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THE DETERMINATION OF THE TRANSFORMATION MATRIX L AND THE COMPLIANCE MATRIX C FOR PLANAR XY_2Z MOLECULES

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The difficulty in extending the mixing parameter method to determine uniquely the transformation matrix L for species containing more than two vibrational modes is pointed out. Then a solution to overcome this is proposed. It is then applied to determine the L matrix for five planar XY_2Z molecules, and the corresponding C matrix which reproduces reasonably well all the previously calculated or observed molecular constants such as vibrational mean amplitudes (two for each molecule), centrifugal distortion constants (four for each molecule), coriolis coupling constants (eleven for each molecule) and inertia defect. The existing discrepancy in the assignment of vibrational frequencies for NO_2F and NO_2Cl has been solved using a criterion partly independent of vibrational frequencies, namely the observed inertia defect.

1. Introduction

It is now common to evaluate the compliance matrix C as $C = L\Phi\tilde{L}$ uniquely, the symbols conveying the usual meaning [1, 2]. Determination of the correct L matrix is a well-known problem and De Wames and Wolfram [3–5] have used the mixing parameter method to fix L uniquely. For species involving only two vibrational modes, determination of the mixing parameter matrix A is straightforward from the isotopic sum rules obtained by Green's function. For 3×3 vibrational cases, the original method is less unique and therefore, requires certain modifications as explained briefly below.

2. Mixing parameter matrix for 3×3 vibrational species

The first difficulty arises from the nature of the method of Green's function as used by De Wames and Wolfram. From the secular determinant we get a product rule, a sum rule and a sum of 2×2 product rule connecting the vibrational frequencies of the parent and perturbed (substituted isotopically) molecules and the mixing parameters. The nature of

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mixing has to be essentially orthogonal and this makes the product rule independent of the mixing parameter. The remaining two rules are quadratic equations of the mixing parameters leading to multiple solutions even with two mixing parameters, except in the case of a proper choice which leads to the same value for the ratio of the mixing parameters [6]. This is in principle equivalent to the assumption of just one mixing parameter.

Secondly, by assuming one mixing parameter, the three normal co-ordinates can be written as linear combinations of the three symmetry co-ordinates orthonormally in a number of ways. The type of mixing which gives an L matrix yielding a satisfactory reproduction of all the molecular constants already calculated or observed has to be taken as the most probable type.

Thirdly, in the trial of various types of mixing, one type may give an imaginary value of the mixing parameter. This does not imply that the symmetry co-ordinates are themselves normal co-ordinates without mixing but only reveals that the type of mixing is not real. In a two dimensional problem however, there is only one way of mixing and an imaginary value of the mixing parameter implies the absence of mixing. (Such a result is obtained by us for the B_2 species of NO_2F).

Planar XY_2Z molecules:

The symmetry co-ordinates are

$$\left.\begin{aligned} S_1 &= \Delta D \\ S_2 &= \frac{\Delta d_1 + \Delta d_2}{\sqrt{2}} \\ S_3 &= \frac{2\Delta\alpha - \Delta\beta_1 - \Delta\beta_2}{\sqrt{6}} \end{aligned}\right\} A_1 \text{ species,}$$

$$\left.\begin{aligned} S_4 &= \frac{\Delta d_1 - \Delta d_2}{\sqrt{2}} \\ S_5 &= \frac{\Delta\beta_1 - \Delta\beta_2}{\sqrt{2}} \end{aligned}\right\} B_2 \text{ species,}$$

$$S_6 = \Delta\gamma \ldots B_1 \text{ species,}$$

where D is the X–Z distance, d_1 and d_2 the X–Y distances, α the Y_1XY_2 angle, β_1 and β_2 the Y_1XZ and Y_2XZ angles and γ the angle X–Z bond makes with the Y_1XY_2 plane. The satisfactory type of mixing found by us led to the following normal co-ordinates:

$$\left.\begin{aligned} Q_1 &= \frac{S_1 + aS_3}{\sqrt{1+a^2}} \\ Q_2 &= S_2 \\ Q_3 &= \frac{S_3 - aS_1}{\sqrt{1+a^2}} \end{aligned}\right\} A_1 \text{ species,}$$

TABLE I

L matrix elements

Molecule	L_{11}	L_{22}	L_{33}	L_{13}	L_{23}	L_{21}	L_{31}	L_{32}	L_{44}	L_{55}	L_{45}	L_{54}
CH_2O	0.3638	1.006	1.9075	0.1165	−0.0495	−0.1546	−0.117	−0.0577	1.0494	1.2541	−0.1069	−0.0758
CF_2O	0.3812	0.2783	0.4504	−0.0223	0.0106	−0.1815	0.4352	−0.1998	0.3939	0.4559	0.0788	−0.6434
CCl_2O	0.3818	0.2255	0.3326	−0.0012	0.0110	−0.1739	0.3609	−0.2086	0.3767	0.5476	0	−0.6156
NO_2F	0.3252	0.2873	0.6747	−0.0223	−0.1316	−0.0112	0.3338	0.3548	0.4305	0.4954	0	−0.4044
No_2Cl	0.2192	0.2975	0.7095	−0.0121	−0.1449	−0.0231	−0.3452	−0.0172	0.3750	0.4226	−0.3639	−0.0101

Note: The element L_{12} is zero for all molecules.

$$\left.\begin{aligned} Q_4 &= \frac{S_4 + bS_5}{\sqrt{1+b^2}} \\ Q_5 &= \frac{S_5 - bS_4}{\sqrt{1+b^2}} \end{aligned}\right\} B_2 \text{ species,}$$

$$Q_6 = S_6 \ldots B_1 \text{ species.}$$

From the mixing parameter matrices for the A_1 and B_2 species, the L matrices are obtained as explained in Ref. [2] and [3]. The L matrix elements are reported in Table I. The compliance matrix elements are reported in Table II. The other molecular constants previously calculated and observed have also been evaluated by us using our L and C matrices and are reported in the Tables III to VII.

TABLE II

Compliance matrix elements (Å/md)

Molecule	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{45}	Ref. for frequencies
CH_2O	0.0839	0.2395	2.7505	−0.0357	0.1449	−0.0744	0.2437	1.7169	−0.1629	[12]
CF_2O	0.0675	0.1539	1.1529	−0.0321	0.0249	−0.1114	0.1932	1.3490	−0.1148	[10]
CCl_2O	0.0742	0.2829	2.4238	−0.0338	0.0701	−0.2794	0.3342	3.5215	−0.5461	[9]
NO_2F	0.2911	0.0815	4.0778	−0.0373	0.5080	−0.0946	0.0979	1.3685	−0.0919	[7, 15]
NO_2Cl	0.2942	0.0899	5.7807	−0.0438	0.8879	−0.1043	0.0851	1.8737	−0.1245	[18]

TABLE III

Force matrix elements (md/Å)

Molecule	F_{11}	F_{22}	F_{33}	F_{12}	F_{13}	F_{23}	F_{44}	F_{55}	F_{45}
CH_2O	13.8861	4.4594	0.4001	1.8582	−0.6811	0.0227	4.3813	0.6219	0.4157
CF_2O	16.4462	7.6939	0.9326	3.4118	−0.0255	0.6698	5.4517	0.7808	0.4639
CCl_2O	14.3814	4.1403	0.4698	1.4754	−0.2458	0.4346	4.0078	0.3804	0.6215
No_2F	4.5537	13.0811	0.3145	1.4651	−0.5333	0.1210	10.9018	0.7779	0.7321
No_2Cl	6.7090	12.0296	0.3234	2.1175	−1.1128	0.1082	13.016	0.5905	0.8649

3. Discussions

The compliance constants for the C–O bond in the molecules CF_2O, CCl_2O and CH_2O respectively are in the order of increasing flexibility as evident from the C–O stretching frequencies of these molecules viz. 1928 cm^{-1}, 1827 cm^{-1} and 1746.1 cm^{-1}. The same trend can also be found for the corresponding force constants F_{11} of these molecules as reported in Table III. The N–O bond in NO_2F and NO_2Cl also shows a similar behaviour.

Table III gives the F elements calculated by inverting the C matrix. We feel that it will not be fair to compare closely our values with those already reported in literature since, to our knowledge, no complete normal co-ordinate analysis has been done for these molecules. Either a particular force field such as, the Urey-Bradley force field is assumed [7, 8] or least square fitting is done by letting one of the force constants be a variable parameter [9], the exception, to our knowledge, being CF_2O [10]. However, we find that there is, in general, satisfactory agreement between our values and those already reported in literature. Also, the general features observed previously by various authors such as, F_{12} being larger than F_{23} and F_{13} being the only negative interaction constant, are also found by us as reported in Table III.

It is also seen from Table IV that the centrifugal distortion constants evaluated by using the compliance matrix elements are in satisfactory agreement with values observed in microwave measurements of the various molecules. These constants are sensitive to the

TABLE IV

Centrifugal distortion constants (MHz)

Molecule	τ_{xxxx}	τ_{yyyy}	τ_{zzzz}	τ_{xyxy}	Remarks
CH_2O	−0.3358	−91.9440	−0,1969	−3.0749	Present work
	−0.3853	−85.390	−.2185	−3.2943	observed [12], [19]
CF_2O	−0.0469	−0.0599	−0.0024	−0.03483	present work
	−0.0452	−0.0654	—	−0.0352	observed [20]
CCl_2O	−0.04696	−0.00589	−0.00096	−0.0101	present work
	−0.04097	−0.00675	−0.0011	−0.0058	observed [9]
NO_2F	−0.04274	−0.0729	−0.00465	−0.0464	present work
	−0.0398	−0.0786	−0.00673	−0.0489	observed [14], [15]
NO_2Cl	−0.0117	−0.1282	−0.0016	−0.0414	present work

values of off-diagonal elements of the compliance matrix [11] and the satisfactory agreement is an indication that the off-diagonal elements evaluated in the present work are fairly reliable.

The coriolis coupling constants evaluated by us are reported in Table V and they are found to obey the well-known sum and product rules applicable for the C_{2v} point group. However, there is poor agreement between individual zetas as found by us and as reported by Oka and Morino [7]. This may be mainly due to the type of normal co-ordinate analysis made by us and the other authors, since we find that for CF_2O, there is good agreement between our values and those reported by Mallinson et al. [10] who have made a complete normal co-ordinate analysis without any assumption. If experimentally observed zeta constants are available, a better comparison would have been possible. The only available observed values to our knowledge are $|\zeta^y_{56}| = 0.548$ [12] for CH_2O and $|\zeta^z_{35}| = 0.866$ [10] for CF_2O and our calculated values are in satisfactory agreement with these.

TABLE V

Coriolis coupling constants

Molecule	ζ^x_{16}	ζ^x_{26}	ζ^x_{36}	ζ^y_{46}	ζ^y_{56}	ζ^z_{14}	ζ^z_{24}	ζ^z_{34}	ζ^z_{15}	ζ^z_{25}	ζ^z_{35}
CH_2O	0.2343	−0.4726	0.8595	0.7902	−0.6128	−0.1124	0.0555	0.9919	−0.5272	0.8425	−0.1069
CF_2O	0.9005	−0.3490	0.2596	0.9562	−0.2928	0.7802	−0.3323	0.5303	−0.5269	0.1075	0.8441
CCl_2O	0.9245	−0.3011	0.2345	0.8897	−0.4565	0.6772	−0.3913	0.6233	−0.7053	−0.1033	0.7010
NO_2F	−0.5781	0.3458	0.7341	0.9549	−0.2968	−0.4009	0.1778	0.8987	0.6572	−0.6195	0.4293
NO_2Cl	−0.6370	0.1827	0.7489	0.9393	−0.3437	−0.4184	−0.0382	0.9097	0.7101	−0.6371	0.2998

We feel that a better criterion for comparison is the observed value of the inertia defect which is totally independent of the normal co-ordinate analysis. Using the L^{-1} matrix elements and zeta constants calculated by us, the inertia defect of these molecules have been calculated. The electronic and centrifugal corrections are taken from Oka and Morino [7]. The calculated inertia defect agrees reasonably well with the observed values as reported in Table VI. The calculated inertia defect is a sensitive function of the force field and its

TABLE VI

Inertia defects (amu Å^2)

Molecule	Δ_{vib}	Δ_{elec}	Δ_{cent}	Δ_{ocalc}	Δ_{oobs}	Reference for Δ_{oobs}
CH_2O	0.0574	−0.0052	0.0016	0.0538	0.0574	[7]
CF_2O	0.1577	−0.0015	0.0005	0.1567	0.1563	[10]
CCl_2O	0.2619	−0.0052	0.0005	0.2572	0.2510	[7]
NO_2F	0.1589	−0.0100	—	0.1489	0.1571	[14]
NO_2Cl	0.2131	−0.0104	0.0012	0.2027	0.2012	[13]

agreement with the observed value is a good indication that the force and compliance constants calculated are fairly accurate.

In fact we have used this criterion to solve a discrepancy regarding the frequency assignment of ν_1 and ν_3 for NO_2F. Morino et al. [13, 14] have already resolved a similar problem involving the correct assignment of ν_3, ν_5 and ν_6 by calculating the inertia defect and comparing it with its experimental value. In their assignment $\nu_1 > \nu_3$ Mirri et al. [15] have calculated two sets of force constants by interchanging ν_1 and ν_3 but were not able to "decide between the two sets even by using rotational data in addition to vibration frequencies". We have performed both assignments separately and calculated the L^{-1} matrix

TABLE VII

Mean amplitudes of vibration

Molecule XY_2Z	l_{x-z} [Å]		l_{x-y} [Å]		Ref. for previous values
	Present	Previous	Present	Previous	
CH_2O	0.0382	0.0377	0.0821	0.0801	[16]
CF_2O	0.0361	0.0362	0.0444	0.0436	[16]
CCl_2O	0.0367	0.0369	0.0485	0.0498	[16]
NO_2F	0.0497	0.0481	0.0374	0.0384	[16]
NO_2Cl	0.0492	0.0434	0.0359	0.0388	[16]

and zeta constants. The latter corresponding to modes 1 and 3 change significantly depending on the assignment. For the assignment where $\nu_1 > \nu_3$, we get an inertia defect 0.1487 amu Å^2 while for the other assignment, we get a value 0.1358 amu Å^2. The former

being nearer the observed value of 0.1571 amu Å^2 [14] clearly reveals that $\nu_1 > \nu_3$. This order has been followed for NO_2Cl also.

In Table VII we report the vibrational mean amplitudes calculated directly from the C matrix and they are found to agree well with those reported by Cyvin [16]. The comparison would have been more effective if observed values from electron diffraction were available.

4. Conclusion

Within the limitations of the Green function method we have evaluated the L and C matrices for five planar XY_2Z molecules and they are able to reproduce satisfactorily for each molecule eighteen other molecular constants observed or calculated such as centrifugal distortion constants, coriolis coupling constants inertia defect and mean amplitudes of vibration. Of all these agreements, the one for inertia defect can be taken as a more reliable criterion since the observed inertia defect is totally independent of the force field and frequency assignments. The difficulty regarding agreement between individual zetas calculated by different methods has already been observed by Ramaswamy and Chandrasekaran [17] for CH_2O. A private communication form the former has shown that they have also laid more emphasis on the agreement between calculated and observed inertia defects.

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