Normal Vibrations of Tetramethylmethane and Tetramethylmethane-d_{12}

By Kazuhiro SHIMIZU and Hiromu MURATA

(Received January 21, 1957)

The Wilson *FG* matrix method for the tetrahedral $M(XY_3)_4$ molecules has been used by Siebert[1] But no symmetry coordinates were given and a valence force field, including only one cross term of M−X and X−M−X internal coordinates, was used. The present investigation was undertaken in an attempt to carry out a normal coordinate treatment with a Urey-Bradley potential function and to assign observed frequencies for $C(CH_3)_4$ and $C(CD_3)_4$ to fundamental modes of vibration.

Normal Coordinate Treatment

A representation of the forty-five normal vibrational modes of the tetrahedral $M(XY_3)_4$ molecules is reduced to fourteen by $\Gamma=3a_1+4e+7f_2$. According to the well-known selection rules, all fundamentals are allowed in Raman spectrum, while only type f_2 fundamentals are allowed in the infrared. In the Raman spectrum, the a_1 vibrations correspond to polarized lines, the others to depolarized. It is possible to show that in both the a_1 and e species, $n^{(\gamma)}=1$ for any sets of equivalent internal coordinates, while in the f_2 species, $n^{(\gamma)}=2$ for the X−Y stretching and the Y−X−Y bending coordinates. For the latter case, it is neccesary to find *K*, which is a subgroup of *G*, and to construct the final symmetry coordinates from nondegenerate symmetry coordinates under *K*, as shown in the following manner:

$G(T_d)$	$K(C_{2v})$	Symmetry coordinates	
	↗ a_1	R_9,	R_{11}
f_2	→ b_1	R_8,	R_{10}
	↘ b_2	None	

From the internal coordinates (Fig. 1), the following orthonormal symmetry coordinates were formed:

for the a_1 vibrations,

$$R_1=\Delta(y_{11}+y_{12}+y_{13}+y_{21}+y_{22}+y_{23}+y_{31}+y_{32}+y_{33}+y_{41}+y_{42}+y_{43})/12^{1/2},$$

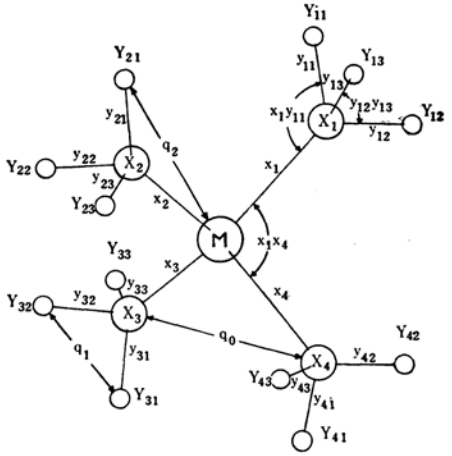

Fig. 1. Internal coordinates of $M(\times Y_3)_4$ molecule.

$$R_2=\Delta(y_{11}y_{12}+y_{11}y_{13}+y_{12}y_{13}+y_{21}y_{22}+y_{21}y_{23}+y_{22}y_{23}+y_{31}y_{32}+y_{31}y_{33}+y_{32}y_{33}+y_{41}y_{42}+y_{41}y_{43}+y_{42}y_{43}-x_1y_{11}-x_1y_{12}-x_1y_{13}-x_2y_{21}-x_2y_{22}-x_2y_{23}-x_3y_{31}-x_3y_{32}-x_3y_{33}-x_4y_{41}-x_4y_{42}-x_4y_{43})/24^{1/2}, \quad \text{and}$$

$$R_3=\Delta(x_1+x_2+x_3+x_4)/2\,;$$

for the e vibrations,

$$R_{4a}=\Delta(2y_{11}-y_{12}-y_{13}+2y_{21}-y_{22}-y_{23}+2y_{31}-y_{32}-y_{33}+2y_{41}-y_{42}-y_{43})/24^{1/2},$$

$$R_{5a}=\Delta(2y_{12}y_{13}-y_{11}y_{12}-y_{11}y_{13}+2y_{22}y_{23}-y_{21}y_{22}-y_{21}y_{23}+2y_{32}y_{33}-y_{31}y_{32}-y_{31}y_{33}+2y_{42}y_{43}-y_{41}y_{42}-y_{41}y_{43})/24^{1/2},$$

$$R_{6a}=\Delta(2x_1y_{11}-x_1y_{12}-x_1y_{13}+2x_2y_{21}-x_2y_{22}-x_2y_{23}+2x_3y_{31}-x_3y_{32}-x_3y_{33}+2x_4y_{41}-x_4y_{42}-x_4y_{43})/24^{1/2}, \text{ and}$$

$$R_{7a}=\Delta(2x_1x_2-x_1x_3-x_1x_4+2x_3x_4-x_2x_3-x_2x_4)/12^{1/2}\,;$$

for the f_2 vibrations,

$$R_{8a}=\Delta(2y_{21}-y_{22}-y_{23}+2y_{33}-y_{31}-y_{32}+2y_{42}-y_{43}-y_{41})/18^{1/2},$$

$$R_{9a}=\Delta(3y_{11}+3y_{12}+3y_{13}-y_{21}-y_{22}-y_{23}-y_{31}-y_{32}-y_{33}-y_{41}-y_{42}-y_{43})/6,$$

$$R_{10a}=\Delta(2y_{22}y_{23}-y_{21}y_{22}-y_{21}y_{23}+2y_{31}y_{32}-y_{31}y_{33}-y_{32}y_{33}+2y_{41}y_{43}-y_{41}y_{42}-y_{42}y_{43})/18^{1/2},$$

$$R_{11a}=\Delta(3y_{11}y_{12}+3y_{11}y_{13}+3y_{12}y_{13}-y_{21}y_{22}-y_{21}y_{23}-y_{22}y_{23}-y_{31}y_{32}-y_{31}y_{33}-y_{32}y_{33}$$

---

[1] H. Siebert, *Z. anorg. allgem. Chem.*, **268**, 177 (1952).

$$\begin{aligned}
&-y_{41}y_{42}-y_{41}y_{43}-y_{42}y_{43}-3x_1y_{11}-3x_1y_{12}\\
&-3x_1y_{13}+x_2y_{21}+x_2y_{22}+x_2y_{23}+x_3y_{31}\\
&+x_3y_{32}+x_3y_{33}+x_4y_{41}+x_4y_{42}\\
&+x_4y_{43})/72^{1/2},\\
R_{12a}&=\Delta(3x_1-x_2-x_3-x_4)/12^{1/2},\\
R_{13a}&=\Delta(2x_2y_{21}-x_2y_{22}-x_2y_{23}+2x_3y_{33}-x_3y_{31}\\
&-x_3y_{32}+2x_4y_{42}-x_4y_{41}-x_4y_{43})/18^{1/2},\ \text{and}\\
R_{14a}&=\Delta(x_1x_2+x_1x_3+x_1x_4-x_2x_3-x_2x_4\\
&-x_3x_4)/6^{1/2}.
\end{aligned}$$

The numbering of these coordinates corresponds to the numbering of the fundamentals in Table III.

From the potential constants of a Urey-Bradley force field[2] and the coefficients of the symmetry coordinates, one obtains the following F matrix elements:

for the a_1 vibrations,

$$\begin{aligned}
F_{11}&=K_1+4s_1{}^2F_1+t_2{}^2F_2'+s_2{}^2F_2,\\
F_{12}&=2^{1/2}t_1s_1(F_1'+F_1)y-(t_2s_3F_2'\\
&\quad+t_3s_2F_2)x/2^{1/2},\\
F_{13}&=3^{1/2}(-t_2t_3F_2'+s_2s_3F_2),\\
F_{22}&=[(H_1-s_1{}^2F_1'+t_1{}^2F_1)y^2+(H_2-s_2s_3F_2'\\
&\quad+t_2t_3F_2)xy+3k_1/2^{1/2}]/2,\\
F_{23}&=-3^{1/2}(t_3s_2F_2'+t_2s_3F_2)y/2^{1/2},\quad \text{and}\\
F_{33}&=K_0+6s_02F_0+3t_3{}^2F_2'+3s_3{}^2F_2;
\end{aligned}$$

for the e vibrations,

$$\begin{aligned}
F_{11}&=K_1+3t_1{}^2F_1'+s_1{}^2F_1+t_2{}^2F_2'+s_2{}^2F_2,\\
F_{12}&=-t_1s_1(F_1'+F_1)y,\\
F_{13}&=(t_2s_3F_2'+t_3s_2F_2)x,\\
F_{22}&=(H_1-s_1{}^2F_1+t_1{}^2F_1)y^2+2^{1/2}k_1/4,\\
F_{23}&=k_1/2^{1/2},\\
F_{33}&=(H_2-s_2s_3F_2'+t_2t_3F_2)xy+2^{1/2}k_1/4,\\
F_{44}&=(H_0-s_0{}^2F_0'+t_0{}^2F_0)x^2-2^{1/2}k_0/4,\ \text{and}\\
F_{14}&=F_{24}=F_{34}=0;
\end{aligned}$$

and for the f_2 vibrations,

$$\begin{aligned}
F_{11}&=K_1+3t_1{}^2F_1'+s_1{}^2F_1+t_2{}^2F_2'+s_2{}^2F_2,\\
F_{13}&=-t_1s_1(F_1'+F_1)y,\\
F_{16}&=(t_2s_3F_2'+t_3s_2F_2)x,\\
F_{22}&=\mathrm{K}_1+4s_1{}^2F_1+t_2{}^2F_2'+s_2{}^2F_2,\\
F_{24}&=2^{1/2}t_1s_1(F_1'+F_1)y-(t_2s_3F_2'\\
&\quad+t_3s_2F_2)x/2^{1/2},\\
F_{25}&=3^{1/2}(-t_2t_3F_2'+s_2s_3F_2),\\
F_{33}&=(H_1-s_1{}^2F_1'+t_1{}^2F_1)y^2+2^{1/2}k_1/4,\\
F_{36}&=-k_1/2^{1/2},\\
F_{44}&=[(H_1-s_1{}^2F_1'+t_1{}^2F_1)y^2+(H_2-s_2s_3F_2'\\
&\quad+t_2t_3F_2)xy+3k_1/2^{1/2}]/2\\
F_{45}&=-3^{1/2}(t_3s_2F_2'+t_2s_3F_2)y/2^{1/2},\\
F_{55}&=K_0+4t_0{}^2F_0'+2s_0{}^2F_0+3t_3{}^2F_2'+3s_3{}^2F_2,\\
F_{57}&=2^{1/2}t_0s_0(F_0'+F_0)x,\\
F_{66}&=(H_2-s_2s_3F_2'+t_2t_3F_2)xy+2^{1/2}k_1/4,\\
F_{77}&=(H_0-s_0{}^2F_0'+t_0{}^2F_0)x^2+3k_0/8^{1/2},\ \text{and}\\
F_{12}&=F_{14}=F_{15}=F_{17}=F_{23}=F_{26}=F_{27}=F_{34}=F_{35}\\
&=F_{37}=F_{46}=F_{47}=F_{56}=F_{67}=0,
\end{aligned}$$

where the following abbreviations are adopted:

$$\begin{aligned}
&t_0=8^{1/2}x/3q_0,\quad t_1=8^{1/2}y/3q_1,\quad t_2=8^{1/2}x/3q_2,\\
&t_3=8^{1/2}y/3q_2,\quad s_0=4x/3q_0,\quad s_1=4y/3q_1,\\
&s_2=(x+3y)/3q_2,\quad s_3=(3x+y)/3q_2,
\end{aligned}$$

and the symbols used for the equilibrium values of the interatomic distances are

$$\begin{aligned}
&x=M-X,\ y=X-Y,\ q_0=X\cdots\cdots X,\\
&q_1=Y\cdots\cdots Y,\ \text{and}\ q_2=M\cdots\cdots Y.
\end{aligned}$$

The G matrix elements, obtained by use of the table of Decius[3] and the method of Crawford[4], are as follows:

for the a_1 vibration,

$$\begin{aligned}
G_{11}&=\mu_X/3+\mu_Y,\\
G_{12}&=-4\mu_X/3y,\\
G_{13}&=-\mu_X/3^{1/2},\\
G_{22}&=2(8\mu_X/3+\mu_Y)/y^2,\\
G_{23}&=4\mu_X/3^{1/2}y,\ \text{and}\\
G_{33}&=\mu_X;
\end{aligned}$$

for the e vibrations,

$$\begin{aligned}
G_{11}&=4\mu_X/3+\mu_Y,\\
G_{12}&=32^{1/2}\mu_X/3y,\\
G_{13}&=-2^{1/2}\mu_X(3/x+1/y)/3,\\
G_{14}&=2\mu_X/x,\\
G_{22}&=(8\mu_X/3+5\mu_Y/2)/y^2,\\
G_{23}&=-2\mu_X(1/3y^2+1/xy)+\mu_Y/2y^2,\\
G_{24}&=8^{1/2}\mu_X/xy,\\
G_{33}&=\mu_X(3/2x^2+1/xy+1/6y^2)+\mu_Y/y^2.\\
G_{34}&=-\mu_X(3/x^2+1/xy)/2^{1/2},\ \text{and}\\
G_{44}&=3\mu_X/x^2;
\end{aligned}$$

and for the f_2 vibrations.

$$\begin{aligned}
G_{11}&=4\mu_X/3+\mu y,\\
G_{13}&=32^{1/2}\mu_X/3y,\\
G_{16}&=-2^{1/2}\mu_X(1/x+1/3y),\\
G_{17}&=8^{1/2}\mu_X/3^{1/2}x,\\
G_{22}&=\mu_X/3+\mu_Y,\\
G_{24}&=-4\mu_X/3y,\\
G_{25}&=-\mu_X/3^{1/2},\\
G_{33}&=8\mu_X/3_Y{}^2+5\mu_Y/2y^2,\\
G_{36}&=-2\mu_X(1/xy+1/3y^2)+\mu_Y/2y^2,\\
G_{37}&=4\mu_X/3^{1/2}xy,\\
G_{44}&=16\mu_X/3y^2+2\mu_Y/y^2,\\
G_{45}&=4\mu_X/3^{1/2}y,\\
G_{55}&=4\mu_M/3+\mu_X,\\
G_{56}&=4\mu_M/3^{1/2}x,\\
G_{57}&=-8\mu_M/3x,\\
G_{66}&=4\mu_M/x^2+\mu_X(3/2x^2+1/xy+1/6y^2)\\
&\quad+\mu_Y/y^2,
\end{aligned}$$

---

[2] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

[3] J. C. Decius, *J. Chem. Phys.*, **16**, 1025 (1948).

[4] B. Crawford, Jr., *J. Chem. Phys.*, **21**, 1108 (1953).

TABLE I

RAMAN AND INFRARED SPECTRAL DATA FOR TETRAMETHYLMETHANE

Type	Silver[a] (Raman)	YKM[b] (Infrared)	Sheppard[c] (Raman)	Siebert[d] (Raman)	SOR (Raman)	SOR (Infrared)
a_1	2913	2911	—	2911	2909	—
	1455	1252	—	—	—	—
	—	733	733	733	733	—
e	2957	2955	—	2955	—	—
	1455	1455	—	1455	1451	—
	925	925	925	—	—	—
	—	335	335	335	335	—
f_2	—	2962	—	2962	2955	2959
	—	2876	—	2876	—	2876
	—	1455	—	1455	—	1475
	—	1370	—	1370	—	1372
	—	1280	1252	1257	1249	1256
	—	925	925	925	921	925
	—	414	414	414	415	418

a See reference 5; b YKM = Young, Koehler and Mckinney, reference 6; c See reference 7; d See reference 1; e SOR = Shull, Oakwood and Rank, reference 9.

$$G_{67}=-8\mu_M/3^{1/2}x^2-\mu_X(3^{1/2}/x^2+1/3^{1/2}xy),$$
$$G_{77}=16\mu_M/3x^2+2\mu_X/x^2, \text{ and}$$
$$G_{12}=G_{14}=G_{15}=G_{23}=G_{26}=G_{27}=G_{34}=G_{35}=G_{46}=G_{47}=0.$$

Here μ_M, μ_X and μ_Y are, respectively, the reciprocals of the masses of the M, X and Y atoms.

Normal Frequencies of Tetramethylmethane

The Raman or the infrared spectral data and the assignments of the observed frequencies for tetramethylmethane have been obtained in previous investigations[1,5–9]. A summary of the fundamentals is given in Table I. A partial normal coordinate treatment was carried out by Silver[5] and by Sheline et al.[8] for the a_1 and e vibrations. Recently, Siebert[1] published the normal coordinate treatment of all vibrations. The disagreement between the results of the different investigations lies in the assignment of two of type f_2 vibrations, i.e. C—C stretching and CH_3 rocking vibration. In this paper, the nature of these vibrations will be clarified. Using the F and G matrix elements given above, the fundamental frequencies were calculated and shown in Table III. Probable values of the observed frequencies and assignment of the Raman and the infrared bands are included in the table. The molecular and potential constants used are listed in Table II. The C—H stretching vibrations were split off by the method of Wilson. The agreement between the calculated and observed fundamentals was almost completely satisfactory. The L

TABLE II

MOLECULAR AND POTENTIAL CONSTANTS OF $C(CH_3)_4$ AND $C(CD_3)_4$

Bond distance	Potential constant (md/A) Type	Set I	Set II
x = C—C	K_0(C—C)	3.440	2.474
= 1.55A	H_0(C—C—C)	0.206	0.105
y = C—H	F_0(C……C)	0.333	0.571
= C—D	$k_0(CC_4)$	0.040A²	0.015A²
= 1.09A	K_1(C—H)	4.50	4.50
	H_1(H—C—H)	0.40	0.40
	H_2(C—C—H)	0.15	0.15
	F_1(H……H)	0.10	0.10
	F_2(C……H)	0.40	0.40
	$k_1(CCH_3)$	0.05A²	0.05A²
	F'	$-F/10$	$-F/10$

The potential constants for the skeletal vibrations were obtained from the observed frequencies of $C(CH_3)_4$:

The values of set I correspond to $\nu_1=733$, $\nu_2=335$, $\nu_3=1089$, and $\nu_4=414\text{ cm}^{-1}$ and those of set II, to $\nu_1=733$, $\nu_2=335$, $\nu_3=925$, and $\nu_4=414\text{ cm}^{-1}$ respectively.

The potential constants for the inner vibrations were obtained directly from the normal frequencies of $H_3C—CH_3$.

---

[5] S. Silver, *J Chem. Phys.*, **8**, 919 (1940).

[6] C. W. Young, J. S. Koehler and D. S. Mckinney, *J. Am. Chem. Soc.*, **69**, 1410 (1947).

[7] N. Sheppard, *J. Chem. Phys.*, **16**, 690 (1948).

[8] R. K. Sheline and K. S. Pitzer, *J. Chem. Phys.*, **18**, 595 (1950).

[9] E. R. Shull, T. S. Oakwood and D. H. Rank, *J. Chem. Phys.*, **21**, 2024 (1953).

TABLE III
PROBABLE VALUES OF THE OBSERVED FUNDAMENTALS, CALCULATED WAVE NUMBERS, AND ASSIGNMENTS FOR $C(CH_3)_4$.

Assignment.			ν calc.		ν obs.
Type	Frequency	Mode of vibration	Set I	Set II	
a_1	ν_1	CH_3 sym. str.	2932	2932	2909
	ν_2	CH_3 sym. def.	1395	1395	—
	ν_3	C—C skel. str.	791	790	733
e	ν_4	CH_3 nonsym. str.	2984	2984	2955
	ν_5	CH_3 nonsym. def.	1443	1442	1451
	ν_6	CH_3 rocking	905	905	925
	ν_7	C—C—C skel. def.	308	307	335
f_2	ν_8	CH_3 nonsym. str.	2984	2984	2959
	ν_9	CH_3 sym. str.	2932	2932	2876
	ν_{10}	CH_3 nonsym. def.	1442	1442	1475
	ν_{11}	CH_3 sym. def.	1390	1377	1372
	ν_{12}	CH_3 skel. str.	1272	1160	1256
	ν_{13}	CH_3 rocking	873	852	925
	ν_{14}	C—C—C skel. def.	372	367	418

matrices, whose components give the modes of vibrations, and the potential energy distributions for the questionable two triply degenerate vibrations were calculated and shown in Tables IV and V. Judging from the values of the contribution of each symmetry coordinate to the normal coordinate Q_{12} in Table IV, it is no longer accurate to designate the frequency ν_{12} as only one mode of vibration, i.e., "C—C stretching". However, it can be seen that, by taking into consideration the distribution of energy in the symmetry coordinates in Table V, the classification given in Table III is reasonable. On the contrary, it is undubitable that the frequency ν_{13}, which is relatively pure, can be assigned to "CH_3 rocking".

TABLE IV
L-MATRICES OF TWO TYPE f_2 VIBRATIONS OF $C(CH_3)_4$.

f_2	Q_{12}		Q_{13}	
	Set I	Set II	Set I	Set II
R_{10}	−0.09	−0.09	−0.07	−0.05
R_{11}	−0.36	−0.00	0.06	0.03
R_{12}	0.36	0.34	−0.16	−0.22
R_{13}	0.64	0.67	0.83	0.72
R_{14}	−0.41	0.36	−0.04	0.01

TABLE V
POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_{ia}^2/\lambda_a$ FOR ν_{12} AND ν_{13} VIBRATIONS

f_2	ν_{12}		ν_{13}	
	Set I	Set II	Set I	Set II
R_{10}	0.00	0.01	0.00	0.00
R_{11}	0.13	0.00	0.01	0.00
R_{12}	0.65	0.57	0.28	0.45
R_{13}	0.19	0.25	0.68	0.53
R_{14}	0.06	0.06	0.00	0.00

Normal Frequencies of Tetramethylmethane-d_{12}

The Raman and the infrared spectral data and the assignments of the observed frequencies for tetramethylmethane-d_{12} have been reported by Shull et al.[9], but a normal coordinate treatment has not been carried out in the literature. According to them, since the observed frequency 765 cm^{-1} is analogous to the band at 921 cm^{-1} in tetramethylmethane, it should be assigned to "C—C stretching" and the observed frequency 1218 cm^{-1} can be assigned to "CD_3 rocking". In general, a normal mode of vibration in which the hydrogen atom in question oscillates with a relatively large amplitude will suffer a greater isotopic change in frequency than that of a normal mode in which this hydrogen moves with a relatively small amplitude. Since the ratio 765/921 is nearly equal to a theoretically expected value $1/2^{1/2}$, it is probably rigorous to designate the frequency observed at 765 cm^{-1} as "CD_3 rocking". Since the frequencies observed at about 1200 cm^{-1} maintain a constant value in both the ordinary and deuterated compounds, it is reasonable to assign these frequencies to "C—C stretching". Using the *F* and *G* matrix elements given above, the fundamental frequencies were calculated and shown in Table VI with

TABLE VI
OBSERVED AND CALCULATED FONDAMENTAL FREQUENCIES AND ASSIGNMENTS FOR $C(CD_3)_4$

Assignment			ν calc.		ν obs.
Type	Frequency	Mode of vibration	Set I	Set II	
a_1	ν_1	CD_3 sym. str.	2110	2110	2128
	ν_2	CD_3 sym. def.	1130	1130	1104
	ν_3	C—C skel. str.	684	684	648
e	ν_4	CD_3 nonsym. str.	2221	2221	—
	ν_5	CD_3 nonsym. def.	1055	1055	1048
	ν_6	CD_3 rocking	695	694	—
	ν_7	C—C—C skel. def.	264	263	276
f_2	ν_8	CD_3 nonsym. str.	2221	2221	2218
	ν_9	CD_3 sym. str.	2110	2110	2058
	ν_{10}	C—C skel. str.	1279	1150	1218
	ν_{11}	CD_3 nonsym. def.	1058	1057	1066
	ν_{12}	CD_3 sym. def.	1029	1020	1037
	ν_{13}	CD_3 rocking	684	679	765
	ν_{14}	C—C—C skel. def.	316	311	342

those observed by Shull et al. The calculation of the L matrix elements (Table VII) and of the potential energy distributions (Table VIII) shows that the assignments given in Table VI are more reasonable.

TABLE VII

L-MATRICES OF TWO TYPE f_2 VIBRATIONS OF $C(CD_3)_4$

f_2	Q_{10} Set I	Q_{13} Set I
R_{10}	−0.04	0.02
R_{11}	0.51	0.13
R_{12}	0.42	−0.10
R_{13}	0.41	0.62
R_{14}	−0.36	−0.10

TABLE VIII

POTENTIAL ENERGY DISTRIBUTION $F_{tt}L_{ta}^2/\lambda_a$ FOR ν_{10} AND ν_{13} VIBRATIONS

f_2	ν_{10} Set I	ν_{13} Set I
R_{10}	0.00	0.00
R_{11}	0.15	0.04
R_{12}	0.87	0.17
R_{13}	0.09	0.72
R_{14}	0.11	0.03

The authors wish to express their gratitude to Drs. Y. Morino and T. Shimanouchi of Tokyo University and Dr. H. Shingu of Kyoto University for many helpful discussions.

Osaka Municipal Technical Research Institute, Kita-ku, Osaka