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Infrared spectrum of matrix isolated CISiO and *ab initio* calculations

Markus Junker and Hansgeorg Schnöckel

Institut für Anorganische Chemie, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

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Cl atoms and SiO molecules are trapped in a solid Ar matrix at 16 K. The formation of the as yet unknown ClSiO molecule has been followed via its IR spectrum. The stretching frequencies of the isotopic isomer ³⁵Cl²⁸Si¹⁶O are observed at 1160.9 and 509.4 cm⁻¹. Experiments with the ¹⁸O isotopic isomers were performed in order to confirm the assignment of the absorptions and to characterize the force field. With the help of quantum chemical calculations (DFT) the optimized ClSiO bond angle is obtained at 125.2°. The computed bond lengths are determined to be 153.6 pm for d(Si-O) and 207.8 pm for d(Si-Cl). The SiCl bond is weak in comparison with that of Cl₂SiO (203.4 pm) which is in line with a decrease in the corresponding Si-Cl force constant. The calculation of its thermodynamic data, $\Delta_f H^0(298) = -167.2 \text{ kJ/mol}; \Delta_f S^0(298) = +279.1 \text{ J/(mol·K)}$, is of high importance for high temperature gas phase reactions of industrial processes, e.g., the combustion of SiCl₄ by O₂. © 1999 American Institute of Physics. [S0021-9606(99)00108-7]

I. INTRODUCTION

Some time ago we studied the reactive species Cl_2SiO ,¹ CICO,² and $CIPO^{3,4}$ under matrix conditions. For CICO and for CIPO the bonding to chlorine is significantly weaker than that in Cl_2CO^2 and Cl_3PO .⁵ For comparison with similar Si–Cl bonding we were interested in the as yet unknown radical CISiO. Furthermore, this reactive species is of interest, since we are involved in studies on the mechanism of the high temperature reaction between SiCl₄ and O₂.⁶ Therefore, in addition to principal interest in bonding of reactive species, the results presented here may contribute to elucidate one of the first steps of this SiCl₄ combustion.

II. EXPERIMENT

Chlorine atoms are produced by thermal dissociation of chlorine molecules. Gaseous chlorine (99.8%, Messer Griesheim GmbH, Krefeld) was passed through a resistor heated oven made of alumina at an input flow rate of about 0.1 mmol/h. The temperature in the center of this furnace was about 1200 °C and the pressure about 10^{-4} atm. Using thermochemical data⁷ the fraction of chlorine atoms generated was determined to be more than 99%.

The chlorine atoms were co-condensed with SiO and an excess of argon on a cooled copper block⁸ at about 16 K. The high temperature molecule SiO was generated by passing an O_2 stream (0.02 mmol/h) over silicon heated to 1200 °C in an alumina furnace. The advantage of this technique is a continuous stream of SiO which can be regulated reproducibly. Furthermore, Si¹⁸O can be prepared easily by application of an ¹⁸O₂ stream. Thus, the relative amount of Ar:Si:Cl in a typical experiment is 100:1:2. After a condensing period of 30 min, IR absorptions were recorded by means of a reflection unit.

Photochemical activation has been performed with the help of a low pressure Hg lamp (Gräntzel, Karlsruhe, Germany). All spectra were recorded with a BRUKER IFS113v FT-IR spectrometer. An MCT detector and a Ge/KBr beamsplitter have been applied in order to obtain the spectra presented. The DFT calculations are carried out on IBM RS 6000/390 workstations using the B3-LYP functional and a TZVPP basis. The program packages GAUSSIAN94⁹ and TURBOMOLE¹⁰ have been used. Contour line diagrams have been realized using the program MOLDEN.¹¹

III. EXPERIMENTAL RESULTS

Figures 1(a) and 1(b) show the two dominant features of the infrared spectrum of ClSi¹⁶O and ClSi¹⁸O in solid argon. The Si-O stretching vibrations are observed with strong intensity at 1160.9 cm^{-1} (ClSi¹⁶O) and 1120.9 cm^{-1} (ClSi¹⁸O). The corresponding frequencies of the ²⁹Si isotopic isomer can be detected unambiguously (Table I). They confirm the assignment to a Si-O motion. the Si-Cl stretching modes are observed at 509.4 cm⁻¹ (ClSi¹⁶O) and 507.6 cm⁻¹ (ClSi¹⁸O). The correctness of this assignment is underlined by a ³⁵Cl/³⁷Cl splitting. The deformation mode has not been observed so far which seems plausible, since, as a result of DFT calculations, its intensity should be only about 10% of that of the Si-Cl stretching mode. Even without the observation of the deformation mode these experimental data clearly show that only a single species is responsible for all these absorptions and that there is present only a single Si-Cl as well as a single Si-O bond in the molecule. No formation of Cl₂SiO was observed in these experiments. Even after irradiation of the matrix with the 254 nm wavelength of a low pressure Hg lamp, no absorptions of Cl₂SiO could be detected. In contrast, former experiments exhibit strong absorptions of Cl₂SiO after Cl₂/SiO codeposition followed by the same irradiation.¹

IV. DFT CALCULATIONS

DFT calculations have been performed in order to get: (a) the equilibrium geometry for the normal coordinate

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FIG. 1. (a) Part of the infrared spectrum of ¹⁶OSiCl in solid argon. Isotopic isomers containing ³⁷Cl, ²⁹Si, and ³⁰Si are marked (\uparrow). (b) Part of the infrared spectrum of ¹⁸OSiCl in solid argon. Isotopic isomers containing ³⁷Cl, ²⁹Si, and ³⁰Si are marked (\uparrow).

analysis, and (b) the energetic relation to solid SiO₂ and SiCl₄ that means a thermodynamic data $\Delta_f H^0$ and $\Delta_f S^0$ of OSiCl and OSiCl₂. In order to check the method applied, we first calculated the corresponding data for OCCl₂ and obtained an excellent agreement in comparison with the experimental values, which is shown by Table II.

The same method has been applied in order to obtain the thermodynamic data for the following reactions:

 $\operatorname{Cl}_2(g) + \operatorname{SiO}(g) \rightleftharpoons \operatorname{Cl}_2 \operatorname{SiO}(g),$ (1)

$$\frac{1}{2}Cl_2(g) + SiO(g) \rightleftharpoons ClSiO(g).$$
 (2)

Combining the calculated reaction energies and entropies for (1) $-335.6 \text{ kJ/mol}/-132.3 \text{ J/(mol}\cdot\text{K})$, and (2) -62.789 kJ/

TABLE I. Observed vibrational modes of different isotopic isomers of ClSiO in solid argon. All values are given in cm^{-1} .

	$\nu(SiO)$	$\nu(SiCl)$
35Cl28Si16O	1160.9	509.4
³⁷ Cl ²⁸ Si ¹⁶ O		503.1
³⁵ Cl ²⁹ Si ¹⁶ O	1153.7	
³⁵ Cl ²⁸ Si ¹⁸ O	1121.0	507.7
³⁷ Cl ²⁸ Si ¹⁸ O		501.5
³⁵ Cl ²⁹ Si ¹⁸ O	1112.9	

TABLE II. Experimental and calculated thermodynamic data for Cl_2CO at 298 K.

Experimental data for Cl ₂ CO (Ref. 16)	DFT calculated values
$\Delta_f H^0 = -220.08 \pm 3.3 \text{ kJ/mol}$	-227.2 kJ/mol
$\Delta_f S^0 = +283.796 \text{ J/(mol}\cdot\text{K})$	+283.84 J/(mol·K)

mol/-44.058 J/(mol·K) with the experimental data for SiO and Cl₂, the following $\Delta_f H^0$ (298) and $\Delta_f S^0$ (298) values in Table III are obtained.

The calculated structural parameters for the molecules SiO, ClSiO, Cl₂SiO, SiCl₂, and SiCl₄ are listed in Table IV. The Si–Cl distance decreases going from SiCl₂/OSiCl to SiCl₄/OSiCl₂. This is in line with the increasing oxidation state of the Si atoms and the atomic charges calculated by the Mulliken population analysis. However, as expected this bond seems to be stronger in OSiCl than in SiCl₂. A different situation is found for the Si–O-bonds: This bond is significantly longer for OSiCl compared to SiO and OSiCl₂. For ClSiO the three calculated vibrational frequencies and their IR-intensities (in km/mol) are listed in Table V.

The general valence force field is described by the following force constants f (mdyn/Å, normalized to unit length):

$f_{\rm SiO}$	8.03,
$f_{\rm SiCl}$	2.30,
$f_{\rm ClSiO}$	0.194,
$f_{\rm SiO/SiCl}$	0.146,
$f_{ m SiO/ClSiO}$	0.405,
f _{sici/cisio}	-0.007.

The electronic structures of the SOMO (${}^{2}A'$) of OSiCl and for comparison of the HOMO (${}^{1}A'$) of OPCl with an additional electron are visualized in Fig. 2. It was calculated on the basis of a Mulliken population analysis. There are *p*-contributions of all three atoms. In order to get SENs, a Roby–Davidson population analysis has been performed using 9 MAOs for Si, P, and Cl and only 5 MAOs for O. In Fig. 3 the results of the population analysis with the charges *q* and the SEN values (DFT/B3-LYP; TZVPP basis) are summarized.

V. NORMAL COORDINATE ANALYSIS

On the basis of the geometrical data obtained from the DFT calculations and of the experimental data from matrix experiments, a normal coordinate analysis has been performed. Due to the lack of experimental information about the frequency of the bending mode it was assumed to be equal to the theoretical value. With the help of the measured

TABLE III. Calculated thermodynamic data for ClSiO and Cl₂SiO.

	Cl ₂ SiO	ClSiO
$\Delta_f H^0$ (298) [kJ/mol]	-440.0	-167.2
$\Delta_f S^0$ (298) [J/(mol·K)]	302.4	279.1

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TABLE IV. Calculated geometrical data for SiO, ClSiO, Cl_SiO, SiCl_2, and SiCl_4.

	SiO	ClSiO	Cl ₂ SiO	SiCl ₂	SiCl ₄
d(SiO)/pm d(SiCl)/pm $\angle (CISiO)/^{\circ}$ $\angle (CISiCl)/^{\circ}$	152.1 	153.6 207.8 125.2 	151.9 202.8 125.7 108.6	 210.5 101.9	 204.7 109

isotopic shifts (¹⁶O/¹⁸O, ³⁵Cl/³⁷Cl and ²⁸Si/²⁹Si) a suitable force field which fits in with all experimental data was obtained. The measured isotopic shifts were corrected for missing differences in anharmonicity (e.g., between that of ¹⁶O and of ¹⁸O species) by application of the following simplification:¹²

$$\Delta \nu_{\rm corr} = \Delta \nu_{\rm exp} + 2x_e \Delta \nu_{\rm ex} \,. \tag{3}$$

With the help of the anharmonicity constants x_e for SiO and SiCl ($x_{SiO}=0.00481$ and $x_{SiCl}=0.00403$,¹³) the following $\Delta \nu_{corr}$ values of Table VI are obtained. Only the corrected isotopic shifts, which represent nearly "harmonic" shifts should restrict the many possible force field data from a normal coordinate analysis. With the following general valence force field (in mdyn/Å, normalized to unit length) the correct frequency shifts were calculated:

$f_{\rm SiO}$	8.00,
$f_{\rm SiCl}$	2.52,
$f_{\rm ClSiO}$	0.226,
$f_{\rm SiO/SiCl}$	0.12,
$f_{\rm SiO/ClSiO}$	0.03,
$f_{\rm SiCl/ClSiO}$	-0.05.

These force constants represent the bonding of ClSiO in solid argon. These constants are slightly different from those of the molecules in the gas phase and also from those of the calculated DFT frequencies. However, these "argon matrix constants" can be compared with those of other matrix isolated species like SiO^{14} and Cl_2SiO .¹

VI. DISCUSSION

The results obtained are discussed on the basis of the experimentally determined force constants. This force field is confirmed by that obtained from DFT calculations. The Si–O force constant (in mdyn/Å) f_{SiO} in ClSiO (8.00) is significantly lower than in the normal valent species SiO (9.01) and Cl₂SiO (8.95). This trend is also demonstrated by the calculated Si–O distances (in pm) (SiO 152.4, ClSiO 153.6, Cl₂SiO 152.2). Likewise the Si–Cl bond in ClSiO is significantly weaker than in Cl₂SiO: f(SiCl): 2.55 (ClSiO)/3.31 (Cl₂SiO). This weakness of the Si–Cl bond is also in line



FIG. 2. Contour diagram (Ref. 11) of the HOMO of OPCl (${}^{1}A'$) and of the SOMO (${}^{2}A'$) of OSiCl, as discussed in the text. The contour lines are plotted in the molecular plane with the values (in a.u.) 0.0, ±0.025, ±0.075, ±0.100, ±0.125, ±0.150, ±0.175.

with the decrease of the bond length 207.7 (ClSiO)—203.4 (Cl₂SiO) and a drastically lower dissociation energy for ClSiO than for Cl₂SiO (calculated values):

 $ClSiO \rightleftharpoons Cl+SiO \quad 184 \text{ kJ/mol}, \tag{4}$

$$\frac{1}{2}\text{Cl}_2\text{SiO} \rightleftharpoons \text{Cl} + \frac{1}{2}\text{SiO} \quad 291 \text{ kJ/mol}, \tag{5}$$

$$\frac{1}{4}\mathrm{SiCl}_{4} \rightleftharpoons \mathrm{Cl} + \frac{1}{4}\mathrm{Si} \quad 365 \text{ kJ/mol.}$$

$$\tag{6}$$

The Si–Cl bond energy of ClSiO is only 63% of that of Cl_2SiO ; for the analogous carbon compounds the situation is even more drastic. For ClCO the Cl–C bond energy is only 18% of that in Cl_2CO (32 kJ/177 kJ).² SiCl₄ possesses the strongest Si–Cl bonds due to the high ionic contributions, although bond distances are longer compared to those of Cl_2SiO .

This discussion clearly shows that the radical character of CISiO with the single electron in the HOMO weakens the Si–Cl as well as the Si–O bond in comparison with bonds of the normal valent species SiO, SiO₂, and Cl₂SiO. This behavior is also observed when going from the 16 valence electron molecule CO₂ to CO₂⁻ (17 valence electrons) for which longer C–O distances and a bond angle of ~130 to 140° is found.¹⁵

In comparison with the analogous carbon compounds, it is evident that in principle the trends are similar for $OSiCl_x$ species. However, especially the strength of the SiO bond exhibits a much smaller variation strength of the CO bonds where multiple bonding up to a triple bond is usual. In contrast, for bonding in the SiO system a maximum bond order is already reached for Cl₂SiO since for the SiO molecule itself no stronger bond is observed. A further comparison seems to be fruitful: By adding an electron to ClSiO the high temperature molecule CIPO is formed (cf. Fig. 2). A very weak P–Cl bond f(PCl)=2.2 and a strong P–O bond with f(PO)=9.8 is observed for this species which is similar to the situation in ClNO for which the description Cl⁻NO⁺ visualizes the presence of nearly an NO triple bond. Further-

TABLE V. Calculated frequencies and intensities (in km/mol) of OSiCl.







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TABLE VI. Experimental and corrected isotopic shifts of OSiCl.

	Experimental	Corrected
¹⁶ O/ ¹⁸ O v(SiO)	39.9	40.3
²⁸ Si/ ²⁹ Si v(SiO)	7.2	7.3
$^{35}\text{Cl}/^{37}\text{Cl}\nu(\text{SiCl})$	6.1	6.2

more, the additional electron completes the lone pair at the P atoms, a fact which makes the smaller bond angle in ClPO (109°) in comparison with 125.2° in ClSiO plausible.

Note added in proof. While correcting the proof we got knowledge about a theoretical work on ClSiO.¹⁷

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