Vibrational Analysis and Isotope Shifts of BEDT-TTF Donor for Organic Superconductors

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Vibrational Analysis and Isotope Shifts of BEDT-TTF Donor for Organic Superconductors

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Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is the best donor for 1-D and 2-D organic superconductors. Since coupling of vibrations with electronic states is critical to the nature of the superconductivity, it is essential to have a good understanding of the vibrational states. Many of the vibrational modes of BEDT-TTF were reported and assigned by Kozlov et al.[5] and more were assigned by Eldridge et al.,[6] who made very complete isotope experiments. However, there remain several disagreements between these assignments. We report here the isotopic shifts for neutral BEDT-TTF based on ab initio calculations [Hartree−Fock (HF) using the 6-31G** basis set] for all fundamental vibrational frequencies. On the basis of these results, we propose new assignments for the fundamental vibrational frequencies of BEDT-TTF that satisfy the isotopic substitutions: (i) D for all H, (ii) ^{13}C for the central carbons, (iii) ^{13}C for all the double bond carbons, and (iv) ^{34}S for all sulfurs. The boat deformation of the neutral BEDT-TTF reduces the point group symmetry from previously accepted D_{2h} (or D_2) to C_2. This deformation explains the existing coincidence infrared (IR) and Raman spectrum.

1. Introduction

In the last two decades, more than 50 1-D and 2-D organic superconductors have been synthesized.[1,2] All organic super-conductors involve derivatives of the organic donor molecules tetrathiafulvalene (denoted as TTF), tetraselenafulvalene (denoted at TSeF), or some mixture of these two molecules, packed into quasi one- and two-dimensional arrays and complexed to appropriate electron acceptors. Bis(ethylenedithio)tetrathiafulvalene (denoted as BEDT-TTF or ET) is the best donor for the organic superconductors (see Figure 1). Using ET, more than 30 organic superconductors have been synthesized, leading to the highest T_c materials. However, the best T_c remains at 12.8 K for κ-(ET)$_2$Cu[N(CN)$_2$]Cl.

The isotopic shift of T_c indicates that the superconductivity involves electron−phonon coupling. However, there remains many questions about the relation between molecular properties and superconductivity. We found[3] that for all known fulvalene-based superconductors, *the neutral fulvalene donor distorts into a boat structure (the cation is planar),* whereas the nonsuper-conductors do not distort. We suggested[3,4] that the coupling between charge transfer and the lowest boat deformation vibrational mode is responsible for the superconductivity. To test such ideas and to develop a more complete understanding of the mechanism for superconductivity, it is very important to know the character of the vibrational states. Such vibrational studies in the crystal will help identify the crucial electron−phonon coupling and clarify the mechanism of the supercon-ductivity. Hopefully this increased understanding can help to develop better organic superconductor materials.

Kozlov et al.[5] reported the vibrational levels of ET and deuterium substituted ET/D$_8$. Recently, Eldridge et al.[6] published extensive vibrational experiments with the isotopic
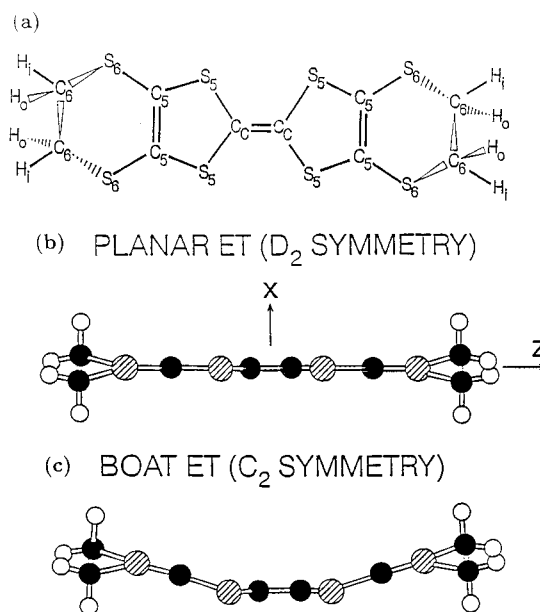

Figure 1. (a) Bis(ethylenedithio)tetrathiafulvalene (denoted as BEDT-TTF or ET). Side view for optimum structures of (b) planar and (c) boat ET.

substitutions: (i) D for all H, (ii) ^{13}C for the central carbons, (iii) ^{13}C for all the double-bond carbons, and (iv) ^{34}S for all sulfurs. Both groups made remarkable progress in identifying and assigning the vibrational modes of ET and isotopic substitutions; however, there remain many disagreements for the assignments of vibrational modes, particularly for deuterated ET. Since there are large isotopic shifts and the vibrational modes cross each other for deuterium substitutions, it is difficult to assign the corresponding modes purely from experiment. Recently, we published[7] the frequencies for ET from ab initio HF calculations and derived the MSX force field calculations to describe the experimental frequencies by Kozlov et al.[5] While

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this material was in the process of publication, newer, much more complete studies of isotopically substituted ET were published by Eldridge et al.[6] Consequently, we have reexamined all the vibrational modes of ET for all available isotopic substitutions, using ab initio quantum chemical calculations [Hartree−Fock (HF) with 6-31G** basis set] to obtain all modes of neutral ET and for the isotope shifts for these substitutions.

Generally the vibrational frequencies for HF ab initio wave functions are about 10% larger than the experimental frequencies. Thus, scaling the calculated frequencies by 0.9 makes the HF frequencies comparable with the experimental frequencies. We report here scaled HF frequencies for ET and its isotopic substitutions. We see that there is a consistent agreement between the scaled HF and the experimental frequencies. This remarkable agreement provides us with a good basis for independent assignments of the vibrational modes for ET and ET/D_8. This allowed us to propose a new set of assignments based on comparing the frequencies, assignments, and isotopic shifts from experiment with the scaled HF (from now on denoted as HF/S) frequencies, symmetries, intensities, and isotopic shifts from theory. The complete isotopic shifts for all the modes of ET should help to identify the crucial phonon mode(s) relevant to the superconductivity.

2. Calculations

Kozlov et al.[5] reported the vibrational levels of ET and for deuterium substitutions. Recently, Eldridge et al.[6] reported much more extensive vibrational experiments with isotopic substitutions: (i) D for all H, (ii) ^{13}C for the central carbons, (iii) ^{13}C for all the double-bond carbons, and (iv) ^{34}S for all sulfurs. Kozlov et al.[5] and Eldridge et al.[6] were aware that only the central C_2S_4 group of the ET is planar, but to simplify the assignments, they considered the ET to be totally flat, leading to D_{2h} symmetry with the fundamental mode distribution

$$\Gamma(D2h) = 12A_g + 7A_u + 6B_{1g} + 11B_{1u} + 7B_{2g} + 11B_{2u} + 11B_{2g} + 7B_{3u} \quad (1)$$

Parts b and c of Figure 1 show the side view of planar and boat ET structures, respectively. Ab initio quantum chemical calculations[3,4] show that *neutral ET is nonplanar*. The stable boat structure of ET has C_2 symmetry, leading to the mode distribution

$$\Gamma(C2) = 37A + 35B \quad (2)$$

The reduction of symmetry is as follows:

$$12A_g + 7A_u + 11B_{3g} + 7B_{3u} \rightarrow 37A \quad (3a)$$

and

$$11B_{1u} + 6B_{1g} + 11B_{2u} + 7B_{2g} \rightarrow 35B \quad (3b)$$

To clarify the vibrational spectrum of the neutral ET molecule, we first compared the experimental frequencies by Kozlov et al.[5] and Eldridge et al.[6] Although most of the frequencies matched numerically within the experimental resolution of 4 cm^{-1}, many assignments disagreed in the symmetry of the modes (in D_{2h}). C−H stretch modes around 2900 cm^{-1}, C−H$_2$ bend modes around 1400 cm^{-1}, and C−H$_2$ twist modes around 1150 cm^{-1}, five modes between 919 and 889 cm^{-1}, and C−H$_2$ rock modes at 687 cm^{-1} were assigned

to different symmetries for ET by Kozlov et al.[5] and Eldridge et al.[6] Almost all the modes of deuterated ET(D$_8$) from C−D stretch modes around 2200 to 600 cm^{-1} except C=C stretch modes around 1500 cm^{-1} were assigned to different symmetries by Kozlov et al.[5] and Eldridge et al.[6] From eqs 3a,b, we see that the symmetries of D_{2h} framework reduce to A and B modes, and both experimental spectra can be unified by considering the exact (C_2) symmetry of the molecule. However, we keep the D_{2h} approximation to compare with the experimental assignments.

Using the quantum mechanical Hessian,[8] we substituted the isotopic masses to obtain the vibrational modes for isotopic substitutions.[9] Table 1 shows the calculated and available experimental frequencies for neutral ET and D(8) substitutions. We report scaled frequencies, intensities, and isotopic shifts for the boat structures. Over the years, the comparison of the HF frequencies with the experimental frequencies for many molecules leads to an empirical scaling factor of 0.9. For the comparisons of the intensities and the symmetries between the HF and the experimental results, we included also the approximate D_{2h} symmetry in all tables and summed the same type (IR or Raman) of intensities of C_2 symmetry modes for the nearly degenerate pair modes such as A(A_g) and B(B_{1u}) at 2914 cm^{-1} in the HF/S spectra. By comparing the experimental frequencies, the assignments, and the isotopic shifts with HF/S frequencies, symmetries, intensities, and isotopic shifts, we propose new sets of assignments for fundamental vibrational frequencies of ET and deuterated ET frequencies in Table 1. The agreement between HF/S and experimental frequencies is very good. We used the frequencies reported by Eldridge et al.[6] when the difference between the reported frequencies by Eldridge et al.[6] and Kozlov et al.[5] is ∼5 cm^{-1}. Table 2 shows the comparisons of HF/S and the experimental frequencies by Eldridge at al.[6] for isotopic substitutions. There is a very good agreement between the experimental and the calculated frequencies for ^{13}C and ^{34}S substitutions. For these substitutions, the order of modes is usually preserved and the shifts are small. Thus, it is relatively easy to assign the modes for these substitutions. The assignments in Table 2 for ^{13}C and ^{34}S substitutions are the same as Eldridge et al.[6] except the 956 and 976 cm^{-1} modes for ^{13}C(6) substitutions. We assigned the 956 cm^{-1} mode to A(B_{3g}) and the 976 cm^{-1} mode to A(A_g) by comparing isotopic shifts. Using the calculated frequencies for the isotopic shifts, we obtained the shifts, $\Delta \nu = \nu_0 - \nu_{iso}$ in Table 3.

3. Discussion

By comparing the HF/S frequencies, symmetries, intensities, and isotopic shifts, we propose new assignments which provide an excellent match between the theory and both sets of experimental results. We account for all the reported frequencies except two modes, at 625 cm^{-1} and 860 and 827 cm^{-1}, in the neutral ET spectra. We believe these modes may be combination bands. Eldridge et al.[6] were also not certain about the last two modes.

We start with the assignments of C−H stretch modes in Table 1. We assigned the strongest Raman mode at 2920 cm^{-1} as A(A_g) and its IR partner at 2922 cm^{-1} as B(B_{1u}). Our calculated values are 2914 cm^{-1} for both. We assigned the second strongest Raman mode at 2964 cm^{-1} as A(A_u) and its IR partner at 2958 cm^{-1} as B(B_{1g}). The calculated values are 2961 cm^{-1} for both. Our calculated intensities agree with these assignments. We assigned the medium strength Raman mode at 2986 cm^{-1} as B(B_{2g}) and its IR partner at 2983 cm^{-1} as B(B_{3u}). We

TABLE 1: Calculated and Experimental Frequencies for Neutral and ET(D(8)) (Deuterium Substitutions). Calculated HF Frequencies Are for Boat (C_2 Symmetry) ET. HF/S Is 0.9 × (HF Frequencies). The Frequencies Are in cm^{-1}, IR Intensities Are in km/mol (1 km/mol = 0.023666 D^2 Å^{-2} amu^{-1}), Raman Intensities Are in Å^4 /amu. Experimental Values Are from Eldridge et al.[6] and Kozlov et al.[5] We Propose New Assignments by Comparing the Following Factors: Experimental Frequencies and Assignments, HF/S Frequencies, Symmetries, and Intensities

		ET							ET/D(8)		
		ν			HF/intensity				ν		
		exp. assignment							exp. assignment		
symmetry C_2 (D_{2h})	HF/S	this paper	Eldridge	Kozlov	IR	Raman	experiment spectra	HF/S	this paper	Eldridge	Kozlov
A (B3u)	2972	2983	2983	2958	14.88		IR, vw^{a,b}	2206	2229	2174	2237
B (B2g)	2972	2986	2986			123.11	Raman, m	2206	2233	2175	
A (Au)	2961	2964				265.90	Raman, s	2201	2175		
B (B1g)	2961	2958			0.38		IR, m	2201	2174		
A (Ag)	2914	2920	2920			610.52	Raman, vs	2121	2147	2147	
B (B1u)	2914	2922	2922	2958	79.91		IR, m	2121	2146	2146	2169
A (B3g)	2906		2964			168.19		2113		2233	
B (B2u)	2906		2958	2916	12.92			2113		2229	
A (Ag)	1634	1551	1551	1552	0.57	345.11	Raman, s	1633	1551	1551	1552
B (B1u)	1611	1509	1509	1505	1.48	0.26	IR/Raman, s	1610	1509	1509	1506
A (Ag)	1595	1493	1493	1494	0.35	509.60	Raman, vs	1594	1493	1493	1494
A (Ag)	1448	1422	1408			25.43	Raman, w	1136	1116	1116	
B (B1u)	1448	1422	1409	1420	4.13		IR, w	1136	1112	1112	1110
A (B3g)	1435	1408	1422	1409		41.63	Raman, m	1059	1029	1029	
B (B2u)	1435	1409	1422	1406	16.13		IR, s	1059	1031	1031	
A (Ag)	1319	1283	1283	1285		2.64	Raman, m	1051	1044	1044	1002 ?
B (B1u)	1319	1284	1284	1282	66.13		IR, s	1050	1042	1042	1011
A (B3g)	1290	1257	1257	1256		1.76	Raman, w	1031	1016	1016	1029
B (B2u)	1290	1261	1261	1259	6.56		IR, m	1030	1013	1013	1041
A (Au)	1189	1174	1126			18.03	Raman, m	927	936	806	
B (B1g)	1188	1174	1125	1175	0.33		IR, m	927	931	804	935
A (B3u)	1134	1126	1174	1125	4.92		IR, m	804	806	793	806
B (B2g)	1134	1125	1174	1132		14.70	Raman, w	803	804	794	805
A (B3g)	1018	1013	1013	1016	0.21	0.34	Raman, m	1010	987		984
B (B2u)	1016	997	997		7.07		IR, m	1016	990	931	990
A (B3g)	1013	1000	1000			0.61	Raman, m	1013	1018	936	1018
B (B1u)	984	992	992	996	0.04		IR, sh	873	905	987	905
A (Ag)	984	990	990	990		7.76	Raman, s	873	881	985	
A (Ag)	930	919	919	911		13.01	Raman, m	787	793	742	794
B (B1u)	930	918	918	905	24.22		IR, s	787	794	742	793
B (B2u)	896	906	906	917	12.99	1.83	IR, s	863	879	905	879
A (B3g)	891	889	889	919	5.72	0.04	Raman, vw	824		881	
B (B1g)	870	890	860 ?	938	31.60		IR, s	746	742		741
A (Au)	870		827 ?			2.58		746	742	678	
B (B2u)	855	875	875^c	875	2.29	0.28	IR, s	824	827	827^c	827
B (B2u)	762				12.03	0.13		692	693		
B (B1u)	761	771	771	772	42.37	0.02	IR, s	761	772	772	772
A (B3g)	758	764	764^c		0.17	1.96	Raman, m	690	693		
A (B3g)	683	687	687	625		17.76	Raman, m	626	634	634	610
B (B2u)	683	687	687	624	2.57		IR, m	626	635	635	609
A (Ag)	644	654	654^d	653		44.70	Raman, s	599	610	610	635
B (B1u)	644	654	654^d	653	6.72		IR, w	599	611	611	634
B (B2g)	561				4.54	11.88		560			
B (B1g)	546					5.07		543			
A (Au)	544				0.11			542			
A (Ag)	485	487	487	486	1.50	15.60	Raman, s	484	487	487	486
B (B2g)	461					2.59		414			
A (B3u)	459				1.53			411			
B (B1u)	446	500	500	499	6.24	0.43	IR, s	447	500	500	500
A (Ag)	435	440	440	440	0.01	14.54	Raman, m	434	440	440	439
B (B1u)	382	390	390	390	6.63	1.16	IR, m	380	388	388	388
B (B2u)	355	335	335	335	0.04	0.80	IR, w	340	327	327	326
A (B3g)	354	348	348	348	0.02	0.10	Raman, w	351	340	340	339
A (B3g)	345	335	335	334	0.09	8.42	Raman, w	331	326	326	323
A (Ag)	321	309	309	308	1.02	4.00	Raman, m	317	298	298	296
B (B1u)	294	277	277	278	3.16	0.17	IR, w	287	270	270	269
A (Au)	284				0.04	2.72		308	277		
B (B2u)	278				0.28	0.05		291	262		
A (B3u)	270				0.04	0.20		286	258		
B (B2u)	258	258	258	257	3.72	0.02	IR, w	254	256	256	257
A (B3u)	243				0.01	0.75		244	220		
B (B1g)	236				4.45	0.61		234	211		
A (B3g)	185	[190]	190^{c,e}	159	0.01	0.72	Raman, sh	182	156	156	155
A (Ag)	156	161	161	151	0.03	14.86	Raman, s	152	147	156	147
A (Au)	117	127	125^{c,e}		0.03	0.18	Raman, vw	116	125		
B (B1g)	116	96			0.00	0.28	Raman, m	114	88		
B (B2u)	54			30	1.14	0.87		53			30
A (Au)	48				0.16	0.19		47			
B (B2g)	39	30		127	2.71	0.37	IR/Raman, w/s	39	30		125
A (B3u)	38			96	7.24	0.26		35			88
B (B2g)	34				0.26	0.63		31			
A (B3u)	18				2.21	1.28		17			

^{a} Relative intensities, vs very strong, s strong, m medium, w weak, vw very weak, sh shoulder, br broad. ^{b} These are the spectra and the relative intensities corresponding to our assignments. ^{c} Symmetries of these modes were not assigned by Eldridge et al.[6] ^{d} These modes were assigned A(B$_{3g}$) and B(B$_{2u}$) in ref 6, but later were reassigned to A(A$_g$) and B(B$_{1u}$) in ref 10. ^{e} These observed shoulders in the spectra by Eldridge et al.[6] may be fundamental modes.

TABLE 2: Scaled HF and Experimental Frequencies for Isotopic Substitutions $^{13}C(6)$, $^{13}C(2)$, $^{34}S(8)$, and D(8). Scaling Factor for HF Frequencies Is 0.9. The Frequencies Are in cm^{-1}. Experimental Values Are from Eldridge et al.[6]

symmetry C_2 (D_{2h})	mode	ET HF/S	ET expt IR	ET expt Raman	$^{13}C(6)$ HF/S	$^{13}C(6)$ expt IR	$^{13}C(6)$ expt Raman	$^{13}C(2)$ HF/S	$^{13}C(2)$ expt IR	$^{13}C(2)$ expt Raman	$^{34}S(8)$ HF/S	$^{34}S(8)$ expt IR	$^{34}S(8)$ expt Raman	D(8) HF/S	D(8) expt IR	D(8) expt Raman
A (B3u)	C−H str.	2972	2983		2972	2983		2972	2983		2972	2983		2206	2229	
B (B2g)	C−H str.	2972		2986	2972		2986	2972		2986	2972		2986	2206		2233
A (Au)	C−H str.	2961		2964	2961		2964	2961		2964	2961		2964	2201		2175
B (B1g)	C−H str.	2961	2958		2961	2958		2961	2958		2961	2958		2201	2174	
A (Ag)	C−H str.	2914		2920	2913		2920	2913		2920	2913		2920	2121		2147
B (B1u)	C−H str.	2914	2922		2913	2922		2913	2922		2913	2922		2121	2146	
A (B3g)	C−H str.	2906			2906			2906			2906			2113		
B (B2u)	C−H str.	2906			2906			2906			2906			2113		
A (Ag)	C=C str.	1634		1551	1570		1486	1617		1522	1633		1549	1633		1551
B (B1u)	C=C str.	1611	1509		1548	1452		1610	1486		1610	1508		1610	1509	
A (Ag)	C=C str.	1595		1493	1532		1437	1547		1465	1594		1493	1594		1494
A (Ag)	CH$_2$ bend	1448		1422	1447			1447		1422	1447		1422	1136		1116
B (B1u)	CH$_2$ bend	1448	1422		1447			1447			1447	1423		1136	1112	
A (B3g)	CH$_2$ bend	1435		1408	1435		1408	1435		1408	1435		1408	1059		1029
B (B2u)	CH$_2$ bend	1435	1409		1435	1409		1435	1408		1435	1409		1059	1031	
A (Ag)	CH$_2$ wag	1319		1283	1319		1283	1319		1283	1319		1283	1051		1044
B B(1u)	CH$_2$ wag	1319	1284		1319	1284		1319	1283		1319	1283		1050	1042	
A (B3g)	CH$_2$ wag	1290		1257	1290		1257	1290		1258	1290		1257	1031		1016
B (B2u)	CH$_2$ wag	1290	1261		1290	1261		1290	1261		1290	1261		1030	1013	
A (Au)	CH$_2$ twist	1189		1174	1188		1174	1188		1174	1188		1174	927		936
B (B1g)	CH$_2$ twist	1188	1174		1188	1173		1188	1172		1188	1173		927	931	
A (B3u)	CH$_2$ twist	1134	1126		1134	1126		1134	1126		1134	1126		803	806	
B (B2g)	CH$_2$ twist	1134		1125	1134		1125	1134		1125	1134		1125	804		804
A (B3g)	ring def. (I.P.)^a	1018		1013	985		1000	1015		1011	1014		1012	1010	987	985
B (B2u)	ring def. (I.P.)	1016	997		985	963		1013	994		1014	996		1016		
A (B3g)	ring def. (I.P.)	1013		1000	981		956	985		965	1011		999	1013		
B (B1u)	C-C str.	984	992		977			984			983	989		873	905	
A (Ag)	C-C str.	984		990	975		976	982		996	983		987	873		881
A (Ag)	CH$_2$ rock	930		919	929		917	929		919	928		917	787		794
B (B1u)	CH$_2$ rock	930	918		928	917		929	918		928	917		787	793	
B (B2u)	CH$_2$ wag	896	906		891	884		895	905		893	903		863	879	
A (B3g)	CH$_2$ wag	891		889	887		883	890		888	889		886	824		
B (B1g)	ring def. (I.P.)	870	890		843	878		869	889		866	887		746	742	
A (Au)	ring def. (I.P.)	870			843			869			865			746		742
B (B2u)	ring def. (I.P.)	855	875		831	848		831	874		850	871		824	827	
B (B2u)	ring def. (I.P.)	762			743			760			757			692	693	
B (B1u)	ring def. (I.P.)	761	771		739	748		737	748		756	767		761	772	
A (B3g)	ring def. (I.P.)	758		764^c	737		747	757		763	754		759	690		693
A (B3g)	CH$_2$ rock	683		687	682		687	683		687	677		680	626		634
B (B2u)	CH$_2$ rock	683	687		682	687		682	687		676	681		626	635	
A (Ag)	CH$_2$ rock	644		654	644		654	644		654	638		648	599		610
B (B1u)	CH$_2$ rock	644	654		644	653		644	654		638	648		599	611	
B (B2g)	ring def. (O.P.)^b	561			542			545			559			560		
B (B1g)	ring def. (O.P.)	546			526			544			545			543		
A (Au)	ring def. (O.P.)	544			524			542			543			542		
A (Ag)	ring def. (O.P.)	485		487	483		486	483		487	471		474	484		487
B (B2g)	ring def. (O.P.)	461			460			460			454			414		
A (B3u)	ring def. (O.P.)	459			458			459			453			411		
B (B1u)	ring def. (O.P.)	446	500		444	487		444	486		435	497		447	500	
A (Ag)	ring def. (O.P.)	435		440	434		440	434		440	422		428	434		440
B (B1u)	ring def. (O.P.)	382	390		380	388		380	388		372	381		380	388	
B (B2u)	ring def. (O.P.)	355	335		354	330		354	335		347	331		340	327	
A (B3g)	ring def. (O.P.)	354		348	352		347	352		347	344		339	351		340
A (B3g)	ring def. (O.P.)	345		335	343		329	344		334	337		329	331		326
A (Ag)	ring def. (O.P.)	321		309	317		308	319		309	315		303			298
B (B1u)	ring def. (O.P.)	294	277		293	278		293	276		288	275		287	270	
A (Au)	ring def. (O.P.)	284			280			282			281			277		
B (B2g)	ring def. (O.P.)	278			273			278			276			262		
A (B3u)	ring def. (O.P.)	270			264			265			268			258		
B (B2u)	ring def. (O.P.)	258	258		255	256		257	258		252	253		254	256	
A (B3u)	ring def. (O.P.)	243			237			242			241			220		
B (B1g)	ring def. (O.P.)	236			232			236			235			211		
A (B3g)	ring def. (O.P.)	185	[190]^{c,d}		184			185			181			182		
A (Ag)	ring def. (O.P.)	156		161	155		160	156		161	153		159	152		156
A (Au)	ring def. (O.P.)	117		127^e	117			117			114			116		125^e
B (B1g)	ring def. (O.P.)	116	96		116			116			113			114	88	
B (B2u)	ring def. (O.P.)	54			54			54			53			53		
A (Au)	ring def. (O.P.)	48			48			48			47			47		
B (B2g)	ring def. (O.P.)	39			39			39			38			39		
A (B3u)	ring def. (O.P.)	38	31^e	30^e	38			38			37			35	30^e	30^e
B (B2g)	ring def. (O.P.)	34			34			34			34			31		
A (B3u)	ring def. (O.P.)	18			18			18			17			17		

^{a} In-plane ring deformation mode. ^{b} Out-of-plane ring deformation mode. ^{c} Symmetries of these modes were not assigned by Eldridge et al.[6] ^{d} These observed shoulders in the spectra by Eldridge et al.[6] may be fundamental modes. ^{e} These frequencies are from Kozlov et al.[5]

TABLE 3: Isotopic Shifts, Δν, for Scaled HF and Experimental Frequencies for the Substitutions ^{13}C(6), ^{13}C(2), ^{34}S(8), and D(8). Scaling Factor for HF Frequencies Is 0.9. The Frequencies Are in cm^{-1}

symmetry C_2 (D_{2h})	ET ν		^{13}C(6) Δν		^{13}C(2) Δν		^{34}S(8) Δν		D(8) Δν	
	HF/S	expt	HF/S	expt	HF/S	expt	HF/S	expt	HF/S	expt
A (B3u)	2972	2983	0	0	0	0	0	0	766	754
B (B2g)	2972	2986	0	0	0	0	0	0	767[a]	753
A (Au)	2961	2964	0	0	0	0	0	0	760	789
B (B1g)	2961	2958	0	0	0	0	0	0	760	784
A (Ag)	2914	2920	0	0	0	0	0	0	792	773
B (B1u)	2914	2922	0	0	0	0	0	0	792	776
A (B3g)	2906		0		0		0		793	
B (B2u)	2906		0		0		0		793	
A (Ag)	1634	1551	64	65	17	29	1	2	1	0
B (B1u)	1611	1509	63	57	1	23	1	1	1	0
A (Ag)	1595	1493	62[a]	56	47	28	1	0	1	+1[b] (0)[c]
A (Ag)	1448	1422	0		0	0	0	0	311	306
B (B1u)	1448	1422	0		0		0	+1	311	310
A (B3g)	1435	1408	0	0	0	0	0	0	376	379
B (B2u)	1435	1409	0	0	0	1	0	0	376	378
A (Ag)	1319	1283	0	0	0	0	0	0	269	239
B (B1u)	1319	1284	0	0	0	1	0	1	268	242
A (B3g)	1290	1257	0	0	0	+1	0	0	259	241
B (B2u)	1290	1261	0	0	0	0	0	0	261	248
A (Au)	1189	1174	0	0	0	0	0	0	261	238
B (B1g)	1188	1174	0	1	0	2	0	1	261	243
A (B3u)	1134	1126	0	0	0	0	0	0	331	320
B (B2g)	1134	1125	0	0	0	0	0	1	331	321
A (B3g)	1018	1013	33	13	3	2	3	1	7	26
B (B2u)	1016	997	31	34	3	3	2	1	0	
A (B3g)	1013	1000	32	44	28	35	2	1	0	
B (B1u)	984	992	7		0		1	3	111	87
A (Ag)	984	990	9	14	2	+6	1	3	111	109
A (Ag)	930	919	1	2	0	0	1	2	143	125
B (B1u)	930	918	1	1	0	0	1	1	143	125
B (B2u)	896	906	5	22	1	1	3	3	33	27
A (B3g)	891	889	4	6	1	2	2	3	67	
B (B1g)	870	890	27	12	1	1	5	3	125	148
A (Au)	870		28		1		5		124	
B (B2u)	855	875	25	27	24	1	6	4	31	48
B (B2u)	762		19		2		5		70	
B (B1u)	761	771	22	23	24	23	5	4	0	+1 (0)
A (B3g)	758	764[d]	21	17	1	1	5	5	68	71
A (B3g)	683	687	1	0	0	0	7	7	57	53
B (B2u)	683	687	1	0	1	0	7	6	57	52
A (Ag)	644	654	1	0	0	0	6	6	45	44
B (B1u)	644	654	1	1	0	0	6	6	45	43
B (B2g)	561		19		15		2		0	
B (B1g)	546		20		2		1		3	
A (Au)	544		20		3		1		3	
A (Ag)	485	487	2	1	1	0	14	13	1	0
B (B2g)	461		1		1		6		47	
A (B3u)	459		1		0		6		48	
B (B1u)	446	500	2	3	2	14	12	3	+1	0 (+1)[c]
A (Ag)	435	440	1	0	1	0	12	12	1	0
B (B1u)	382	390	2	2	2	2	10	9	2	2
B (B2u)	355	335	1	5	1	0	8	4	15	8
A (B3g)	354	348	2	1	1	1	9	9	2	8
A (B3g)	345	335	2	6	1	1	7	6	13	9
A (Ag)	321	309	4	1	2	0	6	6	4	11
B (B1u)	294	277	1	+1	1	1	6	2	7	7
A (Au)	284		4		1		3		7	
B (B2g)	278		4		0		1		16	
A (B3u)	270		6		5		2		12	
B (B2u)	258	258	3	2	1	0	5	5	4	2
A (B3u)	243		6		1		2		23	
B (B1g)	236		4		0		2		26	
A (B3g)	185	[190][d,e]	1		0		4		3	
A (Ag)	156	161	1	1	0	0	3	2	4	5
A (Au)	117	127	0		0		3		1	2
B (B1g)	116	96	0		0		3		2	8
B (B2u)	54		0		0		1		2	
A (Au)	48		0		0		1		1	
B (B2g)	39	30	0		0		1		0	0
A (B3u)	38		0		0		1		3	
B (B2g)	34		0		0		0		3	
A (B3u)	18		0		0		0		1	

[a] 1 cm^{-1} differences between Δν obtained from Table 2 and Δν in Table 3 for some modes are due to rounding off the decimal points. [b] + sign shows the frequency increases for the isotopic substitution. [c] The shifts in the parentheses are from Kozlov et al.[5] [d] Symmetries of these modes were not assigned by Eldridge et al.[6] [e] These observed shoulders in the spectra by Eldridge et al.[6] may be fundamental modes.

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calculated these modes at 2972 cm^{-1} with intensities roughly consistent with the experiment. ET/D(8) modes were assigned by obtaining best fits between HF/S and experimental isotopic shifts. The medium Raman mode at 1408 cm^{-1} is assigned to the A(B$_{3g}$) mode calculated at 1435 cm^{-1}, and the strong IR partner at 1409 cm^{-1} is assigned to the B(B$_{2u}$) mode calculated at 1435 cm^{-1}. Consequently, the 1422 cm^{-1} modes were assigned to the other C−H$_2$ bend modes with A(A$_g$) and B(B$_{1u}$) symmetries. The good match between the experimental and HF/S isotopic shifts supports these assignments. All the modes between 1284 and 918 cm^{-1} were clearly assigned by comparing the symmetries, intensities, and isotopic shifts. The following five modes between 906 and 827 cm^{-1} are difficult to assign since the comparisons between HF/S experimental intensities and isotopic shifts appear not to be clear for these modes. We assigned the 906 cm^{-1} mode to one of the strong IR mode and the 889 cm^{-1} mode to the next HF/S A(B$_{3g}$) mode. We believe the 860 and 827 cm^{-1} modes are not fundamental, and the experimental assignments were also uncertain. We assigned the strong IR mode at 890 cm^{-1} as B(B$_{1g}$) with calculated value 870 cm^{-1} and the medium IR mode at 875 cm^{-1} as B(B$_{2u}$) with calculated value 855 cm^{-1}. The 771 cm^{-1} B(B$_{1u}$) and 764 cm^{-1} A(B$_{3g}$) modes were assigned by obtaining a good match between the HF/S and the experimental isotopic shifts and intensities. Three sets of pair modes around 625, 654, and 687 cm^{-1} were reported by Kozlov et al.[5] and Eldridge et al.[6] However, we obtained only two pairs of modes at 644, 683 cm^{-1} from HF/S results. Comparing the symmetries, the intensities, and the isotopic shifts, we assign them to the experimental frequencies 654, 687 cm^{-1}. We believe that the 625 cm^{-1} mode may be a combination band. The modes between 500 and 258 cm^{-1} were easily assigned by matching the symmetries and intensities. The strong Raman intensity 161 cm^{-1} mode was assigned as A(A$_g$) with the calculated value 156 cm^{-1}. The experimental spectra by Eldridge et al.[6] contain shoulders around 125 and 190 cm^{-1}. These modes may be fundamental modes, and there are some possible corresponding modes in the HF/S spectra. We assigned these low-frequency modes by obtaining the best fit of the isotopic shifts and the intensities between HF/S and the experimental results for ET and ET/D(8).

4. Summary

We reported and compared frequencies for *all vibrational modes* for neutral ET and the substitutions: (i) D for all H, (ii) ^{13}C for the central carbons, (iii) ^{13}C for all the double-bond carbons, and (iv) ^{34}S for all sulfurs. By comparing experimental frequencies, assignments, and isotopic shifts with the scaled HF frequencies, symmetries, intensities, and isotopic shifts, we propose new sets of assignments for fundamental vibrational frequencies of ET and for isotopic substitutions. The agreement between the theoretical and experimental frequencies and isotopic shifts is excellent. These results should be useful in identifying the vibrational states responsible for the superconductivity of these systems.

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