ELECTRON-MOLECULAR VIBRATION COUPLING IN TTF-BASED DONORS

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BEDT-TTF, BMDT-TTF and BEDO-TTF are well known thio-TTF and oxo-TTF (in the former case) derivatives on the basis of which cation-radical salts with 2D type of conductivity can be produced. In this work the comparative analysis of electron-molecular vibration coupling constants (obtained by MNDO quantum-chemical method) that describe the interaction between totally symmetric A_g modes and electron on HOMO level is performed.

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1. Introduction

It is well known that electron–phonon coupling is one of the main reasons of superconductivity (SC). In comparison with the traditional inorganic SC materials the phonon spectra of organic metals are much wider and consist of two types of vibrational modes: intermolecular acoustic phonons and intramolecular vibrations of atoms or atomic groups of organic molecules. It is rather difficult to explain the high value of $T_c \approx 12$ K in some of BEDT-TTF (bis(etylenedithio)-tetrathiafulvalene) [1] salts only by interaction with the phonons of the first type. Intermolecular vibrations could be a significant source of phonon exchange for SC pairing. This idea found its theoretical support in the paper of Yamaji [2]. Thus the correct evaluation of electron-molecular vibration coupling (EMVC) constants for BEDT-TTF and relative donors is of great importance.

2. Results and discussion

There are two main methods of the estimation of EMVC constants. First, the so-called dimer method based on fitting the model reflectivity spectrum (where EMVC constants g_i are model parameters) to the experimental one, which contains the strong vibronic features due to EMVC [3]. The second one is based on the direct calculation of the derivative $(\partial \varepsilon_\gamma / \partial Q_i)$ (where ε_γ is the energy of highest occupied molecular orbital (HOMO) level calculated by MNDO quantum-chemical

method and Q_i is a normal coordinate) which is proportional to g_i [4]. The principal limitation of the first model is the fact that it was designed for the array of insulating dimers. The monocrystals with such structure are not available for BEDT-TTF family substances. The attempt to use this model for describing the reflectivity of β-BEDT-TTF$_2$I$_3$ conductive salt gave obviously understated g_i values $\sum_i g_i N(0) < 0.1$ [5].

The second method is more universal but it takes a lot of spectroscopic work. Taking into consideration the specific features of this method, principal attention was focused on proving the adequacy of a chosen valence force field (VFF) for the description of molecular vibration in this class of donors. The variant of VFF proposed in our earlier work for BEDT-TTF and its deuteroanalogue [6] was easily adopted for substituted terminal groups BMDT-TTF (bis(methylenedithio)TTF) [7] including the case of its cation radicals [9] and for S $\rightarrow$ O substituted BEDO-TTF [8].

Thus, it could be concluded that the chosen VFF adequately describes the vibration in this TTF derivatives. By performing the normal coordinate analysis the displacements of each atom for all modes allowed to couple by symmetry were obtained and after normalization they were used for EMVC constants calculation.

In Table the EMVC constants for all A_g modes of TTF, BMDT-TTF, BEDT-TTF and its cation-radicals together with BEDT-TTF are presented. For TTF and its thio-derivatives the highest values of EMVC constants have modes ω_2, ω_3 (central and ring C=C double bonds stretchings) and modes ω_6 for TTF, ω_7 for BMDT-TTF, and ω_9, ω_{10} for BEDT-TTF (C–S bond stretchings in central and peripheral heterocycles). Orbitals of these atoms give the main input in HOMO and their motion causes the significant shift of HOMO energy. In cation-radicals only in-phase C=C stretching mode ω_3 and C–S modes ω_6, ω_7, ω_9 (for TTF$^+$, BMDT-TTF$^+$ and BEDT-TTF$^+$ respectively) have the biggest g_i values due to the strong form mixing.

In the case of BEDO-TTF the introduction of strongly electronegative oxygen atoms leads to sufficient π-electron density shifts to the peripheral cycles, though the biggest its part retains on central TTF fragment. But EMVC constants of C=C and C–S stretching modes ω_2, ω_3, ω_9, ω_{11} are still the highest and C–O and C–C stretching modes ω_6, ω_7, ω_8 also have the comparable values of g_i. Corresponding vibronic bands were observed in IR spectra of BEDO-TTF compounds [8].

One can see that above mentioned EMVC constants for BMDT-TTF and BEDO-TTF are even higher than those for BEDT-TTF. It might be presumed that the search for SC on their basis is still promising.

Thus the fundamental data obtained allow to perform quantitative theoretical analysis of EMVC input in SC pairing and give grounds for interpretation of the series of intensive bands in IR spectra of the conductive compounds of analyzed donors.

TABLE

EMV-constants for A_g modes of TTF, BEDT-TTF, BMDT-TTF and BEDO-TTF (a) and their cation-radicals (b).

(a)								
	TTF		BEDT-TTF		BMDT-TTF		BEDO-TTF	
i	ω_i [cm^{-1}]	g_i	ω_i [cm^{-1}]	g_i	ω_i [cm^{-1}]	g_i	ω_i [cm^{-1}]	g_i
1	3076	0.028	2932	0.011	2948	0.006	2954	0.027
2	1554	0.675	1556	0.297	1553	0.374	1654	0.425
3	1500	0.697	1509	0.566	1483	0.595	1527	0.549
4	1079	0.124	1394	0.029	1414	0.054	1454	0.045
5	737	0.172	843	0.012	1256	0.076	1279	0.092
6	463	0.560	685	0.163	982	0.014	1203	0.241
7	235	0.120	508	0.336	900	0.030	1014	0.153
8			470	0.027	656	0.156	860	0.300
9			381	0.226	488	0.506	423	0.555
10			146	0.316	440	0.341	590	0.153
11					302	0.035	474	0.463
12					146	0.179	173	0.115
$\sum^*$	201.6		90.8		118.0		152.7	

(b)						
	TTF$^+$		BEDT-TTF$^+$		BMDT-TTF$^+$	
i	ω_i [cm^{-1}]	g_i	ω_i [cm^{-1}]	g_i	ω_i [cm^{-1}]	g_i
1	3078	0.074	2896	0.032	2912	0.022
2	1496	0.054	1461	0.171	1465	0.165
3	1418	0.869	1419	0.765	1427	0.746
4	1074	0.104	1380	0.003	1421	0.102
5	755	0.077	854	0.024	1287	0.063
6	493	0.795	668	0.187	979	0.140
7	260	0.130	516	0.524	896	0.117
8			496	0.098	672	0.192
9			442	0.210	508	0.476
10			174	0.116	483	0.050
11					318	0.025
12					159	0.041
$\sum^*$	178.6		132.0		127.0	

$\sum^* = \sum \hbar\omega_i g_i^2$ (meV) is a "polaron binding energy" which equals the lowering of HOMO level resulting from its coupling with A_g modes.

Acknowledgments

References

[1] A.M. Kini, U. Geiser, H.H. Wang, K.D. Carlson, J.M. Williams, W.K. Kwok, K.G. Vandervoot, J.E. Thompson, D.L. Stupka, D. Jung, M-H. Whangto, *Inorg. Chem.* **29**, 2555 (1990).

[2] K. Yamaji, *Solid State Commun.* **61**, 413 (1987).

[3] M.J. Rice, *Phys. Rev. Lett.* **37**, 36 (1976).

[4] N.O. Lipari, M.J. Rice, C.B. Duke, R. Bozio, A. Girlando, C. Pecile, *Int. J. Quant. Chem.* **11**, 583 (1977).

[5] M.G. Kaplunov, E.B. Yagubskii, L.P. Rosenberg, Yu.G. Borodko, *Phys. Status Solidi A* **89**, 509 (1985).

[6] M.E. Kozlov, K.I. Pokhodnia, A.A. Yurchenko, *Spectrochim. Acta. A* **43**, 323 (1987).

[7] M.E. Kozlov, V.G. Onishchenko, K.I. Pokhodnia, *Zh. Prikl. Spektrosk.* **52**, 622 (1990).

[8] K.I. Pokhodnia, M.E. Kozlov, V.G. Onishchenko, D. Schweitzer, J. Moldenhauer, R. Zamboni, *Synth. Met.* **55-57**, 2364 (1993).

[9] M.E. Kozlov, K.I. Pokhodnia, A.A. Yurchenko, *Spectrochim. Acta A* **45**, 437 (1989).