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Theoretical Studies on Phonon Spectra of High Temperature Tl-Ba-Ca-Cu-O Superconductors

A. Punitha[1], Sujin P. Jose[2*] and S. Mohan[3]

[1,2]Vickram College of Engineering, Enathi 630 561, Tamil Nadu, India
[3]Prist University, Thanjavur, Vallam 613 403, Tamil Nadu, India

*Corresponding author: suja@vickramce.org

Abstract: *Strong electron-phonon coupling may be one of the origins of the high T_c superconductor. Thus, knowledge and understanding concerning phonons in these materials are essential. To investigate phonon spectra, Raman and infrared spectra of these systems have been studied; however, there are a few reports available in the literature with complete Raman and infrared absorption spectra. Due to the nature of these superconductive materials, it is not possible to experimentally obtain all of the phonon frequencies through Raman and infrared spectra. Therefore, a theoretical evaluation of the phonon frequencies of high temperature superconductors becomes important. Due to strong, covalent nature of the bonding in high temperature superconductors, a normal coordinate analysis using Wilson's FG matrix was applied herein to evaluate the phonon frequencies of Tl-Ba-Ca-Cu-O. Calculations of lattice dynamics were also performed using the modified three-body-force shell model. The various interactions between ions were treated in a general way without making them numerically equal. These calculations yielded the zone centre phonon modes and potential energy distributions that helped to identify the pure and mixed frequencies. Thus, the present approach is useful not only to obtain all of the phonon frequencies of the high temperature Tl-Ba-Ca-Cu-O superconductor but also to characterise it. The vibrational frequencies and the potential energy distribution (PED) of the optically active phonon modes are also presented.*

Keywords: high temperature, superconductors, phonon, Raman spectra, infrared spectra

1. INTRODUCTION

Due to the significant potential for applications in superconductivity, a number of interesting studies has been performed in recent years. A variety of rare earth substitutions, such as La-Ba-Cu-O or Y-Ba-Cu-O, led to the discovery of a new superconducting family by Hermann et al.[1,2] in the system A_{111}-B_{11}-Cu-O, where A_{111} is a rare earth element and B_{11} is Ca, Sr or Pb. Thallium cuprates belonging to superconducting families were shown to form two analogous series represented by the formulae $Tl_2Ca_{n-1}A_2Cu_nO_{2n+4}$ and $TlCa_{n-1}A_2Cu_nO_{2n+3}$ (A = Ba, Sr). Various members of these two series up to n = 5 have been observed using electron microscopy. The superconducting transition temperature increases as 'n' increases in both series up to n = 3. A maximum T_c of 125 K has been observed for in phase $Tl_2Ca_2Ba_2Cu_3O_{10}$.[3] In all of these phases, the transition temperature depends considerably on the oxygen stoichiometry and the Tl content. However, in a given series of these Tl cuprates prepared under identical conditions, the transition temperature depends on the hole concentration that is simply defined by the excess charge on the CuO_2 sheets. The origin of holes in these two series is different. In the present understanding, the holes in the bi-layer series are generated by the overlap of the Bi 6s band with the Cu 3d band. However, in the single Tl layer series, the Tl 6s and Cu 3d bands are well-separated. Cation vacancies, cation disorder and oxygen non-stoichiometry may also play a role in the generation of holes.

The structure of the Tl system is built via the inter-growth of perovskite and rock salt structures. Single or double thallium layer materials contain the perovskite-like units $Ba_2Can_{-1}Cu_nO_{2n+2}$ that alternate with either single TlO or double TlO sheets, which are formed by edge sharing TlO_6 octahedra. This series of compounds includes several two dimensional CuO_2 layers between TlO layers. The n = 1 compound has an octahedral CuO_6 block, and the n = 2 compound has two pyramidal CuO_4 blocks.

Thallium cuprates are more symmetric in structure and free from structural modulations and stacking faults than bismuth systems. Although Tl systems and Bi systems are similar in possessing layers of perovskite structure, the Tl system is unique in having both TlO single and double layers, whereas the Bi system exists as only BiO double layer compounds. The layer sequence of the well-studied Tl 2212 or 2201 structures is $(TlO)_m$-(BaO)-(CuO_2)-Ca-(CuO_2)-……….Ca-(CuO_2)-(BaO)-$(TlO)_m$-. A comparison between compounds based on Tl-2212 and Bi-2212 showed interesting, characteristic bond lengths along the c-axis. The TlO double layer block along the c-axis is more compact than the BiO double layer block. Inter-layer bond lengths for Tl-O are approximately 2.0 Å whereas those of Bi-O are 3.7 Å. Moreover, the bond length between Cu and an apical oxygen in the Tl-based compounds is longer than that in the Bi compounds, which may be related to the slightly higher T_c exhibited by the Tl-based superconductors in comparison to that of the iso-structural Bi-based superconductors.[4]

Stoichiometric La_2CuO_4 is not a superconductor under ambient conditions (superconduction may be produced via plasma oxidation) because the presence of 2 x La^{3+} and 4 x O^{2-} requires that all of the copper exist as Cu^{2+} for charge balance. However, high temperature superconductivity requires additional electron/holes (formally, Cu^{2+}), and the T_c increases as the number of holes increases up to a certain limit. Thus, for La_2CuO_4 to become superconducting, either additional oxygen is needed (some La^{3+} must be replaced by Sr^{2+}) or another method must be employed to chemically oxidise the material. Similarly, stoichiometric Sr_2CuO_4TlO is not a superconductor. Again, based on the valence of 2 x Sr^{2+}, 1 x Tl^{3+} and 5 x O^{2-}, all of the copper must be in 3+ valence state for charge balance. Consequently, to induce superconductivity, either some oxygen must be removed (some Sr^{2+} must be replaced by La^{3+}) or another method must be employed to chemically reduce the material. However, the second member of the Tl series, the double TlO layer series (similar to $YBa_2Cu_3O_7$), is naturally superconducting because successive members of the series were obtained by adding Cu^{2+} as $Ca^{2+}Cu^{2+}O_2^{2-}$.

$YBa_2Cu_3O_7$ was the first superconductor for which copper appears to have mixed valence without the need for doping. Assuming valences of Y^{3+}, Ba^{2+} and O^{2-}, the copper in $YBa_2Cu_3O_7$ formally exists as Cu^{2+} and Cu^{3+}. When this material is reduced to $YBa_2Cu_3O_6$ via removal of oxygen from the CuO chains, superconductivity is lost. The valence of Y^{3+} and Ba^{2+} cannot be reduced in $YBa_2Cu_3O_7$, so copper must be formally reduced to Cu^{2+} and Cu^{1+}, with loss of the mixed valence of Cu^{2+} and Cu^{3+} necessary for superconductivity. Similarly, assuming valences of Ca^{2+}, 2 x Ba^{2+}, Tl^{3+} and 7 x O^{2-}, the formula for $Ca_1Ba_2Cu_2O_6TlO$ implies that copper should naturally be of Cu^{2+} and Cu^{3+} mixed valence, and the material should be superconducting. Reduction, which is necessary for superconductivity in the first member of the single TlO layer series, might instead be expected to reduce superconductivity in this second member of the series. Thus, in general, the redox conditions during preparation will have a profound effect on the superconductivity of these materials.

A normal coordinate calculation of the Raman and infrared active modes of four Tl-based high temperature superconductors, i.e., $Tl_2Ba_2CuO_6$ (2:0:2:1:6) and $Tl_2Ca_2Ba_2Cu_3O_{10}$ (2:2:2:3:10) with body-centred tetragonal structures (bct, space group I_4/mmm) and $TlCaBa_2Cu_2O_7$ (1:1:2:2:7) and $TlCa_3Ba_2Cu_4O_{11}$ (1:3:2:4:11) with simple tetragonal structures (St, space group P_4/mmm) have been attempted in the present work for the first time.

From group theoretical considerations, the optical modes involved in an irreducible representation for the above compounds are as follows:

(i) 2:0:2:1:6 system
$\Gamma = 4A_{1g}\,(R) + 4E_g\,(R) + 5A_{2u}\,(IR) + 1B_{2u}\,(IR) + 6E_u\,(IR)$

(ii) 2:2:2:3:10 system
$\Gamma = 7A_{1g}\,(R) + 1B_g\,(R) + 8E_g\,(R) + 8A_{2u}\,(IR) + 2B_{2u}\,(IR) + 10E_u\,(IR)$

(iii) 1:1:2:2:7 system
$\Gamma = 4A_g\,(R) + 1B_g\,(R) + 5E_g\,(R) + 6A_{2u}\,(IR) + 1B_{2u}\,(IR) + 7E_u\,(IR)$

(iv) 1:3:2:4:11 system
$\Gamma = 7A_{1g}\,(R) + 2B_{1g}\,(R) + 9E_g\,(R) + 9A_{2u}\,(IR) + 2B_{2u}\,(IR) + 11E_u\,(IR)$

2. EXPERIMENTAL

A previously cited method[5–7] was used to evaluate the phonon frequencies of the thallium high temperature superconductors $Tl_2Ba_2CuO_6$, $Tl_2Ca_2Ba_2Cu_3O_{10}$, $TlCaBa_2Cu_2O_7$ and $TlCa_3Ba_2Cu_4O_{11}$. A simple valence force under Wilson's FG matrix method was used for this purpose. In the present work, we started with a more general approach in the framework of the three-body-force shell model (TSM) with $R \neq S \neq T$ to calculate the lattice dynamics frequencies. The values of the phonon frequencies calculated herein at the zone centre using the TSM are in good agreement with the available Raman and infrared values. Furthermore, a normal coordinate analysis was also attempted for the superconductor $TlCa_3Ba_2Cu_4O_{11}$ using Wilson's FG matrix method for confirmation of our present study. The vibrational frequencies and the potential energy distribution (PED) of the optically active modes are also reported.

Tables 1, 2, 3 and 4 summarise the bond lengths and force constants used in the present work for evaluating the phonon frequencies for the thallium 2:0:2:1:6, 2:2:2:3:10, 1:1:2:2:7 and 1:3:2:4:11 systems, respectively. A complete phonon spectrum derived from the two different methods along with the observed frequencies[8,9] and the potential energy distributions are given in Tables 5, 6, 7 and 8 for the 2:0:2:1:6, 2:2:2:3:10, 1:1:2:2:7 and 1:3:2:4:11 systems, respectively. The normal coordinate analysis calculations reproduce the observed frequencies of the Raman active modes reasonably well.

Table 1: Bond distance and force constants* for $Tl_2Ba_2CuO_6$.

Force constants	Bond type	Distance (Å)	Initial values of potential constants
f_b	Ba-O(1)	2.798	0.75
f_c	Ba-O(2)	2.819	1.10
f_d	Ba-O(3)	2.851	0.81
f_e	Tl-O(2)	2.003	0.30
f_g	Tl-O(3)	2.097	0.30
f_h	Tl-O(3)	3.108	0.61
f_k	Tl-O(3)	2.402	0.48
f_l	Cu-O(1)	1.932	0.145
f_m	Cu-O(2)	2.648	1.65
f_n	Tl-O(3)-Tl	-	0.31
f_p	O(1)-Cu-O(1)	-	0.25
f_α	Tl-O(2)-Ba	-	0.46
f_β	O(2)-Tl-O(3)	-	0.80

*Units of 10^2 Nm^{-1} for stretching and 10^{-18} Nm rad^{-2} for bending modes.

Table 2: Bond lengths and force constants* for $Tl_2Ca_2 Ba_2Cu_3O_{10}$.

Force constants	Bond type	Distance (Å)	Initial values of potential constants*
f_a	Ca-O(1)	2.410	1.10
f_b	Ca-O(2)	2.467	1.08
f_c	Cu(1)-O(1)	1.945	1.44
f_d	Cu(1)-O(2)	1.827	1.62
f_e	Cu(2)-O(3)	1.930	1.47
f_g	Cu(2)-O(4)	1.964	1.38
f_h	Cu(2)-O(2)	2.332	1.09
f_k	Ba-O(1)	2.911	0.70
f_l	Ba-O(2)	2.753	1.16
f_m	Ba-O(3)	2.945	0.84
f_n	Ba-O(4)	2.845	0.98
f_p	Tl-O(2)	2.030	0.70
f_q	Tl-O(3)	2.098	0.75
f_r	Tl-O(4)	3.103	0.64
f_s	O(1)-Cu(1)-O(2)		0.99
f_t	O(1)-Cu(2)-O(4)		1.01
f_u	Tl-O(2)-Ba		0.41
f_v	O(2)-Tl-O(3)		0.76

*Units of 10^2 Nm^{-1} for stretching and 10^{-18} Nm rad^{-2} for bending modes.

Table 3: Bond lengths and force constants* for $TlCaBa_2Cu_2O_7$.

Force constants	Bond type	Distance (Å)	Initial values of potential constants*
f_a	Ca-O(1)	2.467	1.08
f_b	Ba-O(1)	2.822	0.78
f_c	Ba-O(2)	2.804	1.10
f_d	Ba-O(3)	2.801	0.81
f_e	Tl-O(2)	2.030	0.70
f_g	Tl-O(3)	2.098	0.71
f_h	Tl-O(4)	3.103	0.64
f_k	Cu(2)-Cu(2)	3.405	0.50
f_l	Cu-O(1)	1.932	0.16

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Table 3: *(continued)*

Force constants	Bond type	Distance (Å)	Initial values of potential constants*
f_m	Cu-O(2)	2.610	1.59
f_n	Tl-O(3)-Tl	-	0.35
f_p	O(1)-Cu-O(1)	-	0.28
f_α	Tl-O(2)-Ba	-	0.41
f_β	O(2)-Tl-O(3)	-	0.76

*Units of 10^2 Nm^{-1} for stretching and 10^{-18} Nm rad^{-2} for bending modes.

Table 4: Bond lengths and force constants* for $TlCa_3Ba_2Cu_4O_{11}$.

Force constants	Bond type	Distance (Å)	Initial values of potential constant*
f_a	Ca-O(1)	2.410	1.10
f_b	Ca-O(2)	2.467	1.08
f_c	Cu(1)-O(1)	1.945	1.44
f_d	Cu(1)-O(2)	1.827	1.62
f_e	Cu(2)-O(3)	1.930	1.47
f_g	Cu(2)-O(4)	1.964	1.38
f_h	Cu(2)-O(2)	2.332	1.09
f_k	Ba-O(1)	2.911	0.70
f_l	Ba-O(2)	2.753	1.16
f_m	Ba-O(3)	2.945	0.84
f_n	Ba-O(4)	2.845	0.98
f_p	Tl-O(2)	2.030	0.70
f_q	Tl-O(3)	2.098	0.75
f_r	Tl-O(4)	3.103	0.64
f_s	O(1)-Cu(1)-O(2)	-	0.99
f_t	O(1)-Cu(2)-O(4)	-	1.01
f_u	Tl-O(2)-Ba	-	0.41
f_v	O(2)-Tl-O(3)	-	0.76

*Units of 10^2 Nm^{-1} for stretching and 10^{-18} Nm rad^{-2} for bending modes.

Table 5: Phonon frequencies of $Tl_2Ba_2CuO_6$.

Symmetry species	Frequency (cm^{-1})			Potential energy distribution (%)*
	Using lattice dynamics	Using normal coordinate analysis	Observed	
A_{1g} (Raman)	130	117	125	$f_\beta(61)f_d(21)f_k(11)$
	159	158	165	$f_c(64)f_l(28)$
	470	474	485	$f_l(71)f_d(12)f_p(11)$
	617	620	603	$f_h(68)f_k(20)f_c(10)$
E_g (Raman)	98	102	–	$f_c(68)f_e(12)f_\beta(10)$
	139	151	–	$f_m(71)f_i(21)$
	385	392	–	$f_l(46)f_m(27)f_c(11)$
	496	490	–	$f_l(44)f_g(31)f_n(12)$
A_{2u} (IR)	101/98	106	–	$f_n(71)f_\alpha(16)$
To/Lo	125/141	135	–	$f_m(65)f_k(20)f_d(11)$
	299/315	305	–	$f_g(81)f_e(16)$
	428/450	444	–	$f_p(56)f_n(29)$
	615/632	621	–	$f_p(60)f_\beta(18)f_n(11)$
B_{2u} (IR)	260	262	–	$f_p(54)f_n(26)f_e(15)$
E_u (IR)	85/87	97	–	$f_n(71)f_c(15)$
To/Lo	160/172	171	–	$f_m(68)f_e(22)$
	315/330	333	–	$f_p(49)f_d(16)f_c(24)$
	391/409	398	–	$f_p(51)f_e(14)f_k(18)$
	436/450	448	–	$f_p(60)f_b(11)f_k(14)$
	561/569	572	–	$f_\beta(64)f_p(26)$

*Only contributions greater than 10% are included.

Table 6: Phonon frequencies of $Tl_2Ca_2Ba_2Cu_3O_{10}$.

Symmetry species	Frequency (cm^{-1})			Potential energy distribution (%)*
	Using lattice dynamics	Using normal coordinate analysis	Observed	
A_{1g} (Raman)	108	112	99	$f_h(56)f_c(22)f_d(12)$
	131	128	133	$f_n(62)f_k(26)f_c(16)$
	152	146	159	$f_c(49)f_m(30)f_e(19)$
	277	290	270	$f_s(58)f_v(20)f_a(10)$
	411	420	401	$f_t(64)f_b(11)f_s(14)$
	490	481	498	$f_c(71)f_d(14)$
	608	605	601	$f_g(69)f_h(28)$
	256	251	245	$f_s(44)f_t(32)$
E_g (Raman)	68	71	–	$f_m(49)f_c(15)f_b(15)$
	140	142	–	$f_c(52)f_b(18)f_k(20)$
	152	148	–	$f_u(63)f_p(20)f_r(11)$
	260	262	–	$f_s(66)f_t(22)f_v(12)$
	384	385	–	$f_u(54)f_v(29)$
	431	421	–	$f_h(59)f_k(11)f_p(10)$
	501	500	–	$f_g(71)f_c(15)$
	572	565	–	$f_d(73)f_b(22)$
A_{2u} (IR)	75/108	81	–	$f_r(42)f_d(24)f_e(21)$
To/Lo	111/132	116	–	$f_n(48)f_q(29)$
	161/159	160	–	$f_n(51)f_h(29)$
	184/197	187	–	$f_s(60)f_t(14)f_d(15)$
	296/364	299	–	$f_v(52)f_a(16)f_s(13)$
	389/411	395	–	$f_s(64)f_t(21)f_b(12)$
	448/452	452	–	$f_b(69)f_d(15)f_k(11)$
	586/604	589	–	$f_c(72)f_l(10)f_q(10)$
B_{2u} (IR)	141	140	–	$f_s(51)f_t(25)f_u(15)$
	320	311	–	$f_t(49)f_s(29)f_v(22)$
E_u (IR)	75/81	79	–	$f_e(56)f_u(33)$

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Table 6: *(continued)*

Symmetry species	Frequency (cm^{-1})			Potential energy distribution (%)*
	Using lattice dynamics	Using normal coordinate analysis	Observed	
To/Lo	104/110	112	–	$f_n(59)f_t(20)f_e(10)$
	149/154	138	–	$f_n(64)f_s(15)f_v(10)$
	261/268	264	–	$f_s(55)f_n(25)f_u(15)$
	362/366	354	–	$f_t(51)f_b(14)f_k(16)$
	387/402	411	–	$f_a(63)f_s(21)f_v(18)$
	405/452	389	–	$f_t(66)f_u(19)f_v(22)$
	461/472	468	–	$f_c(73)f_k(14)f_s(10)$
	555/561	557	–	$f_d(80)f_p(10)f_t(10)$
	568/587	581	–	$f_g(69)f_n(12)f_r(13)$

*Only contributions greater than 10% are included.

Table 7: Phonon frequencies of $TlCaBa_2Cu_2O_7$.

Symmetry species	Frequency (cm^{-1})			Potential energy distribution (%)*
	Using lattice dynamics	Using normal coordinate analysis	Observed	
A_{1g} (Raman)	109	111	120	$f_c(58)f_d(24)f_a(11)$
	155	155	148	$f_c(61)f_l(26)$
	370	361	–	$f_l(65)f_d(15)$ $f_p(16)$
	520	518	525	$f_a(61)f_\alpha(29)$
B_{1g} (Raman)	271	288	278	$f_a(52)f_k(19)f_\alpha(17)$
E_g (Raman)	65	–	–	$f_c(61)f_e(16)f_\beta(10)$
	126	131	–	$f_m(70)f_l(18)f_\beta(10)$
	340	333	–	$f_a(49)f_g(29)$ $f_n(11)$
	380	386	–	$f_\beta(51)f_k(18)$ $f_g(19)$
	561	560	–	$f_n(64)f_h(20)$ $f_m(14)$
A_{2u} (IR)	69/97	75	–	$f_n(74)f_\alpha(12)$
To/Lo	128/134	138	–	$f_m(61)f_k(18)f_d(12)$
	215/221	209	–	$f_a(80)f_e(14)$
	364/400	355	–	$f_p(60)f_\beta(14)f_n(19)$
	418/438	429	–	$f_\beta(40)f_p(24)f_m(20)$
	515/572	525	–	$f_\alpha(48)f_n(26)f_p(21)$

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Table 7: *(continued)*

Symmetry species	Frequency (cm^{-1})			Potential energy distribution (%)*
	Using lattice dynamics	Using normal coordinate analysis	Observed	
B_{2u} (IR)	201	210	–	f_p(51)f_n(21)f_e(19)
E_u (IR)	70/78	84	–	f_b(64)f_c(14)f_d(12)
To/Lo	101/109	115	–	f_a(71)f_e(20)
	255/245	258	–	f_a(55)f_e(18)f_k(10)
	360/372	368	–	f_β (60)f_p(22)f_α(11)
	425/433	402	–	f_n(61)f_α(28)
	484/451	448	–	f_d(44)f_β(21)f_c(11)
	578/562	588	–	f_e(51)f_n(21)f_α(20)

To/Lo corresponds to frequencies of the transverse optical and longitudinal modes. *Only contributions greater than 10% are included.

Table 8: Phonon frequencies of $TlCa_3Ba_2Cu_4O_{11}$.

Symmetry species	Frequency (cm^{-1})		Potential energy distribution (%)*
	Using lattice dynamics	Using normal coordinate analysis	
A_{1g} (Raman)	105	102	f_h(59)f_c(25)f_d(15)
	130	126	f_n(61)f_k(24)f_c(18)
	146	141	f_c(51)f_m(25)f_e(19)
	274	242	f_d(49)f_v(22)f_a(15)
	369	362	f_u(51)f_v(33)
	440	452	f_t(61)f_b(10)f_s(14)
	521	508	f_c(72)f_d(15)
B_{1g} (Raman)	245	201	f_s(41)f_t(38)
	296	302	f_s(46)f_t(21)f_v(15)
E_g (Raman)	65	68	f_m48)f_c(20)f_b(20)
	109	111	f_n(49)f_q(32)
	126	138	f_u(61)f_p(21)f_n(15)
	275	256	f_s(67)f_t(20)f_v(11)
	340	360	f_u(55)f_v(30)
	380	384	f_v(59)f_u(16)f_p(10)
	410	402	f_h(56)f_k(15)f_p(12)

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Table 8: *(continued)*

Symmetry species	Frequency (cm^{-1})		Potential energy distribution (%)[*]
	Using lattice dynamics	Using normal coordinate analysis	
	561	569	$f_d(74)f_b(21)$
A_{2u} (IR)	81/97	81	$f_n(44)f_d(22)f_e(21)$
To/Lo	128/134	130	$f_n(49)f_q(30)$
	147/142	134	$f_n(55)f_h(26)$
	186/188	165	$f_s(64)f_t(16)f_d(11)$
	304/328	305	$f_v(53)f_a(17)f_s(14)$
	352/364	360	$f_s(61)f_t(22)f_b(14)$
	418/438	438	$f_b(70)f_d(16)f_k(10)$
	460/447	451	$f_h(64)f_k(20)f_p(10)$
	575/572	568	$f_e(72)f_e(10)f_q(10)$
B_{2u} (IR)	201	205	$f_s(50)f_t(20)f_u(16)$
	330	326	$f_t(46)f_s(29)f_v(22)$
E_u (IR)	70/78	65	$f_e(41)f_u(31)$
To/Lo	101/109	110	$f_r(59)f_t(22)f_e(10)$
	139/135	134	$f_r(61)f_s(15)f_v(12)$
	242/247	251	$f_s(54)f_r(26)f_u(16)$
	255/245	260	$f_r(36)f_s(32)f_v(18)$
	356/358	369	$f_t(49)f_b(16)f_k(19)$
	360/372	372	$f_a(62)f_s(20)f_v(19)$
	425/433	432	$f_t(60)f_u(20)f_v(15)$
	484/451	478	$f_c(74)f_k(10)f_s(10)$
	578/562	571	$f_d(72)f_p(15)f_t(10)$
	599/568	582	$f_g(71)f_n(12)f_r(12)$

[*] Only contributions greater than 10% are included.

3. RESULTS AND DISCUSSION

The lattice dynamics calculations using Raman spectra have permitted detailed assignments of vibrational frequencies in the superconducting system. Kulkarni et al.[10] have studied the optical modes of thallium-based high T_c superconducting compounds using the lattice dynamics of high T_c superconductors. Their calculations were based on a shell model that incorporates short-range repulsive potential, long-range coulombic potential and ionic polarisabilities. In the present investigation, the lattice dynamics of high temperature Tl-based compounds have been investigated on the basis of a modified TSM.[11–20] This model considers the effect of many body interactions on the lattice potential. The various interactions between ions are treated in a general way without making them numerically equal. The model parameters determined using the TSM for 2:0:2:1:6, 2:2:2:3:10, 1:1:2:2:7 and 1:3:2:4:11 Tl-based compounds are given in Tables 9, 10, 11 and 12, respectively.

Table 9: Shell parameters of the model for $Tl_2Ba_2CuO_6$ a,b are Born-Mayer constants Z, Y, K: ionic charge, shell charge and on-site core-shell force constants of the ion

Interaction	a_{ij} (eV)	b_{ij} (A^{-1})
Tl-O (same plane)	3020	2.90
Tl-O(adjacent plane)	3020	3.50
Ba-O	3245	3.00
Cu-O	1260	3.45
O-O	1000	3.00

Ion	Z(|e|)	Y(|e|)	K(e^2/Va)
Tl	2.90	2.00	916
Ba	1.95	2.39	195
Cu	2.00	3.22	1110
O(Cu-O plane)	–2.10	–2.90	284
O(Tl-O plane)	–2.20	–2.90	371
O(Ba-O plane)	–2.20	–2.90	$289(K_{\parallel})/1961(K_{\perp})$

Table 10: Shell parameters of the model for $Tl_2Ca_2\ Ba_2Cu_3O_{10}$; a, b are Born-Mayer constants; Z, Y, K: ionic charge, shell charge and on-site core-shell force constants for the ions.

Interaction	a_{ij} (eV)	b_{ij} (A^{-1})
Tl-O (same plane)	3035	3.00
Tl-O (adjacent plane)	3035	3.55
Ba-O	3245	3.10
Ca-O	2513	3.25
Cu-O	1260	3.45
O-O	1000	3.00

(continued on next page)

Table 10: *(continued)*

Ion	Z (|e|)	Y (|e|)	K (e^2/V_a)
Tl	2.90	2.00	975
Tl	3.00	2.00	869
Ba	1.95	2.32	210
Ca	2.02	0.60	171
Cu	2.00	3.22	1115
O (Cu-O plane)	–2.10	–2.90	295
O (Tl-O plane)	–15	–2.90	376
O (Ba-O plane)	–2.15	–2.90	294($K_{\|\|}$)/1974($K_\perp$)

Table 11: Shell parameters of the model for $TlCaBa_2Cu_2O_7$; a, b are Born-Mayer constants; Z, Y, K: ionic charge, shell charge and on-site core-shell force constants for the ions; V_a is the volume of the unit cell.

Interaction	a_{ij} (eV)	b_{ij} (A^{-1})
Tl-O(1)	3740	3.20
Tl-O(2)	3740	3.70
Ba-O(1)	3218	3.20
Ca-O(3)	3508	3.46
Cu-O(3)	1271	3.38
O-O	520	3.10

Ion	Z (|e|)	Y (|e|)	K (e^2/V_a)
Tl	2.85	3.16	946
Ba	2.20	3.49	179
Ca	1.98	3.74	1085
Cu	2.16	3.28	1085
O	–1.86	–2.72	520

Table 12: Shell parameters of the model for $TlCa_3Ba_2Cu_4O_{11}$; a, b are Born-Mayer constants; Z, Y, K: ionic charge, shell charge and on-site core-shell force constants for the ions; V_a is the volume of the unit cell.

Interaction	a_{ij} (eV)	b_{ij} (A^{-1})
Tl-O(1)	3740	3.20
Tl-O(2)	3740	3.70
Ba-O(1)	3218	3.20
Ca-O(3)	3508	3.46
Cu-O(3)	1271	3.38
O-O	520	3.10

Ion	Z (|e|)	Y (|e|)	K (e^2/V_a)
Tl	2.85	3.16	946
Ba	2.20	3.49	179
Ca	1.98	3.74	1085
Cu	2.16	3.28	1085
O	–1.86	–2.72	520

The phonon frequencies for these Tl-based compounds using normal coordinate calculations are presented here for the first time. There are no spectroscopic data available for $TlCa_3Ba_2Cu_4O_{11}$ in the literature. Due to the high cost of this compound, the Raman spectra could not be measured by the authors. It is gratifying to note that all of the general features explained for the earlier superconductors were also observed in these thallium superconductors. The phonon frequencies evaluated using normal coordinate analysis and the modified three body force shell model agree quite well for the four high T_c thallium superconductors. It is also interesting that the Raman data available for the A_{1g} and B_{1g} modes for 2:0:2:1:6, 1:1:2:2:7 and 2:2:2:3:10 agree very well with the evaluated phonon frequencies. All of the calculations reported by Kulkarni et al.[10] for these thallium compounds in their theoretical study agree with the results of the present work.

Displacements in Cu-O planes are known to be responsible for high temperature superconductivity. Superconductivity and lattice vibrations are found in the B_{1g} modes. Thus, a pair of opposite oxygen ions in the Cu-O plane vibrate 180° out of phase. Progressing through our compounds from 2:2:2:3:10 to 1:3:2:4:11, the vibrating oxygens are separated by the stretching C-O plane, and the phonon frequency is expected to decrease in the displacement of Cu-O planes. This conclusion is consistent with the evaluated frequencies obtained for these systems.

Because the dipole moment of the unit cell does not vary during oxygen motion, the Raman frequencies in the B_{2u} mode are absent, and B_{2u} is known as a silent mode. The phonon frequency was evaluated via the two different methods for this silent mode, which are reasonably consistent with each other. In the A_{1g} mode, the oxygen ion in the same Cu-O plane vibrates in phase. As explained earlier, the O(1), O(4) and Ca motions yield a lower frequency of 247 cm^{-1} in the 1:3:2:4:11 compound in comparison with a frequency of 277 cm^{-1} in the 2:2:2:3:10 compound. This frequency is observed at 361 cm^{-1} in the 1:1:2:2:7 compound. The O(1) and O(4) vibrational frequency is also observed to be greater in the A_{1g} mode than in the B_{1g} mode in all of the cases studied here. The addition of Ca and Cu-O units has the least effect on the oxygen and copper ions within the Cu-O planes, which is evident from the frequencies of the various E_g and E_u modes in these compounds.

The Tranverse optical and Longitudinal optical modes (To-Lo) splitting of the infrared active modes results from the dynamic dipole moment associated with these modes. The A_{2u} mode shows large To-Lo splitting whereas the E_u mode shows the least splitting, with both modes involving oxygen vibrations.

4. CONCLUSION

In conclusion, the modified three-body-force shell model (TSM) and normal coordinate analysis produce satisfactory results for the determination of phonon frequencies in a set of Tl-based compounds. Each of the observed Raman frequencies reported in the literature are well-represented by the evaluated frequencies in the present work. The theoretical phonon frequencies obtained by the lattice dynamics and the normal coordinate analysis method agree very well with the available Raman and infrared frequencies. The calculated vibrational phonon frequencies using two different techniques yield the same result. These calculations yielded not only the phonon frequency in the centre of the Brillouin zone but also support the presence of a strong electron-phonon interaction in the high-temperature superconductor TlCaBaCuO. The potential energy distribution confirms the reliability and accuracy of the vibrational spectral analysis as well as the present assignments. The PED calculation also validates the reliability and precision of the spectral assignments of the fundamental vibrational mode.

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