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Short Communication

Gas phase structure of diiodosilane SiH_2I_2

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Abstract

The molecular structure of diiodosilane has been determined by gas electron diffraction. Assuming C_{2v} symmetry, only the S–I bond length (2.423(3) Å) and the I–Si–I bond angle (110.8(4)°) could be determined accurately in this experiment. The experimental geometric parameters and vibrational frequencies which were reported earlier are compared to calculated values derived with the HF approximation and DFT methods (B3LYP and SVWN) using 3-21G* basis sets and effective core potentials.

Keywords: Diiodosilane; Infrared spectra; Gas electron diffraction; Quantum Chemical Calculations

Infrared spectra of gaseous, liquid and solid diiodosilane as well as Raman spectra of the liquid phase have been published previously [1,2]. In this communication we report the molecular structure of this compound as determined by gas electron diffraction (GED) and quantum chemical calculations. Furthermore, the calculated vibrational frequencies are compared to the experimental values.

The compound was synthesized by reacting diphenylsilane with hydrogen iodide at −40 °C [3]. Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2 [4] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample, inlet system and nozzle with 0.7 mm inner diameter were at room temperature. The photographic plates (KODAK Electron Image Plates, 13 × 18 cm) were analyzed with the usual methods [5]. Averaged molecular intensities in the s-ranges 2–18 and 8–25 $Å^{-1}$, in intervals of $\Delta s = 0.2$ $Å^{-1}$ ($s = (4\pi/\lambda)sin\ \theta/2$, where λ is the electron wavelength and θ is the scattering angle), are presented in Fig. 1.

Geometry optimizations and frequency calculations were performed with the Hartree–Fock approximation and DFT methods (B3LYP and SVWN), using 3-21G* basis sets and effective core potentials SSD [6] with an additional set of d functions for Si. Vibrational amplitudes were calculated from cartesian force constants which were derived with the HF/3-21G* method and multiplied with a scaling factor of 0.85. All quantum chemical calculations were done with the GAUSSIAN 98 program suite [7] and amplitudes were derived with the program ASYM40 [8].

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Table 1
Experimental and calculated geometric parameters of SiH_2I_2

	GED[a]	HF/3-21G*	B3LYP/3-21G*	SVWN/3-21G*	HF/SDD[b]	B3LYP/SDD[b]	SVWN/SDD[b]
Si–H	1.470(28)	1.463	1.479	1.493	1.448	1.464	1.481
Si–I	2.423(3)	2.455	2.458	2.423	2.480	2.513	2.471
I–Si–I	110.8(4)	112.6	113.4	112.9	112.2	112.9	112.8
I–Si–H	107.3(33)	108.2	108.1	108.2	108.0	107.9	108.1

Bond distances in Å, bond angles in degree.
[a] r_g values with 3σ uncertainties.
[b] With set of d functions for Si.

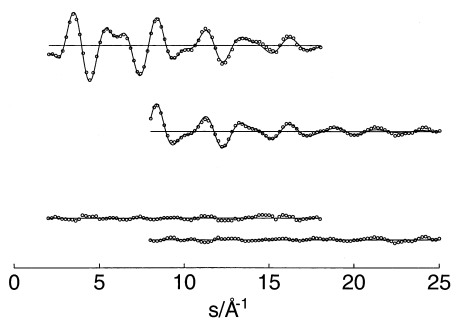

Fig. 1. Experimental (dots) and calculated (full line) electron diffraction intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

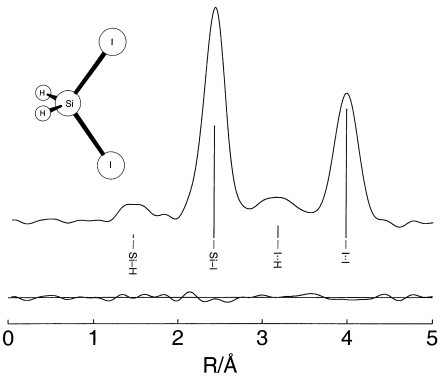

Fig. 2. Experimental radial distribution function and difference curve.

The radial distribution function (Fig. 2) was derived by Fourier transformation of the molecular intensities which were modified with a damping function $\exp(-\gamma s^2)$, $\gamma = 0.0037$ Å^2.

The geometric parameters were refined by least squares fitting of the molecular intensities. Assuming C_{2v} symmetry, four geometric parameters and two vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than |0.5|: Si–I/ISiI = −0.66 and Si–H/ISiH = −0.52. The final results are listed together with calculated values in Tables 1 and 2.

Only two geometric parameters, Si–I and I–Si–I, are well determined in the GED experiment. The S–I bond length in diiodosilane (2.423(3) Å) is somewhat shorter than that in iodosilane (2.4384(6) Å [9]) or in tetraiodosilane (2.430(5) Å [10]). The I–Si–I bond angle (110.8(4)°) is slightly larger than tetrahedral. This contradicts the VSEPR model which predicts this angle to be smaller than tetrahedral, since iodine possesses a higher electronegativity (2.5) than hydrogen (2.1).

Only a very limited number of quantum chemical calculations for compounds containing Si–I bonds has been reported in the literature and thus little experience is available about the performance of different methods and basis sets for such compounds. Comparison of predicted Si–I bond lengths with the experimental value in Table 1 reveals, that the HF approximation and DFT methods with small basis sets (3-21G*) provide satisfactory agreement. The

Table 2
Interatomic distances (r_g values from GED), experimental and calculated (HF/3-21G*) vibrational amplitudes

	Distance	Amplitude (GED)[a]	Amplitude (HF)
Si–H	1.47	0.087[b]	0.087
Si–I	2.42	0.070(4)	0.060
H···H	2.50	0.148[b]	0.148
I···H	3.19	0.141[b]	0.141
I···I	3.99	0.131(5)	0.109

[a] Uncertainties are 3σ values.
[b] Not refined.

Table 3
Experimental and calculated vibrational frequencies (unscaled)

Species	Mode	Experiment	HF/3-21G*	B3LYP/3-21G*	B3LYP/SDD[a]	SVWN/SDD[a]
A_1	ν_1	2195[b]	2452	2287	2290	2224
	ν_2	925[b]	1020	932	930	881
	ν_3	328[b]	348	330	283	301
	ν_4	91[c]	93	86	81	82
A_2	ν_5	664[c]	756	687	675	654
B_1	ν_6	2215[b]	2464	2306	2314	2249
	ν_7	501[b]	542	487	488	474
B_2	ν_8	797[b]	909	824	811	779
	ν_9	399[b]	427	409	340	366

[a] With set of d functions for Si.
[b] IR(gas) [1].
[c] Raman(liquid) [2].

experimental value is reproduced best with the SVWN method. HF and DFT methods with the SSD basis sets predict the Si–I bond too long by 0.05–0.09 Å. The calculated bond lengths are even longer without d functions for silicon.

The HF/3-21G* approximation predicts all vibrational frequencies systematically too high by 2–13%. The two Si–I stretching vibrations (ν_3 and ν_9) are too high by about 6%. No systematic trends between calculated and experimental vibrational frequencies are observed for the other methods listed in Table 3. Calculated frequencies are either too high or too low. The B3LYP method which is known to reproduce vibrational frequencies for molecules containing lighter elements satisfactorily, results in the case of SiH_2I_2 in values which vary between 4% too high and 18% too low (B3LYP/SSD). Especially the two Si–I stretching frequencies are predicted too low by 15 and 18%. This trend is contrary to that observed for compounds containing lighter elements for which stretching frequencies are always predicted too high.

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