

ASSIGNMENT OF FUNDAMENTAL VIBRATIONS AND ESTIMATION OF ELECTRON-MOLECULAR
VIBRATION COUPLING CONSTANTS FOR BIS(ETHYLENEDIOXY)TETRATHIAFULVALENE (BEDO)

K. I. POKHODNIA, M. E. KOZLOV AND V. G. ONISCHENKO,

Institute of Semiconductors, Ukr. Acad. of Sci., Kiev, Ukraine

D. SCHWEITZER AND J. MOLDENHAUER

3. Physicalisches Institute, Universitat Stuttgart, Germany

R. ZAMBONI

ISM CNR Bologna, Italy

ABSTRACT

The i.r. absorption and Raman spectra of BEDO are investigated. All fundamental vibrations are assigned using correlations between the obtained data and those for a well-known compound BEDT-TTF (ET). Comparative normal coordinate analysis has been done. The results are used for calculation of electron-intramolecular vibration coupling constants of BEDO based superconducting charge-transfer complexes. Comparison of these values with the constants obtained earlier for ET shows that BEDO is a perspective donor for searching new superconductors on its basis.

INTRODUCTION

Application of ET for the synthesis of organic superconductors (SC) sufficiently widened the class of such materials. Within a short period of time the SC transition temperature (T_c) has been raised by nearly 10 times [1]. Such an impressive T_c rise was achieved basically due to changing of the anion part of the cation radical ET salts. The evident approach in looking for the new superconductors seems to be a modification of the donor itself. Introduction of the substance in which sulfur atoms in 6-member rings were substituted by the oxygen ones, the so called BEDO, is one of the variants, of such an approach [2]. At present there were synthesized many BEDO-based conductors, though only two of them exhibited superconductivity: $(BEDO)_3Cu(NCS)_3$ ($T_c \sim 1K$) and $(BEDO)_2ReO_4(H_2O)$ ($T_c \sim 2.5$) [3,4,9].

It is known that one of the reasons of superconductivity in organic solids is a strong coupling of the electrons on the HOMO level of the donor with its intramolecular vibrations (EMVC) [5]. This interaction tells on the conductive

properties and reveals itself in the i.r. spectra as intensive vibronic bands [6]. Taking into account the similarity of geometrical structure of ET and BEDO it seems interesting to compare the values of EMVC constants in both of them.

The EMVC constant calculations for ET were reported earlier [7]. In this paper the assignment of fundamental vibrations in the Raman and i.r. spectra of BEDO is performed. This assignment is confirmed by the normal coordinate analysis. Further the calculation of EMVC constants for BEDO is carried out by the method described in [8]. These data may be used for developing the SC theory in organics. Besides they help to interpret some peculiarities in the i.r. spectra of conductive BEDO salts.

EXPERIMENTAL

BEDO was synthesized by the method described in [2]. During recrystallisation the red-brown thin plates (of irregular shape) of BEDO monocrystals were obtained, which were then used for polarization measurements. The i.r. powder, monocrystal and solution (in CS₂) spectra were recorded by a BOMEM FT spectrometer (model DA3.01) in the range 450-5000 cm⁻¹. The Raman spectra in the range 100-3600 cm⁻¹ were carried out on a Bruker FT spectrometer with the laser excitation ($\lambda = 1064$ nm). When the laser light with $\lambda < 800$ nm was used there appeared a very intensive sample fluorescence in the whole investigated spectral range what made registration of a weak Raman signal practically impossible.

RESULTS AND DISCUSSION

According to [9] the BEDO monocrystals crystallize in the orthorhombic space group, and the elementary cell consists of the two pairs of molecules with nearly perpendicular long axes. As in the case of ET only the central C₂S₄ fragment of BEDO is planar, other atoms of skeleton are somewhat out of plane, particularly it is characteristic of the terminal C₂H₄ fragments. Due to this some product rule inaccuracies have to be taken into consideration when BEDO fundamental modes assignment on presumption of its D_{2h} symmetry (as it was done for ET) is performed. Modes distribution amongst symmetry species for BEDO is the same as for ET [7].

The Raman and i.r. polycrystal spectra of BEDO are shown in Fig.1 (a, b). Unfortunately the molecular arrangement in the unit cell of BEDO doesn't give chances to divide the observed i.r. bands related to different symmetry species by polarization measurements with the only exception for CH₂ groups vibrations.

Fundamental vibrations of BEDO are assigned using correlations between the obtained spectral data and those for ET. It was assumed that spectral position of the bands corresponding to the common fragment should be close. Quite definitely the characteristic vibrations of C=C, C-S and C-H bonds might be identified. In the Raman spectrum the most intensive band 1527 cm⁻¹ is

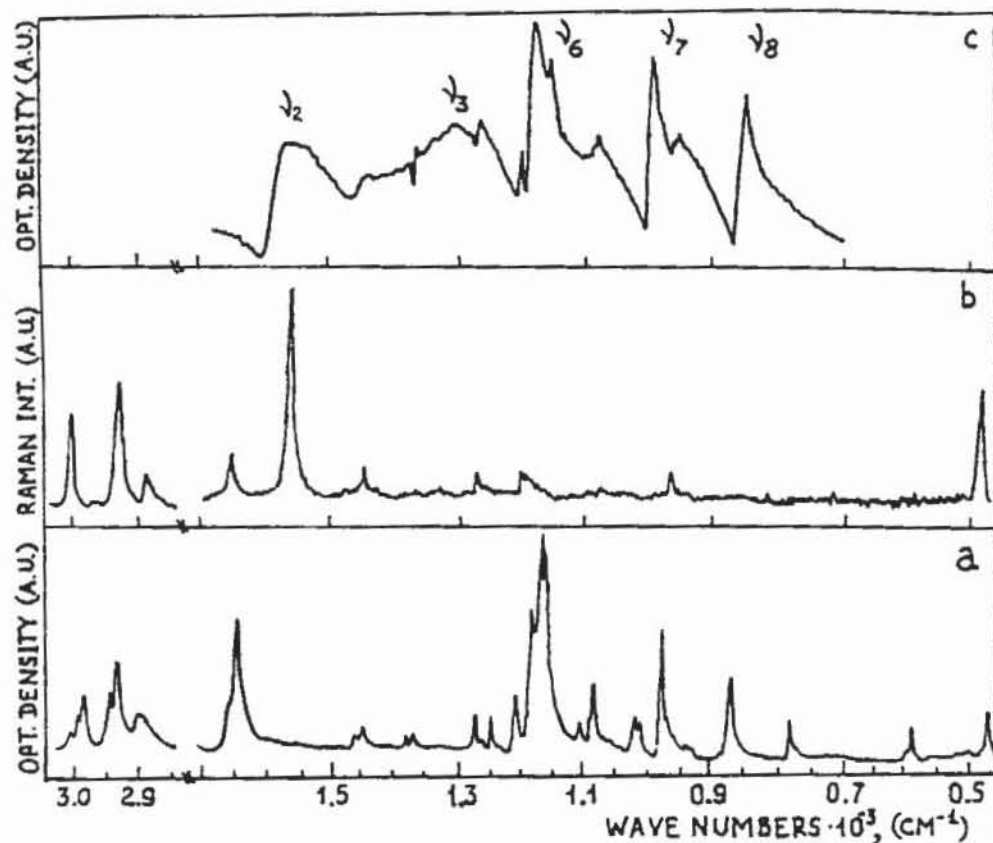


Fig. 1. The Raman spectrum of BEDO (b) and i.r. spectra of BEDO (a) and $(\text{BEDO})_2\text{Cl}(\text{H}_2\text{O})$ (c).

assigned to A_g stretching of central C=C bond. Its frequency is close to the frequency of the same mode in ET (1551 cm^{-1}). In this spectral range two bands related to the C=C bonds vibrations in the fulvalene rings have to be observed both in the Raman and i.r. spectra. According to X-ray crystallographic data the length of this bond in BEDO (1.303 \AA) is somewhat shorter than in ET (1.332 \AA) [9], what means its higher rigidity and higher frequency of its stretching. On this basis the bands 1657 (Ram) and 1647 cm^{-1} (i.r.) are assigned to A_g and B_{1u} vibrations of these C=C bonds.

It is known that in ET the C-S stretching modes in TTF-fragment reveal themselves as two pairs of A_g (440 and 448 cm^{-1}) and B_{1u} (777 and 500 cm^{-1}) in the Raman and i.r. spectra respectively. In the Raman spectrum of BEDO only one rather intensive band near 472 cm^{-1} was observed (the intensity of the lower frequency band is apparently very small). This band and the two i.r. active bands

near 463 and 764 cm^{-1} are assigned as A_g and B_{1u} C-S bonds stretchings in TTF-fragment.

While the frequency range of C-H stretching modes is well known their assignment in BEDO requires special considerations. In the i.r. spectrum one can distinguish two groups of bands in the regions 2980-3010 cm^{-1} and 2930-2950 cm^{-1} and a broad band near 2870 cm^{-1} . It is known that the asymmetric stretching mode of individual CH_2 group has higher frequency than the symmetric one and their polarizations are perpendicular. On this basis we assume that B_{3g} , B_{2u} , B_{1g} modes formed by asymmetric vibration of each CH_2 fragment (in different phases) belong to the first group of bands and A_g , B_{1u} , B_{2g} , B_{3u} modes - to the second one. Such an assignment is confirmed by the intensity changes of the band 2987 cm^{-1} in the mono and polycrystal spectra. In fact this band doesn't reveal itself in monocrystal spectra where light polarization coincides with the molecule planes, and in our experimental set mainly the second group of modes can be excited. In the spectrum of polycrystals, where microcrystals are arbitrarily oriented and all types of modes can be excited, this band is one of the most intensive.

Rather strong broad band near 2870 cm^{-1} has not been observed earlier in ET spectra. Taking into consideration the common tendency of blue shift for all C-H stretching modes of BEDO such a decrease of its frequency must have been caused by some special reasons. In our opinion, it may result from the interaction between H atoms (at C_2H_4 fragment conformation of "staggered" type [10]) and O atoms bearing a strong negative charge of the neighbouring BEDO molecules. Though this question has not been specially considered in reference materials on BEDO structure, the existence of short C-H...O contacts has been observed in the structure of conductive salts of this donor [9]. Splitting of bending CH_2 modes near 1450 cm^{-1} (A_g , B_{1u}) and 1370 cm^{-1} (B_{3g} , B_{2u}) and also B_{2u} mode of C-O-C bonds stretchings (1156 and 1159 cm^{-1}) can be explained by this effect. The last splitting disappears in the solution spectrum.

By analogy with ET the bands 1262 cm^{-1} (A_g), 1270 cm^{-1} (B_{1u}), 1170 cm^{-1} ($B_{1g}-A_u$) are interpreted as ethylene fragment bending modes. Product rule inaccuracy together with C-H...O interaction makes assignment of C-H vibrations somewhat relative. But as it will be shown further these modes do not mix up with the other skeleton modes and get coupled with electrons on HOMO very weakly.

The bands 1196 cm^{-1} (Ram) and 1199 cm^{-1} (i.r.) can be quite definitely interpreted as A_g and B_{1u} vibrations of C-O-C bonds and the band near 188 cm^{-1} (Ram), which has its analogue in ET spectrum, is assigned as A_g bending of the whole TTF-fragment.

The remaining the bands are apparently related to 6-member rings vibrations and are strongly shifted to higher frequencies with respect to their analogues

Table 1

The fundamental frequencies of BEDO (cm^{-1})

Sym	i	ν		Potential energy distribution (%)	Sym	i	ν		Potential energy distribution (%)
		obs	calc				obs	calc	
A _g	1	2937	2954	K ₂₂ (99)	B _{2g}	37	2954	K ₂₂ (100)	
B _{1u}	26	2934	2954		B _{3u}	66	2944		2954
A _g	2	1656	1654	K ₁₀ (68)	B _{2g}	38	1175	K _{16,22} (47), K _{20,22} (40)	
B _{1u}	27	1647	1647	K ₁₀ (73)	B _{3u}	67	1175		
A _g	3	1527	1527	K ₁ (74)	B _{2g}	39	683	K _{16,22} (49), K _{20,22} (51)	
A _g	4	1445	1454	K ₂₀ (23), K _{20,22} (27) K _{22,23} (40)	B _{3u}	68	683		
B _{1u}	28	1444	1454			B _{3g}	55	2937	K ₂₂ (99)
A _g	5	1262	1279	K ₂₀ (18), K _{16,22} (36) K _{22,23} (26)	B _{2u}	44	2934	2954	
B _{1u}	29	1270	1279			B _{3g}	56	1398	K _{20,22} (23), K _{22,23} (71)
A _g	6	1196	1203	K ₁₂ (17), K ₁₆ (35)	B _{2u}	45	1374	1398	
B _{1u}	30	1199	1203			B _{3g}	57	1246	K _{16,22} (44), K _{20,22} (32)
A _g	7	1010	1014	K ₆ (36), K ₁₂ (37)	B _{2u}	46	1240	1246	
B _{1u}	31	1015	1014			B _{3g}	58	1164	K ₁₂ (29), K ₁₆ (40)
A _g	8	865	860	K ₁₆ (48), K ₂₀ (15)	B _{2u}	47	1159	1164	
B _{1u}	32	864	861			B _{3g}	59	1080	K ₆ (30)00, K _{16,20} (2)
A _g	9	423	423	K ₂ (67)	B _{2u}	48	1082	1080	
B _{1u}	33	769	776	K ₂ (52), K _{2,3} (25)	B _{3g}	60	1096	K ₂ (56), K _{1,2} (39)	
A _g	10	590	590	K ₁₂ (29), K _{12,16} (25)	B _{2u}	49	941	933	K ₂ (36), K ₁₂ (34)
B _{1u}	34	588	589			B _{3g}	61	945	
A _g	11	476	474	K ₆ (19), K _{12,16} (25)	B _{2u}	50	962	966	K ₂ (49), K ₁₂ (15)
B _{1u}	34	463	466	K ₂ (34), K _{12,16} (19)	B _{3g}	62	811	K ₆ (33), K ₁₆ (26), K _{16,20} (27)	
A _g	12	188	173	K _{2,3} (23), K _{2,6} (26)	B _{2u}	51	825?		810
B _{1u}	36	373	373	K ₂ (18), K ₆ (19)	B _{3g}	63	437	K ₁₂ (26), K _{6,10} (27)	
B _{1g}	20	2997	2993	K ₂₂ (99)	B _{2u}	52	56	K _{1,2} (89)	
A _u	13	2995	2993			B _{3g}	64	381	K _{1,2} (36), K _{6,12} (21)
B _{1g}	21	1169	1169	K ₂₂ (15), K _{16,22} (30)	B _{2u}	53	440	K ₁₂ (24), K _{6,10} (27)	
A _u	14	1170	1169	K _{20,22} (56)	B _{3g}	65	208	K _{1,2} (19), K _{6,12} (31)	
B _{1g}	22	870	870	K _{16,22} (70)	B _{2u}	54	296	K ₁₂ (22), K _{6,12} (40)	
A _u	15	870	870	K _{20,22} (30)					

Table 2

The valence force constants of BEDO (10^6 cm^{-2})^a

Symb.	Value	Symb.	Value	Symb.	Value	Symb.	Value	Symb.	Value
K ₁	11.434	K _{2,3}	1.423	K _{22,23}	0.734	A ^{1,2}	0.458	A ^{10,12}	1.036
K ₂	5.408	K _{2,6}	1.755	H ²	0.274	A ^{2,3}	0.661	A ^{12,16}	1.751
K ₆	6.347	K _{6,10}	1.202	H ³	-0.687	A ^{2,6}	0.798	A ^{12,16}	0.132
K ₁₀	12.320	K _{6,12}	1.423	H ¹⁰	0.188	A ^{2,6}	0.060	A ^{16,20}	0.968
K ₁₂	6.989	K _{10,12}	0.545	H ¹²	0.356	A ^{6,10}	0.851	A ^{16,22}	0.672
K ₁₆	7.536	K _{12,16}	1.582	H ¹²	0.157	A ^{6,12}	0.119	A ^{16,20}	0.176
K ₂₀	7.115	K _{16,20}	2.512	H ²⁰	0.618	A ^{6,10}	0.451	A ^{20,22}	0.170
K ₂₂	7.241	K _{16,22}	0.827	H ²³	0.123	A ^{10,12}	0.398	A ^{16,22}	-0.404
K _{1,2}	0.898	K _{20,22}	0.903	A ^{1,2}	0.339	A ^{6,12}	-0.099	A ^{20,22}	0.911

^a Only values of force constants for symmetrically nonidentical bonds (*i, j*) or angles (*n, m*) are included. Force constants: K₁ - stretch, K_{*n, m*} - bend, H₁^{*j*} - stretch-stretch, A₁^{*n, m*} - stretch-bend.

in ET spectra due to S→O substitution. For their assignment it's necessary to perform normal coordinate analysis (NCA) because of their strong mixing.

For NCA it was assumed that BEDO is flat and has a D_{2h} symmetry. All bonds lengths and angles between them were taken after averaging the structure data [9]. The same number of force field (FF) constants as for ET was used for description of BEDO fundamental vibrations. The final values of calculated frequencies of normal modes and their description in terms of the potential energy distribution among internal coordinates (PED) are presented in Table 1, the values of force constants - in Table 2. One can see that the agreement between experimental and calculated values is quite acceptable (the highest deviations are observed for the vibrations of ethylene fragments due to the reasons mentioned above) and PED confirms the proposed assignment of the bands in BEDO spectra.

The FF analysis shows that substitution of S by O leads to considerable increase (up to 25%) of all force constants in 6-member ring (K_{10} , K_{12} , K_{16} , K_{20}), what gives evidence of rigidity increase of this fragment in BEDO. Knowing FF of BEDO one can calculate the atomic displacement vectors for 12 A_g modes. After their reduction by zero-point amplitudes they were used for EMVC constant calculation.

The computation of BEDO electronic structure obtained by quantum chemical calculations (MNDO method) gives the value of HOMO energy 8.9 eV which is close to ET value (8.7 eV). Comparison of π -electron density distribution on atoms of BEDO and ET (Fig.2) shows that the charges on atoms of the central C_2S_4

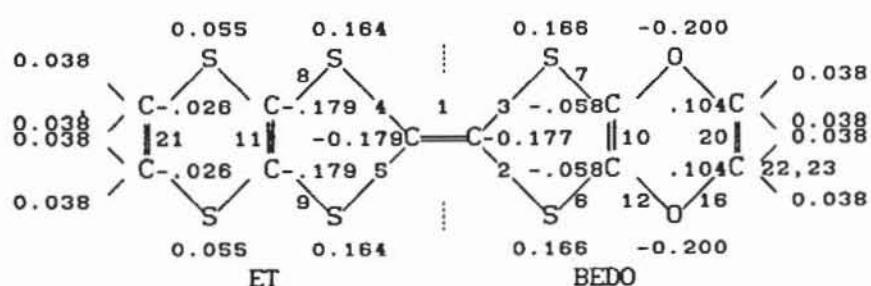


Fig.2. Calculated charge values on the atoms of ET (right) and BEDO (left), and numeration of bonds used in normal coordinate analysis.

fragments for both molecules are practically the same what is in agreement with bands positions related to this fragment. The main differences were observed in 6-member rings. Oxygen almost completely transfers electron density from the carbon atoms to itself what apparently makes the ring C=C bonds more rigid.

The EMVC constant value describing strength of interaction between the i th mode and HOMO electrons was determined by the equation: $g_i = (h\nu_i)^{-1}(\partial E/\partial Q_i)_0$, where $\nu_i = A_g$ mode frequencies; $E =$ HOMO energy. The results of calculation are shown in Table 3.

Table 3

Calculated dimensionless EMVC constants g_i for BEDO (i = number of A_g mode). For comparison g_i ET⁺ values for similar modes are presented in brackets.

i	g_i	$(g_i \text{ ET}^+)$	i	g_i	$(g_i \text{ ET}^+)$	i	g_i	$(g_i \text{ ET}^+)$	i	g_i	$(g_i \text{ ET}^+)$
1	0.027	(0.022)	4	0.045	(0.102)	7	0.153	(0.117)	10	0.153	(0.050)
2	0.425	(0.165)	5	0.092	(0.063)	8	0.300	(0.192)	11	0.463	(0.476)
3	0.549	(0.746)	6	0.241	(0.140)	9	0.555	(0.025)	12	0.115	(0.041)

One can see that the EMVC constant values both for ET and BEDO are high for the vibrations in which heavily charged atoms take part. Presence of electronegative O atoms in 6-member rings of BEDO leads to a sharp increase of constants values for the A_g modes related to this fragments ($i > 5$) in comparison with g_i values for the similar ET modes, because the charge on S atoms in ET is much smaller.

The EMVC constants values are in a good qualitative agreement with experimental data. If the vibronic bands related to A_g C=C ($i=3$) and C-S ($i=9$) modes dominate in the i.r. spectra of ET salts [11], additional intensive vibronic bands related to ν_6 , ν_7 , ν_8 appear in the i.r. spectrum of $(\text{BEDO})_2\text{Cl}(\text{H}_2\text{O})$ (Fig.1c).

Thus as for EMVC constant values BEDO is a very perspective donor for searching new superconductors on its basis. The lowering of HOMO energy of it due to EMV coupling or "polaron binding energy" $\sum h\nu_i g_i^2 = 152$ meV is 20% higher than the ET value. But there are some other important factors (Coulomb interaction, structure disorder etc.) determining T_c value which also have to be taken into account. They might be on the way of achieving higher T_c in the structures already obtained. That's why additional work has to be done on looking for such acceptors the combination of which with BEDO would minimize their negative influence.

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