Rapid Raman Spectroscopic Determination of the Stoichiometry of Microscopic Quantities of BEDT–TTF-based Organic Conductors and Superconductors

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An approximately linear dependence exists between the degree of charge transfer and the Raman-active C=C stretching frequencies in insulating, conducting, and superconducting salts of the electron-donor molecule BEDT–TTF, which may be used to rapidly deduce the stoichiometry of newly synthesized materials.

A major difficulty in the field of new organic conducting and superconducting salts is the characterization of reaction products from electrocrystallization reactions due to the frequent occurrence of multiple crystalline phases, in small quantities, each with differing stoichiometry, crystal structure and electrical/magnetic properties.[1] Since the available techniques for characterization (spectroscopic, X-ray crystallographic) require reasonably 'large' samples, no single technique exists for rapid and precise characterization of microscopic samples, but this situation is changing rapidly with the advent of new instrumentation and techniques.

Laser Raman spectroscopy offers great potential for characterization of organic conducting materials by measuring certain diagnostic vibrations in these salts[2–7] (*e.g.* the symmetric C=C stretching modes in TTF derivatives), and correlating them with compound stoichiometry, but past attempts to use this technique have been quite incomplete and of very limited scope, because of the tendency of the existing lasers to destroy these materials. With recent dramatic breakthroughs in the development of Raman microscope spectrometers, these limitations have been largely removed. With this new technique, an adjustable low power (*ca.* 1 mW) He : Ne laser† is used, and the reflective Raman measurement samples a tiny area on the order of 1 μ^2 (10^{-12} m^2), providing a rapid and nondestructive characterization, as well as imaging capabilities. Here, we report the first study of the correlation between the C=C double bond Raman frequencies of the BEDT–TTF based organic conductors/superconductors and the degree of charge transfers in these salts, where BEDT–TTF (abbreviated ET) is bis(ethylenedithio)-tetrathiafulvalene.

The degree of charge transfer (Z) has previously been correlated to the frequency of the IR active CN stretching vibration for charge-transfer complexes of the electron-acceptor tetracyanoquinodimethane (TCNQ) with a host of electron-donor molecules.[8,9] A linear correlation between Z (independently measured by use of diffuse X-ray scattering from the periodicity of the charge-density-wave) and the observed frequencies was obtained, which in turn was widely used as a rapid means to estimate Z in newly synthesized salts. In the TCNQ complexes, which all possess a 1 : 1 donor : acceptor stoichiometry, Z can span the entire continuum from zero (van der Waals solid) to one (ionic crystal), depending on the difference in redox potentials of the donor molecule compared to that of TCNQ. In contrast, almost all the ET salts are prepared with anodic oxidation and contain anions with fixed, integer charge (usually −1), thus the average charge of the donor-radical-cation is given by the ET : anion stoichiometric ratio. In a few cases, the anion possesses non-integral charge (per formula unit), but even there, the anion charge is determined by the composition of the anion, and not by partial charge transfer. For the present study, a broad sampling of ET-salts with the commonly observed stoichiometries 2 : 1 ($Z = 0.5$), 3 : 2 ($Z = 0.667$), and 1 : 1 ($Z = 1$), as well as crystals of the neutral donor molecule, were investigated. The non-stoichiometric salts $(ET)Hg_{0.776}(SCN)_2$ ($Z = 2.0–2 \times 0.776 = 0.448$) and $(ET)Ag_{1.6}(SCN)_2$ ($Z = 0.4$) were also included in the study.[10,11]

Previous calculations have shown that the two totally symmetrical (Raman-active) C=C stretching modes between 1400 and 1550 cm^{-1} had large electron-phonon coupling constants, and therefore were especially sensitive to the charge state of the donor molecule.[2] The effect of the positive electrical charge residing on the ET molecule is to decrease the electron population in the HOMO, whose coefficients are bonding with respect to both types of C=C (central and external/ring) double bonds. Consequently, the weakening of the bonds leads to lower vibrational frequencies. According to the normal coordinate analysis,[2] the two totally symmetric C=C modes (ν_3 and ν_4 have approximately equal contributions from the stretching vibrations of the central C=C bond and from the C=C bonds connecting the five- and six-membered rings of the ET molecule, with in-phase and out-of-phase signs, respectively, for the two modes. In this study, the ν_3 and ν_4 frequencies were recorded for the salts mentioned, in order to correlate their frequencies with the partial charge of the ET molecule in the salts and to provide an easy calibration curve

Table 1 Raman absorption frequency of the symmetric C=C vibration modes for ET salts at room temperature[a]

ET salts	ν_4/cm^{-1} (intensity)	ν_3/cm^{-1} (intensity)
Neutral:		
ET (this work)	1489 (12 925)	1546 (3 630)
ET (ref. 2)	1494(vs)	1554(s)
Nonstoichiometric:		
$(ET)Hg_{0.776}(SCN)_2$	1480 (7 630)	1500(sh)
$(ET)Ag_{1.6}(SCN)_2$	1476 (4 570)	1500(sh)
2 : 1 Salts:		
α-$(ET)_2(NH_4)Hg(SCN)_4$[b]	1469 (1 330)	1488 (1 600)
	1469 (2 700)	1488 (1 500)
α-$(ET)_2RbHg(SCN)_4$	1469 (1 200)	1488 (500)
	1469	1490
β-$(ET)_2I_3$[b]	1457 (4 907)	1488(sh)
β-$(ET)_2AuI_2$[b]	1470 (700)	
κ-$(ET)_2Cu[N(CN)_2]Br$[b]	1464 (860)	1488 (710)
	1459 (4 630)	
κ-$(ET)_2Cu[N(CN)_2]Cl$[c]	1463 (530)	1489 (500)
	1462 (3 100)	1490 (650)
κ-$(ET)_2Cu(NCS)_2$[b]	1461 (1 500)	
κ-$(ET)_2Cu_2(CN)_3$[c]	1471 (400)	1498 (200)
	1471 (1 250)	1498
κ-$(ET)_4Hg_3Cl_8$[c]	1464 (2 980)	1486 (1 800)
	1462 (5 140)	1489 (1 880)
3 : 2 Salts:		
$(ET)_3Cl_2 \cdot 2H_2O$[c]	1468 (4 000)	1487(sh)
	1464 (6 000)	
$(ET)_3(HSO_4)_2$	1460 (1 900)	1476(sh)
1 : 1 Salts:		
$(ET)Cu[N(CN)_2]_2$	1411 (4 060)	1448 (860)
	1412 (1 120)	1448 (760)
$(ET)BiI_4$	1407 (3 840)	1465 (5 630)
$(ET)AuBr_2Cl_2$	1406 (1 800)	1457 (1 800)
	1416 (6 230)	1462 (1 310)

[a] Results are based on signal averaging (*ca.* 10 scans with scan time 10 s). The error in the measured Raman shift is *ca.* ±2 cm^{-1}. For some samples, two sets of data are provided with 90° rotation in the crystal plane. [b] Ambient pressure organic superconductor. [c] Organic superconductors under pressure.

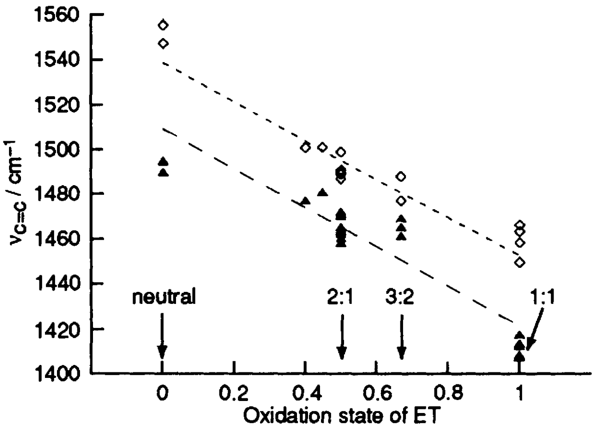

Fig. 1 Correlation of the ν_4 (▲) and ν_3 (◇) symmetric C=C vibration frequencies with the oxidation states of various ET salts. The dashed lines are linear fits to the data with correlation coefficient $R = 0.93$ and 0.96 for ν_4 and ν_3 modes, respectively.

for a rapid test of the stoichiometry present in future, newly synthesized materials.

All measurements were carried out at room temperature by use of a Raman microscope spectrometer (Renishaw, Ltd.) equipped with a He : Ne (λ_0 = 6328 Å) laser. A 180° reflective geometry with the analyser polarization parallel to the incident laser beam polarization was adopted. The samples were mounted on a glass microscope slide, and the monochromator was calibrated against a diamond thin film standard (ν = 1332 cm^{-1}). The various ET-salts were synthesized according to published methods.[1] Room temperature ESR spectra of each crystal were recorded, to ascertain its phase identity, since in many cases, multiple phases may be grown simultaneously during electrocrystallization.[1] Most of the spectra were obtained in reflection from the surfaces parallel to the most highly conducting plane of the crystals, which usually coincide with the best-developed faces of the crystal. Significant differences between orthogonal polarization directions within the plane were observed for the transition intensities, but not for the Raman shift frequencies. In most salts, one of the transitions was virtually unobserved for a particular polarization direction, thus care must be taken to record spectra at different polarization angles. Furthermore, the conductive salts exhibit increased background, broader transitions, and more noise compared to the crystals of the neutral donor molecule. In the latter, a mode of different symmetry at 1511 cm^{-1} is also visible.[12]

The results obtained are summarized in Table 1 and Fig. 1. In the neutral ET crystals, as expected, the highest values of ν_3 and ν_4 in the series were observed, *i.e.*, 1546 and 1489 cm^{-1}, respectively, within 5 cm^{-1} of literature data.[2] In the salts, ν_3, usually the less intense of the two modes, decreased approximately linearly to (on the average) *ca.* 1492 cm^{-1} in the 2 : 1 salts, 1481 (3 : 2 salts), and 1458 cm^{-1} (1 : 1 salts), respectively. The stronger transition, ν_4, similarly decreased by ca. 80 cm^{-1} between the neutral and the fully-charged samples. the frequency decrease for ν_4 was somewhat less linear than for ν_3. Some scatter of the experimental data around the mean values may be seen on Fig. 1. Besides measurement uncertainties, an important potential source of deviation from the mean values could be additional shifts due to intermolecular interactions, which could vary from sample to sample depending on the detailed packing in the crystals. We have found no systematic correlation of Raman frequencies with the overall crystallographic packing motif, *e.g.*, α, β, or κ-phases in the 2 : 1 salts.[1] For the other stoichiometries, the number of samples within each packing type was too small to observe any systematic deviations.

In the absence of any specific theoretical functional dependence of Raman frequency *vs.* Z, we have employed a linear fitting model, shown on Fig. 1, for both modes. The straight lines are given by eqns. (1) and (2):

$$\nu_3\ (\mathrm{cm}^{-1}) = -Z \times 86.0 + 1539; \qquad (1)$$

$$\nu_4\ (\mathrm{cm}^{-1}) = -Z \times 88.4 + 1508; \qquad (2)$$

The slopes for both modes are almost the same, in good agreement with the calculated coupling constants.[2] The inverse of these equations may be used to determine Z from the observed Raman peaks in the case of a newly synthesized sample whose stoichiometry is still unknown, eqn. (3)

$$Z = w_3 \frac{1539 - \nu_3}{86.0} + w_4 \frac{1508 - \nu_4}{88.4} \qquad (3)$$

where w_3 and w_4 are suitably normalized ($w_3 + w_4 = 1.0$) weighting factors, *e.g.*, $w_3 = w_4 = 0.5$. For the two non-stoichiometric salts included in Table 1, the following values of Z were obtained by this method (equal weighting factors): $Z = 0.38$ for (ET)Hg$_{0.776}$(SCN)$_2$ and $Z = 0.41$ for (ET)Ag$_{1.6}$(SCN)$_2$. The corresponding values obtained from the much more time-consuming X-ray structural analysis were 0.448 and 0.40, respectively, in reasonably good agreement with the Raman data.

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† Long wavelength excitation was chosen for minimal sample decomposition and maximal light penetration in order to suppress surface effects.

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