^{35}Cl Nuclear Quadrupole Interaction in Thionyl Chloride

Fernando Mata and Norberto Carballo

Departamento de Química Física, Universidad de Valladolid (Spain)

21 hyperfine multiplets, up to $J = 12$, have been measured for thionyl chloride ($^{32}S^{16}O^{35}Cl_2$), by means of microwave spectroscopy in the region $18.0 - 26.5$ GHz. Nuclear quadrupole coupling constants along the principal axes of inertia were determined to be $\chi_{aa} = -25.004 \pm 0.040$ MHz, $\chi_{bb} = -0.009 \pm 0.025$ MHz and $\chi_{cc} = 25.013 \pm 0.031$ MHz. Also, coupling constants along the S–Cl bond axis (z axis) and two axes perpendicular to this have been calculated to be $\chi_{xx} = 65.93$ MHz, $\chi_{yy} = 30.36$ MHz and $\chi_{zz} = -96.30$ MHz. These values have been compared with those of other workers and with those of other related molecules. Information about the electronic distribution in the S–Cl bond has been obtained from the values of these constants, and the results have been discussed.

I. Introduction

The microwave spectra of three isotopic species of thionyl chloride, $^{32}S^{16}O^{35}Cl_2$, $^{32}S^{16}O^{35}Cl^{37}Cl$ and $^{32}S^{16}O^{37}Cl_2$, have been studied in our laboratory. In a previous paper [1] we have reported the rotational constants and quartic centrifugal distortion constants of those species, and several structures of thionyl chloride have been proposed and discussed. In the present paper we deal with the nuclear quadrupole effect of the parent molecule, $^{32}S^{16}O^{35}Cl_2$.

Thionyl chloride has a complicated quadrupole effect, because of the presence of two chlorine atoms, which has already been studied by several authors. Journel [2], by assigning Q- and R-lines with medium and high J values in the parent molecule, determined the approximate values of the coupling constants χ_{aa} and χ_{cc}. But his work was based on transitions with small hyperfine splittings of around 1 MHz, and the coupling constants could not be calculated with sufficient accuracy.

Later, Wenger et al. [3] studied three hyperfine multiplets in °Q lines by assigning a total of 14 hyperfine components; the analysis of these results, by using the rotational constants of Destombes [4], permitted them to calculate the three coupling constants with good accuracy.

More recently, Suzuki et al. [5], for the parent molecule also, achieved a notable improvement in

the precision of these constants by assigning 13 hyperfine multiplets, with a total of 46 components, and J values up to 9.

With our work we have further improved these values. Effectively, the assignment of 21 multiplets, with J up to 12 and a total of 81 components, in an analysis where (differing from Suzuki et al. [5]) we have also considered the centrifugal distortion effects [1], has permitted us to reduce the nuclear quadrupole coupling constant errors.

II. Experimental

The thionyl chloride utilized was Merck "for synthesis". The microwave spectrum was taken using a Hewlett-Packard MRR 8460 A spectrometer, in K-band, $18.0 - 26.5$ GHz, and with 33.33 kHz square wave Stark modulation.

Transitions were measured at room temperature and at pressures from 10 to 25 µHg. Stark fields ranging from 400 to 4000 Vcm^{-1} were applied, at regular intervals of 800 Vcm^{-1}, to select the most suitable value in each measurement. These Stark field variations have been done in order to separate the Stark components from unperturbed spectrum lines, so they do not interfere with the measurement of the latter.

Finally, the sweep rate depends on the characteristics of the transition which we wish to measure. In order to obtain a good separation between the multiplet components, we have utilized rates from 0.010 to 0.005 MHz/s.

III. Assignment

The analysis of the hyperfine multiplets serves two purposes: the correct assignment of transitions, which is done with much confidence by means of the quadrupole effect, and the determination of nuclear quadrupole coupling constants, which are of interest in order to discuss the electronic distribution in the molecule's bonds.

A theoretical precalculated spectrum was obtained from rotational constants given in the bibliography [6], which permitted us to know the unperturbed frequencies. We have employed the χ_{aa}, χ_{bb} and χ_{cc} constants given by Wenger et al. [3] as initial data in order to know the splitting due to the nuclear quadrupole effect. The first-order treatment proposed by Robinson and Cornwell [7] was used. These authors follow the $I_1 I_2 I J F M_F$ notation of Foley [8], which is the most useful for coupling of two identical nuclei.

The quadrupole coupling energy, i.e., the splitting of a hyperfine level about the unperturbed level is, on the one hand, a function of the field gradient created by the electrons along an axis fixed in space [9], and, on the other hand, a function of the energy matrix secular determinant roots, $\lambda_{\varepsilon J F}$; ε is a pseudo-spin quantum number [7] which defines the energy states.

The frequency of a multiplet component must be:

$$\nu_{Qi} = \nu_0 + \Delta E_{Qi},$$

where ν_0 is the unperturbed transition frequency and ΔE_{Qi} is the splitting originating from the quadrupole effect.

In the Q branch selection rules are (for the most intense multiplet components) $\Delta J = \Delta F = \Delta \varepsilon = 0$, while in the R branch they are $\Delta J = \Delta F = 1$ and $\Delta \varepsilon = 0$.

In the Q branch as well as in the R branch there are four multiplets components which have the splitting $\Delta E_{Qi} = 0$. This has an important practical consequence: the unperturbed transition, differing from the quadrupole effect of a single nucleus, appears in the multiplet, and it is precisely the line of greatest intensity. This has allowed us to determine the frequency centres of $^{32}S^{16}O^{35}Cl_2$, in transitions up to $J = 12$, which is the maximum value of $\lambda_{\varepsilon J F}$ in tables [7], and, besides, to measure these frequency centres in $^{32}S^{16}O^{35}Cl^{37}Cl$ and $^{32}S^{16}O^{37}Cl_2$, in which the quadrupole effect has not yet been resolved with accuracy [1, 5].

As we have just pointed out, we have not analyzed the quadrupole effect in $J > 12$ transitions. But it is not a great disappointment; these high J value lines have the smallest splittings, and this phenomenon is stressed in Q lines, where, e.g., the $12_{67} \leftarrow 12_{57}$ transition has a multiplet whose splitting is a little higher than half a MHz. Higher J lines will have even smaller splittings.

IV. Results

71 transitions ($J \leq 29$) were assigned in the parent molecule, and from this analysis we could obtain the rotational constants and quartic centrifugal distortion constants [1].

The nuclear quadrupole hyperfine structure of 21 of these transitions was resolved and this yielded a

Table 1. Measured nuclear quadrupole splittings (a) of two of the observed transitions of $^{32}S^{16}O^{35}Cl_2$ (MHz).

Transition	Centre Frequency				Hyperfine Components				
	ν_0 obs	ν_0 calc	ν_0 obs-ν_0 calc	Centrifugal distortion	ε	F	obs[a]	calc[a]	obs-calc
$6_{52} \leftarrow 6_{43}$	23710.000	23710.317	−0.317	−1.322	3	9	−3.050	−3.003	−0.047
					1	6	−3.777	−3.790	0.013
					3	4	−2.030	−2.047	0.017
					3	3	−4.740	−4.777	0.037
					2	6	−3.777	−3.787	0.010
$10_{55} \leftarrow 9_{63}$	21824.700	21824.718	−0.018	−3.132	3	11	−0.685	−0.706	0.021
					3	9	−2.335	−2.371	0.036
					1	8	−2.115	−2.121	0.006
					3	6	3.000	2.957	0.043
					0	9	−2.527	−2.533	0.006

[a] The hyperfine component splittings are $\Delta E_{Qi} = \nu_{Qi} - \nu_0$; ν_{Qi} being the frequency of each multiplet component, and ν_0 the unperturbed frequency.

A	5086.831 ± 0.011	
B	2822.657 ± 0.007	
C	1960.369 ± 0.005	
D_J	1.000 ± 0.019	
D_{JK}	-2.397 ± 0.028	
D_K	6.200 ± 0.031	
δ_J	0.371 ± 0.004	
δ_K	1.402 ± 0.046	

Table 2. Rotational parameters utilized in the nuclear quadrupole coupling constants fitting [1]. Rotational constants in MHz; centrifugal distortion constants in kHz.

total of 81 components. The multiplet resolution could not always be done completely, due to the interferences made by the other two isotopic species present in the sample, whose transitions coincide sometimes with the multiplet components, making difficult, or even obstructing, its measurement. These hyperfine components which coincide accidentaly with absorption lines of the other species must be omitted from the fit of the nuclear quadrupole coupling constants [3].

The multiplets have been measured with hyperfine splittings lower than 10 MHz, and with a maximum number of 7 components (centre excluded) by multiplet. As an example, the nuclear quadrupole splittings of two transitions are shown in Table 1. One of them is a Q line, and the other is a R one. The complete list of assigned multiplet hyperfine components can be obtained from Fernando Mata and from Dr. Frank J. Lovas of the Microwave Center at the National Bureau of Standards, Washington, DC (USA), or from Dr. Barbara Stark, University of Ulm (West Germany).

V. Quadrupole Coupling Constants

From the experimental values of ΔE_{Qi} we have calculated, by means of a least-squares fitting, the nuclear quadrupole coupling constants of the parent molecule. We have used our own rotational parameters in these calculations [1], and they are shown in Table 2. The quadrupole coupling constants along

the principal inertia axes, a, b, c, can be seen in Table 3, next to the results obtained by other authors.

In order to relate the coupling constants to physical properties of the S−Cl bond, the values of the constants along the bond axis were obtained. This was achieved by transformation from the principal axis system, a, b and c, to a system x, y and z, where the z-axis coincides with the S−Cl bond, and the x- and y-axes are perpendicular to this; and they are situated so that the y-axis is contained in the molecule symmetry plane. This transformation was carried out simply by performing two consecutive rotations; first, by turning around the a-axis an angle φ (equal to the one formed by the c-axis and the y-axis), and then, by turning around the y-axis an angle θ (equal to the half of the Cl−S−Cl angle).

The values of χ_{xx}, χ_{yy} and χ_{zz} are given in Table 3, and they are calculated from the r_0 structure obtained by us with the b-coordinate of chlorine atom, determined by monosubstitution [1]. With these structural parameters, which can be seen in Table 4, the angle values are $\varphi = 22.77°$ and $\theta = 48.48°$.

To obtain the coupling constants along the S−Cl bond axis and the two other ones perpendicular to this, Suzuki et al. [5] have used their own r_0 structure, whereas Wenger et al. [3] have accepted the electron diffraction structure proposed by Hargittai [10]. The χ_{xx}, χ_{yy} and χ_{zz} values obtained by these authors are shown also in Table 3.

VI. Discussion

By observing Table 3, one can see that there is an excellent agreement among the results derived by Suzuki et al. [5], Wenger et al. [3], and ourselves, especially between the later two. Our accuracy is slightly better, and it can be due to the larger

Table 3. ³⁵Cl Nuclear quadrupole coupling constants (MHz) of $^{32}S^{16}O^{35}Cl_2$.

	This work	Suzuki et al. [5]	Wenger et al. [3]	Journel [2]
χ_{aa}	-25.004 ± 0.040	-25.02 ± 0.04	-25.01 ± 0.07	$\pm 22.1 \pm 0.1$
χ_{bb}	$-\ 0.009 \pm 0.025$	$-\ 0.25 \pm 0.04$	$-\ 0.03 \pm 0.45$	
χ_{cc}	25.013 ± 0.031	25.27 ± 0.08	25.04 ± 0.45	$\pm 22.8 \pm 0.1$
χ_{xx}	65.93	65.62	64.1	
χ_{yy}	30.36	31.13	31.0	
χ_{zz}	-96.30	-96.75	-95.1	

Table 4. r_0 structure, obtained by the authors [1] and utilized in transformation from χ_{aa}, χ_{bb}, χ_{cc} to χ_{xx}, χ_{yy}, χ_{zz}. Distances in Å and angles in degrees.

r(S−O)	1.4278 ± 0.0005
r(S−Cl)	2.0744 ± 0.0003
< Cl−S−Cl	96.9547 ± 0.0013
< O−S−Cl	107.958 ± 0.022

number of multiplets we have assigned and measured. The good concordance between the observed and calculated splittings (see Table 1) justifies the use of the first order perturbation treatment [7], and makes it unnecessary to calculate the off-diagonal elements of the χ tensor.

Also, a comparison among the χ_{xx}, χ_{yy} and χ_{zz} constants of thionyl chloride and those of other related molecules, such as SO_2Cl_2 [11], $COCl_2$ [12], and $CSCl_2$ [13] can be interesting. The values are listed in Table 5. In $CSCl_2$ it has been necessary to interchange χ_{xx} and χ_{yy} because the x- and y-axis designation of those authors is the opposite of this paper and the other authors.

The χ_{zz} value of thionyl chloride is close to that of SO_2Cl_2, which is the most similar molecule. The χ_{zz} values of $COCl_2$ and $CSCl_2$, both with C−Cl bonds, are logically alike and a little different from those of the other two molecules.

Moreover, as we have said above, information about the S−Cl (or C−Cl) bond properties can be obtained from the χ_{xx}, χ_{yy} and χ_{zz} constants. Several simplifications can be used in the interpretation of quadrupole constants (see Ref. [14], Chapt. 14). In the case of these molecules, the most reasonable assumption is to neglect the s and d electrons and overlap, or, in other words, to attribute the field gradient only to the 3p electrons of the chlorine atom. If the three 3p orbitals hold, respectively, n_x, n_y and n_z electrons, then, according to Eq. (14.107) in Ref. [14],

$$n_x + n_y - 2n_z = -2\chi_{zz}/\chi_0,$$

where $\chi_0 = 109.74$ MHz [15] represents the largest possible value of χ_{zz} when the $3p_z$ orbital holds only one electron.

Besides, the Eq. (14.108) of [14] is

$$n_x - n_y = \frac{2}{3}\left(\frac{\chi_{zz}}{\chi_0}\right)\eta,$$

$\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$ being the asymmetry parameter in the tensor of nuclear quadrupole coupling. It measures the deviation of the electronic charge distribution along the S−Cl (or C−Cl) bond from cylindrical symmetry, that is to say, it informs us about the possible double bond character between the Cl and the other atom.

However, one further assumption is necessary to obtain the electron populations of the p_x, p_y and p_z orbitals, and, consequently, the double bond character; and the most suitable one is that the double bond is made only with the p_y orbital, perpendicular to the Cl−S−Cl (or Cl−C−Cl) plane. This is the same as supposing $n_x = 2$, and then it is possible to calculate n_y and n_z (see [13]).

The relation between the electron populations, n_x, n_y and n_z, and the bond characteristics is established in the following way: the double bond character is $\pi_c = n_x - n_y$, since it is related to the electron loss in the p_x orbital. And the partial ionic character of the σ bond is $i_c = n_z - 1$, for in order to know the electron excess in the p_z orbital it is required to take away the electron of the chlorine atom.

In Table 5 the values of η, n_y, n_z, π_c and i_c obtained for these four molecules are listed. At a glance we can see that $SOCl_2$ is somewhat of a special case, since it has a high double bound character and a low ionic character.

From the point of view of the electronegativity difference between S and Cl one could expect a higher ionic character. Nevertheless, Table 5 itself shows us that it is not possible to argue this so easily; the C atom has nearly the same electro-

Table 5. Comparison of the nuclear quadrupole coupling constants (MHz), asymmetry parameter, 3p electron population of the chlorine atom and the double bond and ionic character of the S−Cl or C−Cl bond.

	Ref.	χ_{xx}	χ_{yy}	χ_{zz}	η	n_y	n_z	π_c	i_c
$SOCl_2$	This work	65.93	30.36	−96.30	−0.369	1.784	1.014	0.216	0.014
SO_2Cl_2	[11]	50.14	40.37	−95.51	−0.102	1.941	1.100	0.059	0.100
$COCl_2$	[12]	49.72	27.30	−77.02	−0.291	1.864	1.230	0.136	0.230
$CSCl_2$[a]	[13]	46.01	27.69	−73.70	−0.249	1.889	1.273	0.111	0.273

[a] χ_{xx} and χ_{yy} interchanged in relation to [13]. See text.

negativity as S, $x_C = x_S = 2.5$ [16], and therefore the S$-$Cl and C$-$Cl bonds would have identical ionic character. The point is that in SOCl$_2$ the Cl atom is not bonded only to a S atom, but to the $-$SOCl group; and for this reason the discussion has to be referred to the electronegativity difference between the Cl atom and the rest of the molecule. According to this, we could suggest an increasing order of group electronegativities as $-$CSCl $<$ $-$COCl $<$ $-$SO$_2$Cl $<$ $-$SOCl. A more detailed discussion would need the theoretical calculation of the group electronegativities [17], but they are difficult to evaluate and are not too accurate; usually it is better to obtain them just from the quadrupole coupling constants (see [14], Sect. 14.15).

It is even more surprising that the double bond character is as high as 21.6%, especially if we consider that the sum of the single bond covalent radii is 2.03 Å [18], while the S$-$Cl bond length obtained

by other authors [5, 10] and by us (Table 4) is about 2.07 Å. So it is a rather high double bond character for such a long interatomic distance.

We think that the explanation of those anomalies can lie in the merely approximate nature of the theories developed so far to interpretate the nuclear quadrupole coupling constants in terms of electronic distribution. Those theories seem to be rather suitable for many molecules, but in SOCl$_2$ they lead to slightly peculiar results. But the elaboration of a more accurate and rigorous treatment is beyond the aim of this paper.

Acknowledgement

[1] F. Mata and N. Carballo, J. Mol. Struct., in press.
[2] G. Journel, Thesis, University of Lille, 1969.
[3] H. U. Wenger, A. Bauder, and Hs. H. Gunthard, Chem. Phys. **1**, 441 (1973).
[4] J.-L. Destombes, Thesis, University of Lille, 1970.
[5] S. Suzuki, M. Yamaguchi, M. Onda, T. Sakaizumi, O. Ohashi, and I. Yamaguchi, J. Mol. Struct. **73**, 41 (1981).
[6] G. Journel, A. Dubrulle, J.-L. Destombes, and C. Marlière, Compt. Rend. Acad. Sci., Paris **267 B**, 48 (1968).
[7] G. W. Robinson and C. D. Cornwell, J. Chem. Phys. **21**, 1436 (1953).
[8] H. M. Foley, Phys. Rev. **71**, 747 (1947).
[9] J. J. Bragg and S. Golden, Phys. Rev. **75**, 735 (1949).
[10] I. Hargittai, Acta Chim. Hung. **60**, 231 (1969).

[11] S. Kinuta, see Ref. [5].
[12] J. H. Carpenter and D. F. Rimmer, J. C. S. Faraday Trans. II **74**, 466 (1978).
[13] J. H. Carpenter, D. F. Rimmer, J. G. Smith, and D. H. Whiffen, J. C. S. Faraday, Trans II **71**, 1752 (1975).
[14] W. Gordy and R. L. Cook, Microwave Molecular Spectra, Interscience Publishers, New York 1970.
[15] V. Jaccarino and J. G. King, Phys. Rev. **83**, 471 (1951).
[16] W. Gordy and W. J. Orville-Thomas, J. Chem. Phys. **24**, 439 (1956).
[17] P. R. Wells, Progr. Phys. Org. Chem. **6**, 111 (1968).
[18] L. Pauling, Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, New York 1960.