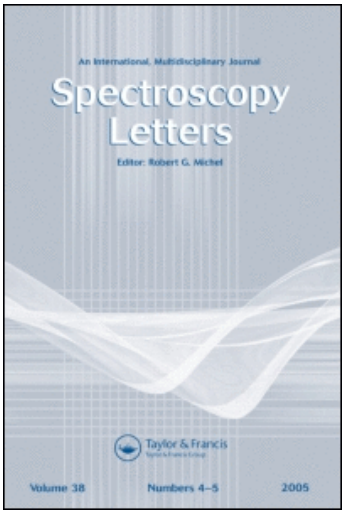

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

The Infrared Spectra of Diiodosilane

A. Ben Altabef[a]; E. L. Varetti[a]; P. J. Aymonino[a]
[a] Cátedra de Química Inorgánica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, R. Argentina

To cite this Article Altabef, A. Ben , Varetti, E. L. and Aymonino, P. J.(1979) 'The Infrared Spectra of Diiodosilane', Spectroscopy Letters, 12: 6, 445 — 450
To link to this Article: DOI: 10.1080/00387017908069171
URL: http://dx.doi.org/10.1080/00387017908069171

SPECTROSCOPY LETTERS, 12(6), 445-450 (1979)

THE INFRARED SPECTRA OF DIIODOSILANE

A.Ben Altabef [1], E.L.Varetti [2] and P.J.Aymonino [2]

Cátedra de Química Inorgánica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esquina 115, 1900 La Plata, R.Argentina.

ABSTRACT

The IR spectra of SiH_2I_2 was recorded in the gaseous, liquid and solid phases, in the range 4000-250 cm^{-1}. An assignment of the observed bands is proposed and the measured frequencies are compared with the existing data for the other members of the series SiH_2X_2 (X: halogen).

INTRODUCTION

Infrared spectroscopic data for SiH_2F_2, SiH_2Cl_2 and SiH_2Br_2 were published by several groups [3,4,5]. An Urey-Bradley force field for these molecules was

also reported [6]. However, no information could be found in the literature about the vibrational properties of SiH_2I_2, save a brief reference to its bands above the NaCl-prism limit (600 cm^{-1}) [7]. We report now the results of an IR study of this last compound in different aggregation states.

EXPERIMENTAL

SiH_2I_2 was prepared using the method of Fritz and Kummer [8]; the IR bands of the gaseous substance were coincident with those previously reported [7]. The spectra were measured with a Perkin-Elmer 457 spectrophotometer, calibrated with H_2O, CO and NH_3 bands. Spectra of the gaseous, liquid and solid substance were obtained in cells provided with CsI windows. The weaker bands were observed in some gas spectra using a heated gas cell, which allowed the use of higher vapour pressures. Low temperature spectra of the substance condensed from the gas phase on a CsI window cooled at 85 K were obtained by means of a RIIC (model VTL-2) variable temperature cell.

RESULTS AND ASSIGNMENT

The SiH_2I_2 molecule must have C_{2v} symmetry, as found for example in SiH_2F_2 by microwave spectroscopy [9]. Therefore, the nine normal modes of vibration should be classified as $4\ A_1 + A_2 + 2\ B_1 + 2\ B_2$, being the A_2 mode active only in Raman whereas the other modes are active both in Raman and infrared.

We observed six bands in the spectra of gaseous and liquid SiH_2I_2 (Table 1). The assignment of these bands is immediate after comparison with the data published for the other members of the series [3,4,5]. A schematic correlation with these data can be appreciated in Figure 1.

The two Si-H stretching modes originate the feature centered at 2200 cm^{-1}, which must result from the overlapping of two bands, as evidenced by its complex profile in the gas spectra and by the splitting in two components in the spectra of the solid

TABLE 1

Wavenumbers and Assignment of the Observed Bands in the Infrared Spectra of SiH_2I_2.

Mode		Gas		Liquid	Solid	Assignment
A_1:	1	2205[a]	s	2200	2200	Symm. Si-H stretch
	2	928 921	s	900	925	H-Si-H deformation
	3	333	w	323	b	Symm. Si-I stretch
	4	c		c	c	I-Si-I deformation
B_1:	6	2205[a]	s	2200	2152	Antisym. Si-H stretch
	7	505	w	502	b	SiH_2 rock
B_2:	8	799 793	vs	780	735	SiH_2 wag
	9	402 396	m	388	b	Antisym. Si-I stretch

a: center of complex band; b: not observed; c: not accessible; s: strong, m: medium, w: weak, v: very.

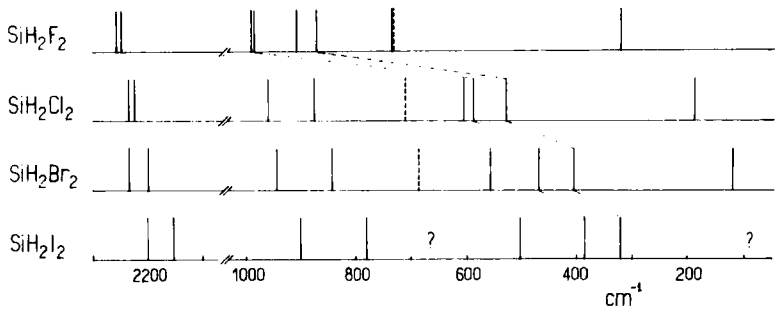

FIG. 1: Relative location of vibrational bands in the dihalosilanes. The vertical dashed lines indicate the position of torsional bands. The shift of the Si-X stretching modes along the series is also remarked.

substance at low temperatures as well. The weaker component (2200 cm^{-1}) is assigned to the symmetric Si-H stretching and the stronger one (2152 cm^{-1}) to the antisymmetric mode.

The Si-I stretching mode was found at 362 cm^{-1} in the spectra of SiH_3I [10] and at 306 cm^{-1}(symmetric stretching) and 385 cm^{-1} (antisymmetric stretching) in a study of diiododimethylsilane [11]. Such data justify the assignment of the 323 cm^{-1}(weak) and 388 cm^{-1}(medium) bands of SiH_2I_2 to the symmetric and antisymmetric Si-I stretching modes, respectively. The gradual shift of the Si-X modes towards lower wavenumbers along the series, as remarked in Figure 1, is justified not only by the increase of mass of the halogen atoms but also by the decrease

of the associated force constant with decreasing electronegativity of the halogen [6].

The deformation modes associated with the SiH_2 moiety show a rather uniform shift along the series and are immediately assigned (Table 1 and Figure 1).

There are still two normal modes to be considered. One is the I-Si-I deformation, which should originate a band near 100 cm^{-1} (122 cm^{-1} in the bromine derivative [5]) and therefore could not be observed with our spectrophotometer. The second mode is the torsion (species A_2, active only in Raman) for which a wavenumber of about 660 cm^{-1} can be predicted (Figure 1).

REFERENCES

1. On leave of absence from Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, R.Argentina.
2. Members of the Carrera del Investigador Científico, CONICET, R.Argentina.
3. S.Cradock, E.A.V.Ebsworth and A.G.Robiette, Trans.Faraday Soc. 60, 1502 (1964).
4. D.H.Christensen and O.F.Nielsen, J.Mol.Spectrosc. 27, 489 (1968).
5. D.W.Mayo, H.E.Opitz and J.S.Peake, J.Chem.Phys. 23, 1344 (1955); K.Kawai and H.Murata, Nippon Kagaku Zasshi 77, 504 (1956).
6. K.Ohno, M.Hayashi and H.Murata, J.Sc.Hirosh.Univ. 37 A, 325 (1973).
7. H.J.Emeleus, A.G.MacDiarmid and A.G.Maddock, J.inorg.nucl.Chem. 1, 194 (1955).
8. G.Fritz und D.Kummer, Chem.Ber. 94, 1143 (1961).
9. V.W.Laurie, J.Chem.Phys. 26, 1359 (1957).

10. H.Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie", Springer - Verlag, Berlin, 1966.
11. J.R.Durig and C.W.Hawley, J.Chem.Phys. 58, 237 (1973).

Received 3-15-79
Accepted 4-04-79