main thrust in O_2 electrocatalysis. Rather the search is on for catalysts that promote the direct dissociation of O_2. Some evidence exists that O_2 reduction on Pt, the best catalyst available today, proceeds in this manner.[6-9]

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Registry No. O_2, 7782-44-7; graphite, 7782-42-5; Co–TSP, 28802-06-4.

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Gas-Phase Raman Spectrum of Pentafluorosulfur Chloride, SF_5Cl

AIC70260E

Sir:

The recent paper by Marsden and Bartell[1] has prompted us to report some results that we have obtained concerning the assignments of vibrational frequencies for SF_5Cl.

In earlier work on the vibrational properties of SF_5Cl,[2] Raman bands at 398 and 271 cm^{-1} were assigned to ν_{11}(e) [ρ_w(S–Cl)] and $\nu_6(b_1)$ [$\pi(SF_4)$], respectively. In another study these assignments were reversed.[3] Christe and co-workers[4] commented on the possibility that the band observed at 398 cm^{-1} might be ascribed to the ^{37}Cl component of the S–Cl stretching mode on the basis of force constant calculations and by analogy with SeF_5Cl. Although several workers have accepted this interpretation based on force constant calculations,[1,5] no definitive experimental work has appeared in the literature prior to this report. In a previous paper,[6] we reported the results of a Raman and infrared argon matrix isolation study of SF_5Cl and were able to obtain high-resolution spectra of the bands in the region of 400 cm^{-1} associated with ν_4 (ν(S–Cl)). Since publication of that work, we have obtained polarization data for the Raman spectrum of gaseous SF_5Cl which leave little doubt that the band we observed at 395 cm^{-1} is the ^{37}Cl component of ν(S–Cl).

Spectra were recorded on a Jarrel-Ash Model 500 laser Raman spectrometer equipped with a 5-W Spectra-Physics Model 165 argon ion laser using a multipass gas cell with quartz windows. Other details of the optical system have been described elsewhere.[7] Spectra were observed using 5145- and 4880-Å excitation; the average values of the Raman frequencies are presented in Table I.

Table I. Raman Spectral Data for SF_5Cl(g)

ν, cm^{-1}	I/I_0[a]	ρ[b]	Assignments[c]	
909.1	3	0.82	ν_8(e)	SF_4 eq square str
951.4	3	0.12	$\nu_1(a_1)$	S–F ax. str
797.2	2	0.44	$2\nu_4(a_1)$	
705.4	93	0.11	$\nu_2(a_1)$	SF_4 eq square str
622.2	6	0.79	$\nu_5(b_1)$	SF_4 eq square str
602.7	3	0.64	$\nu_3(a_1)$	SF_4 out-of-plane def
592.2	2	0.70	ν_9(e)	S–F wag
504.1	2	0.71	$\nu_7(b_2)$	SF_4 in-plane def
440.9	5	0.74	ν_{10}(e)	SF_4 in-plane def
403.8	100	0.16	$\nu_4(a_1)$	S–^{35}Cl str
395.0	47	0.20	$\nu_4(a_1)$	S–^{37}Cl str
273.0	4	0.75	ν_{11}(e)	S–Cl wag

[a] Relative peak heights. [b] Estimated from relative peak heights; curve resolution employed for bands at 403.8 and 395.0 cm^{-1}. [c] Assignments from Cross et al.[2] [except band at 395.0 cm^{-1}].

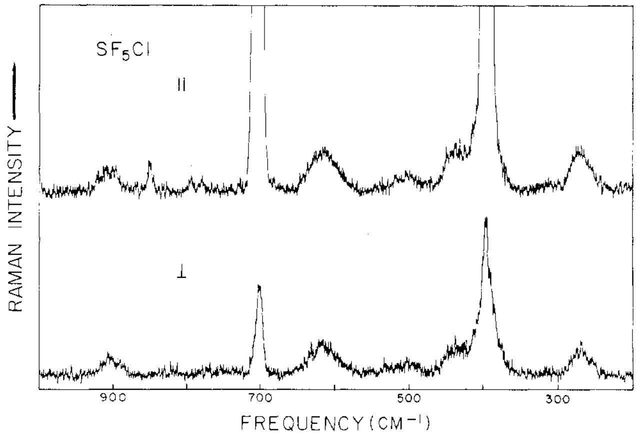

Figure 1. Gas-phase laser-Raman spectrum of SF_5Cl with polarization parallel and perpendicular; 4880-Å excitation (1.3 W), pressure 500 Torr, slits 120 μ, scan speed 0.5 cm^{-1}/s, 1-s time constant, sensitivity 400 Hz.

Raman spectra of SF_5Cl in the gas phase at 500 Torr are shown in Figure 1 under conditions of parallel and perpendicular polarization over the region 200–1000 cm^{-1}. The a_1 modes associated with ν(S–Cl) [ν_4] at 403.8 and 395.0 cm^{-1}, $\nu(SF_4)$ [ν_2] at 705.4 cm^{-1}, and $\nu(S–F_{ax})$ [ν_1] at 851.4 cm^{-1} are still strongly polarized while the band at 602.7 cm^{-1} associated with ν_3 [$\pi(SF_4)$] is weakly polarized. All other bands are depolarized.

A portion of the high-resolution spectrum in the vicinity of 400 cm^{-1} (S–Cl stretch) is shown in Figure 2. The bands shown in Figure 2a are split by approximately 8.8 cm^{-1} and have a relative *integrated* intensity ratio of ca. 3:1. The bands in Figure 2b were observed with the analyzer aligned parallel to the polarization of the incident radiation, and the bands in Figure 2c resulted from scanning the same sample under identical conditions with the analyzer oriented perpendicular to the polarization of the incident radiation. Table I lists the frequencies, relative peak heights, and depolarization ratios for SF_5Cl.

The fact that the Raman band at 395.0 cm^{-1} is strongly polarized indicates that it is due to a mode of symmetry species a_1 and, hence, cannot be assigned to either $\nu_6(b_1)$ or ν_{11}(e). This result and the magnitude of the splitting between the bands at 403.8 and 395.0 cm^{-1} as well as the observed integrated intensities establish the less intense band as the ^{37}Cl component of the S–Cl stretching mode. Moreover, we wish to point out that our observed frequency separation between the S–^{35}Cl and S–^{37}Cl stretching vibrations of 8.8 cm^{-1} in the gas phase (8.2 cm^{-1} in the argon matrix) agrees very well with

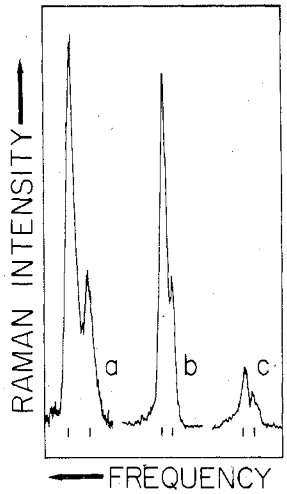

Figure 2. Chlorine isotopic components of ν(S–Cl) in SF$_5$Cl; frequency scale 10 cm^{-1}/division. (a) High-resolution scan: pressure 500 Torr, slits 45 μ, scan speed 0.1 cm^{-1}/s, 1-s time constant, sensitivity 800 Hz. (b) Polarization parallel: slits 62 μ, scan speed 1.0 cm^{-1}/s, 1-s time constant, sensitivity 800 Hz. (c) Polarization perpendicular: conditions identical with those of part b.

the predictions made by Marsden and Bartell[1] (8 cm^{-1}) and by Brooks et al.[5] (8.4 cm^{-1}) and is consistent with their analyses of the force field of SF$_5$Cl. The force constants calculated by both groups were also in good agreement. One of the expected 11 bands for SF$_5$Cl has never been observed. Christe et al.[4] have suggested that this band is ν_6, the SF$_4$ out-of-plane deformation, which either is obscured by other bands or is of low intensity. The frequency of ν_6 has been calculated to be 322.1 cm^{-1} by Brooks et al.[5] and 317 cm^{-1} by Marsden and Bartell.[1] Although it is probable that the missing band is ν_6, the assignment of the band at 273 cm^{-1} as ν_6 by Griffiths[3] cannot be ruled out.

Registry No. SF$_5$Cl, 13780-57-9.

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A Coordination Chemistry Guide to Structural Studies of Chemisorbed Molecules

AIC70454U

Sir:

An understanding of surface chemistry at the molecular level in the context of the chemisorbed state and of the dynamic processes of corrosion, adhesion, and catalysis represents a major scientific challenge.[1,2] Such a "molecular" understanding requires as a first step the delineation of the structure of the molecules, atoms, or groups of atoms chemisorbed at the surface; the issues of bonding and dynamic chemistry cannot be properly examined without such structural information. Surface crystallography, based on the interpretation of low-energy electron diffraction (LEED)[2,3] data, can rigorously define the simplest and ideal case of an ordered chemisorption of atoms[4] on a single crystal but requires supplementary information for an accurate structural analysis of more complex chemisorbed species. It is the purpose of this article to describe a simple supplementary structural technique which is based on a known, but not exploited, surface reaction, the displacement reaction.[5] In addition, a convention is proposed for the notation or description of chemisorbed states wherein there is some unification of surface chemistry and inorganic terms so as to facilitate communication through such interfaces as inorganic and surface science and homogeneous and heterogeneous catalysis.

Before discussing displacement reactions at metal surfaces,[6] it is essential to describe the various classes of chemisorbed states for molecules. At very low temperatures, <100 K, the chemisorption process is in all cases associative (no fragmentation or rearrangement of the molecule); however, this elementary step may be followed by processes other than reversible desorption as the temperature is raised and it is these processes that occur above 200 K that are of primary interest.

In the simplest case of chemisorption, a molecular associative step is the only process that occurs from very low metal surface temperatures to some higher temperature where a desorption step occurs. This limiting case, class 1, of fully reversibly molecular associative chemisorption may have the notation mA$_R$, mA for molecular associative[7] and subscript R for thermally reversible. Molecules that display this type of chemisorption behavior are carbon monoxide on nickel and platinum[8] and acetonitrile on nickel (111).[9] In these examples, only one atom of the molecule is within bonding distance of metal atoms and may be described as an η^1 ligand following the hapto notation of Cotton,[10] i.e., mA$_R$–η^1. Metal atom connexity with respect to the donor atom of the molecule could be specified,[10] e.g., mA$_R$–$\eta^1\mu_2$ for a CO bridge bonded between two metal atoms. In contrast to the CO and CH$_3$CN examples, the reversible chemisorption of ethylene on copper[11] probably involves a bonding approach of both carbon atoms to the metal surface atom(s) and could be differentiated by the notation mA$_R$–η^2.

An alternative sequence for a chemisorption process would be an initial molecular associative adsorption followed by a dissociative reaction step at some higher temperature and then reversible molecular desorption at a still higher temperature. This process, class 2, would be molecular dissociative and reversible, mD$_R$. Typical molecules that exhibit such behavior are the diatomics like hydrogen, nitrogen (on some metals) and cyanogen,[12] the heavier halogens, and oxygen on the more noble metals. Closely related to class 2 is a molecular dissociative chemisorption which, on thermal desorption,[13] yields a relatively clean surface and a set of gaseous desorption products that are not reactants. This class 3 process would be typical of the behavior of HX (X = I and CN) on the noble metals with H$_2$ and X$_2$ desorbed from the surface at different temperatures. To distinguish this class from a fully irreversible chemisorption, the notation mD$_I$–M$_R$ could be used since a "clean" metal (M) surface is regenerated (subscript R). Classes 2 and 3 are analogous to oxidative addition reactions in coordination chemistry.

The fourth class of chemisorption is molecular dissociative and completely irreversible, mD$_I$. For this class, neither the original molecule nor a clean metal surface is formed on flash heating of the crystal. Hydrocarbons, e.g., ethylene on tungsten, commonly show this type of chemisorption behavior.