On the Ratio L_{12}/L_{21} For $n=2$ Eigenvalue Problems: An Empirical Constraint For The Calculation of Force Constants (Extended L Matrix Approximation)

A. MÜLLER, N. MOHAN, and U. HEIDBORN

Institut für Chemie, Universität Dortmund

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The variation of the ratio L_{12}/L_{21} (where L_{ij} refers to the element of the L matrix) as a function of the mass coupling term $T=G_{12}/|G|^{1/2}$ has been studied for molecules of the type $XY_4(Td)$, $XY_3(D_{3h})$ and $XY_2(C_{2v})$ using the exact force field data. In the case of the XY_4 and XY_3 type molecules, the ratio L_{12}/L_{21} is nearly independent of the mass coupling and in the case of the XY_2 type, it shows a nearly linear dependence on T. The force constants have been evaluated using an empirically determined constraint for L_{12}/L_{21}. The values are generally in good agreement with the exact ones. In all cases except VCl_4 the exact interaction term of the F matrix is in agreement with the sign rule of Müller et al.

Introduction

For a unique solution of the second order secular equation in the vibrational eigenvalue problem, an additional constraint apart from the values of the frequencies of vibration is needed. The L matrix approximation [1–4] has been found to be useful in calculating a reasonable set of force constants in the case of molecules with small mass coupling [5]. But the method is generally applicable for the calculation of mean amplitudes of vibration even in the case of strongly coupled vibrations [1, 6].

In the case of a 2×2 secular determinant in the vibrational eigenvalue problem, this constraint implies a completely characteristic ν_2 vibration [4, 5]. It was shown by us [2] that this condition is equivalent to TORKINGTON's [7] condition that F_{22} is a minimum.

In this paper we want to investigate the properties of the ratio L_{12}/L_{21} for a large number of molecules of the $XY_4(T_d)$, $XY_3(D_{3h})$, and $XY_2(C_{2v})$ type for which the force constants have been determined from additional data. Both the elements are zero in the limiting case of completely uncoupled vibrations.

General Study of the Behaviour of L_{12}/L_{21}

We have summarized the values of the elements of the L matrix determined from the exact force constant data for some molecules of the $XY_4(T_d)$, $XY_3(D_{3h})$, and $XY_2(C_{2v})$ type in Tables 1, 2 and 3 respectively.

It should be mentioned that in all cases the F_{12} elements are in agreement with the sign rule of MÜLLER et al. [3], that means F_{12} has the opposite sign of G_{12}.

Graphical study of the variation of L_{12}/L_{21} with respect to the mass coupling term T is presented in Figs. 1, 2, and 3 for the three types of molecules mentioned above.

For the nonhydrides one immediately notices that in the case of the XY_4 and XY_3 type molecules, the ratio L_{12}/L_{21} is nearly independent of the mass coupling term and further that the absolute value is itself very small. However in the case of the XY_2 type, L_{12}/L_{21} varies nearly linearly with the mass coupling term. It may be noteworthy to point out that such a linear relation holds exactly for the molecules NO_2, NF_2, OF_2, and CF_2, which exhibit relatively large mass coupling.

Evaluation of Force Constants

The following conclusions may be drawn regarding the behaviour of L_{12}/L_{21} for these molecules from the empirical study.

1. For the XY_4 and XY_3 type molecules an average value of the factor L_{12}/L_{21} may be taken as a constraint in fixing the force constants (for $XY_4: L_{12}/L_{21}=-0.075$, and for $XY_3: L_{12}/L_{21}=-0.020$).
2. In the case of the XY_2 type the linear relation between L_{12}/L_{21} and T may be used as a con-

Reprint requests to Prof. Dr. A. MÜLLER, Lehrstühle für Anorganische Chemie der Universität Dortmund, *D-4600 Dortmund-Eichlinghofen*, August-Schmidt-Straße.

Table 1. Elements of the L matrix (a. m. u.) $^{-1/2}$ for the XY_4(Td) type molecules.

Molecule	L Matrix Elements L_{11}	L_{12}	L_{21}	L_{22}	Exact Force Field Data (F_2) F_{11}	F_{12}	F_{22}	Reference
CF_4	0.403	0.040	− 0.594	0.443	6.907 ± 0.459	0.938 ± 0.112	0.971 ± 0.046	8
CCl_4	0.373	0.013	− 0.614	0.351	3.35 ± 0.75	0.52 ± 0.21	0.38 ± 0.03	9
SiF_4	0.316	0.010_5	− 0.314	0.443	6.406 ± 0.371	0.291 ± 0.154	0.438 ± 0.102	8
$SiCl_4$	0.273	0.021	− 0.371	0.329	2.96 ± 0.09	0.14_5 ± 0.03	0.236 ± 0.005	10
GeF_4	0.266	− 0.017	− 0.109	0.409	5.807 ± 0.237	0.283 ± 0.143	0.274 ± 0.014	8
$GeCl_4$	0.216	0.006	− 0.172	0.317	2.73 ± 0.13	0.13 ± 0.08	0.170 ± 0.003	10
RuO_4	0.275	0.007	− 0.107	0.408	6.49 ± 0.05	0.07 ± 0.05	0.381 ± 0.002	11
OsO_4	0.264	0.007	− 0.062	0.386	8.01 ± 0.08	− 0.012 ± 0.08	0.454 ± 0.018	12
BF_4^-	0.414	0.066	− 0.632	0.229	4.68	0.72	0.69	13
VCl_4	0.230	0.040	− 0.276	0.243	2.09 ± 0.16	− 0.15 ± 0.06	0.12 ± 0.02	14
$TiCl_4$	0.235	0.030	− 0.245	0.064	2.56 ± 0.47	0.06 ± 0.22	0.12 ± 0.02	14
CH_4	1.052	− 0.057	− 0.149	1.556	5.383	0.206	0.458	15
SiH_4	1.023	− 0.034	− 0.090	1.477	3.032	0.025	0.24	15
GeH_4	1.007	− 0.063	0.029	1.435	2.807	0.083	0.208	15
SnH_4	1.024	− 0.047	0.040	1.429	2.266	0.064	0.143	16

Table 2. Elements of the L matrix (a. m. u.) $^{-1/2}$ for the XY_3(D_{3h}) type molecules.

Molecule	L Matrix Elements L_{11}	L_{12}	L_{21}	L_{22}	Exact Force Field Data (E′) F_{11}	F_{12}	F_{22}	Reference
SO_3	0.330	− 0.003	0.254	0.513	10.605 ± 0.312	− 0.359 ± 0.218	0.616 ± 0.015	8
BF_3	0.434	− 0.021	0.570	0.554	6.683 ± 0.05	− 0.37 ± 0.02	0.5095 ± 0.0020	17
BCl_3	0.406	− 0.011	0.596	0.496	3.47 ± 0.13	− 0.247 ± 0.004	0.25 ± 0.04	18
BBr_3	0.386	− 0.010	0.619	0.251	2.79 ± 0.23	− 0.195 ± 0.07	0.191 ± 0.007	18
BI_3	0.380	− 0.007	0.624	0.207	2.25	− 0.17	0.13	19

Table 3. Elements of the L matrix (a. m. u.) $^{-1/2}$ for the XY_2(C_{2v}) type molecules.

Molecule	L Matrix Elements L_{11}	L_{12}	L_{21}	L_{22}	Exact Force Field Data (A_1) F_{11}	F_{12}	F_{22}	Reference
SO_2	0.280	0.009_5	− 0.126	− 0.330	10.41 ± 0.20	0.32 ± 0.21	0.815 ± 0.007	20
NO_2	0.289	0.023	− 0.273	0.286	12.43	0.76	1.10	21
SiF_2	0.285	0.007	− 0.185	0.453	5.33	0.17	0.44	22
CF_2	0.324	0.073_5	− 0.415	0.304	7.45	0.68	1.40	23
NF_2	0.321	0.057_5	− 0.371	0.371	6.05	0.42	1.08	23,24
OF_2	0.314	0.049	− 0.334	0.381	4.76	0.19	0.72	25
ClO_2	0.277	0.037	− 0.164	0.269	6.85	0.01	0.65	26
O_3	0.306	0.054	− 0.333	0.431	7.66 ± 0.14	0.59 ± 0.04	1.31 ± 0.04	27

straint. This means that $L_{12}/L_{21} = m\,T + c$ with $m = +0.325$ and $c = 0.063$, T being different for different molecules.

Thus the force constants for these molecules have been recalculated using the empirically determined constraint. For the sake of completeness some hydrides have also been included in the determination of the force field for these types. However it may be noted that in the case of the hydrides the value of the force constants are not critically dependent on the constraint since the vibrations are rather characteristic[5] because the mass coupling is extremely small.

As pointed out[28], the matrix can be parametrically represented in the form:

$$\boldsymbol{L} = \boldsymbol{B}\,\boldsymbol{M}^{1/2}\,\boldsymbol{X} \tag{1}$$

where $\boldsymbol{B}$ is the eigenvector matrix of $\boldsymbol{G}$, $\boldsymbol{M}$ a diagonal matrix containing the eigenvalues of $\boldsymbol{G}$, and $\boldsymbol{X}$ an arbitrary orthogonal matrix of the form

$$\boldsymbol{X} = \begin{bmatrix} \cos\Theta & -\sin\Theta \\ \sin\Theta & \cos\Theta \end{bmatrix}. \tag{2}$$

The use of the constraint

$$L_{12}/L_{21} = K \text{ (constant)} \tag{3}$$

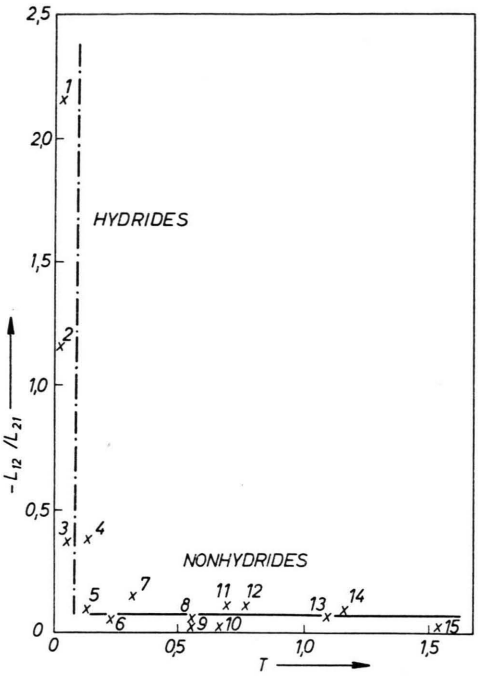

Fig. 1. The ratio L_{12}/L_{21} versus the mass coupling term T for $XY_4(T_d)$ type molecules:

1. GeH_4 2. SnH_4 3. SiH_4 4. CH_4 5. OsO_4
6. RuO_4 7. GeF_4 8. $GeCl_4$ 9. $SiCl_4$ 10. SiF_4
11. $TiCl_4$ 12. VCl_4 13. CF_4 14. BF_4 15. CCl_4

In the case of 3, 4 and 7 the value of L_{12}/L_{21} used in the graph corresponds to the other solution of Equation (4).

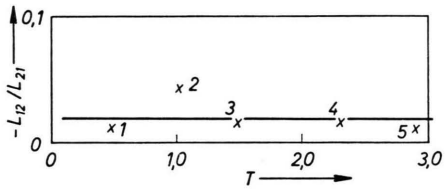

Fig. 2. The ratio L_{12}/L_{21} versus the mass coupling term T for $XY_3(D_{3h})$ type molecules:

1. SO_3 2. BF_3 3. BCl_3 4. BBr_3 5. BI_3

leads to the following equation for the parameter

$$\text{i. e. } \tan\Theta = \frac{B_{12}M_2^{1/2} - K B_{21} M_1^{1/2}}{B_{11}M_1^{1/2} + K B_{22} M_2^{1/2}}. \qquad (4)$$

The F matrix has been calculated using the diagonal matrix Λ containing the frequencies from the equation

$$\boldsymbol{F} = \boldsymbol{L}^{-1}\,\Lambda\,\boldsymbol{L}^{-1}. \qquad (5)$$

The solution of Eq. (4) leads to two solutions of $\tan\Theta$ corresponding to whether B_{12} and B_{21} have the same or the opposite sign. The two solutions

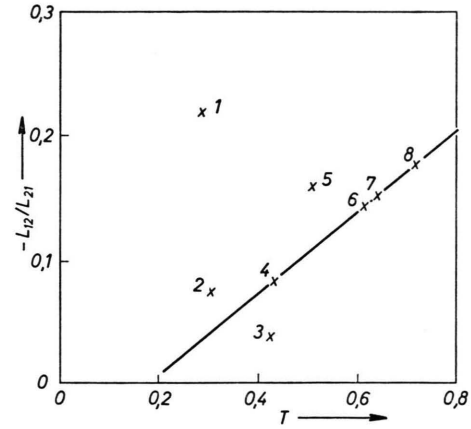

Fig. 3. The ratio L_{12}/L_{21} versus the mass coupling term T for $XY_2(C_{2v})$ type molecules:

1. ClO_2 2. SO_2 3. SiF_2 4. NO_2 5. O_3
6. OF_2 7. NF_2 8. CF_2

Table 4. Force constants for $XY_4(T_d)$ type molecules in mdyn/Å determined from the constraint: $L_{12}/L_{21} = -0.075$.

Molecule	$F_{11}(F_2)$	$F_{12}(F_2)$	$F_{22}(F_2)$
CF_4	6.81	0.91	0.98
CCl_4	2.80	0.39	0.42
SiF_4	6.08_5	0.14	0.45
$SiCl_4$	2.83	0.10	0.24
GeF_4	5.79	0.005	0.27
$GeCl_4$	2.54	0.04	0.18
RuO_4	6.55	0.02	0.38
OsO_4	8.02	0.01	0.45
BF_4^-	4.37	0.66	0.67
VCl_4	2.40	−0.04	0.10
$TiCl_4$	2.41_5	0.03	0.11
CH_4	5.32	0.13	0.45
SiH_4	3.01	0.03	0.24
GeH_4	2.79	0.01	0.20
SnH_4	2.24	0.00_5	0.14

Table 5. Force constants for $XY_3(D_{3h})$ type molecules in mdyn/Å determined from the constraint: $L_{12}/L_{21} = -0.02$.

Molecule	$F_{11}(E')$	$F_{12}(E')$	$F_{22}(E')$
SO_3	10.63	− 0.37	0.62
BF_3	7.04	− 0.50	0.50
BCl_3	3.50	-0.26_5	0.25
BBr_3	2.75	− 0.18	0.19
BI_3	1.99	− 0.10	0.13_5

Table 6. Force constants for $XY_2(C_{3v})$ type molecules in mdyn/Å determined from the constraint: $L_{12}/L_{21} = m\,T + c$.

Molecule	L_{12}/L_{21}	$F_{11}(A_1)$	$F_{12}(A_1)$	$F_{22}(A_1)$
SO_2	− 0.036	10.53	0.49	0.82
ClO_2	− 0.030	7.12	0.24	0.64
SiF_2	− 0.076	5.22	0.11	0.45
O_3	− 0.103	7.82	0.72	1.22_5

approach each other as the ratio L_{12}/L_{21} decreases. In Tables 4, 5, and 6 the calculated values of the empirically determined constraint are given. The solutions correspond to the same sign of the L matrix elements as determined for the exact force constants.

Discussion

It can be seen from Tables 4 – 6, that the values of the force constants determined from this empirical approach are generally in good agreement with the exact ones. One feature that may be noted is that in any case, the values calculated in the present study are better than those obtained using the L matrix approximation method [1–4]. This may be expected since in our study we have assumed general mixing in both the normal modes, contrary to the basic postulate of the L matrix approximation method according to which the lower vibrational mode is assumed to be completely characteristic [4, 5]. The results obtained in the present study are encouraging specially in the case of molecules like CF_4, BF_3, BCl_3, and BI_3 for which the mass coupling is large. However, in the case of O_3 the agreement is not very good.

There is close agreement of our results with the exact ones for the hydrides, though our constraint is not valid in such cases (see Fig. 1). The most interesting result is that for different types of molecules (XY_4, XY_3 and XY_2) the ratio L_{12}/L_{21} shows special dependence on the mass coupling term T.

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