Catalysis in Molten Salt Media

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Abstract: The low-melting tetraalkylammonium salts of the $SnCl_3^-$ and $GeCl_3^-$ anions are convenient solvents for some homogeneous catalytic reactions of olefins. These salts, when fused, dissolve up to 7% $PtCl_2$ to give deep red solutions which catalyze the hydrogenation, isomerization, hydroformylation, and carboalkoxylation of olefins. In the hydrogenation of 1,5,9-cyclododecatriene, considerable selectivity to cyclododecene is attainable at *ca.* 150° and 100 atm hydrogen pressure. The catalytic solutions of $PtCl_2$ in $[(C_2H_5)_4N][SnCl_3]$ appear to contain $SnCl_3^-$ complexes of platinum including the known anions $[Pt(SnCl_3)_5]^{3-}$ and $[HPt(SnCl_3)_4]^{3-}$.

A major problem in homogeneous catalysis is the separation of products from catalyst and solvent without decomposition of the catalyst. Recent approaches to solution of this problem have emphasized restraint of the catalytic complex by semipermeable membranes[1] or by polymeric ligands.[2] An approach that seems to have been under-utilized is the use of molten salts as stable, nonvolatile solvents[3] from which organic products are readily separated by distillation. Although molten salts have been employed as solvents in a variety of catalytic oxidation reactions,[4] their use has been limited by their physical properties. As pointed out by Rony,[4j] who has carried out one of the few studies of homogeneous catalytic reactions of olefins in molten salt media, most conventional molten electrolytes are corrosive and present mass transfer problems.

These problems are avoided by using tetraalkylammonium salts of $GeCl_3^-$ and $SnCl_3^-$ as solvents for catalytic reactions of olefins. These salts are stable and low melting and are good solvents for many olefins and complexes of the platinum metals. In addition, these salts act as ligands[5] which stabilize the complexes against reduction to free metal and, as described below, confer good selectivity in many reactions.

Results

Fused Salt Solutions. The tetraethylammonium salts of the trichlorogermanate$(1-)$[6] and trichlorostannate$(1-)$[7] ions melt at relatively low temperatures (68 and 78°, respectively) to give clear, colorless liquids. The molten salts are stable in the absence of oxygen for prolonged periods at 150–200° and are good solvents for olefins. For example, at 84° and *ca.* 1 atm, ethylene gives a 0.013 *M* solution in molten $[(C_2H_5)_4N][SnCl_3]$. Chlorides of all the group VIII metals dissolve to give deeply colored solutions[8] which presumably contain complexes bearing the $GeCl_3^-$ and $SnCl_3^-$ ligands.

Platinum dichloride dissolves in $[(C_2H_5)_4N][SnCl_3]$ to give deep red solutions (up to 7% w/w) which display striking catalytic activity in hydrogenation, hydroformylation, and carboalkoxylation of olefins. By adjustment of reaction conditions, considerable selectivity for a particular reaction can be obtained as illustrated below in the hydrogenation of cyclododecatriene to cyclododecene. The $PtCl_2$ solutions seem to be considerably stabilized toward reduction by hydrogen since no metal deposition occurs at 160° and 100 atm pressure. Palladium chloride solutions are less stable, but are unchanged at 100° under 1 atm of hydrogen.

Hydrogenation Reactions. Solutions of $PtCl_2$ in $[R_4N][SnCl_3]$, like the discrete complex $[R_4N]_3[Pt(SnCl_3)_5]$,[9,10] are efficient catalysts for the hydrogenation of olefins. For example, ethylene is cleanly reduced to ethane in the presence of an equimolar amount of hydrogen. The deep red solution remains clear with no evidence of metal deposition. (The rate is much slower than that produced by an equivalent amount of platinum metal suspended in the molten salt.) The solutions can be used repeatedly without apparent loss of catalytic activity if oxidation by adventitious air is avoided.

The rate of ethylene hydrogenation is quite sensitive to changes in the medium. In matched experiments with 1.3 mmol each of ethylene and of hydrogen and 0.1 mmol of catalyst at 100°, the following extents of reaction were attained in 5 hr: $PtCl_2$–Et_4NGeCl_3, 20; $PtCl_2$–Et_4NSnCl_3, 50; *cis*-$(Et_3As)_2PtCl_2$–Et_4NSnCl_3, 27; *cis*-$(Ph_3P)_2PtCl_2$–Et_4NSnCl_3, 20; *cis*-$(Et_3P)_2PtCl_2$–Et_4NSnCl_3, 17%. The rates attained with the phosphine and arsine complexes are significantly lower than that for the $PtCl_2$ solution even though these complexes, used in conjunction with $SnCl_2$, are known to be olefin hydrogenation catalyts.[11] Hydrogenation of ethylene

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Table I. Hydrogenation of 1,5,9-Cyclododecatriene by Fused Salt Solutions of $PtCl_2$[a]

Medium	Temp, °C	Pressure atm	Time, hr	Products, %: Triene	Diene	Monoene[b]	$C_{12}H_{24}$
Et_4NSnCl_3	100	100	6	85	2	12	Trace
	140	100	8	2	18	80	Trace
	160	100	8	2	10	87	Trace
	140	500	6	5	18	73	4
	140	30	6	7	23	65	5
$Ph_3MePSnBr_3$	150	100	6	0		64	18

[a] In each experiment 5.0 ml of *cis,trans,trans*-1,5,9-cyclododecatriene and *ca.* 50 g of a 1% $PtCl_2$ solution were allowed to react under the conditions indicated in an 80-ml Hastelloy shaker tube. [b] The cyclododecene appeared to contain roughly equal amounts of the cis and trans isomers.

in molten tetra-*n*-butylammonium trichlorostannate is slightly slower than in the tetraethylammonium salt, but the lower melting point (59–60°) permits operation at lower temperatures. Hydrogenation activity was observed even at 50° in a solution of $PtCl_2$ in a eutectic mixture of the two trichlorostannate salts.

Vinyl chloride is cleanly hydrogenated to ethane at 120° and 3 atm pressure in a $PtCl_2$ solution in molten $[(C_2H_5)_4N][SnCl_3]$. The reduction appears to proceed *via* dechlorination to give ethylene which is subsequently hydrogenated since some ethylene is detectable when the reaction is stopped after a short time. The appearance of ethane rather than butane or butenes as the product is surprising because vinyl chloride is readily coupled to butadiene by $SnCl_3^-$ salts in the presence of $PtCl_2$ in aqueous dimethylformamide.[7] However, when vinyl chloride is exposed to a $PtCl_2$ solution in $[(C_2H_5)_4N][SnCl_3]$ in the absence of hydrogen at 95°, the olefin partially dissolves (0.045 *M* at 610 mm pressure) but no reaction is apparent.

Platinum dichloride solutions in molten $[(C_2H_5)_4N][SnCl_3]$, like trichlorostannate complexes in more conventional media,[11–13] selectively hydrogenate dienes and trienes to monoolefins. A substantial advantage of the molten salt medium, however, is that the product may be separated by decantation or simple distillation. This simplicity of isolation is especially useful in the reduction of high-boiling polyenes such as the linoleate esters in soyabean oil.[12,13] Methyl linoleate is hydrogenated at 150° and 100 atm pressure in the presence of a 1% solution of $PtCl_2$ in $[(C_2H_5)_4N][SnCl_3]$ to give a mixture of esters containing 63% methyl oleate.

As shown in Table I, the hydrogenation of 1,5,9-cyclododecatriene (cis,trans,trans) can be directed to give primarily cyclododecene under similar conditions. In the range of 30–500 atm, hydrogen pressure does not seem to be a critical variable but choice of time and temperature is important in production of a maximum yield of cyclododecene. A single experiment at 150° with the all-trans triene likewise gave 80+% selectivity to the monoolefin. When *cis*-$PtCl_2[As(C_2H_5)_3]_2$ was used as the catalyst, the reaction was selective to cyclododecene but much slower. After 10 hr at 150° *ca.* 75% triene remained but most of the cis,trans,trans isomer charged had been isomerized to the all-trans and other isomers. Isomerization appears to be much more rapid than hydrogenation in the $PtCl_2$–molten salt solutions. Treatment of 1,5-cyclooctadiene with hydrogen at 1 atm and 100° gave over 90% 1,3 isomer but only traces of cyclooctene and no cyclooctane.

Carbonylation Reactions. Platinum dichloride solutions in molten $[(C_2H_5)_4N][SnCl_3]$ catalyze both hydroformylation and carboalkoxylation of olefins. Reaction of a 1:2:10 mixture of hydrogen, ethylene, and carbon monoxide at 90° and 400 atm gave a 65% combined yield of propionaldehyde and its aldol dimer, 2-methyl-2-pentenal. Carbomethoxylation of 1-hexene at 90° and 450 atm CO pressure gave a 4:1 mixture of methyl heptanoate and the isomeric 2-methylhexanoate. This activity in carbonylation of olefins is again reminiscent of that observed with a mixture of H_2PtCl_6 and $SnCl_2 \cdot 2H_2O$ in alcoholic media.[14]

Discussion

The great similarity in catalytic activity between a solution of $PtCl_2$ in a molten trichlorostannate salt and that observed with preformed $SnCl_3^-$ complexes suggests that the catalytic species may be similar or identical in the two systems. In the presence of a large excess of $SnCl_3^-$ ligand (75Sn/Pt for 1% $PtCl_2$ in Et_4NSnCl_3), the predominant platinum species is expected to be the known[10] five-coordinate complex $[Pt(SnCl_3)_5]^{3-}$. Indeed $[(C_2H_5)_4N]_3[Pt(SnCl_3)_5]$ was isolated by extraction of a concentrated (7%) solution of $PtCl_2$ in $[(C_2H_5)_4N][SnCl_3]$. Fractional extraction of the salt medium recovered from one hydrogenation disclosed the presence of another previously characterized[10] five-coordinate complex, $[HPt(SnCl_3)_4]^{3-}$.

The identification of this hydrido–platinum species suggests that the hydrogenation in this medium proceeds by a conventional olefin insertion mechanism[15] as shown in Figure 1. (A similar mechanism has been proposed for the isomerization of olefins by $PtCl_2$–$SnCl_2$ solutions.[16]) In steps 3 and 4 the olefin competes with excess $SnCl_3^-$ ligand for a coordination site in the hydridoplatinum complex. The large excess of ligand in the molten salt probably accounts for the selective hydrogenation of polyenes to monolefins. Conjugated dienes, such as those formed by isomerization of 1,5,9-cyclododecatriene, compete more successfully for coordination sites than do monolefins by virtue of their ability to form π-allyl complexes in step 5. The mechanism for the cleavage of the alkyl– or allyl–platinum bond in this medium has not been established. The oxidative addition of H_2 (step 6) followed by elimination of alkane (or alkene) seems plausible, but there is strong evidence for protolysis of the C–Pt bond in hydroxylic media.[17]

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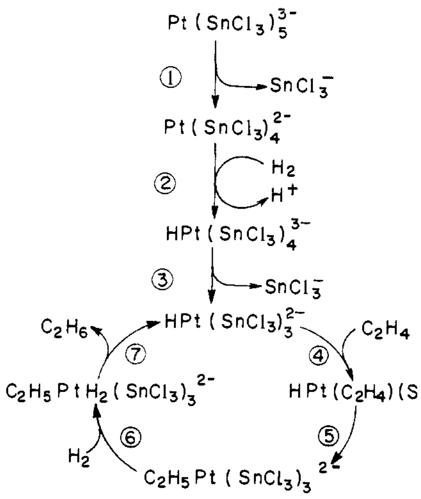

Figure 1. Proposed hydrogenation mechanism in molten trichlorostannate salts. All steps except 7 are reversible.

The observed selectivity for polyene hydrogenation together with the convenient separation techniques available in the fused salt reaction medium suggests that it may be the solvent of choice in a number of homogeneous catalytic reactions. The limiting factors seem to be the relatively low reaction rates and the need to operate above the melting point of the salt.

Experimental Section

Preparation of Fusible Salts. All the trichlorostannate and trichlorogermanate salts studied are very sensitive to oxygen in solution and also slowly oxidize in the solid state. Therefore, storage of the salts as well as manipulation of the solutions was done in a nitrogen atmosphere.

$[(C_2H_5)_4N][SnCl_3]$. Tetraethylammonium trichlorostannate(II) was prepared by the method of Stolberg and Jones[7] and was recrystallized from ethanol–ether before use. The molten salt (mp 78–79°) was found to have a density of 1.48 g/ml at 100°. Hence the molarity of the pure liquid is 4.2 mol/l.

$[(C_2H_5)_4N][GeCl_3]$. Tetraethylammonium trichlorogermanate(II) was prepared by a modification of Poskozim's method[18] for the analogous cesium salt.

Germanium tetrachloride (15.1 ml, 0.13 mol) was added to a warm solution of 70 g of 50% H_3PO_2 in 80 ml of 3 *M* HCl. The mixture was stirred at *ca.* 85° for 5 hr and cooled to 50°, and a solution of 25 g of tetraethylammonium chloride in 15 ml of 3 *M* HCl was added. An oil separated on cooling. The partially solidified oil was dissolved in ethanol and was precipitated as white needles by addition of 700 ml of ether. The solid trichlorogermanate salt was washed with ether in an N_2 atmosphere and was dried under vacuum, mp 67.5–69°, yield 19.3 g (48%).

Anal. Calcd for $C_8H_{20}Cl_3GeN$: C, 31.07; H, 6.52; N, 4.53. Found: C, 30.48; H, 6.41; N, 4.29.

$[(n\text{-}C_4H_9)_4N][SnCl_3]$. A solution of 22.6 g (0.1 mol) of $SnCl_2 \cdot 2H_2O$ in 100 ml of 1 *N* HCl was stirred at 25° while 100 ml of aqueous 1 *M* tetra-*n*-butylammonium chloride was added. A colorless oil separated. The mixture was briefly warmed to boiling and the layers were separated. The residual oil crystallized on cooling. An attempt to recrystallize it from $CHCl_3$-CCl_4 was unsuccessful, but white solid crystallized from methanol or ethanol solutions on cooling, mp 58–59°. Recrystallization of the tetra-*n*-butylammonium trichlorostannate from ethanol gave white crystals, mp 59.5–60°.

Anal. Calcd for $C_{16}H_{36}Cl_3NSn$: C, 41.10; H, 7.76; N, 3.00. Found: C, 40.81; H, 8.14; N, 2.62.

$[CH_3P(C_6H_5)_3][SnBr_3]$. A solution of 34 g of methyltriphenylphosphonium bromide in 270 ml of H_2O was added with stirring to a solution of 27.8 g of stannous bromide in 45 ml of 48% hydrobromic acid. An off-white precipitate formed and was filtered, washed with ethanol and ether, and was dried under vacuum. Recrystallization from ethanol gave off-white crystals of methyltriphenylphosphonium tribromostannate(II), mp 113–114°, yield 38.3 g.

Anal. Calcd for $C_{19}H_{18}Br_3PSn$: C, 35.90; H, 2.86. Found: C, 36.17; H, 2.96.

$[C_6H_5N(CH_3)_3][SnCl_3]$. A solution of 25 g of trimethylanilinium chloride in 50 ml of 0.5 *N* HCl was added to a solution of 31 g of $SnCl_2 \cdot 2H_2O$ in 100 ml of 0.5 *N* HCl. The mixture was heated briefly and then was cooled to give long white needles of trimethylanilinium trichlorostannate(II), mp 106–106.5°; yield 46.3 g.

Anal. Calcd for $C_9H_{14}NSnCl_3$: C, 29.9; H, 3.91; N, 3.88. Found: C, 30.08; H, 3.90; N, 3.65.

Preparation of $PtCl_2$ Solutions. Although $PtCl_2$ dissolves in $[(C_2H_5)_4N[SnCl_3]$ at concentrations up to 7%, typical catalytic runs were made with 0.5–1.2% solutions (1.0% = 0.055 *M*, including a correction for the small volume expansion when $PtCl_2$ dissolves). Appropriate weights of $PtCl_2$ and the tin salt were mixed and gently heated under nitrogen until the salt melts. The $PtCl_2$ dissolved rapidly when stirred to give a deep red solution which was filtered before use. The solution may be cooled and stored as a solid under N_2. Such solutions seem unaffected by repeated use at temperatures up to 160°.

In an experiment to determine the species present in solution, 4.0 g of platinum(II) chloride was dissolved in 53.2 g of molten $[(C_2H_5)_4N][SnCl_3]$. The very deep red solution was filtered and the filtrate was heated at 100° for 1 hr. The melt was cooled and was extracted with several 200-ml portions of hot ethanol. The residual red-orange solid was dissolved in acetone to give a red solution which was filtered to remove a little gray solid. Dilution with methanol gave 3.0 g of orange crystalline $[(C_2H_5)_4N][Pt(SnCl_3)_5]$ with an X-ray powder pattern identical with that previously characterized.[19] A sample was recrystallized from acetone–methanol before elemental analysis.

Anal. Calcd for $C_{24}H_{60}Cl_{15}N_3PtSn_5$: C, 16.85; H, 3.53; Cl, 31.08; N, 2.46. Found: C, 17.70; H, 3.81; Cl, 30.62; N, 2.41.

Ethylene Hydrogenation. Comparative rate experiments were carried out in a 22-ml glass pressure bottle fitted with magnetic stirrer and a transducer or a mechanical pressure gauge and heated by a stirred oil bath. The reactor containing a preformed solution of 0.10 mmol of $PtCl_2$ or complex in 5.0 g of $[(C_2H_5)_4N]$-$[SnCl_3]$ was heated to 70°, slightly below the melting point, and the reactor was evacuated to 0.1 Torr and was repressured to 25 psig with an equimolar mixture of ethylene and hydrogen. The reactor was then heated to 100° with stirring and the rate of reaction monitored by pressure change. The extent of reaction after 8–18 hr was verified by gas chromatographic analysis of the gases.

Cyclododecatriene Hydrogenation. A mixture of 5.0 g of *cis,-trans,trans*-1,5,9-cyclododecatriene and 54 g of a preformed 1% solution of $PtCl_2$ in $(C_2H_5)_4NSnCl_3$ was heated at 160° under 100 atm hydrogen pressure for 10 hr in an 80-ml Hastelloy shaker tube. At the conclusion of the run, the organic products were extracted from the congealed salt with benzene. Distillation of the extract gave the C_{12} products as clear liquid, bp *ca.* 60° at 1 mm, $n^{25}\text{D}$ 1.4977. (Direct distillation of the entire reaction mixture was a generally more convenient procedure. Product recovery seemed to be equivalent.) Gas chromatographic analysis on a butanediol succinate column at 150° showed 87% *cis*- + *trans*-cyclododecene, *ca.* 10% dienes, little or no cyclododecane, and a trace of unchanged triene.

The salt residue after extraction was dissolved in ethanol to leave *ca.* 1 g of a yellow-brown powder (no Pt metal observed). Further extraction with acetone left 0.79 g of a yellow-green powder with a spectrum (ν_{Pt-H} 2060 cm^{-1}) and analysis approaching that of their known $(Et_4N)_3[HPt(SnCl_3)_4]$.

Anal. Calcd for $C_{24}H_{61}Cl_{12}N_3PtSn_4$: C, 19.38; H, 4.13; N, 2.83. Found: C, 20.85; H, 4.33; N, 2.80.

Methyl Linoleate Hydrogenation. A mixture of 5.0 ml of methyl linoleate and 50 g of a 1.0% solution of $PtCl_2$ in tetraethylammonium trichlorostannate was shaken at 150° for 6 hr under a hydrogen pressure of 100 atm in an 80-ml stainless steel vessel. The organic products were distilled directly away from the molten salt at 200° at 0.2 Torr. Redistillation gave 2.0 g of clear colorless liquid, $n^{26}\text{D}$ 1.4522 (identical with that of a commercial sample of

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methyl oleate). The gas chromatogram on a 10% butanediol succinate column on Chromosorb W at 175° showed 63% methyl oleate.

Vinyl Chloride Hydrogenation. A 1.0% solution of $PtCl_2$ in a mixture of 44 g of $[(n\text{-}C_4H_9)_4N][SnCl_3]$ and 17 g of $[(C_2H_5)_4N][SnCl_3]$ was melted, evacuated, and cooled to 25°. The glass reactor was pressured to 25 psig with vinyl chloride and was reheated to 70°. Some vinyl chloride dissolved but no reaction occurred over 3 hr. The reactor was heated to 120° and the gas was replaced with an equimolar mixture of hydrogen and vinyl chloride. A rapid pressure drop occurred. Gas chromatographic analysis showed only ethane and vinyl chloride.

In a subsequent experiment, an equimolar mixture of H_2 and vinyl chloride was heated at 105° for 3 hr with a 1% solution of $PtCl_2$ in Et_4NSnCl_3. The conversion level (*ca.* 20%) was lower than in the earlier experiment, but even at this stage the predominant product was ethane. A small amount of ethylene also appeared.

Ethylene Hydroformylation. A solution of 0.6 g of platinum dichloride and 51 g of tetraethylammonium trichlorostannate was placed in a glass-lined 400-ml Hastelloy pressure vessel. The vessel was pressured to 1000 atm with a 1:2:10 mixture of hydrogen, ethylene, and carbon monoxide and was agitated at 90° for 6 hr. The volatile products were fractionated by vacuum distillation. The product retained by a trap cooled to −119° was propionaldehyde. Treatment with 2,4-dinitrophenylhydrazine gave a yellow-orange product. Recrystallization from ethanol gave orange needles of the 2,4-dinitrophenylhydrazone of propionaldehyde, melting point 154–156°. A mixture melting point with an authentic sample was not depressed. Vacuum distillation of the residual liquid clinging to the frozen salt in the pressure vessel gave 2.8 g of clear colorless liquid. Gas chromatographic analysis showed the presence of propionaldehyde and 2-methyl-2-pentenal.

Carbomethoxylation of Hexene. A mixture of 45 g of 1% $PtCl_2$ in $[(C_2H_5)_4N][SnCl_3]$ solution, 8.4 g of 1-hexene, and 4.8 g of methanol was heated at 90° for 6 hr under 450 atm CO pressure in a 400-ml glass-lined shaker tube. Gas chromatography of the crude supernatant liquid showed methyl heptanoate and methyl 2-methylhexanoate in a ratio of 4.1:1.

Nuclear Magnetic Resonance Spectra of 1:1 Adducts of 1,10-Phenanthroline and α,α′-Bipyridyl with Tris[2,2,6,6-tetramethylheptane-3,5-dionato] Complexes of the Lanthanides[1,2]

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Abstract: The pmr spectra of solutions of 1:1 adducts of dpm_3 complexes of Eu, Pr, and Yb with 1,10-phenanthroline (phen) and α,α′-bipyridyl (bipy) have been studied. The pseudocontact shifts recorded for these complexes do not accord with the Robertson–McConnell expression, which assumes axial symmetry about the metal–Lewis base atom bond. Whereas the spectra of the phen complexes are rather insensitive to variations in temperature, a conformational process involving biphenyl-type rotational isomerization is deduced from the temperature dependence of $Eu(dpm)_3 \cdot$ bipy. These complexes do not coordinate efficiently with added substances and are, therefore, of no value as shift reagents.

In the mere 3 years following the illustration by Hinckley[4] of the effect of tris(diketonato)europium (III) complexes upon the chemical shifts of protons in the vicinity of Lewis basic centers, literally hundreds of reports[5] have appeared describing facets of the interaction between a variety of lanthanide complexes and supernumerary substrates and of the influences thus wrought upon the field position of proximal, resonating nuclei in these substrates. The examples employed in studies of the shift-inducing properties[6] have in common the feature that all behave as monodentate ligands in their coordination to the metal, even though some are in fact multifunctional[7,8] and exhibit (mono) coordination at more than one functional group. In such lanthanide–Lewis base complexes it was found that the magnetic susceptibility tensor of the paramagnetic feature exhibits apparent $C_{\infty v}$ symmetry about the metal atom–Lewis basic atom bond, and that induced shifts (ΔH_i) can be calculated from the relationship[9]

$$\frac{\Delta H_i}{H_0} = \frac{k(g)(3\cos^2\theta_i - 1)}{r_i^3}$$

in which H_0 is the static field, θ_i is the angle about the metal ion between the bond defining the $C_{\infty v}$ axis and the *i*th nucleus, r_i is the distance of the *i*th nucleus from the electron cloud around the metal ion, and $k(g)$ is an empirically determined (generally) value that reflects the relative size of the components of the susceptibility tensor along ($g_{\parallel}$) and normal to ($g_{\perp}$) the $C_{\infty v}$ axis.[5,9] Numerous successful applications[5] have shown that the dependence upon θ_i can be overlooked in most cases without altering drastically the calculated shifts, although a few examples have been reported for which the errors introduced by this neglect are astronomical.[10]

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