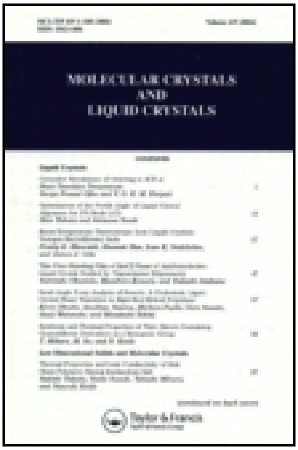

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Raman Scattering From TMTSF-Salts

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RAMAN SCATTERING FROM TMTSF-SALTS

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Experimental results for Raman scattering from TSeF, TMTSF-D12, $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ excited with blue-green laser light at liquid nitrogen temperature are reported. A strong resonance effect for excitation of TMTSF with 4579 Å was observed and an assignment for the a_g modes was obtained by comparison with results from TTF. Methyl group modes were identified at 328 cm^{-1}, 472 cm^{-1} and 916 cm^{-1}, respectively.
Charging the TMTSF molecule resulted in a strong frequency shift of -122 cm^{-1} and -76 cm^{-1} for the $a_g\nu_2$ mode, respectively. A study of the temperature dependence of the scattering from molecular modes between 2 K and 300 K did not reveal any correlation with the phase transitions in the conducting compounds.

INTRODUCTION

Experimental results of Raman scattering from various

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quasi-one-dimensional compounds containing selenium are reported for the first time. The experiments have been performed in order to check on relations between charge transfer (CT)[1-3] or phase transitions[4-7] and the scattering from molecular modes.

EXPERIMENTAL PROCEDURE

Raman scattering experiments were performed for the compounds TSeF, TMTSF, TMTSF-D12, $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$. Single crystals and powdered material of TMTSF, $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ were prepared by standard methods.[4,8] TMTSF-D12 was prepared as recently reported by F. Wudl and E. Aharon-Shalom[9] and TSeF was supplied by E. Engler from IBM. All spectra were excited at liquid nitrogen temperature with laser light in the blue-green spectral region. In addition the temperature dependence of the vibrational modes of the charged molecules was studied between 2 K and 300 K. In order to prevent sample damage the laser intensity was kept around 5mW. For the weak scatterers like $(TMTSF)_2PF_6$ a total scanning time of more than 40 hours was necessary to get a reasonable signal to noise ratio. In order to assign the vibrational modes Raman spectra of TTF were studied as well. In the case of TMTSF the optical absorption between 3600 Å and 7000 Å was measured for a solution of TMTSF in $ChCl_3$ and for a single crystal.

EXPERIMENTAL RESULTS

Raman spectra of TSeF, TMTSF and TTF are shown in Figure 1. The selenium compound and the sulfur compound were excited with 4579 Å and 6061 Å laser light, respectively. Details of the vibrational frequencies are compiled in Table I.

The spectrum of TSeF is dominated by 3 strong peaks at 272 cm^{-1}, 1526 cm^{-1} and 1549 cm^{-1}, respectively. As compared to TTF the third strong mode in the 1500 cm^{-1} region is missing. The spectrum of TMTSF shows 4 strong peaks at 276 cm^{-1}, 453 cm^{-1}, 1503 cm^{-1} and 1539 cm^{-1}. Substituting the hydrogen of the methyl group by deuterium results in a considerable shift of the modes at 263 cm^{-1}, 328 cm^{-1}, 472 cm^{-1} and 916 cm^{-1} to 236 cm^{-1},

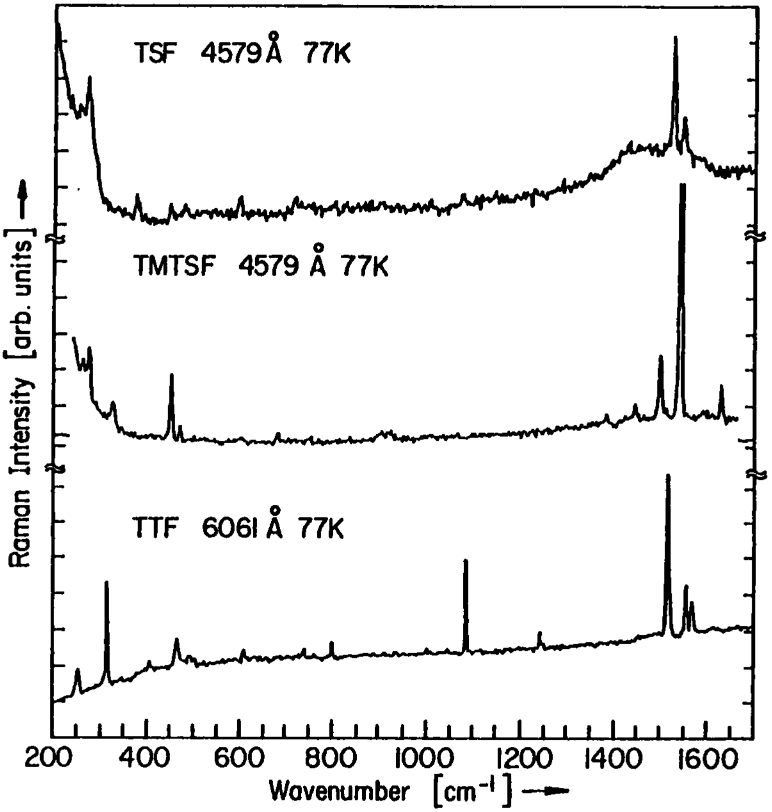

FIGURE 1. Raman spectra for TSeF, TMTSF and TTF as excited at liquid nitrogen temperature with laser light of 4579 Å and 6061 Å, respectively.

241 cm^{-1}, 439 cm^{-1} and 752 cm^{-1}, respectively. A detailed discussion of the change of the Raman spectrum upon deuteration will be given elsewhere. The Raman spectrum of TTF was very similar to what has been reported previously.[10-12] A strong dependence of the scattering intensity on the wavelength of the exciting laser was observed for TMTSF. Changing the excitation from 4579 Å to 5145 Å resulted in a decrease of the scattering intensity by two orders of magnitude. A study of the frequency dependence of the optical transmission revealed a moderate absorption band center-

Table I Raman Lines of TSeF and TMTSF, [cm^{-1}]

Mode	TTF°	TSeF°	TMTSF°	Normal coordinate
			173	
$a_g\nu_7$	256s	231w	180w	ring deformation
		260m	263s	
$b_{3g}\nu_{33}$	316vs	272s	276s	
	420m	379m	328m	methyl in TMTSF
$a_g\nu_6$	469m	451m	453vs	ν_{C-S}, inner in TTF
	480w	480w	472m	methyl in TMTSF
$b_{3g}\nu_{32}$	612w	599m	603w	
$a_g\nu_5$	740m	718m	682m	ν_{C-S}, outer in TTF
$b_{3g}\nu_{31}$	800w		916m	methyl in TMTSF
$b_{3g}\nu_{30}$	1010w	1010w	1018w	
$a_g\nu_4$	1086vs	1075w		ν_{C-H} in TTF
			1167w	
$b_{3g}\nu_{29}$	1246		1225w	combination tones
			1384w	and methyl in
		1430w	1420w	TMTSF
		1480w	1444w	
$a_g\nu_3$	1520vs	1526vs	1503vs	$\nu_{C=C}$ center
			1530w	
$a_g\nu_2$	1556vs	1549vs	1539vs	$\nu_{C=C}$ ring
	1569s		1589w	

ed at 5400 Å and a very strong absorption starting at 4200 Å. As a consequence the ratio of the optical density as measured at 4579 Å and 5145 Å was 0.4 which evidently cannot account for the strong decrease in scattering intensity. Resonance enhancement for excitaation with 4579 Å must rather be the dominate reason for the strong scattering intensity at this wavelength. Details on the optical properties including a strong luminescence and the resonance Raman effect in TMTSF will be published elsewhere.

Highly conducting compounds of TMTSF containing the charged molecule turned out to the very weak Raman scatterers. Figure 2 shows spectra from $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$. A comparison with TTF-TCNQ revealed that

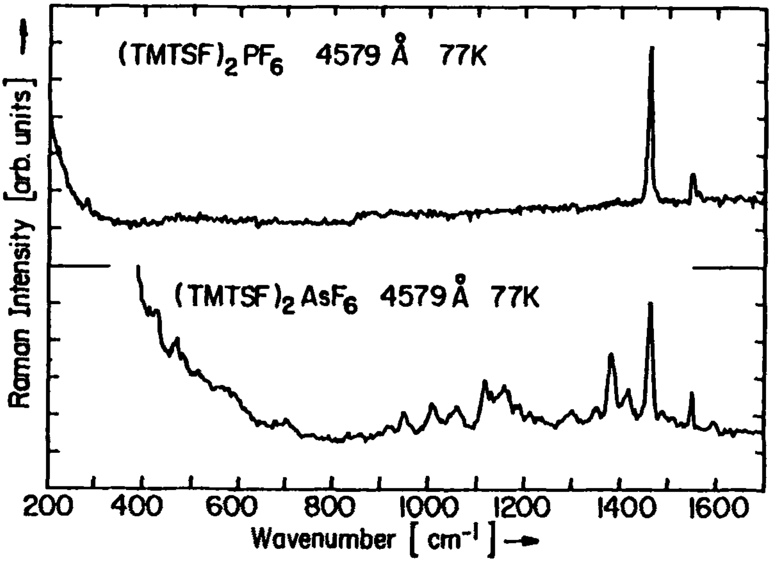

FIGURE 2. Raman spectra of $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ as excited with 4579 Å laser light at liquid nitrogen temperature.

the scattering intensity of these compounds is about a factor 10 smaller than for TTF-TCNQ. In the case of $(TMTSF)_2AsF_6$ the spectrum was taken from the edge of the crystal which considerably increased the total amount of scattering light. Table II shows a detailed compilation of the observed Raman lines for $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ as compared to TTF^+. The values in parenthesis indicate the frequency shift as compared to the uncharged molecule. The temperature dependence of the Raman spectra from the PF_6 and AsF_6 compounds did not exhibit any significant change in mode frequencies.

DISCUSSION

For the assignment of the Raman lines a direct comparison between the well-known lines of TTF and those of the

Table II Raman lines of $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ $[cm^{-1}]$

Mode	TTF^+	$(TMTSF)_2PF_6$	$(TMTSF)_2AsF_6$
$a_g\nu_7$	256(0)		
$a_{3g}\nu_{33}$	263	278(2)	
$a_g\nu_6$	493(24)	478(25)	469(16)
$a_g\nu_5$	750(10)	675(7)	675(7)
		917	944
$a_{3g}\nu_{30}$	1010	1010	1006
$a_g\nu_4$	1078(-8)		1056
			1116
			1156
			1294
			1350
$a_g\nu_3$	1415(-105)	1381(-122)	1381(-122)
			1419
$a_g\nu_3$	1477(-79)	1463(-76)	1463(-76)
		1547	1544
		1559	1590

selenium compounds has been performed. The proximity in frequency and the similarity in line intensity have been used as the primary criteria for the comparison. In the case of TMTSF simplified symmetry of D_{2h} was assumed by replacing the methyl group by point masses. Thus it must be kept in mind that in particular the C-H in plane bending mode $a_g\nu_4$ of TTF cannot be observed in TMTSF but is rather replaced by modes from the methyl group. With this exception the relation between TTF and the selenium compounds leads to a tentative assignment at least for the a_g mode as shown in Table I. The similarity of the molecules suggests that the normal coordinates for TTF as evaluated by Bozio et al[10] should apply at least qualitatively for the selenium compounds. In the latter work it was found that the sulfur motion contributes only to $a_g\nu_5$, $a_g\nu_6$ and $a_g\nu_7$. Only these modes should therefore be sensitive to a replacement of sulfur by selenium in agreement with the results of Table I. Also $a_g\nu_6$ is the only mode in TTF which does not contain hydrogen motion. Thus there is no change in this mode frequency by replacing hydrogen by methyl.

The assignment of the modes $a_g\nu_5$ and $a_g\nu_6$ is problematic since they contain the motion of the chalcogen atom directly. A simple consideration of the difference in the reduced masses (C-S versus C-Se) requires a 9% reduction of frequency for the heavier selenium compound. The reduction from Table I is only 5%. On the other hand it is known from the study of vibrational modes in various selenium compounds that the force constants change strongly if sulfur is substituted by selenium.[13] Changes in vibrational frequency of 30% have been observed for SF_6 and SeF_6, respectively.[14] To account for that the only possible alternative assignment for the $a_g\nu_6$ mode would be to 272 cm^{-1} in TSeF and 276 cm^{-1} in TMTSF. The $a_g\nu_5$ mode would then be assigned to 451 cm^{-1} and 453 cm^{-1} and the $b_{3g}\nu_{33}$ mode to 260 cm^{-1} and 263 cm^{-1} in TSeF and TMTSF, respectively. These relations are indicated in Table I by arrows. The substitution induced frequency shifts are then as high as 39% and 42% for the $a_g\nu_6$ and $a_g\nu_5$ mode, respectively. This seems to be not unreasonable with respect to the strong influence of the chalcogen substitutions on the bond length. While Gaunt[14] reports a 7.5% increase of the chalcogen-fluorine bond by selenium subsitution of sulfur in SF_6 the results of Dr. Kistenmacher et al.[15] on TTF and the results of LaPlaca[16] on TSeF yield on 8.7% and 9.5% increase of the length for the inner and the outer carbon-chalcogen bond, respectively. This result indeed favours the strong downshift of the $a_g\nu_5$ and $a_g\nu_6$ modes.

From a comparison with other compounds where hydrogen is substituted by a methyl group[17] (as in toluene or xylene) and in particular from the results

hydrogen is substituted by a methyl group[17] (as in toluene or xylene) and in particular from the results

obtained for the deuterated TMTSF, the lines at 328 cm^{-1} (242 cm^{-1}, 472 cm^{-1} (426 cm^{-1}) and 916 cm^{-1} (752 cm^{-1}) were identified as originating from the methyl group. The values in parenthesis refer to the deuterated material. For the mode at 752 cm^{-1} a contribution of the combination of the two fundamentals at 294 cm^{-1} and 450 cm^{-1} cannot be excluded. Higher frequency modes induced by the methyl group could be in the range between 1400 cm^{-1} (1050 cm^{-1}) and 1520 cm^{-1} (1500 cm^{-1}). However, overlapping of fundamentals and combination tones made a definite assignment in this frequency region impossible.

In the case of the charged TMTSF molecule an assignment of the a_g modes was possible as shown in Table II. The assignment corresponding to the strong substitutions-induced frequency shift is again indicated by arrows. The CT-induced frequency shift is slightly positive for the low frequency modes whereas $a_g\nu_3$ and $a_g\nu_2$ exhibit a strongly negative shift. This is very similar to what is known for TTF.[11,18] It must be kept in mind, however, that TMTSF in the present compound is only partially charged. The CT-induced frequency shift is thus much larger than in the TTF molecule. It appears to be even larger than in the sulfur compound TMTTF for which Bozio and Pecile[3] reported a shift of 119 cm^{-1} for the $a_g\nu_2$ mode for full CT. The same response applied to TMTSF would yield a CT of 0.6 which is slightly higher than the value of 0.5 obtained from stoichiometry. The maximum CT-induced frequency shift thus increases from 7% to 8% and 16% for TTF, TMTTF and TMTSF, respectively.

CONCLUSION

Raman scattering from TMTSF salts showed a strong relaxation of their vibrational modes to the more simple compounds TTF and TSeF. The uncharged molecule has a strongly enhanced Raman cross section for blue light excitation. Vibrational modes of the methyl group were identified at 328 cm^{-1}, 472 cm^{-1} and 916 cm^{-1}. The charged molecule behaves similar to TTF but the CT-induced frequency shifts for the $a_g\nu_2$ and the $a_g\nu_3$ modes are much larger.

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