COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B : Chimie

TOME : 31 ANNÉE : 1985

THE FRANCK-CONDON PRINCIPLE AND THE GEOMETRY OF $SCCl_2$ IN THE EXCITED ELECTRONIC STATE

by

A. ABDEL-RAHMAN, E.M. NOUR, M.H. ABDELLA and E. SAMY.

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les diciplines scientifiques représentées à la Faculté des Sciences de l'Université d'Ankara.

La Revue, jusqu'à 1975 a l'exception des tomes, I, II, III etait composée de trois séries

Série A : Mathématiques, Physique et Astronomie,
Série B : Chimie,
Série C : Sciences Naturelles.

A partir de 1975 la Revue comprend sept séries:

Série A_1 : Mathématiques,
Série A_2 Physique,
Série A_3 : Astronomie,
Série B : Chimie,
Série C_1 : Géologie,
Série C_2 : Botanique,
Série C_3 : Zoologie.

A partir de 1983 les séries de C_2 Botanique et C_3 Zoologie ont été réunies sous la seule série Biologie C et les numéros de Tome commencerons par le numéro 1.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté des Sciences de l'Université d'Ankara. Elle accepte cependant, dans la mesure de la place disponible les communications des auteurs étrangers. Les langues Allemende, Anglaise et Française seront acceptées indifféremment. Tout article doit être accompagné d'un resumé.

Les articles soumis pour publications doivent être remis en trois exemplaires dactylographiés et ne pas dépasser 25 pages des Communications, les dessins et figures portés sur les feuilles séparées devant pouvoir être reproduits sans modifications.

Les auteurs reçoivent 25 extraits sans couverture.

l'Adresse : Dergi Yayın Sekreteri
Ankara Üniversitesi,
Fen Fakültesi,
Beşevler-Ankara
TURQUIE

THE FRANCK-CONDON PRINCIPLE AND THE GEOMETRY OF $SCCl_2$ IN THE EXCITED ELECTRONIC STATE

A. ABDEL - RAHMAN, E.M. NOUR*, M.H. ABDELLA and E. SAMY

Faculty of Science, Zagazig University, Zagazig, Egypt.

(Received August 8, 1984 *and Accepted May* 1, 1985)

ABSTRACT

The geometry of the $SCCl_2$ molecule in the electronic excited state, $^1A_2 \rightarrow {}^1A_1$, has been determined using the polydimentional Franck-Condon method. The molecule in the ground electronic state is plannar and belongs to the C_{2v} point group, while in the excited state in becomes non-plannar and changes symmetry to the C_s point group. This change in symmetry is accompanied by the increase of the values of the molecular dimensions compared with those in the ground state. Increase in the in C = S, C — Cl bond lengths and in ClCCl angle are evaluated to be 0.1838, 0.06845 Å and 9.01°, respectively.

INTRODUCTION

The Franck-Condon method has been used successfully in evaluating quantitatively the geometry of many diatomic as well as polyatomic molecules in the excited electronic state [1,2,3] where the molecules undergo changes in dimensions and in some cases a change of symmetry also occurs. However, the information about the excited electronic state may be obtained from the positions and intensities of the vibronic transitions which are located within the electronic spectrum. The $SCCl_2$ molecule undergoes electronic transition [4] of the type $^1A_2 \rightarrow {}^1A_1$ in the visible region. Fluorscence [4,5], Microwave [6] as well as vibrational studies (7,8,9) have been reported for the $SCCl_2$ molecule. From these studies, it was concluded that the molecule in the ground electronic state is plannar and possesses the C_{2v} symmetry.

In this study we report the evaluation of the structural parameters of $SCCl_2$ in the excited electronic state using the Franck-Cordon principle.

---

* To whom correspondance should be addressed.

RESULTS AND DISCUSSION

To determine the structure of the excited using the Franck-Condon principle requires that the geometry as well as the normal coordinates of the molecule in the ground state to be known. The method also requires a full vibrational assignments and that the intensities of selected bands within each progression have been determined. However, the quantitative feature of the vibrational structure in electronic transition depends on the evaluation of the overlap integral [10], M;

$$M = \int \overset{*}{\psi}'' (Q'') \, \psi' (Q') \, dQ' \qquad (1)$$

where Q′ and Q″ are the normal coordinates of the ground and excited states, respectively, and ψ', ψ'' are the corresponding vibrational wavefunctions. The relation between the overlap integrals, M′s, and the displacement D_i in normal coordinates of the excited state are well established [1,3]. The form of these relations depend on the nature of progression $V' \rightarrow V''$ involved where V′ and V″ are the vibrational quantum numbers for the ground and excited states, respectively. On the other hand, the values of the overlap integrals can be evaluated on the basis of the intensities of the emission or absorption lines [10]. However, the change in normal coordinate D_i is of little value unless it converts to a change in the symmetry coordinates; $\triangle S = S'' - S'$, where S′ and S″ are the symmetry coordinates of the ground and excited states, respectively. The relation [10,11] between D_i and $\triangle S$ is expressed as;

$$\triangle S = G_i{}^{1/2} \, . \, D_i \qquad (2)$$

and

$$G_i{}^{1/2} = L_i \qquad (3)$$

where G_i and L_i are diagonal matrices. The first is the kinetic energy matrix while the latter connects the symmetry coordinates, S, to the normal coordinate, Q. The symmetry coordinates of the $SCCl_2$ in the ground state with C_{2v} symmetry distributed among the symmetry blocks $3A_1 + B_1 + 2B_2$ are:

$$S_1 = t \qquad S_4 = \alpha$$

$$S_2 = \frac{1}{\sqrt{2}} (r_1 + r_2) \qquad S_5 = \frac{1}{\sqrt{2}} (r_1 - r_2)$$

$$S_3 = \frac{1}{\sqrt{2}} (\beta_1 + \beta_2) \qquad S_6 = \frac{1}{\sqrt{2}} (\beta_1 - \beta_2)$$

where t, $r_1, r_2, \beta_1, \beta_2$ and α are the internal coordinates defined in Figure 1. The G-matrix for each symmetry block was calculated according to the equation (12):

$$G = UgU' \tag{4}$$

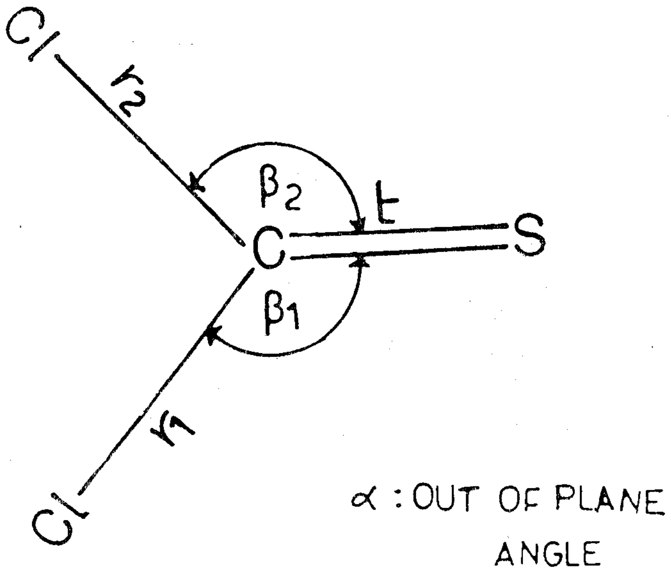

Figure 1. Definition of the internal coordinates in $SCCl_2$.

where U is the matrix formed by the coefficients of symmetry coordinates, U′ is the transpose of U and g is a matrix involves kinetic energy elements. The diagonalized elements of G-matrix for the A_1 symmetry used in our calculation are;

$$G_{diag} = [0.03463 \quad 0.16109 \quad 0.14480]$$ and

the corresponding values of the diagnolized L matrix elements;

$$L_{diag} = [0.18610 \quad 0.40136 \quad 0.38053] .$$

The vibrational data [7] related to the symmetric motions in both the ground (A_1) and excited (A') states as well as the progression [4] of the A_1 modes and their intensities used in the calculations are given in Tables 1 and 2, respectively. These data were used to evaluate the in plane D_i displacement quantities related to the change in C = S and

Table 1. Symmetric vibrational wavenumbers (cm^{-1}) for $SCCl_2$ in the ground and excited states.

Mode	ground	excited
υ (C = S)	1139	907
υ (C — Cl)	503	480
g (ClCCl)	288	245

Table 2. Intensities of vibrational lines (cm^{-1}) their assignments for $SCCl_2$ molecule.

$\Delta\upsilon$	Intensity	A_1		B_1	
		υ_1	υ_2	υ_3	υ_4
290	16	1	0	1	0
1230	2	0	0	1	2
2169	6	0	0	1	4
497	3	0	1	0	0
1435	98	0	1	0	2
2374	22	0	1	0	4
3312	10	0	1	0	6
4246	5	0	1	0	8
582	14	0	0	2	0
1521	13	0	0	2	2
2463	8	0	0	2	4

C — Cl bonds and ClCCl° angle in the excited state. These displacements were transferred to the change in symmetry coordinates S_i according to the equations:

$$\triangle S_1 = G_{11}^{1/2} \cdot D_1 \qquad ; C = S$$

$$\triangle S_2 = G_{22}^{1/2} \cdot D_2 \qquad ; C — Cl$$

$$\triangle S_2 = G_{33}^{1/2} \cdot D_3 \qquad ; ClCCl^{\circ}$$

This led to the evaluation of the new dimentional parameters of $SCCl_2$ in the excited state as given in Table 3. The data clearly demonstrate that the $SCCl_2$ in the excited state shows increase in the values of C = S, C — Cl bond lengths and ClCCl° angle, compared with those of the ground state. These results agree with the decrease of the vibrational wavenumber values of the excited state compared with those of the ground state (see Table 2). Force constant [13] calculations on both state also support our results. These indicate that the C = S and C — Cl bonds in the excited state is 0 .72 and 0 .46 weaker than in the ground state.

Table 3. Structural data for $SCCl_2$ (in Å and degrees) in the ground and excited states.

Parameter	ground	excited*		
		a	b	c
C = S	1.601	1.785	1.756	1.730
C — Cl	1.729	1.797	1.853	1.745
ClCCl	111.19°	120.15°	119.22°	112.3°
out of plane angle	0.0	——	——	27.2°

* (a) Calculation based on anharmonic motions,
(b) Calculation based on harmonic mitons.
(c) Ref. 14.

However, Lombardi [14] calculated the parameters of $SCCl_2$ in the excited state and his data is given beside ours in Table 3. Although, both data agree in the increase of molcular dimensions compared with those of the ground state they differ in their values. This may be related to the tact that Lombardi obtained his data using methods based on the values of the rotation constants of the species in the excited state.

Finally, the out of plane angle in the excited state can not be calculated using the Franck-Condon principle because the symmetry coordinate related to this angle is not the same in the ground and excited states.

REFERENCES

[1] D.C., MOULE, in. Vibrational spectra and structure, vol. 6, P. 227, ed. J.R. Durig, R1977).

[2] Y. FUJIMURA AND H. YMAGUCHI, Bull. Chem. Soc. Japan, 46, 2034 (1973).

[3] J.B., COON, R.E., DEWANDES AND C.M., LOYED, J. Mol. Spectr, 8, 285 (1962).

[4] J.C.D., BRAND, J.L., HARDWICK AND K.E., TEO, J. Mol. Spectr., 57, 215 (1975).

[5] J.R., GROVER AND D.M., BRENNER, M. Chem. Phys. 78, 4385 (1983).

[6] J.H., CARPER, D.F., RIMMER, J.G., SMITH AND D.H., WHIFFEN, J. Chem. Soc. Faraday Trans. act., 2, 1752 (1975).

[7] J.C.D., BRAND, J.H., COLLOMON, D.C., MOULE, J. TYRRELL AND T.H., GOODWIN, Trans. Faraday Soc., 61, 2365 (1965).

[8] T., OKA, A.R., NIGHT AND R.P., STEER, J. Chem. Phys., 63, 2414 (1975).

[9] D.C., MOULE, C.R., SUBRAMANIAN, J. Mol. Spectr., 48, 336 (1973).

[10] W.L., SMITH AND P.A., WARSOP, Trans. Faraday Soc., 46, 1165 (1968).

[11] T.E., SHARP AND H.M., ROSENSTOCK, J. Chem. Phys., 41, 3453 (1964).

[12] E.B., WILSON, J.C., DECIUS AND P.C., CROSS, Molecular Vibrations, McGraw-Hill, New York, 1955.

[13] E.M., NOUR, A., ABDEL RAHMAN AND E., SAMY, Results to to be published.

[14] J., LOMBARDI, J. Chem. Phys., 52, 6126 (1970).