absorbed by

**Table I.** Totally Symmetric Raman Fundamentals of TCNQ and TCNQ<sup>•-</sup> [ $\rho_1 = 1/6$ ]

Assign $\nu_i$	PED, % <sup>a</sup>	TCNQ (4579 Å), cm <sup>-1</sup>	TCNQ <sup>•-</sup> (6471 Å), cm <sup>-1</sup>	$\Delta\nu_i$ (TCNQ - TCNQ <sup>•-</sup> ), cm <sup>-1</sup>	$\Sigma_i(\text{PED})_{K_i}$ , $\Delta P_i^d$	$\Sigma_i(\text{PED})_{K_i}$ , $\Delta P_i^e$
$\nu_1$	$K_6(99)$	3048 <sup>b</sup> vw				
$\nu_2$	$K_5(87)$	2223 m	2192 m	+31	+0.044	+0.026
$\nu_3$	$K_1(46), K_2(22),$ $K_3(25), H_3(20)$	1603 m	1613 s	-10	+0.053	+0.060
$\nu_4$	$K_1(30), K_3(59)$	1453 s	1389 s	+64	+0.145	+0.170
$\nu_5$	$H_3(81)$	1192 m	1195 m	-3	0	0
$\nu_6$	$K_2(45), K_4(21)$	948 vw	976 <sup>c</sup> m	-28	-0.077	-0.077
$\nu_7$	$K_2(32), K_4(17)$	707 vw	724 vw	-17	-0.057	-0.056
$\nu_8$	$K_4(23), H_6(43),$ $H_7(18)$	598 w	612 w	-14	-0.021	-0.015
$\nu_9$	$H_1(18), H_6(18)$	331 w	336 s	-5	0	0
$\nu_{10}$	$H_6(28), H_7(49)$	140 <sup>b</sup> vw				

<sup>a</sup> Potential energy distribution (PED) obtained from normal coordinate calculations in ref 27. <sup>b</sup> Solid, 5145-Å excitation. <sup>c</sup>  $3 \times 10^{-3}$  M solution; 5145-Å excitation. <sup>d</sup>  $\Delta P_i = P_i(\text{TCNQ}^0) - P_i(\text{TCNQ}^{\bullet-})$ ; ref 50. <sup>e</sup>  $\Delta P_i = P_i(\text{TCNQ}^0) - P_i(\text{TCNQ}^{\bullet-})$ ; ref 51.

**Table II.** Overtone and Combination Bands of TCNQ<sup>•-</sup>

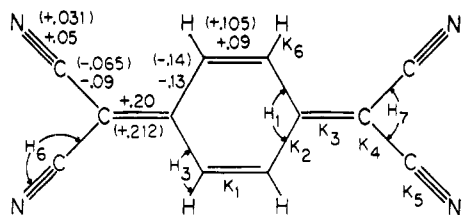
Frequency shift, cm <sup>-1</sup>	Assignment
670	$2 \times 336 = 672; 2\nu_9$
1057	$724 + 336 = 1060; \nu_7 + \nu_9$
1725	$1389 + 336 = 1725; \nu_4 + \nu_9$
1948	$1613 + 336 = 1949; \nu_3 + \nu_9$
2521	$2192 + 336 = 2528; \nu_2 + \nu_9$
2584	$1195 + 1389 = 2584; \nu_5 + \nu_4$
2776	$2 \times 1389 = 2776; 2\nu_4$
3003	$1613 + 1389 = 3002; \nu_3 + \nu_4$
3224	$2 \times 1613 = 3226; 2\nu_3$

TCNQ<sup>•-</sup>. Complete resolution of the C≡N stretch in TCNQ<sup>•-</sup> from that in CH<sub>3</sub>CN, as seen in Figure 3, would not be possible in infrared spectroelectrochemistry.<sup>13-15,19</sup>

Pecile and co-workers<sup>23</sup> prepared the Rb(1:1) salt of TCNQ and have reported its solid state (powder) Raman spectrum excited at 5145 Å. In addition Chi and Nixon<sup>24</sup> have reported powder Raman spectra of RbTCNQ and KTCNQ excited at 6471, 5682, 5145, 4880, and 4579 Å. Although there is overall agreement between these solid state results and those obtained in our solution work, there are also some significant differences. In the solution spectra excited in the 6000–6600-Å range, of which the 6471-Å spectrum is representative, only seven of ten possible totally symmetric fundamentals are observed.  $\nu_6$  and  $\nu_{10}$  are apparently too weakly resonance enhanced to be observable under these conditions (i.e., these normal modes do not undergo large changes in their equilibrium nuclear configurations in the  $^2B_{1u}^{(1)}$  state) while  $\nu_1$ , the C–H stretching mode, is probably masked by either solvent modes or the 3003-cm<sup>-1</sup> band we have assigned as the  $\nu_3 + \nu_4$  combination. In contrast the solid RbTCNQ spectra show a medium intensity  $\nu_6$  band at 980 cm<sup>-1</sup><sup>23,24</sup> as well as a low-frequency mode which may be  $\nu_{10}$ .<sup>23</sup> No  $\nu_1$  is, however, reported.<sup>23,24</sup> We have found that  $\nu_6$  can be observed in a 3.0 mM solution of electrogenerated TCNQ<sup>•-</sup> at 976 cm<sup>-1</sup> if it is excited with 5145-Å light. We tentatively suggest that  $\nu_6$  is preresonance enhanced at this exciting wavelength through the  $^2B_{1u}^{(2)}$  excited state and that the equilibrium nuclear configuration for the  $\nu_6$  mode is substantially displaced in this excited state relative to that in the ground state. Further discussion on this observation is reserved for another paper.<sup>46</sup> In addition to the presence of  $\nu_6$  and possibly  $\nu_{10}$ , the solid state spectra show nontotally symmetric modes and apparent splitting of certain fundamentals.<sup>23,24</sup> These solid state effects complicate the measurement of the frequency shifts which accompany formation of TCNQ<sup>•-</sup>. Such complications are absent in RRSE

spectra although only the totally symmetric mode frequency shifts can be measured. One substantial advantage of using electrochemical methods to generate TCNQ<sup>•-</sup> in solution as compared to the chemical redox methods used by Pecile<sup>23</sup> and Nixon<sup>24</sup> to prepare solid state MTCNQ salts is that we can rigorously attribute our Raman spectra to a minimally perturbed TCNQ monoanion radical. It is not yet clear that in the solid state spectra of RbTCNQ and KTCNQ all of the observed bands are associated with TCNQ<sup>•-</sup>. In fact the solid state Raman bands reported by Chi and Nixon<sup>24</sup> at 2214, 1622, 1330, 1280, 1181, 1005, 962, 725, and 356 cm<sup>-1</sup> (Table I in ref 24) for room-temperature RbTCNQ excited at 5145, 4880, or 4579 Å are remarkably similar to the Raman bands at 2214, 1638, 1327, 1281, 1174, 1000, 963, 735, and 349 cm<sup>-1</sup> which we have recently reported for the cyanocarbonyl containing carbanion  $\alpha,\alpha$ -dicyano-*p*-toluoyl cyanide (DCTC<sup>-</sup>) in CH<sub>3</sub>CN solution.<sup>47</sup> DCTC<sup>-</sup> is formed by the reaction of O<sub>2</sub> with TCNQ<sup>2-</sup>. Furthermore these bands which have been assigned by Nixon to nontotally symmetric modes of TCNQ<sup>•-</sup> exhibit identical dependence on laser excitation wavelength to those of DCTC<sup>-</sup>. Recent results on the solid state RR spectra of RbTCNQ, CsTCNQ, and KTCNQ in our laboratory<sup>48</sup> show that DCTC<sup>-</sup> can always be observed in MTCNQ samples prepared according to the alkali metal iodide reduction procedure of Melby<sup>49</sup> unless contact between the MTCNQ and O<sub>2</sub> is rigorously prevented at all times. We conclude that Nixon's assignment of these bands in RbTCNQ and KTCNQ and the conclusions concerning the nature of the vibronic coupling among the upper electronic states of TCNQ<sup>•-</sup> which are based on this assignment are incorrect. Further discussion on this topic including the methods for preparation of MTCNQ samples and the methods for obtaining their RR spectra free from DCTC<sup>-</sup> interferences is deferred to a forthcoming paper.<sup>48</sup>

The vibrational frequency shifts which accompany the transformation of TCNQ to its radical anion have been listed in Table I. These shifts are an important type of chemical information which can be directly provided by RRSE experiments. This is especially true for the TCNQ system where resonance enhanced spectra can be obtained for both the oxidized and reduced forms of the TCNQ couple. This was not the case in the TCNE system studied previously (a uv laser was not available to us to excite into the region of the first singlet-singlet transition of TCNE neutral) where the comparison had to be made between the resonance Raman spectrum of TCNE<sup>•-</sup> and the normal Raman spectrum of the neutral. A qualitative understanding of the frequency shifts,  $\Delta\nu_i$ , can be obtained from an examination of the  $\pi$  bond order changes from SCF-LCAO-MO calculations on TCNQ and TCNQ<sup>•-</sup>.



**Figure 4.**  $\pi$  bond order changes,  $\Delta P_i = P_i(\text{TCNQ}) - P_i(\text{TCNQ}^-)$ , and internal symmetry coordinate definitions. The  $\pi$  bond order changes given in parentheses refer to those calculated by a CNDO/S procedure with configuration interaction,<sup>51</sup> whereas, those not in parentheses are obtained from ref 50.

The bond order changes computed by Jonkman and Kommandeur<sup>50</sup> are shown in Figure 4 along with the internal symmetry coordinate designations used by Girlando and Pecile to describe the potential energy distribution (PED) of the totally symmetric normal modes of TCNQ. The numbers in parentheses in Figure 4 are the corresponding bond order changes for  $\text{TCNQ} + e^- \rightarrow \text{TCNQ}^-$  calculated using a CNDO/S scheme with configuration interaction.<sup>51</sup> Approximately 70 singly excited configurations were incorporated into this calculation. The geometries for TCNQ and  $\text{TCNQ}^-$  were those determined by Trueblood<sup>52</sup> and Fritchie,<sup>53</sup> respectively. Consider the  $\nu_2$   $\text{C}\equiv\text{N}$  stretching vibration which shows a  $+31\text{-cm}^{-1}$  shift on reduction. The corresponding bond order change for  $\text{C}\equiv\text{N}$  is  $+0.044$  ( $+0.026$ ) which accounts for the plus direction of the shift since  $\nu_2$  is dominated by the  $\text{C}\equiv\text{N}$  internal coordinate ( $K_5$ ). For normal modes whose PED contains contributions from several internal coordinates, it is not valid to compare the frequency shift with just one bond order change. A more reasonable approach is to compare the frequency shift with a weighted bond order change in which the weighting coefficient of a bond stretching coordinate is its fractional contribution to the PED,  $(\text{PED})_{K_i}$ , and the weighting coefficient of an angle bending coordinate is arbitrarily set to zero. This follows from the observation that nearly pure bending modes show small frequency shifts on radical anion formation (viz.,  $\nu_5$  which is almost entirely C–H bending;  $\Delta\nu_5 = -3\text{ cm}^{-1}$ ). The weighted bond order changes calculated in this manner are listed in Table I under the heading  $\Sigma_i (\text{PED})_{K_i} \Delta P_i$ . With the prominent exception of  $\nu_3$ , this procedure adequately rationalizes the direction of the frequency shift and correctly orders the relative shift magnitudes for both positively shifted modes (viz.,  $\Delta\nu_4 > \Delta\nu_2$ ) and negatively shifted modes (viz.,  $\Delta\nu_6 > \Delta\nu_7 > \Delta\nu_8$ ). The actual relative magnitudes of the shifts are not in good agreement with the relative values of the weighted bond order change. For example,  $\Delta\nu_4/\Delta\nu_2 \approx 2$ , whereas the corresponding weighted bond order ratio is ca. 3.3 (6.5). Neither the direction nor the magnitude of  $\Delta\nu_3$  is accounted for by comparison with the appropriately weighted bond order change. Qualitatively similar results are obtained using either set of  $\pi$  bond order changes. The reason for this discrepancy is not clear although it might suggest that either the PED for this mode changes dramatically from TCNQ to  $\text{TCNQ}^-$  or that the force constant for  $\nu_3$  is not a strong function of the detailed composition of the PED thereby making it difficult to compute a unique PED from the normal coordinate analysis.

**Acknowledgment.** The authors wish to thank the National

Science Foundation (Grant No. MPS-7412573) for financial support of this work. We are also grateful to Miss Mary R. Suchanski who obtained the electronic absorption spectra shown in Figure 2 and carried out many of the electrochemical experiments. In addition we want to thank Professor Mark A. Ratner for access to and assistance in the interpretation of Mr. Karsten Krogh-Jespersen's CNDO/S calculations on TCNQ and  $\text{TCNQ}^-$  prior to their publication. One of us (D.L.J.) acknowledges a fellowship from the ACS Analytical Division sponsored by The Perkin-Elmer Corp.

## References and Notes

- (1) Alfred P. Sloan Foundation Fellow, 1974–1976
- (2) E. T. Kaiser and L. Kevans, Ed., "Radical Ions", Wiley, New York, N.Y., 1968.
- (3) Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964).
- (4) Y. Matsunaga, *J. Chem. Phys.*, **42**, 1982 (1965).
- (5) M. G. Kaplunov, T. P. Panova, E. B. Yagubskii, and Y. G. Borod'ko, *Zh. Strukt. Khim.*, **13**, 440 (1972).
- (6) M. G. Kaplunov, T. P. Panova, and Y. G. Borod'ko, *Phys. Status Solidi*, **13**, K67 (1972).
- (7) J. Stanley, D. Smith, B. Latimer, and J. P. Devlin, *J. Phys. Chem.*, **70**, 2011 (1966).
- (8) J. C. Moore, D. Smith, Y. Youhne, and J. P. Devlin, *J. Phys. Chem.*, **75**, 325 (1971).
- (9) P. C. Li, J. P. Devlin, and H. A. Pohl, *J. Phys. Chem.*, **76**, 1026 (1972).
- (10) J. J. Hinkel and J. P. Devlin, *J. Chem. Phys.*, **58**, 4750 (1973).
- (11) G. R. Anderson and J. P. Devlin, *J. Phys. Chem.*, **79**, 1100 (1975).
- (12) R. Bozio, A. Girlando, and C. Pecile, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1237 (1975).
- (13) D. Laser and M. Ariel, *J. Electroanal. Chem. Interfacial Electrochem.*, **41**, 381 (1973).
- (14) D. R. Tallant and D. Evans, *Anal. Chem.*, **41**, 835 (1969).
- (15) B. R. Clark and D. H. Evans, unpublished results.
- (16) D. H. Eargle, Jr., and E. W. Cox, *Chem. Soc. Spec. Publ.*, **No. 22**, 116–124 (1967).
- (17) D. H. Eargle, Jr., *J. Org. Chem.*, **39**, 1295 (1970).
- (18) I. N. Juchnovski and I. G. Biner, *Chem. Phys. Lett.*, **12**, 40 (1971).
- (19) K. Ezumi, H. Miyazaki, and T. Kubota, *J. Phys. Chem.*, **74**, 2397 (1970).
- (20) C. Takahashi and S. Maeda, *Chem. Phys. Lett.*, **22**, 364 (1973).
- (21) C. Takahashi and S. Maeda, *Chem. Phys. Lett.*, **24**, 584 (1974).
- (22) C. Takahashi and S. Maeda, *Chem. Phys. Lett.*, **28**, 22 (1974).
- (23) A. Girlando, R. Bozio, and C. Pecile, *Chem. Phys. Lett.*, **25**, 409 (1974).
- (24) C. K. Chi and E. R. Nixon, *Spectrochim. Acta, Part A*, **31**, 1739 (1975).
- (25) E. Mayer, R. B. Girling, and R. E. Hester, *J. Chem. Soc., Chem. Commun.*, 192 (1973).
- (26) D. L. Jeanmaire, M. R. Suchanski, and R. P. Van Duyne, *J. Am. Chem. Soc.*, **97**, 1699 (1975).
- (27) A. Girlando and C. Pecile, *Spectrochim. Acta, Part A*, **29**, 1859 (1973).
- (28) M. E. Peover, *Trans. Faraday Soc.*, **58**, 2370 (1962); **60**, 417 (1964).
- (29) D. Acker and W. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).
- (30) W. J. Middleton, *J. Org. Chem.*, **30**, 1402 (1965).
- (31) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).
- (32) M. Ratner, J. R. Sabin, and E. E. Ball, *Mol. Phys.*, **26**, 1177 (1973).
- (33) H. T. Jonkman, G. A. Van der Velde, and W. C. Nieupoort, *Chem. Phys. Lett.*, **25**, 62 (1974).
- (34) A. Bieber and J. J. Andre, *Chem. Phys.*, **5**, 166 (1974), and references therein.
- (35) J. Ladik, A. Karplen, G. Stollhoff, and P. Fulde, *Chem. Phys.*, **7**, 267 (1975).
- (36) A. Karplen, J. Ladik, G. Stollhoff, and P. Fulde, *Chem. Phys. Lett.*, **31**, 291 (1975).
- (37) S. Efrima and M. Bixon, *Chem. Phys. Lett.*, **25**, 34 (1974).
- (38) R. P. Van Duyne and S. F. Fischer, *Chem. Phys.*, **5**, 183 (1974).
- (39) J. Ulstrup and J. Jortner, *J. Chem. Phys.*, **63**, 4358 (1975).
- (40) R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).
- (41) S. Hiroama, H. Kuroda, and H. Akamatsu, *Bull. Chem. Soc. Jpn.*, **44**, 9 (1971).
- (42) D. A. Lowitz, *J. Chem. Phys.*, **46**, 4698 (1967).
- (43) O. S. Mortensen, *Chem. Phys. Lett.*, **3**, 4 (1969).
- (44) T. Takenaka, *Spectrochim. Acta, Part A*, **27**, 1735 (1971).
- (45) W. Kiefer, *Appl. Spectrosc.*, **28**, 115 (1974).
- (46) M. R. Suchanski, D. L. Jeanmaire, and R. P. Van Duyne, manuscript in preparation.
- (47) M. R. Suchanski and R. P. Van Duyne, *J. Am. Chem. Soc.*, **98**, 250 (1976).
- (48) M. R. Suchanski and R. P. Van Duyne, manuscript in preparation.
- (49) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Moche, *J. Am. Chem. Soc.*, **84**, 3374 (1962).
- (50) H. T. Jonkman and J. Kommandeur, *Chem. Phys. Lett.*, **15**, 496 (1972).
- (51) M. A. Ratner and K. Krogh-Jespersen, private communication, 1975.
- (52) R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, **18**, 932 (1965).
- (53) C. J. Fritchie and P. Arthur, *Acta Crystallogr.*, **21**, 139 (1966).