Parametric Study of Functions of Molecular Vibrations

IV. Coriolis Coupling Constants for the Molecules XY^2 and X^3 (Symmetry C_{2v})

A. Alix and L. Bernard

Laboratoire de Recherches Optiques Faculté des Sciences, Reims (France)

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In this work, the authors give the parametric form of the Zeta constants for the case of the molecules XY^2 and X^3 (symmetric species C_{2v}), as a function of the mathematical parameter α which generates all the solutions, and of the molecular coupling coefficient ψ_{12} between two symmetry coordinates $S_1(A_1)$ and $S_2(A_1)$.

Introduction

As is the case for various functions in the theory of molecular vibrations such as the force constant matrix F [1,2,3,4], the energy distributions $M_i^{(k)}$ [4,5], the compliance matrix (F^{-1}) and mean square amplitudes of vibration Σ_{ij} [6,7], the Coriolis coupling constants ζ_{ij} can be studied using the parametric form in the general case of second order equations. The expressions we obtain are, then, dependent on the type of symmetry of the molecule which is studied.

As far as this work is concerned, the parametric study of the vibrations of molecules XY^2 or X^3 of point group C_{2v} leads to results which are very simple.

I. Parametric Study of the Coriolis Constants ζ_{ij}

Meal and Polo [8,9] have defined the matrix Zeta of the Coriolis coupling constants

$$\zeta^\alpha = L^{-1} C^\alpha L^{-1t}$$

in which L is the well known matrix of the eigenvectors of the matrix product (GF). C^α is a characteristic matrix of the studied molecule which has a certain analogy from the point of view of the definition and the transformation properties, with the matrix G which defines the inverse kinetic energy of the molecule. These matrices are easily obtained by the "vector method" [10,11]

with
$$G_{ij} = \sum_a \mu_a (s_{i_a} \cdot s_{j_a}),$$
$$C_{ij}^\alpha = \sum_a \mu_a (s_{i_a} \times s_{j_a}) e_\alpha .$$

Reprint requests to A. Alix, Laboratoire de Recherches Optiques BP 347, *51-Reims*, France.

The matrix ζ being invariant under scaling is then studied in the normed system S^N of the symmetry coordinates by using the definition of the molecular coupling coefficient ψ_{ij} between two symmetry coordinates S_i and S_j which are defined by the relations [6,12],

$$L^N = \sigma L, \quad \sigma_i = (G_{ii})^{-1/2} .$$

Thus we get: $C^{N\alpha} = \sigma^{-1} C^\alpha \sigma^{-1}$,

$$\zeta^{N\alpha} = L^{N-1} C^{N\alpha} L^{Nt-1} = L^{-1} C^\alpha L^{-1t} = \zeta^\alpha .$$

By using the parametric form of the matrix L^N related to the solution L^{N^0} corresponding to a completely characteristic lower vibrational mode, which is identical to the model of "progressive rigidity of molecules" [13] and to the approximation [14] $L_{ij} = 0$ for $i > j$ [15], we get

$$L^N = L^{N^0} R \quad \text{with:} \quad R R^t = I .$$

We have then

$$\zeta^\alpha = \zeta^{N\alpha} = R^t (\zeta^{N^0})^\alpha R .$$

1. Case of non-linear molecules XY^2 (group C_{2v})

This is the very well known case of the water molecule model with

$$S_1(A_1) = (1/\sqrt{2})(R_1 + R_2),$$
$$S_2(A_1) = L \cdot \alpha ,$$
$$S_3(B_1) = (1/\sqrt{2})(R_1 - R_2) .$$

The different matrices G^N, C^{Ny} and ζ^y take the form

$$G^N = \begin{vmatrix} 1 & -\sin 2\psi_{12} & 0 \\ -\sin 2\psi_{12} & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

$$\text{with } \sin 2\psi_{12} = -\frac{G_{12}}{\sqrt{G_{11} G_{22}}} = -G_{12}^N,$$

$$C^{Ny} = \begin{vmatrix} 0 & 0 & \sin 2\psi_{12} \\ 0 & 0 & -1 \\ -\sin 2\psi_{12} & 1 & 0 \end{vmatrix},$$

$$\zeta^y = \begin{vmatrix} 0 & 0 & \xi_{13} \\ 0 & 0 & \xi_{23} \\ -\xi_{13} & -\xi_{23} & 0 \end{vmatrix} .$$

The matrix L^N of order 3, taking into account the expression for the sub-matrix of order 2 ($L^N(A_1)$), is written as

$$L^N(A_1) = L^{N^0}(A_1)\, R(\alpha)\,,$$

$$L^N = \left|\begin{array}{ccc} 1 & 0 & 0 \\ -\sin 2\psi_{12} & \cos 2\psi_{12} & 0 \\ 1 & 0 & 1 \end{array}\right| \left|\begin{array}{ccc} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{array}\right| = \left|\begin{array}{ccc} \cos\alpha & -\sin\alpha & 0 \\ -\sin(2\psi_{12}-\alpha) & \cos(2\psi_{12}-\alpha) & 0 \\ 0 & 0 & 1 \end{array}\right|.$$

Thus we get the final expressions for the constants ζ^y_{13} and ζ^y_{23} as

$$\zeta^y_{13} = \sin(2\psi_{12}-\alpha) = -\sqrt{G_{22}}\, L_{12} = -L^N_{12}\,,$$
$$\zeta^y_{23} = -\cos(2\psi_{12}-\alpha) = -\sqrt{G_{22}}\, L_{22} = -L^N_{22}\,.$$

We notice, in agreement with HERSCHBACH and LAURIE[16] that the constant ζ^y_{23} is always negative.

Remarks

The solution of the molecular potential function based on the hypothesis of complete uncoupling of the vibrations corresponds to the case of the "splitting" of vibration[9,16]

$$\zeta^0_{13} = \sin 2\psi_{12}\,, \quad \zeta^0_{23} = -\cos 2\psi_{12}$$

with

$$\zeta^\alpha_H = (L^{-1})_H\, C^\alpha_H\, (L^{-1t})_H$$

in which $(L^{-1})_H$ is the part of the matrix L^{-1} corresponding to the high frequency vibrations and we deduce that

$$\zeta^y_{13} \simeq \frac{{}^tC^y_{13}}{\sqrt{G_{11}\,G_{22}}} = C^{Ny}_{13} = \sin 2\psi_{12}\,.$$

Different authors[14,17,18] have shown that this approximation is suited very well to the molecules XY_n when the coupling between S_1 and S_2 is not too important ($|\sin 2\psi_{12}| < 0{,}3$ with our definition[6] of the coupling between S_1 and S_2).

The influence of the value of the masses m_x and m_y on the values of the Coriolis constants has been studied recently[14,18,19].

We can find again one of the limits of ζ_{13} by taking into consideration the variation of the molecular coupling coefficient $\sin 2\psi_{12}$

$$\sin^2 2\psi_{12} = \frac{\varrho^2 \sin^2\varphi}{1+2\varrho+\varrho^2\sin^2\varphi} \text{ with } \frac{m_y}{m_x} = \frac{\mu_x}{\mu_y} = \varrho\,.$$

Let

$$\sin^2 2\psi_{12}(\varrho\to\infty) = 1$$

or

$$\sin 2\psi_{12} = \pm 1, \quad \psi_{12} = \pm\pi/4\,.$$

This solution corresponds to the maximum coupling between the symmetry coordinates S_1 and S_2. The application of the energy criterium[5] defines the only solution that is physically acceptable and is given by $\alpha = 0$. Thus

$$(\zeta_{13})_{\varrho\to\infty} = (\zeta^0_{13})_{\varrho\to\infty} = \sin 2\psi_{12_{\varrho\to\infty}} = +1\,.$$

2. Case of linear molecules XY^2 (group $D_{\infty h}$)

These molecules behave in the same way as the diatomic molecules: the molecular potential model for these diatomic-like molecules is given by the solution corresponding to completely characteristic vibrations.

Let $\psi_{ij} = 0\,, \quad i,j = 1,2,3\,.$

We get the classical result[18]

$$\zeta_{23} = -1\,, \quad \zeta_{13} = 0\,.$$

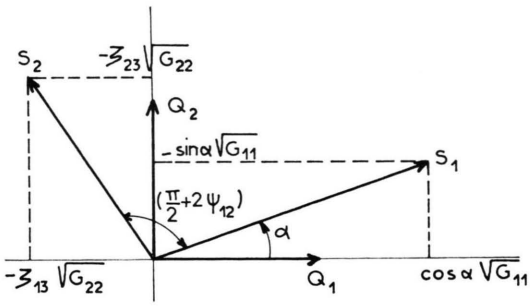

Fig. 3. Vibrations of bent XY^2 type molecules.

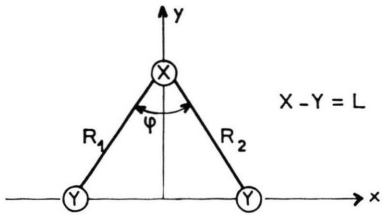

Fig. 1. Internal coordinates and the coordinates axes for $XY^2(C_{2v})$ type molecules.

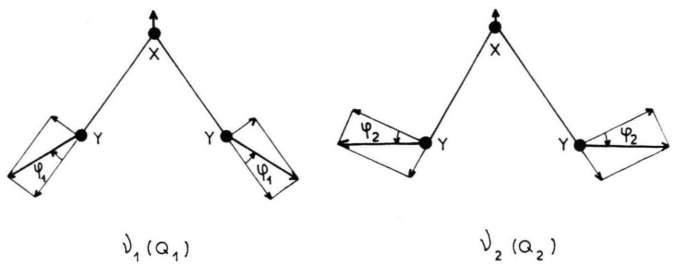

Fig. 2. Mixing of the symmetry coodinates in normal coordinates (Q_1 and Q_2) for $n = 2$ cases.

II. Molecular Potential F and Coriolis Constants ζ_{ij}

The force constant matrix F, the parametric expressions for which have been given[1], is entirely defined by knowledge of the parameter α and can be related to ζ_{ij} as

$$F(A_1) = L^{0-1}_{(A_1)}{}^t \, R(\alpha) \, \Lambda^{A_1} \, R(-\alpha) \, L^{0-1}_{(A_1)},$$
$$F(B_1) = \Lambda^{B_1} \, (G^{-1})^{B_1}$$

with

$$\tan\alpha = \frac{\tan 2\psi_{12} + (\xi_{13}/\xi_{23})}{1 - \tan 2\psi_{12}(\xi_{13}/\xi_{23})}.$$

Besides, it is possible to find again the Coriolis constants, except for the sign, by developing the relation of MEAL and POLO[9]

$$L^t(F\,C^y)\,L^{t-1} = \Lambda\zeta^y$$

which gives

$$\zeta^2_{13} = \frac{\lambda_1[F_{11}/(G^{-1})_{11}]}{\lambda_1 - \lambda_2} \quad \text{and} \quad \zeta^2_{13} + \zeta^2_{23} = 1.$$

Consequently, by using the parametric expression of F_{11}, we get

$$F_{11} = (G^{-1})_{11}\left(\frac{\lambda_1 - \lambda_2}{2} + \frac{\lambda_1 - \lambda_2}{2}\cos 2(2\psi_{12} - \alpha)\right)$$

which leads to

$$\zeta^2_{13} = \frac{1 - \cos 2(2\psi_{12} - \alpha)}{2} = \sin^2(2\psi_{12} - \alpha).$$

III. Energy Distributions and Normal Coordinates

1. *Energy distributions* $M_i^{(k)}$

The energy contributions of the symmetry coordinates S_i to the normal modes of vibration Q_k are defined by[20]

$$M_i^{(k)} = \sum_j L_{ik} L_{jk} F_{ij} \lambda_k^{-1} = L_{ik} L_{ki}^{-1} = L^N_{ik} L^{N-1}_{ki}.$$

Factorization of the matrices G, F, L, Λ ... leads to

$$M = \begin{vmatrix} M_i^{(i)} & 1 - M_i^{(i)} & 0 \\ 1 - M_i^{(i)} & M_i^{(i)} & 0 \\ 0 & 0 & 1 \end{vmatrix},$$

$$M_i^{(i)} = \frac{1 + \tan 2\psi_{12} \tan\alpha}{1 + \tan^2\alpha}, \quad i = 1, 2, .$$

Hence with $\tan\alpha = \tan(2\psi_{12} - (2\psi_{12} - \alpha))$

$$M_i^{(i)} = \frac{1 + \tan(2\psi_{12} - \alpha)\,\mathrm{tg}\,2\psi_{12}}{1 + \tan^2(2\psi_{12} - \alpha)} = \frac{1 - \tan 2\psi_{12}(\xi_{13}/\xi_{23})}{1 + (\xi_{13}/\xi_{23})^2}.$$

Table 1

Molecules	$\xi^0_{13} = \sin 2\psi$	ξ_{13}	$\xi^0_{23} = -\cos 2\psi$	α_{real}	coupling $M_i^{(i)}(\alpha)$ %	φ_1	φ_2	$\varphi_2(0)$	$2\psi_{12}$
H_2Se	0.012 44	− 0.015 60	− 0.999 92	+ 1.60°	99.956	+ 1.60°	− 0.89°	+ 0.71°	0.71°
H_2S	0.030 53	− 0.000 20	− 0.999 53	+ 1.76°	99.999	+ 1.75°	− 0.01°	+ 1.75°	1.74°
H_2O	0.057 38	− 0.000 60	− 0.998 35	+ 3.32°	99.996	+ 3.26°	− 0.03°	+ 3.33°	3.28°
$S^{s0}O_2$	0.152 85	0.181 60	− 0.988 24	− 1.67°	99.464	− 1.58°	+ 10.99°	+ 9.28°	+ 8.79°
$Cl^{35}O_2$	0.281 20	0.364 00	− 0.959 64	− 5.01°	96.685	− 4.63°	+ 22.92°	+ 18.03°	+ 16.33°
$S^{32}O^{18}$	0.294 66	0.306 60	− 0.955 59	− 0.71°	99.598	− 0.63°	+ 19.87°	+ 19.16°	+ 17.13°
$Cl^{35}O_2$ (excited)	0.300 82	0.302 00	− 0.953 68	− 0.07°	99.960	− 0.06°	+ 18.35°	+ 18.28°	+ 17.50°
$N^{14}O_2$	0.411 47	0.583 10	− 0.911 42	− 11.37°	87.385	− 9.32°	+ 41.32°	+ 31.30°	+ 24.29°
O_3^{16} or O_3^{18}	0.457 81	0.600 00	− 0.889 04	− 9.62°	88.717	− 9.42°	+ 37 45°	+ 29.95°	+ 27.24°

Remark: $\varphi_2 + \varphi_1 \simeq \varphi_2(0)$.

From the vibrational energy distributions point of view, we find that the exact coupling of the vibrations is entirely defined by the constants ζ_{ij} (see Table 1).

2. Form of the normal vibrations (symmetry species A_1)

a) in the space of symmetry coordinates: S

The use of the molecular coupling coefficients ψ_{ij} and of the normed system of the symmetry coordinates makes it possible to define the normal coordinates Q_k in the space S^N [6, 21] as

$$\cos(S_i, Q_k) = \frac{L_{ik}}{\sqrt{G_{ii}}} = L_{ik}^N = \cos(S_i^N, Q_k) .$$

Then we get

$$\tan(S_i, Q_i) = L_{ij}^N / L_{ii}^N , \quad \tan(S_2, Q_2) = \zeta_{13}/\zeta_{23}$$

and $$(S_1, S_2) = \pi/2 + 2\,\psi_{12} .$$

b) in the space of the internal coordinates R

The relation between the internal symmetry coordinates S and the internal valence coordinates R can be written as

$$S = U\,R \quad \text{or} \quad R = U^t S$$

so that the form of the normal coordinates Q_k is

$$S = L\,Q,\ R = l\,Q \text{ yielding } Q = l^{-1}\,R = (L^{-1}\,U^t)\,R .$$

The deviations of the normal coordinates Q_1 and Q_2 from the symmetry coordinates S_1 and S_2 are defined, by the angles φ_1 and φ_2 as

$$\cot\varphi_1(\alpha) = \sqrt{G/2\,G_{11}^2}\,(\tan 2\,\psi_{12} + 1/\tan\alpha) ,$$

$$\tan\varphi_2(\alpha) = \sqrt{G/2\,G_{11}^2}\,(\tan 2\,\psi_{12} - \tan\alpha) .$$

The solution of non-coupling based on the consideration of energy distributions is limited by

$$\tan\varphi_1(0) = 0 , \quad \varphi_1(0) = 0 \quad \text{or} \quad Q_1 = L_{11}^{-1}\,S_1 ,$$

$$\tan\varphi_2(0) = \sqrt{\frac{G_{22}}{G_{11}}}\,\frac{\sin 2\psi_{12}}{\sqrt{2}} = \frac{-\,G_{12}}{\sqrt{2}\,G_{11}} .$$

Thus, the bigger the molecular coupling coefficient ψ_{12}, the more the normal vibration $\nu_2(Q_2)$ will be a mixture of the coordinates S_1 and S_2, although these coordinates contribute respectively to Q_1 and Q_2 only from the energy point of view (see Table 1).

IV. Mean Square Amplitudes of Vibration Σ_{ij} and Centrifugal Stretching Constants [6, 7, 19]

The parametric study [6, 7] of the mean amplitudes of vibration Σ_{ij} leads in that particular case to a study of a fundamental relation between the constants Σ_{22} and the ζ_{ij} [19] which is

$$\Sigma_{22} = G_{22}\left(\frac{\delta_1+\delta_2}{2} - \frac{\delta_1-\delta_2}{2}\cos 2\,(2\,\psi_{12} - \alpha)\right)$$
$$= G_{22}[\delta_1 \sin^2(2\,\psi_{12} - \alpha) + \delta_2 \cos^2(2\,\psi_{12} - \alpha)] .$$

Hence we get

$$\Sigma_{22} = G_{22}(\delta_1\,\zeta_{13}^2 + \delta_2\,\zeta_{23}^2) \quad \text{with} \quad \zeta_{13}^2 = 1 - \zeta_{23}^2 ,$$

$$\zeta_{13}^2 = \frac{\dfrac{\Sigma_{22}}{G_{22}} - \delta_2}{\delta_1 - \delta_2} = \frac{\dfrac{(F^{-1})_{22}}{G_{22}} - \sigma_2}{\sigma_1 - \sigma_2} = \frac{\lambda_1 - \dfrac{F_{11}}{(G^{-1})_{11}}}{\lambda_1 - \lambda_2} .$$

These relations between Σ_{22} and $(F^{-1})_{22}$ are a simplified form of the ones we obtained in the general case of second order [7].

It may also be possible to express the various elements of the matrices ζ, θ and Φ in the matrix theory of the centrifugal constants [22], which are, for instance, given by

$$\zeta_{13}^2 = \frac{(\Phi_{22}/G_{22}) - \lambda_2}{\lambda_1 - \lambda_2} = \frac{\sigma_1 - [\theta_{11}/(G^{-1})_{11}]}{\sigma_1 - \sigma_2} \quad \text{etc.}$$

These relations make it possible to test the results we get with the different experimental data for a given molecule (Σ, Λ, $t_{\alpha\beta\gamma\delta}$, ...).

Conclusion

The parametric study of the Coriolis coupling constants leads to some expressions which are particularly simple and which directly define the molecular potential, the energy distributions and the normal modes of vibration. The relations between the matrices ζ, F, Σ, Φ and θ are obviously explicit.

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Zum Rotations-Zeeman-Effekt in Dimethylketen

D. SUTTER, L. CHARPENTIER und H. DREIZLER

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

(Z. Naturforsch. **27 a**, 597—600 [1972]; eingegangen am 19. Dezember 1971)

Molecular Zeeman Effect and the Determination of the Molecular g Values, Paramagnetic Susceptibilities, and Molecular Quadrupole Moments in Dimethylketene

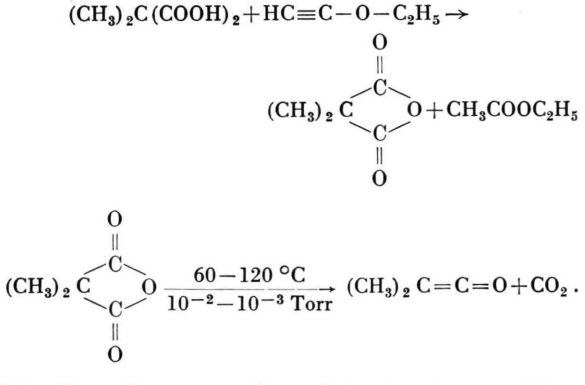
The rotational Zeeman-Effect in the microwave spectrum of dimethylketene was investigated at fieldstrengths close to 22 kG. Only $\Delta J=1$ rotational transitions with $\Delta M=\pm 1$ selection rules did show appreciable splittings due to the magnetic field. From the splittings the diagonal elements of the molecular g-tensor were determined to be:

$$g_{aa}=\mp 0.020\,(3)\,; \qquad g_{bb}=\mp 0.0165\,(8)\,; \qquad g_{cc}=\mp 0.0126\,(5)\,.$$

(Only the relative signs of the g-values are obtained from the experiment). The susceptibility anisotropies were found to be close to zero.

Über das Mikrowellenspektrum von Dimethylketen, $(CH_3)_2C=C=O$, wurde mehrfach berichtet [1]. In der vorliegenden Arbeit werden die Ergebnisse einer Untersuchung des Rotations-Zeeman-Effekts bei magnetischen Feldstärken um 22 kG vorgelegt. Der verwendete Zeeman-Spektrograph ist in einer früheren Arbeit [2] beschrieben worden.

Im Vergleich zu anderen Präparationen [3] hat sich folgende hinsichtlich der Reinheit des Endproduktes und der Ausbeute (60%) gut bewährt.



Die Herstellung von Dimethylmalonsäure erfolgte nach [4].

Eine 60-proz. Lösung von Ethoxyacetylen (Fluka) wurde durch Destillation bei -30 °C, 10^{-2} Torr, von einem Rückstand befreit. 2,2 ml der so gereinigten Ethoxyacetylen-Hexan-Mischung (11 mmol Ethoxyacetylen) wurden auf -10 °C gekühlt und zu einer ebenso gekühlten Lösung von 0,6 g (4,5 mmol) Dimethylmalonsäure in 4 ml getrockneten Äthyläther gegeben. Die Mischung wird 40 Minuten unter Rückfluß und Feuchtigkeitsabschluß ($CaCl_2$) gekocht. Das Produkt wurde anschließend im Exsikkator abgekühlt.

Essigsäureäthylester, Äther und Hexan wurden in einem Stickstoffstrom bei etwa 10^{-2} Torr entfernt, zunächst 4 h bei Zimmertemperatur, danach 12 h bei 30 °C und schließlich 24 h bei 40 °C. Es verbleibt das Dimethylmalonsäureanhydrid als weißes Pulver. Nach Anschluß eines mit flüssiger Luft gekühlten Auffanggefäßes wurde unter Vakuum ($10^{-2}-10^{-3}$ Torr) bei 60 °C bis 120 °C ansteigend die Pyrrolyse durchgeführt. Das Dimethylketen und Kohlendioxid sammelt sich als hellgelbe Substanz im Auffanggefäß. Bei etwa -60 °C wird das CO_2 abgetrennt. Dimethylketen ist bei -180 °C über Monate haltbar.

Viele Rotationsübergänge des Dimethylketens (DMKT) erscheinen im Magnetfeld lediglich etwas verbreitert. Nur die Übergänge mit $\Delta J=1$, $\Delta M=\pm 1$ Auswahlregeln werden nennenswert aufgespalten. Sie erscheinen im Magnetfeld als annähernd symmetrische Dubletts (vgl. Abb. 1). Die beiden Kom-