

corresponding to the b stretch. This has to be related with the high stretching force constant k_t and the high electronic density carried by the Mo-O_t bonds. When considering that the bending constant reflects the ability of electronic densities carried by adjacent bonds to repel each other, it is easy to understand that higher localized electronic density (i.e., more dense valence orbitals in the VSEPR approach) will induce a higher bending constant.

On the other hand, the bending constant k_β has a very low value consistent with the very loose Mo-O_c bonds, carrying a very low electronic density. The k_β value cannot be given accurately because of the nonobservation of the F_{1u} band assigned to δ bending. Since this band is expected below 200 cm⁻¹, k_β is certainly less than 0.5 mdyn Å⁻¹, which is also consistent with a bend constant of an angle between two single bonds, Mo-O_b.

So far as the k_α value is concerned, we observe that the replacement of 0.005 by 0.00 does not affect significantly the calculated frequencies. We only can say that k_α has a very low value, which is again consistent with the loosely bonded O_c atom.

The four above bend constants concern each MoO₆ octahedron and the O₆Mo₆ octahedron of the framework. The k_e constant gives information about the ability of deformation of the MoO₆Mo angles between two adjacent octahedra, i.e., the bridge angles characteristic of the structure. Its value is as well consistent with the single-bond character of the Mo-O_b bonds. Let us notice that k_e is higher than k_β . This could be related to the electronic density along the Mo-O_b bonds: the electronic cloud should be more dense around the O_b atoms.

When considering the PED column of Table I, we can see that, except for δ bending, there are no pure bending modes. The γ bend significantly contributes to many modes at relatively high frequency. It even appears that the F_{1u} 598-cm⁻¹

and A_{1g} 598-cm⁻¹ modes, previously assigned as Mo-O_b stretching modes, present a predominant γ character, with some b-stretch character. The other bend modes appear as mixed modes in the medium- and low-frequency regions. The ϵ character is never predominant, as seen in Table I.

(iii) **Torsional Constants.** The torsions over c bonds were always found to be unnecessary. The torsions over b bonds act in some low-frequency vibrations. However, the values 0.02 and 0.00 mdyn Å⁻¹ practically lead to the same results. We must admit there is no serious basis for discussion of such a low-value force constant: it is better to neglect it.

Conclusion

In this paper devoted to the normal-coordinate analysis of hexamolybdate anion of the Lindqvist structure, we have demonstrated the importance of using isotopic molecules as a support of assignments. The outstanding feature of this study is certainly the complete assignment of the vibrational spectra of this anion.

On this basis, we were able to propose a reasonable force field which accounts for all the experimental data (four isotopic species). The three stretching force constants k_t (7.46 mdyn Å⁻¹), k_b (2.35 mdyn Å⁻¹), and k_c (0.47 mdyn Å⁻¹) are consistent with double Mo-O_t bonds, single Mo-O_b bonds, and very loose Mo-O_c bonds, respectively.

From this study, by assumption of the transferability of the force field, investigations on other polyoxometalates will be carried out.

Acknowledgment. We wish to thank the late Dr. M. T. Forel, who encouraged us to undertake this study, and Dr. M. Fournier for helpful discussions about polyoxometalates: success in synthesizing the ¹⁸O derivative was certainly due to his valuable advice.

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Microwave, Infrared, and Raman Spectra, Structure, Quadrupole Moment, and Normal-Coordinate Analysis of Disilyl Iodide¹

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The microwave spectra of H₃SiSiH₂I and D₃SiSiD₂I have been recorded from 26.5 to 38.5 GHz. a -Type transitions were observed, and R-branch assignments have been made for the ground vibrational state. The rotational constants were found to have the following values: for H₃SiSiH₂I, $A = 8602.22 \pm 8.63$, $B = 1179.79 \pm 0.02$, $C = 1062.47 \pm 0.02$ MHz; for D₃SiSiD₂I, $A = 6571.01 \pm 5.80$, $B = 1078.87 \pm 0.03$, $C = 969.96 \pm 0.06$ MHz. From a diagnostic least-squares adjustment to fit the six rotational constants, the following structural parameters were obtained: $r(\text{Si}-\text{H}_3) = 1.491 \pm 0.010$ Å, $r(\text{Si}-\text{H}_2) = 1.478 \pm 0.010$ Å, $r(\text{Si}-\text{Si}) = 2.336 \pm 0.007$ Å, $r(\text{Si}-\text{I}) = 2.440 \pm 0.009$ Å, $\angle\text{SiSiI} = 106.7 \pm 0.3^\circ$, $\angle\text{SiSiH(I)} = 111.8 \pm 1.8^\circ$, $\angle\text{SiSiH} = 111.3 \pm 1.9^\circ$. These parameters are compared to the corresponding ones in some other silanes. The quadrupole coupling constants were found to have the values $\chi_{aa} = -938$, $\chi_{bb} = 255$, and $\chi_{cc} = 683$ MHz with $\eta = -428$ MHz. The infrared (3500-20 cm⁻¹) and Raman spectra (3500-0 cm⁻¹) have been recorded for both the gas and solid. Additionally, the Raman spectra of the liquids were recorded and qualitative depolarization values were obtained. All of the normal modes except the SiH₃ torsion have been assigned on the basis of band contours, depolarization values, and group frequencies. A normal-coordinate calculation has been carried out by utilizing a modified valence force field to calculate the frequencies and the potential energy distribution. Some mixing was found among the SiH₃ symmetric deformation, the SiH₂ scissors, and the SiH₂ wagging motions. These results are compared to similar quantities in some corresponding molecules.

Introduction

Disilyl iodide was first prepared and isolated by Ward and MacDiarmid^{2a} in 1959. Prior to this time, the only other

monohalogenated disilyl compounds reported were H₃SiSiH₂Br and H₃SiSiH₂Cl.^{2b,3} Neither of these compounds was obtained in high purity, and because of the proposed ready

(1) Taken in part from the thesis of J. S. Church, which will be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

(2) (a) L. G. L. Ward and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **82**, 2151 (1960); (b) A. Stock and C. Somieski, *Chem. Ber.*, **53**, 759 (1920).
(3) J. M. Gamboa, *An. Real Soc. Esp. Fis. Quim., Ser. B*, **46**, 699 (1950); *Chem. Abstr.* **49**, 6766 (1955).

disproportionation according to the equation



it was impossible to fully characterize them.^{2a} Recently, it has been suggested that the rapid decomposition of disilyl iodide is catalyzed by traces of aluminum iodide, which was difficult to remove.⁴

Other than the original work of Ward and MacDiarmid^{2a} where the physical properties, thermal stability, and gas-phase infrared spectra above 700 cm⁻¹ were reported, disilyl iodide has been the subject of a limited number of investigations. Fehér et al.⁵ recorded and assigned the Raman spectrum of disilyl iodide; however, no depolarization data were reported. The NMR spectra were reported in two independent investigations.^{6,7} The most complete of these studies was that of Van Dyke and MacDiarmid,⁷ where the proton chemical shifts and ²⁹Si-H coupling constants were measured for a series of compounds containing the disilyl group. The trend in the relative values of the proton chemical shifts of the SiH₃ and SiH₂ groups in the series H₃SiSiH₂X (X = F, Cl, Br, I) was found to be analogous to that observed in the ethyl halide series.⁸ The SiH₂ resonances move to lower field as the electronegativity of the attached halogen decreases. However, in the case of H₃SiSiH₂I, the NMR spectrum differs markedly from that of H₃CCH₂I as the SiH₂ and SiH₃ resonances cross over in frequency with the SiH₂ resonance falling at higher field than the SiH₃ resonance.⁷⁻¹⁰

Ward and MacDiarmid^{2a} suggest that such a crossover of the SiH₃ and SiH₂ resonance frequencies in the H₃SiSiH₂X series can be attributed to a decrease in the "effective" electronegativity of the halogens in the silicon compounds with respect to the carbon-bonded compounds. Furthermore, they suggest that such a reduction in electronegativity could arise through p_π → d_π back-bonding between the halogen and silicon atoms. Evidence of this type of bonding has been reported by Cradock and Ebsworth¹¹ for the Si-Cl bond in H₃SiCl.

In a recent Raman investigation, we¹² have determined the barrier to internal rotation around the Si-Si bond in gaseous disilane by the direct observation of the torsional overtones. A value of 1.26 kcal/mol was obtained for this barrier, which is consistent with the results obtained by various indirect methods. With the successful determination of the rotational barriers in the ethyl compounds,¹³ it becomes of interest what effect monosubstitution of halogens would have on the barriers for the corresponding disilyl compounds. Although vibrational spectroscopy provides a direct method for the determination of torsional barriers, it should be noted that microwave spectroscopy also affords information on the determination of these barriers through the relative intensity measurements of excited-state transitions as well as from the observation of splitting of the rotational transitions. This has been demonstrated by Cox and Varma,¹⁴ who determined the barrier to internal rotation in H₃SiSiH₂F to be 1.048 kcal/mol by the measurement of the observed A-E splitting of the rotational lines.

In a continuing effort to characterize the H₃Si moiety, an investigation of the vibrational and rotational spectra of disilyl iodide was undertaken. It was hoped that along with yielding information relevant to the possible p_π → d_π bonding in the S-I bond and the barrier to internal rotation of the H₃Si moiety, information on the quadrupole ¹²⁷I nuclei would also be obtained. The results of these investigations are reported herein.

Experimental Section

Disilyl iodide was prepared by the reaction of anhydrous hydrogen iodide and disilane in the presence of a catalytic amount of aluminum iodide.^{2a} The hydrogen iodide was prepared from red phosphorus (Baker), pulverized iodine, and distilled water and purified by passing through a trap at -96 °C. Disilane was prepared by the reduction of hexachlorodisilane (PCR Research Chemicals Inc.) with lithium aluminum hydride (Alfa) in a solution of dibutyl ether.¹⁵ Disilane-d₆ was either prepared with use of lithium aluminum deuteride (Merck Sharp and Dohme) in the manner described above or purchased directly from Merck Sharp and Dohme.

The aluminum iodide was prepared from the elements in boiling benzene.¹⁶ The resulting aluminum iodide was purified for catalytic use by sublimation in vacuo. In order to avoid isotopic contamination, the reaction vessel was thoroughly cleaned and then charged with fresh catalyst prior to preparing the deuterium compound. During sample preparation and handling, care was taken to exclude all traces of mercury and mercury vapor with which H₃SiSiH₂I is known to readily react. Both disilane and disilyl iodide were purified prior to their use on a low-temperature sublimation column.

The microwave spectra were obtained by using a Hewlett-Packard 8460A MRR spectrometer with a Stark modulation of 33.3 kHz. The Stark cells were maintained at a temperature slightly below room temperature by lightly packing them in dry ice. The sample was continuously flowed through the wave guide in order to minimize decomposition effects. Mid-infrared spectra were recorded on a Digilab Model FTS-14C Fourier transform interferometer equipped with a high-intensity Globar source, Ge/KBr beam splitter, and TGS detector. Spectra of the gaseous samples were recorded both at their ambient vapor pressure and at 10 mmHg with use of a 10-cm cell fitted with KBr windows. Spectra of the crystalline solids were recorded by condensing the samples on a CsI plate held at liquid-nitrogen temperature and then annealing until no further change in the spectra was observed. All mid-infrared spectra were recorded at a resolution of 2 cm⁻¹. The far-infrared spectra were recorded on a Digilab Model FTS-15B Fourier transform interferometer equipped with a high-pressure Hg arc lamp source and TGS detector. Atmospheric water vapor was removed from the interferometer housing by purging with dry nitrogen. The spectral region from 650 to 80 cm⁻¹ was obtained by using a 5.09-μm Celenar polyester-film beam splitter, and the region from 80 to 20 cm⁻¹ was obtained by using a 25-μm Mylar beam splitter. Far-infrared spectra of the gases were recorded at 1-cm⁻¹ resolution by containing the samples at their ambient vapor pressure in 10-cm cells fitted with polyethylene windows. Spectra of the crystalline solids were recorded at 2-cm⁻¹ resolution. The samples were condensed on a silicon plate held at liquid-nitrogen temperature and annealed until no further spectral changes were noted. Raman spectra were recorded on a Cary Model 82 spectrophotometer equipped with a Spectra-Physics Model 171 argon ion laser. The laser power was varied from 0.25 to 1 W at the sample depending upon the physical phase under investigation. Spectra of the crystalline solids were recorded at 20 K in a Cryogenics Technology Inc. Spectrim cryostat equipped with a Lake Shore Cryotronics Model DTL 500 temperature controller. The samples were annealed with use of standard techniques. Spectra of the liquids were recorded at ~20 °C by sealing the samples in Pyrex capillaries under high vacuum. The capillaries were then placed in a vacuum-jacketed tube through which cool nitrogen gas was passed. This cell is similar to the one described by Miller and Harney.¹⁷ Raman spectra of the gases were recorded with use of the standard Cary multipass accessories by holding the samples at their ambient

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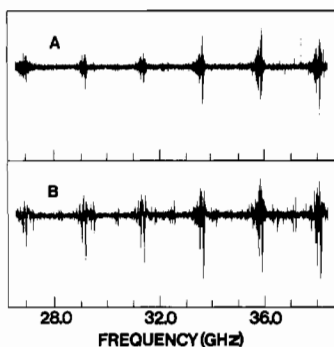


Figure 1. Low-resolution microwave spectrum of disilyl iodide in the region 26.5–38.5 GHz. The base voltage in trace A is 200 V whereas in trace B it is 800 V.

vapor pressure in cells fitted with greaseless stopcocks. Depolarization measurements were made with use of the standard Cary accessories. All Raman spectra were recorded at a resolution of 4 cm^{-1} , and frequencies of sharp resolvable lines are expected to be accurate to at least $\pm 2\text{ cm}^{-1}$. It was found that the samples were considerably more stable than previously reported. After most experiments, 95% of the sample used was recovered by refractionation. The only notable amount of decomposition occurred in the Raman studies of the gaseous samples. So that impurities could be minimized, the compounds were frequently resampled during these experiments.

Microwave Spectrum

On the basis of the assumed molecular structure, disilyl iodide is very nearly a prolate top with the symmetry plane formed by the "a" and "b" axes. Since the a axis is nearly parallel to the Si–I bond, one anticipates mainly a-type transitions. Transitions of the b type may also be observed, but their intensity relative to the a-type transitions should be very weak. The microwave spectrum of disilyl iodide from 26.5 to 38.5 GHz as recorded at base Stark voltages of 200 and 800 V appear in Figure 1. Attempts to investigate the rotational transitions of disilyl iodide below 27.0 GHz were difficult due to their extreme weakness. The weakness of the spectrum can be attributed in part to splitting due to the quadrupole ^{127}I nuclei as well as splitting due to internal rotation. The initial assignment of the rotational lines of disilyl iodide was made for the two R-branch series $J + 1_{1,J} \leftarrow J_{1,J-1}$ and $J + 1_{2,J-1} \leftarrow J_{2,J-2}$, where $J = 11$ or 12 . The assignment was confirmed by checking the qualitative Stark effect, the hyperfine structure due to the interaction between the nuclear spin and the molecular rotation, as well as the rigid rotor model fitting. Due to the high J values of the observed spectrum, the individual Stark components were not resolvable, which made the determination of the electric dipole impossible. It is interesting to note that the Stark components of the $K = 1$ transitions on the high-frequency side of the main band modulated so slowly that these transitions were not observed until Stark voltages of over 1200 V were reached. Rotational lines for several excited vibrational states were observed in the spectra of both isotopic species. As a typical example, the ground- and excited-vibrational-state lines of the $14_{2,12} \leftarrow 13_{2,11}$ transition of disilyl iodide are shown in Figure 2. These transitions are of interest since their analysis could possibly lead to information about the SiH_3 torsional barrier. There are two possible low-frequency vibrations from which the excited-state vibrational transitions could arise: the SiH_3 torsional mode and the Si–Si–I bending mode. From crude relative intensity measurements of several of the excited-state transitions it seemed likely that the series of weaker lines originate from the molecules in the excited states of the Si–Si–I bending vibration and not the torsional mode. This assignment was confirmed by the careful examination of the line shapes and the similarity of the Stark effect of the excited-state transitions. If the observed series of excited-state lines were

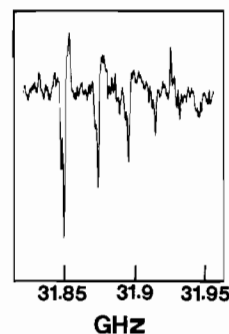


Figure 2. Microwave absorption of the $14_{2,12} \leftarrow 13_{2,11}$ transition of disilyl iodide. The series of weaker lines is due to rotation of the molecule in excited vibrational states.

Table I. Rotational Transitions (MHz) of Disilyl Iodide and Disilyl- d_5 Iodide in the Ground Vibrational State

| molecule | transition | $\nu(\text{obsd})$ | $\Delta\nu$ (obsd – calcd) ^a | |
|------------------------------------|------------------------------------|----------------------------------|--|-------|
| $\text{H}_3\text{SiSiH}_2\text{I}$ | $12_{1,11} \leftarrow 11_{1,10}$ | 27 505.21 | 0.24 | |
| | $12_{2,10} \leftarrow 11_{2,9}$ | 27 214.64 | –0.01 | |
| | $13_{0,13} \leftarrow 12_{0,12}$ | 28 692.32 | 0.01 | |
| | $13_{1,12} \leftarrow 12_{1,11}$ | 29 773.93 | –0.22 | |
| | $13_{2,11} \leftarrow 12_{2,10}$ | 29 529.40 | –0.02 | |
| | $14_{0,14} \leftarrow 13_{0,13}$ | 30 834.96 | 0.12 | |
| | $14_{1,13} \leftarrow 13_{1,12}$ | 32 037.24 | 0.21 | |
| | $14_{1,14} \leftarrow 13_{1,13}$ | 30 439.86 | –0.03 | |
| | $\text{D}_3\text{SiSiD}_2\text{I}$ | $16_{2,14} \leftarrow 15_{2,13}$ | 33 444.59 | 0.53 |
| | | $17_{1,16} \leftarrow 16_{1,15}$ | 35 349.49 | –0.17 |
| | | $17_{2,15} \leftarrow 16_{2,14}$ | 35 573.52 | 0.10 |
| | | $17_{3,14} \leftarrow 16_{3,13}$ | 35 081.79 | 0.31 |
| | | $18_{1,17} \leftarrow 17_{1,16}$ | 37 366.33 | 0.17 |
| | | $18_{2,16} \leftarrow 17_{2,15}$ | 37 698.70 | –0.46 |
| | $18_{3,15} \leftarrow 17_{3,14}$ | 37 186.45 | –0.42 | |

^a Calculated from the rotational constants listed in Table III.

due to the rotation of the molecules in higher torsional states, one would anticipate that the transitions of the third, fourth, and fifth excited states would be split. Such splitting was not observed for any of the excited-state transitions, which indicates that the excited states are due to the bending mode or that the barrier to internal rotation is extremely high. The latter can be ruled out on the basis of the barrier values of 1.26 and 1.048 kcal/mol reported for disilane¹² and disilyl fluoride,¹⁴ respectively. For these reasons as well as for the conditions under which the experiments were carried out it was felt that more accurate measurements of the relative intensities of the excited-state transitions would not be worth pursuing.

In Table I the rotational assignments and their frequencies after making first-order corrections for the hyperfine contributions are listed for the ground vibrational state of disilyl iodide and disilyl- d_5 iodide. The experimental frequencies were obtained by adding the quadrupole hyperfine component frequency shift, $\nu - \nu_0$, given in Table II to the frequencies listed in Table I. In the cases where the hyperfine structure was not resolvable, the band center was used directly for the experimental frequency. Only a-type transitions are reported; because of the overall weak intensity of the rotational spectrum, attempts to observe b-type transitions were abandoned. The effective rotational constants and moments of inertia for both isotopic species of disilyl iodide are given in Table III. Because the measured transitions are very insensitive to the rotational constant A , the accuracy of this rotational constant is poor.

Quadrupole Coupling Constants. Hyperfine splitting due to the coupling of the ^{127}I nuclear electric quadrupole moment with the overall internal rotation was observed in the spectra of both disilyl iodide and disilyl- d_5 iodide. The quadrupole hyperfine component shifts for the ground vibrational state

Table II. Quadrupole Hyperfine Component Frequency Shifts (MHz), $\nu - \nu_0$, for the Ground Vibrational State of Disilyl Iodide and Disilyl- d_5 Iodide

| molecule | $J' \leftarrow J$ | $F' \leftarrow F$ | $\nu - \nu_0$ (obsd) | $\nu - \nu_0$ (calcd) | | |
|----------------------------------|----------------------------------|----------------------------------|-------------------------|--------------------------|-------|--|
| H_3SiSiH_2I | $12_{1,11} \leftarrow 11_{1,10}$ | $21/2 \leftarrow 19/2$ | 2.11 | 2.00 | | |
| | | $23/2 \leftarrow 21/2$ | | | | |
| | | $29/2 \leftarrow 27/2$ | 1.93 | 1.83 | | |
| | $12_{2,10} \leftarrow 11_{2,9}$ | $25/2 \leftarrow 23/2$ | | | | |
| | | $29/2 \leftarrow 27/2$ | 0.73 | 0.62 | | |
| | | $27/2 \leftarrow 25/2$ | 1.41 | 1.52 | | |
| | $13_{0,13} \leftarrow 12_{0,12}$ | $27/2 \leftarrow 25/2$ | -1.32 | -1.34 | | |
| | | $31/2 \leftarrow 29/2$ | 2.83 | 2.85 | | |
| | $13_{1,12} \leftarrow 12_{1,11}$ | $21/2 \leftarrow 19/2$ | | | | |
| | | $29/2 \leftarrow 27/2$ | 0.51 | 0.62 | | |
| | | $27/2 \leftarrow 25/2$ | -0.66 | -0.68 | | |
| | D_3SiSiD_2I | $17_{1,16} \leftarrow 16_{1,15}$ | $31/2 \leftarrow 29/2$ | 1.83 | 1.74 | |
| $39/2 \leftarrow 37/2$ | | | 2.00 | 1.97 | | |
| $37/2 \leftarrow 35/2$ | | | 0.22 | 0.26 | | |
| $18_{1,17} \leftarrow 17_{1,16}$ | | $35/2 \leftarrow 33/2$ | -1.13 | -1.13 | | |
| | | $31/2 \leftarrow 29/2$ | | | | |
| | | $41/2 \leftarrow 39/2$ | 1.99 | 2.03 | | |
| | | | $39/2 \leftarrow 37/2$ | 0.13 | 0.16 | |
| | | | $37/2 \leftarrow 35/2$ | -1.07 | -1.14 | |
| | | | $33/2 \leftarrow 31/2$ | | | |
| | | | | | | |

Table III. Ground Vibrational State Rotational Constants (MHz) and Moments of Inertia ($U \text{ \AA}^2$)^a of Disilyl Iodide and Disilyl- d_5 Iodide

| | H_3SiSiH_2I | D_3SiSiD_2I |
|----------|--------------------|--------------------|
| A | 8602.22 \pm 8.63 | 6571.01 \pm 5.80 |
| B | 1179.79 \pm 0.02 | 1078.87 \pm 0.03 |
| C | 1062.47 \pm 0.02 | 969.96 \pm 0.06 |
| κ | -0.97 | -0.96 |
| I_a | 58.751 | 76.912 |
| I_b | 428.374 | 468.445 |
| I_c | 475.676 | 521.043 |

^a Conversion factor: 505 391 MHz $U \text{ \AA}^2$.

of disilyl iodide and disilyl- d_5 iodide are listed in Table II. The initial approximation of the quadrupole coupling constants was made by transforming the constants reported for silyl iodide by Kewley et al.¹⁸ to the principal axis system of disilyl iodide. The splittings measured for the $12 \leftarrow 11$ and $13 \leftarrow 12$ transitions were then used to obtain the diagonal elements of the quadrupole coupling constant tensor in the principal axis system. Only the first-order theory¹⁹ was used, as second-order corrections are very small for transitions of these high J values. The values obtained for χ_{aa} (-938 MHz), χ_{bb} (255 MHz), and χ_{cc} (683 MHz) of disilyl iodide (where $n = -428$ MHz) were transferred directly to disilyl- d_5 iodide since the rotation of the principal axis due to isotopic substitution was found to be very small ($<1^\circ$). The splitting observed for several of the rotational lines of disilyl iodide could not be explained in terms of the nuclear quadrupole moment alone. This additional splitting observed in the spectrum of H_3SiSiH_2I can possibly be from the interaction of the quadrupole nuclear spin with the internal rotation of the SiH_3 group. The correction of the observed frequencies for the contribution of the A-E splitting was impossible with our current computer program since the J quantum numbers of the observed transitions are too high. In the case of the deuterium compound, the splitting of the A-E levels is anticipated to be small. All observed splittings of the rotational lines of D_3SiSiD_2I were accountable in terms of the quadrupole interaction. Due to the high J values of the observed transitions this splitting was not resolvable in most cases. The observed band widths and centers, however, were consistent with their predicted values. The inability to correct

for the additional splitting due to internal rotation in the case of disilyl iodide, along with the inability to resolve many of the quadrupole components of disilyl- d_5 iodide, account for the rather large deviation from the rigid rotor model, depicted in the values of $\nu - \nu_0$ listed in Table II.

It is interesting to compare the values obtained for the quadrupole tensor along the M-I bond (eQq) of several silicon compounds and their carbon analogues. With the availability of the nuclear quadrupole coupling constants for a fairly sizeable series of alkylhalides, Daily²⁰ was able to present a detailed analysis of the observed trends in terms of ionicity and s hybridization. Since the data available for the corresponding silicon series are still rather meager, only a few qualitative statements can be made. Kewley et al.¹⁸ reported a value of -1245 MHz for the eQq tensor of silyl iodide. Comparison of this value to the value of -1422 MHz calculated from the χ_{aa} coupling constant of disilyl iodide indicates that the charge distribution along the Si-I bond of these two molecules differs significantly. It is evident from these values of eQq that the effect of the substitution of an SiH_3 group for a hydrogen atom in H_3SiI is to decrease the ionic character of the Si-I bond. This decrease in ionicity is also noted in the Si-I bond of trifluorosilyl iodide where Sams and Jache²¹ reported a value of -1450 MHz for eQq . They²¹ state that the large difference in values of eQq reported for H_3SiI and F_3SiI can be attributed to two possible causes. One of these causes is that the more electronegative fluorine atoms tend to withdraw electrons and thus shrink the silicon bond radius. The second possible cause is structural in nature. Since Sheridan and Gordy²² have found the structure of the SiF_3 group to be insensitive to the group to which it is attached, Sams and Jache²¹ assumed values for the Si-F distance and $FSiF$ angle. By using the B value obtained from their microwave study, they²¹ calculated a value of $2.387 \pm 0.02 \text{ \AA}$ for the Si-I bond distance. This value is fairly small in comparison to the Si-I bond distances found in silyl iodide¹⁸ and disilyl iodide; however, similar bond-shortening effects were observed by Sheridan and Gordy²² in F_3SiCl and F_3SiBr . This bond contraction is attributed to the increased double-bond character.

The values reported for the quadrupole coupling tensor along the C-I bonds of H_3CI , H_3CCH_2I , and F_3CI do not exactly fall in line with the values reported for their silicon analogues discussed above. Kasiya and Oka²³ reported a value of -1771 MHz for the eQq of ethyl iodide while Mallinson²⁴ determined the eQq of methyl iodide to be -1934 MHz. This denotes a decrease in ionic character due to the substitution of a CH_3 group for a hydrogen in H_3CI . However, the effect of the substitution of all three hydrogen atoms by fluorine atoms in the hydrocarbon has nearly the same effect on the hydrocarbon as on the silicon-containing compound, since a value of -2150 MHz was reported²⁵ for the eQq of F_3CI . From these results it can be concluded that the effect on the charge distribution along the M-I bond from substitution of an H_3M group for a hydrogen atom of the H_3MI molecule is significantly different depending upon whether $M = Si$ or C . However, the effect of complete substitution by fluorine atoms is very similar. It would be of great interest to determine the quadrupole tensor along the M-I bonds of H_3CSiH_2I and H_3SiCH_2I .

Structure. Because of the number of parameters involved in the structure of disilyl iodide, it is impossible to obtain a complete structure from the results of the present microwave study. The good agreement between the observed rotational

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Table IV. Diagnostic Least-Squares Adjustment of the Structural Parameters in Disilyl Iodide

| parameter, Å or deg | init value | estd uncertainty | adjusted value |
|--------------------------|---------------|---------------------|-------------------|
| $r(\text{Si-I})$ | 2.437 | ± 0.010 | 2.440 ± 0.009 |
| $r(\text{Si-Si})$ | 2.331 | ± 0.010 | 2.336 ± 0.007 |
| $r(\text{Si-H(I)})$ | 1.477 | ± 0.010 | 1.478 ± 0.010 |
| $r(\text{Si-H})$ | 1.490 | ± 0.010 | 1.491 ± 0.010 |
| $\angle \text{SiSiI}$ | 109.5 | ± 2.0 | 106.7 ± 0.3 |
| $\angle \text{SiSiH(I)}$ | 111.1 | ± 2.0 | 111.8 ± 1.8 |
| $\angle \text{SiSiH}$ | 110.9 | ± 2.0 | 111.3 ± 1.9 |
| $\angle \text{HSiH(I)}$ | 110.0 | fixed | |

| | rotational constants | obsd | calcd |
|------------------------------------|-------------------------|---------|---------|
| $\text{H}_3\text{SiSiH}_2\text{I}$ | A | 8602.22 | 8564.41 |
| | B | 1179.79 | 1179.17 |
| | C | 1062.47 | 1061.86 |
| $\text{D}_3\text{SiSiD}_2\text{I}$ | A | 6571.01 | 6617.46 |
| | B | 1078.87 | 1075.92 |
| | C | 969.96 | 966.69 |

constants and the rotational constants calculated from the appropriate structural parameters obtained from disilane²⁶ and silyl iodide¹⁸ indicates that the assumed structure is very close to the actual structure of disilyl iodide in the ground vibrational state.

In order to obtain the uncertainty in the structural parameters, we allowed them to vary using the method of diagnostic least squares as described by Curl.²⁷ The computer program utilized for these calculations was obtained from Wells and Malloy.²⁸ The initial values with their estimated uncertainties as well as the refined parameters are listed in Table IV. During the initial adjustment of the structural parameters, the Si-Si-I angle was allowed to vary; however, it was held fixed in the final refinement. These refined parameters give the following rotational constants for disilyl iodide and disilyl- d_3 iodide, respectively: $A = 8564.41$, $B = 1179.17$, $C = 1061.86$ MHz; $A = 6617.46$, $B = 1075.92$, $C = 966.69$ MHz. By a comparison of these calculated values to the experimental values of the rotational constants given in Table III it is evident that they are in good agreement. The largest discrepancy is found between the observed and calculated values of the A rotational constants. The diagnostic least-squares fit resulted in a value for the A rotational constant of disilyl iodide that is ~ 38 MHz smaller than the observed value whereas for disilyl- d_3 iodide, a value ~ 46 MHz larger was obtained. It should be noted, however, that the A rotational constant has the largest degree of experimental uncertainty since no b -type transitions were assigned.

The skeletal parameters of the refined structure of disilyl iodide listed in Table IV are in excellent agreement with the corresponding parameters reported for other silyl and disilyl compounds. These parameters also have the smallest uncertainties. The most invariant of these parameters is the Si-Si bond distance. Values of 2.331 and 2.332 Å have been reported for this distance in disilane²⁶ and disilyl fluoride,¹⁴ respectively. These values are in excellent agreement with the value of 2.336 Å determined for the Si-Si bond distance in disilyl iodide. It is interesting to compare the silicon-halogen bond distances found for several silyl and disilyl halides. Cox and Varma¹⁴ reported a value of 1.598 Å for the Si-F bond distance of disilyl fluoride, while Kewley et al.¹⁸ obtained a distance of 1.593 Å for the corresponding distance in silyl fluoride. This trend in the silicon-halogen bond distances is also found for the iodide compounds; however, the differences

in the bond lengths are not as significant. Kewley et al.¹⁸ reported a value of 2.437 Å for the Si-I bond distance in silyl iodide, while a value of 2.440 Å was obtained for this parameter in disilyl iodide. The skeletal parameter that changed in value the most during the structural refinement was the Si-Si-I angle. The closing of this angle in disilyl iodide from the value of 109.5° found in disilyl fluoride¹⁴ was anticipated. The refined value of 106.7° is well within the expected limits for the Si-Si-I angle. Along with the other skeletal parameters, it should be noted that the uncertainty in the Si-Si-I angle is very small (0.3°).

The uncertainty in the out-of-plane bond distances and angles is somewhat larger than those reported for the skeletal parameters. This uncertainty is also reflected in the differences found between the observed and calculated values of the inertial defect ($\Delta_c = I_a + I_b - I_c$). A value for Δ_c of 11.449 MHz is calculated from the experimental rotational constants whereas the rotational constants of the refined structure yield a value of 11.661 MHz. The values reported for the Si-H bond distance are found to vary considerably from one compound to another. The longest Si-H bond length is the 1.492-Å distance reported for disilane by Beagley et al.²⁶ whereas the shortest is a 1.45-Å distance determined from the rotational fine structure of the infrared bands of silane.²⁹ The values of the Si-H bond distances obtained in the final refinement of the disilyl iodide structure are consistent with the majority of the reported Si-H bond distances.^{14,18,26} The Si-Si-H angles obtained for disilyl iodide are slightly larger than those reported for disilane²⁶ and disilyl fluoride;¹⁴ however, there are fairly large uncertainties in the angles calculated for disilyl iodide ($\sim \pm 2.0^\circ$). It is worth noting that attempts to adjust the H-Si-H angle of the SiH_2I group had little effect on improving the agreement between the observed and calculated rotational constants.

Vibrational Assignment

The assignments presented in this paper are based upon a structure with C_2 symmetry. In accordance with the known structure of the ethyl halides,³⁰⁻³² the two silyl tops were assumed to be in a staggered conformation. Under C_2 symmetry, the 18 fundamental vibrational modes of disilyl iodide are distributed as $11 A' + 7 A''$, all modes being both infrared and Raman active. The A' vibrations will give rise to polarized Raman lines whereas the A'' modes will be depolarized. For all of the $\text{H}_3\text{M}-\text{MH}_2\text{X}$ molecules, the A'' modes are predicted to have C-type band contours since the largest principal inertial axis occurs out of the molecular plane. The A' (in-plane) vibrations are predicted to have A, B, or A/B hybrid band contours depending on the orientation of the dipole moment. With use of the rotational constants obtained in the present study, the P-R separations for the A- and B-type band contours were calculated to be 8.7 and 11.2 cm^{-1} , respectively. The A-type bands are characterized by a single sharp Q branch of moderate intensity while the B-type bands are expected to exhibit two sharp Q branches. The P-R separation of the C-type bands was calculated to be 19 cm^{-1} . Like the A-type band contour, the C type also exhibits a single Q branch; however, it is much more intense. Calculation of the band contours using the same rotational constants, but at higher resolution, produced the same values for the P-R separation; however, the actual shape of the B- and C-type bands changed dramatically. At 1- cm^{-1} resolution, both the B- and the C-type

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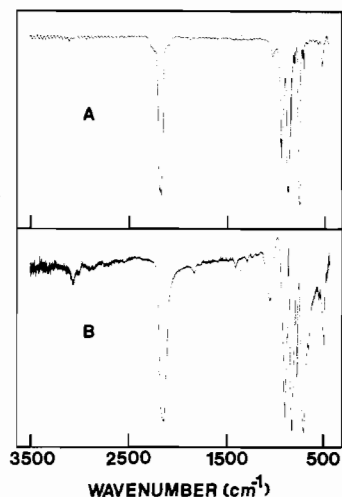


Figure 3. Mid-infrared spectra of disilyl iodide: (A) gas; (B) crystalline solid.

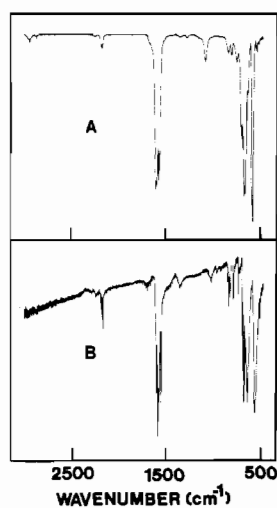


Figure 4. Mid-infrared spectra of disilyl- d_5 iodide: (A) gas; (B) crystalline solid.

bands are characterized by strong R branches and greatly depressed P branches. The fundamentals observed to possess band contours were found to be consistent with their predicted characteristics. All observed frequencies are listed in Tables V and VI. The mid-infrared spectra of disilyl iodide and disilyl- d_5 iodide are shown in Figures 3 and 4, respectively. The Raman spectra of the two isotopic species are shown in Figures 5 and 6, and the far infrared spectra are shown in Figures 7 and 8. The assignment that follows was made through the consideration of group frequencies, Raman depolarization ratios, and infrared band contours.

Skeletal Modes. The skeletal modes of disilyl iodide include the Si-Si and Si-I stretching modes and the Si-Si-I bending mode. All three of these modes are in-plane motions and thus belong to the A' symmetry species. The Si-Si stretching fundamental, ν_9 , has been assigned to a polarized Raman line of medium intensity that is observed at 446 cm^{-1} in the spectrum of gaseous disilyl iodide. The corresponding infrared band is of weak intensity and exhibits a band contour characteristic of an A/B hybrid. In the spectra of gaseous disilyl- d_5 iodide, the Si-Si stretching mode shifts to 427 cm^{-1} . These observed frequencies are consistent with those reported¹² for the corresponding modes in disilane and disilane- d_6 , 432 and 408 cm^{-1} , respectively. The Si-I stretching fundamental, ν_{10} , has been assigned to the very intense polarized Raman line observed at 333 cm^{-1} in the spectrum of gaseous disilyl iodide. In the spectrum of the deuterated compound this mode is

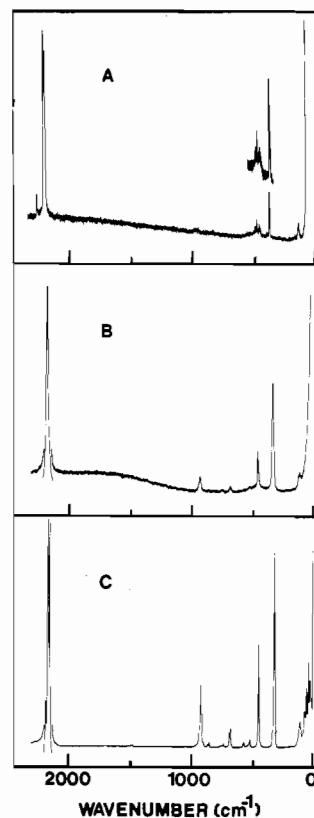


Figure 5. Raman spectra of disilyl iodide: (A) gas; (B) liquid; (C) crystalline solid.

observed at 314 cm^{-1} . The infrared counterparts to these Raman lines are also strong in intensity. In the infrared spectra^{33,34} of gaseous silyl iodide and silyl- d_5 iodide, the Si-I stretching fundamentals have been assigned to strong bands observed at 362 and 351.5 cm^{-1} , respectively. Upon crystallization, the ν_{10} fundamental splits into two components. One of these components appears more intense in the infrared spectrum while the other component is of greater intensity in the Raman effect. The final skeletal mode, the Si-Si-I bending fundamental, ν_{11} , is anticipated to have the lowest frequency of all of the normal modes. This mode has been assigned to the polarized Raman line of weak intensity appearing at 105 cm^{-1} in the spectrum of gaseous disilyl iodide. In the Raman spectrum of the crystalline solid this mode shifts to 107 cm^{-1} . The infrared counterpart of this mode is not observed. The ν_{11} fundamental of the deuterated compound is observed at 90 cm^{-1} in the Raman spectrum of the gas, and upon crystallization this mode shifts to 106 cm^{-1} and again is only observed in the Raman spectrum.

SiH₃ Modes. The SiH₃ modes include three Si-H stretching fundamentals and six bending fundamentals. The three stretching fundamentals consist of two A' modes, one antisymmetric, ν_1 , and one symmetric, ν_3 , and an antisymmetric A'' mode, ν_{13} . The SiH₃ antisymmetric stretching mode, ν_1 , has been assigned to the strong, polarized band observed at 2158 cm^{-1} in the Raman spectrum of liquid disilyl iodide; on deuteration this mode shifts to 1560 cm^{-1} . The SiH₃ symmetric stretching mode, ν_3 , has been assigned to the Raman band of very strong intensity observed at 2147 cm^{-1} in the spectrum of the solid. The corresponding mode of the deuterated compound is observed at 1544 cm^{-1} . For disilyl iodide, the A'' SiH₃ antisymmetric stretching fundamental, ν_{13} , appears degenerate in frequency with the A' SiH₃ antisymmetric

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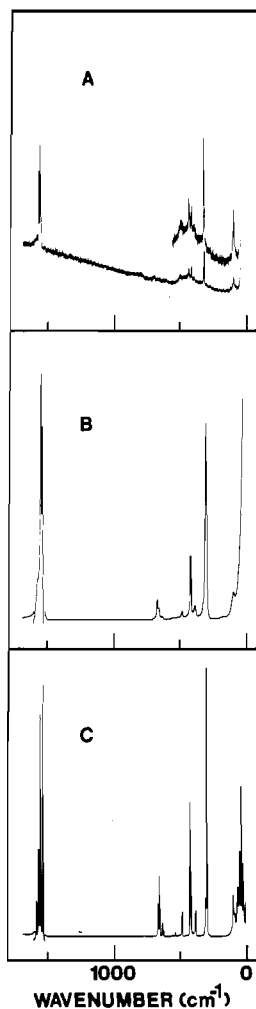


Figure 6. Raman spectra of disilyl- d_5 iodide: (A) gas; (B) liquid; (C) crystalline solid.

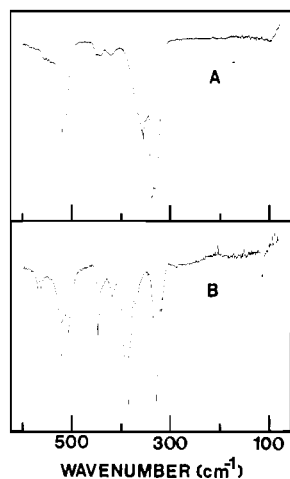


Figure 7. Far-infrared spectra of disilyl iodide: (A) gas; (B) crystalline solid.

stretching mode. In the deuterium compound, however, these modes are no longer unresolvable and the ν_{13} fundamental is observed at 1578 cm^{-1} in the spectrum of the crystalline solid. It is worth noting that only one band is observed in the Si-H stretching region of the infrared spectrum of crystalline disilyl iodide. This may be due to the lower quality of the molecular crystal obtained during these measurements.

The six silyl bending motions can be characterized as three deformations, two rocking modes and one torsional mode. The two A' deformations, one antisymmetric, ν_4 , and one sym-

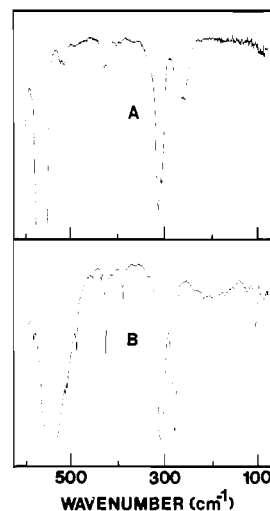


Figure 8. Far-infrared spectra of disilyl- d_5 iodide: (A) gas; (B) crystalline solid.

metric, ν_5 , have been assigned to bands observed in the infrared spectrum of gaseous disilyl iodide at 872 and 844 cm^{-1} , respectively. Both of these bands are strong in intensity; the band appearing at 872 cm^{-1} exhibits a B-type band contour while the band at 844 cm^{-1} has a C-type contour. In the spectra of gaseous disilyl- d_5 iodide, the ν_4 and ν_5 fundamentals are observed at 647 and 625 cm^{-1} , respectively. The A'' antisymmetric deformation, ν_{14} , has been assigned to the band of medium intensity observed at 934 cm^{-1} in the spectrum of gaseous $\text{H}_3\text{SiSiH}_2\text{I}$. On deuteration this mode shifts to 674 cm^{-1} . The two SiH_3 rocking modes can be described as an A' symmetric mode, ν_8 , and an A'' antisymmetric mode, ν_{16} . In the Raman spectrum of methylsilane, Ball et al.³⁵ have assigned the SiH_3 rocking fundamental to a band observed at 532 cm^{-1} . In the infrared spectrum of gaseous disilyl iodide, the ν_8 fundamental is observed at 515 cm^{-1} . This band is of medium intensity and exhibits the A/B hybrid type band contour anticipated for the A' vibrational modes. The ν_8 fundamental appears at 400 cm^{-1} in the infrared spectrum of gaseous disilyl- d_5 iodide. The antisymmetric rocking fundamental, ν_{16} , has been assigned to the weak infrared band observed at 562 cm^{-1} in the spectrum of crystalline disilyl iodide. On deuteration this mode shifts to 411 cm^{-1} and appears as a weak shoulder. The SiH_3 torsional fundamental was not observed in the vibrational spectra of disilyl iodide. Attempts to observe the overtone of this fundamental in the Raman spectrum of the gas were also unsuccessful as they were hampered by both the decomposition of the sample induced by the laser beam and the low vapor pressure of the sample.

SiH_2 Modes. The SiH_2 motions can be broken down into two stretching modes and four bending modes. The stretching modes include the A' symmetric and the A'' antisymmetric stretching fundamentals, ν_2 and ν_{12} , respectively. The SiH_2 stretching vibrations are expected to fall at slightly higher frequencies than the SiH_3 stretching modes when the SiH_2 moiety is bound to a halogen. The symmetric SiH_2 stretching fundamental, ν_2 , has been assigned to a moderately intense line observed at 2155 cm^{-1} in the spectrum of the crystalline solid. The SiD_2 symmetric stretching mode is observed at 1564 cm^{-1} in the Raman spectrum of the molecular crystal. The A'' antisymmetric SiH_2 stretching fundamental has been assigned to the Raman line of medium intensity appearing at 2183 cm^{-1} in the spectrum of the annealed solid. Upon deuteration, this mode shifts to 1595 cm^{-1} .

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Table V. Observed^a Infrared and Raman Frequencies (cm⁻¹) for Disilyl Iodide

| IR | | | Raman | | | | | | | assign | |
|--------------|------------|-------|------------|------|----------------------|--------|----------------------|-------|------------|----------------------|---|
| gas | rel intens | solid | rel intens | gas | rel intens and depol | liquid | rel intens and depol | solid | rel intens | ν_i | approx description |
| 2186 R | | | | | | | | | | | |
| 2180 Q, C | s | | | | | | | 2183 | m | ν_{12} | SiH ₂ antisym str |
| 2171 | s | | | 2166 | vs, p | 2158 | vs, p | 2162 | vs | ν_{11}, ν_{13} | SiH ₃ antisym str |
| 2162 R | | | | 2162 | sh | | | | | | |
| 2156 Q, A/B | s | 2155 | s | 2156 | m, p | 2154 | vs, p | 2155 | m | ν_2, ν_3 | SiH ₂ and SiH ₃ sym str |
| 2152 P | | | | | | | | 2147 | s | | |
| 1027 | w, br | 1062 | w, br | | | | | | | | ? |
| 940 R | | 926 | w, br | | | | | 926 | w, sh | | |
| 934 Q, A/B | s | 911 | s | 934 | vvw | 920 | w, p | 918 | m | ν_{14} | SiH ₃ antisym def |
| 924 P | | | | 924 | vvw | | | 911 | w, sh | | |
| 876 R | | | | | | | | | | | |
| 872 ctr, B | s | 890 | m, sh | | | | | | | ν_4 | SiH ₃ antisym def |
| 867 P | | | | | | | | 863 | w | | ? |
| 854 R | | | | | | | | | | | |
| 844 Q, C | m | 846 | s | | | | | 846 | w | ν_5 | SiH ₃ sym def |
| 835 P | | 830 | m, sh | | | | | | | | |
| 814 R | | | | | | | | | | | |
| 807 Q, A/B | w | 790 | m | | | | | | | ν_6 | SiH ₂ def |
| 800 P | | | | | | | | | | | |
| 756 | vs | 730 | vs | | | | | 752 | w | | |
| 720 | w | | | | | | | 730 | w | ν_7 | SiH ₂ wag |
| 705 | m | 710 | m, sh | | | | | 710 | vvw | | ? |
| 701 | m | | | | | | | | | | |
| 678 | vw | 673 | m | | | 674 | w, dp | 687 | m | ν_{15} | SiH ₂ twist |
| | | | | | | | | 673 | w, sh | | |
| | | | | | | | | 570 | w | | |
| 556 | w | 568 | w | | | | | 565 | w | ν_{16} | SiH ₃ rock |
| 549 | w | 562 | w | | | | | | | | |
| 520 R | | | | | | | | | | | |
| 515 Q, A/B | m | 520 | m | | | 515 | vw, p | 520 | w, br | ν_8 | SiH ₃ rock |
| 510 P | | 507 | w | | | | | 517 | w | | |
| 451 R | | | | | | | | | | | |
| 446 ctr, A/B | w | 446 | m | 446 | m, p | 447 | m, p | 447 | s | ν_9 | Si-Si str |
| 441 P | | | | | | | | | | | |
| 420 | w | 417 | w | | | | | | | | ? |
| 366 R | | | | | | | | | | | |
| 358 Q | | | | | | | | | | | } hot bands |
| 356 Q | | | | | | | | | | | |
| 354 Q, C | m | 383 | s | 354 | w, dp | | | | | ν_{17} | SiH ₂ rock |
| 350 P | | 371 | w, sh | | | | | | | | |
| 333 | s | 328 | s | 333 | s, p | 330 | m, sh | 326 | w, sh | | |
| | | 315 | w, sh | 327 | sh | 326 | s, p | 318 | vs | ν_{10} | Si-I str |
| | | | | | | | | 313 | w, sh | | |
| | | | | 105 | w, p | 105 | w, p | 107 | w | ν_{11} | SiSi bend |

^a Abbreviations used: s, strong; m, medium; w, weak; v, very; p, polarized; dp, depolarized; br, broad; sh, shoulder; P, Q, R, vibrational-rotational branches; A, B, C and A/B, type of band contour; ctr, center of B-type band.

The SiH₂ bending fundamentals are given by the representations $2A' + 2A''$. The two A' modes are the SiH₂ deformation, ν_6 , and the SiH₂ wag, ν_7 . These modes are generally observed at higher frequencies than the two A'' modes, the SiH₂ twist, ν_{15} , and the SiH₂ rock, ν_{17} . In the vibrational spectra of methylchlorosilane, Durig and Hawley³⁶ assigned the SiH₂ deformation and SiH₂ wag to bands observed at 900 and 700 cm⁻¹, respectively. Ball et al.³⁷ assigned these modes to spectral features that appeared at 842 and 636 cm⁻¹ in the spectra of dimethylsilane. The ν_6 fundamental of disilyl iodide has been assigned to a weak infrared band with A/B hybrid contour. This fundamental is observed at 790 cm⁻¹ in the infrared spectrum of the crystalline solid. In the vibrational spectrum of the deuterium compound, ν_6 is observed in the infrared spectrum of the annealed solid at 564 cm⁻¹. The SiH₂ wagging fundamental has been assigned to the infrared band of very strong intensity observed at 730 cm⁻¹ in

the spectrum of the solid. The Raman counterpart of this mode is weak in intensity. In the spectrum of polycrystalline D₃SiD₂I the wagging mode is observed at 542 cm⁻¹. The SiH₂ twisting mode has been assigned to a band observed at 685 cm⁻¹ in the Raman spectrum of methylchlorosilane.³⁶ In the vibrational spectrum of dimethylsilane³⁷ this fundamental was assigned to a C-type band observed at 467 cm⁻¹. The ν_{15} fundamental of disilyl iodide is assigned to an infrared band of medium intensity observed in the spectrum of the crystalline solid. In the Raman spectrum of the liquid this mode is observed as a weak depolarized feature at 674 cm⁻¹. The SiD₂ twist is observed at 488 cm⁻¹ in the spectrum of the annealed solid. The SiH₂ out-of-plane rocking fundamental is anticipated to have the lowest frequency of all of the A'' modes excluding the SiH₃ torsion. This fundamental has been assigned to the C-type infrared band of medium intensity centered at 354 cm⁻¹ in the spectrum of gaseous disilyl iodide. In the infrared spectrum of gaseous disilyl-d₃ iodide the ν_{17} fundamental appears at 263 cm⁻¹. Durig and Hawley³⁶ have assigned the SiH₂ rocking fundamental of methylchlorosilane to a band observed at 527 cm⁻¹. The corresponding rocking

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(37) D. F. Ball, P. L. Goggin, D. C. McKean, and L. A. Woodward, *Spectrochim. Acta*, **16**, 1358 (1960).

Table VI. Observed^a Infrared and Raman Frequencies (cm⁻¹) for Disilyl-d₂ Iodide

| IR | | | | Raman | | | | | | assign | |
|------------|------------|-------|------------|-------|----------------------|--------|----------------------|-------|------------|------------|------------------------------|
| gas | rel intens | solid | rel intens | gas | rel intens and depol | liquid | rel intens and depol | solid | rel intens | ν_i | approx description |
| 1598 R | | | | | | | | | | | |
| 1594 Q, C | vs | 1595 | s | | | 1581 | w, dp | 1595 | w | ν_{12} | SiD ₂ antisym str |
| 1587 R | | | | | | | | | | | |
| 1584 Q, A | s | 1583 | m, sh | | | | | 1578 | m | ν_{13} | SiD ₃ antisym str |
| 1579 P | | 1574 | s | | | | | | | | |
| 1573 | s, sh | 1567 | m | 1566 | s, p | 1560 | vs, p | 1574 | m | ν_1 | SiD ₃ antisym str |
| | | 1557 | m | 1557 | vs, p | | | 1564 | s | ν_2 | SiD ₂ sym str |
| 1558 R | | | | | | | | | | | |
| 1554 Q, A | s | 1544 | s | | | 1548 | s, p | 1544 | vs | ν_3 | SiD ₃ sym str |
| 1549 P | | | | | | | | | | | |
| 682 R | | | | | | | | 674 | w | | |
| 674 Q, C | m | 674 | s | | | 669 | m, dp | 662 | m | ν_{14} | SiD ₃ antisym def |
| 671 P | | 660 | s | | | | | 660 | w | | |
| 652 R | | | | | | | | | | | |
| 647 ctr, B | s | 656 | m | | | 647 | m, p | 656 | vw | ν_4 | SiD ₃ antisym def |
| 643 P | | | | | | | | 638 | w | | |
| 625 Q, A/B | s | 626 | vs | | | 617 | w, p | 626 | vw | ν_5 | SiD ₃ sym def |
| 615 P | | 614 | m, sh | | | | | | | | |
| 566 | vs | 564 | m, sh | | | | | 562 | vs | ν_6 | SiD ₂ def |
| | | 562 | vw | | | | | | | | |
| | | 542 | vs | | | 545 | w, p | 542 | w | ν_7 | SiD ₂ wag |
| 526 R | | | | | | | | | | | |
| 521 ctr, B | w | 513 | m | | | 520 | vw, p | | | | ? |
| 516 P | | 509 | m | | | | | | | | |
| | | 488 | m | 486 | vw, dp | 490 | w, dp | 488 | w | ν_{15} | SiD ₂ twist |
| | | 476 | w, sh | | | | | | | | |
| 433 R | | 436 | w, sh | | | | | | | | |
| 428 ctr, B | w | 426 | m | 427 | m, p | 428 | w, p | 428 | m | ν_9 | Si-Si str |
| 424 P | | | | | | | | | | | |
| | | 411 | w, sh | | | | | 411 | w, sh | ν_{16} | SiD ₃ rock |
| 405 R | | | | | | | | | | | |
| 400 ctr, B | vw | 398 | m | | | 394 | w, p | 398 | w, br | ν_8 | SiD ₃ rock |
| 395 P | | | | | | | | | | | |
| 314 | s | 314 | w, sh | 314 | s, p | 312 | s, p | 313 | m | | |
| 309 | m | 308 | s | | | | | 307 | w, sh | ν_{10} | Si-I str |
| 303 | m, sh | | | | | | | 302 | s | | |
| 272 R | | | | | | | | | | | |
| 263 Q, C | m | 279 | s | | | | | 279 | w, sh | ν_{17} | SiD ₂ rock |
| 256 P | | | | | | | | | | | |
| | | | | | | 184 | w, p | | | | } impurities |
| | | | | | | 167 | w, dp | | | | |
| | | | | 90 | w, p | 103 | w, p | 106 | w | ν_{11} | |

^a For abbreviations used, see Table V.

motion of methylphosphinosilane has been assigned by Carter et al.³⁸ to a band observed at 582 cm⁻¹. The rather large shift of the SiH₂ rocking frequency in disilyl iodide relative to its group frequency helps bring to attention the fact that all of the SiH₃ and SiH₂ bending fundamentals of H₃SiSiH₂I are observed at lower frequencies than expected.

Teller-Redlich product rule calculations were carried out in an attempt to confirm the proposed assignment. Generally, an agreement of 3-5% between the calculated and observed ratios is sufficient to support the assignment. The calculated product rule values for the A' and A'' blocks are 0.0729 and 0.0982, respectively. Since all of the A' fundamentals were only observed in the spectra of the solid phase, these frequencies were used for the calculation. Ideally, frequencies from the spectra of the gas phase should be used for this calculation as intermolecular interactions are at a minimum in this phase. A value of 0.0744, which results in a 2.1% error, was obtained for the A' block. The calculations for the A'' block were also made with use of the frequencies observed for the polycrystalline solids. Since the SiH₃ torsional fundamental was not observed, a shift factor of 1.4 was assumed.

With use of these values a product rule ratio of 0.1041 was obtained. This value is within 5.8% of the theoretical value; however, since the torsional shift factor was assumed and all frequencies used were taken from the spectra of the crystalline samples, this error is acceptable.

Crystal Structure

Several constraints can be placed on the crystal structure of disilyl iodide on the basis of both theoretical considerations and observed spectral data. The site symmetry of a molecule in its ordered crystalline lattice must be equal to, or a subgroup of, the point group of the free molecule. Thus, for the C_s symmetry of gaseous disilyl iodide, the possible site groups include C_s, C₂, or C₁. The splitting of many of the intramolecular fundamentals into two components upon crystallization indicates that there are two molecules per unit cell. This splitting is particularly pronounced in the Si-I stretching fundamental where, as discussed previously, one of the components is observed as a weak infrared feature with a strong Raman-active counterpart. The converse is true for the infrared and Raman intensities of the second component. These results can be rationalized in terms of the in-phase and out-of-phase motions of the two molecules making up the unit cell. The in-phase and out-of-phase synchronization of these motions of the two molecules creates a symmetry condition

(38) R. O. Carter, W. J. Natter, and J. R. Durig, *J. Phys. Chem.*, **82**, 2728 (1978).

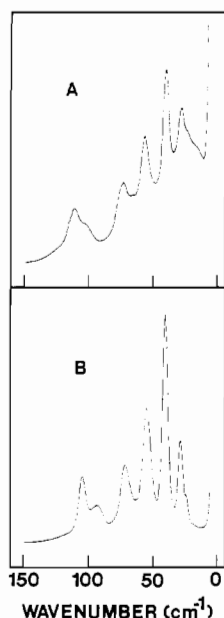


Figure 9. Low-frequency Raman spectra of crystalline disilyl iodide: (A) disilyl iodide; (B) disilyl- d_5 iodide.

within the unit cell, where in one case the dipole changes of the two molecules cancel each other out but the changes in polarizability reinforce each other. In the second case, the dipole changes reinforce each other and the polarizability changes cancel.

The intermolecular fundamentals yield information on the factor group symmetry of the crystal as well as the number of molecules per unit cell. For two molecules per unit cell, three librational and six translational vibrations are anticipated. Theoretically, the intermolecular fundamentals may be distinguished by analyzing the observed frequency shifts of the motions upon deuteration of the molecule. The shift factor for a translation upon deuteration of disilyl iodide should be proportional to the square root of the mass of $\text{Si}_2\text{D}_5\text{I}$ to that of $\text{Si}_2\text{H}_3\text{I}$ or 1.01. Similarly, the shift factors associated with the librations depend upon the moments of inertia around the three principal axes of the molecule and its isotopic species. The principal moments of inertia for disilyl iodide were calculated with use of the structural parameters obtained in this study. The theoretical shift factor for the libration that occurs about the "a" principal axis of disilyl iodide is 1.14, while it is calculated to be 1.04 and 1.05 for librations about the "b" and "c" axes, respectively. The shift factors obtained experimentally are usually much smaller than the predicted values due to the large amount of anharmonicity associated with intermolecular fundamentals.

The Raman spectra of the lattice mode regions of disilyl iodide and disilyl- d_5 iodide appear in Figure 9. From the Raman spectrum of disilyl iodide six of the nine predicted intermolecular fundamentals are readily observed. Because of the great similarity between the spectra of the "light" and "heavy" species, all of the corresponding bands are easily identified. The frequencies for the observed fundamentals, their shift factors, and their assignments are given in Table VII. The three librational modes appear in the far-infrared spectra of the crystalline compounds as fairly intense features. Only three of the six anticipated translational modes are resolved in the Raman spectra of the molecular crystals. In the far-infrared spectra these translations appear as a weak, very broad unresolvable band. The broadness of this band is probably due to the concentration of all six translational modes within this spectral feature. The translational vibrations, which in general appear at lower frequencies than the librations, are probably all active in both the infrared and Raman effect;

Table VII. Observed and Calculated Shift Factors for the Lattice Vibrations for Disilyl Iodide and Disilyl- d_5 Iodide

| disilyl iodide | disilyl- d_5 iodide | obsd shift factor at 20 K | calcd ^a shift factor | assign |
|--------------------|-----------------------|---------------------------|---------------------------------|--------------------|
| 112.5 ^b | 104 ^b | 1.08 | 1.14 | libration <i>a</i> |
| 74 ^b | 71.5 ^b | 1.04 | 1.04 | libration <i>b</i> |
| 57 ^b | 54.5 ^b | 1.05 | 1.05 | libration <i>c</i> |
| 40 | 40 | 1.00 | 1.01 | translation |
| 28 | 28 | 1.00 | 1.01 | translation |
| 23 | 23 | 1.00 | 1.01 | translation |

^a Librational shift factors were calculated on the basis of the structural parameters obtained in the present work. ^b Observed in both the infrared and Raman spectra; other lattice modes were observed in the Raman effect only.

however, they are all not resolvable. The results of the analysis of the lattice modes confirm that there are two molecules per unit cell as predicted from the intramolecular vibrations. These results also restrict the space group of the cell to one of fairly low symmetry.

Normal-Coordinate Analysis

Since the observed frequencies for the SiH_3 and SiH_2 bending modes were found to be considerably lower than those observed for the corresponding motions in similar silyl compounds, a normal-coordinate analysis was undertaken to ascertain the amount of mixing among the normal modes. Along with obtaining a more accurate description of the fundamental vibrations, it was also of interest to determine whether the force constants for the SiH_3 moiety previously reported for some silyl-containing compounds were transferable to disilyl iodide. The calculations were carried out by the Wilson FG matrix method³⁹ with a computer program written by Schachtschneider.⁴⁰ The molecular parameters used were taken from the present study. All of the vibrational frequencies used in the calculations were measured from the polycrystalline phase. The unnormalized symmetry coordinates used in the present study are similar to those described previously for ethyl iodide.⁴¹

The observed and calculated frequencies along with their approximate potential energy distributions (PED) are reported for disilyl iodide and disilyl- d_5 iodide in Table VIII. With use of a force field of 13 constants (10 main diagonal elements and 3 interaction terms) given in Table IX, an average error of 7.6 cm^{-1} or 0.97% was obtained for disilyl iodide. By the employment of the same force field, an average error of 9.4 cm^{-1} or 1.50% was obtained for disilyl- d_5 iodide. Addition of more interaction force constants would probably improve the frequency fit; however, it was felt that further pursuit of this calculation would not significantly increase the information already acquired. All of the A' modes of both disilyl iodide and disilyl- d_5 iodide are relatively pure. The Si-Si stretching fundamentals of both isotopic species are mixed slightly with the Si-I stretching fundamentals; however, this was anticipated. In the case of the deuterium compound, the PED of the Si-Si stretching mode also includes a small contribution from the SiD_3 rocking and SiD_2 wagging motions. The remainder of the A' fundamentals are relatively pure, with the exception of the SiH_3 antisymmetric deformation, the SiH_2 deformation, and the SiH_2 wag. All three of these modes mix with each other to a small degree. This mixing is considerably

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(40) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules", Parts V and VI, Technical Reports No. 231-64 and 57-65, Shell Development Co., Houston, Texas.

(41) J. R. Durig, J. W. Thompson, V. W. Thyagesan, and J. D. Witt, *J. Mol. Struct.*, **24**, 41 (1975).

Table VIII. Observed^a and Calculated Frequencies (cm⁻¹) and Potential Energy Distribution (PED) for the Normal Modes of H₃SiSiH₂I and D₃SiSiD₂I

| vib no. | H ₃ SiSiH ₂ I | | | D ₃ SiSiD ₂ I | | |
|-----------------|-------------------------------------|-------|--|-------------------------------------|-------|--|
| | obsd | calcd | assign and PED | obsd | calcd | assign and PED |
| A' Mode | | | | | | |
| ν ₁ | 2162 | 2176 | 100% SiH ₃ str | 1574 | 1575 | 100% SiD ₃ str |
| ν ₂ | 2154 | 2155 | 99% SiH ₂ str | 1564 | 1544 | 98% SiD ₂ str |
| ν ₃ | 2147 | 2140 | 100% SiH ₃ str | 1544 | 1525 | 100% SiD ₃ str |
| ν ₄ | 890 | 900 | 82% SiH ₃ antisym def, 10% SiH ₂ wag, 4% SiH ₂ scissors | 656 | 657 | 71% SiD ₃ antisym def, 15% Si-Si str, 9% SiD ₂ wag |
| ν ₅ | 846 | 848 | 99% SiH ₃ sym def | 626 | 643 | 97% SiD ₃ sym def |
| ν ₆ | 790 | 781 | 67% SiH ₂ scissors, 25% SiH ₂ wag, 8% SiH ₃ sym def | 564 | 577 | 50% SiD ₂ scissors, 29% SiD ₂ wag, 20% SiD ₃ sym def |
| ν ₇ | 730 | 720 | 78% SiH ₂ wag, 10% SiH ₂ scissors, 10% SiH ₃ sym def | 542 | 546 | 46% SiD ₂ wag, 26% SiD ₂ scissors, 12% SiD ₃ sym def, 10% Si-Si str |
| ν ₈ | 520 | 536 | 99% SiH ₃ rock | 398 | 393 | 87% SiD ₃ rock, 10% SiD ₂ wag |
| ν ₉ | 446 | 457 | 89% Si-Si str, 4% Si-I str | 426 | 406 | 71% Si-Si str, 18% SiD ₃ rock, 6% SiD ₂ wag |
| ν ₁₀ | 328 | 326 | 86% Si-I str, 4% Si-Si str | 307 | 307 | 82% Si-I str, 7% Si-Si-I bend, 6% SiD ₂ wag |
| ν ₁₁ | 107 | 107 | 98% Si-Si-I bend | 106 | 103 | 98% Si-Si-I bend |
| A'' Mode | | | | | | |
| ν ₁₂ | 2183 | 2179 | 100% SiH ₂ str | 1595 | 1577 | 100% SiD ₂ str |
| ν ₁₃ | 2162 | 2176 | 100% SiH ₃ str | 1578 | 1575 | 100% SiD ₃ str |
| ν ₁₄ | 911 | 900 | 99% SiH ₃ antisym def | 662 | 642 | 98% SiD ₃ antisym def |
| ν ₁₅ | 687 | 687 | 98% SiH ₂ twist | 488 | 491 | 95% SiD ₂ twist |
| ν ₁₆ | 565 | 548 | 97% SiH ₃ rock | 411 | 408 | 91% SiD ₃ rock, 9% SiD ₂ twist |
| ν ₁₇ | 383 | 381 | 100% SiD ₂ rock | 279 | 284 | 100% SiD ₂ rock |

^a All observed frequencies were measured from samples held in their crystalline phase.

Table IX. Internal Force Constants for H₃SiSiH₂I and D₃SiSiD₂I

| force const | description | value, ^a mdyn/Å |
|-----------------|---|----------------------------|
| K _q | Si-H(SiH ₃) str | 2.682 |
| K _d | Si-H(SiH ₂) str | 2.690 |
| K _r | Si-Si str | 1.919 |
| K _s | Si-I str | 1.571 |
| H _α | HSiH(SiH ₃) bend | 0.397 |
| H _β | SiSiH(SiH ₃) bend | 0.419 |
| H _δ | HSiH(SiH ₂) bend | 0.295 |
| H _θ | SiSiH(SiH ₂) bend | 0.410 |
| H _γ | HSiI bend | 0.327 |
| H _φ | SiSiI bend | 0.563 |
| F _{θξ} | SiSiH bend, HSiI (SiH ₂) bend | -0.045 |
| F _{rβ} | Si-Si stretch, SiSiH (SiH ₃) bend | -0.026 |
| F _{βφ} | SiSiH(SiH ₃) bend, SiSiI bend (trans) | -0.218 |

^a Bending coordinates are weighted by 1 Å.

greater in the deuterium compound. In general, the mixing of the normal modes of disilyl iodide was found to be very similar to the mixing reported by Durig et al.⁴¹ for ethyl iodide.

It is interesting to note that a limited number of interaction terms were utilized in reproducing a majority of the normal modes. All of the interaction force constants used involve the SiH₃ and SiH₂ bending coordinates. The interaction between the Si-Si-I angle bend and the H-Si-Si angle bend on the adjacent top that is in the trans conformation has the largest magnitude of all of the interactions.

By comparison of the force fields obtained for disilyl iodide and disilane,¹² it is evident that several of the corresponding force constants are nearly identical while others differ significantly. The values of 2.682 and 2.690 mdyn/Å reported for the SiH₃ and SiH₂ stretching force constants of disilyl iodide are consistent with the value of 2.692 mdyn/Å obtained for the Si-H stretching force constant of disilane. For the Si-Si stretching force constant, values of 1.919 and 1.838 mdyn/Å were obtained for disilyl iodide and disilane, respectively. It is interesting to note that the value of 1.571 mdyn/Å obtained for the Si-I stretching force constant of disilyl iodide is considerably smaller than the 1.951 mdyn/Å value reported by Linton and Nixon for silyl iodide.³⁴ This may indicate a weakening of the Si-I bond in the disilyl

compound relative to the corresponding bond of the silyl compound. The major difference in the force fields determined for disilyl iodide and disilane is found to be in the values reported for the main diagonal force constants H_{α} and H_{β} . The force constant H_{α} represents the H-Si-H angle bend and has a value on the order of 0.43 mdyn Å/rad² for disilane, silyl isocyanate and silyl isothiocyanate.¹² For disilane, the force constant for the H-Si-Si angle bend, H_{β} , has a reported value of 0.396 mdyn Å/rad². The values for the corresponding force constants of disilyl iodide are $H_{\alpha} = 0.397$ and $H_{\beta} = 0.419$ mdyn Å/rad². It is immediately evident that the values obtained for H_{α} in disilyl iodide are very similar to the values of H_{β} reported for H₃SiSiH₃, H₃SiNCO and H₃SiNCS. This same similarity is also found between H_{β} of disilyl iodide and H_{α} of disilane. In actuality, it appears as if the values of H_{α} and H_{β} have switched in going from disilane to disilyl iodide. This same trend is noted for the bending force constants of the SiH₂ group. Attempts to transfer the force constant values of H_{α} and H_{β} obtained for disilane directly to the force field of disilyl iodide resulted in the calculation of the A' SiH₃ symmetric deformation at a higher frequency than the A' SiH₃ antisymmetric deformation.

In the rationalization of the inability to transfer the H_{α} and H_{β} force constants, two major differences between the results obtained from the investigation of disilane, silyl isocyanate, silyl isothiocyanate, and disilyl iodide come to light. First, as noted previously, the observed frequencies of the SiH₃ and SiH₂ bending modes of disilyl iodide are in general lower than the frequencies observed for the corresponding modes of the other silyl compounds. This lowering of the observed bending frequencies is probably due, in part, to the increased mixing of the normal modes of this low-symmetry molecule, whereas the bending modes of disilane, silyl isocyanate, and silyl isothiocyanate were found to be relatively pure.

It is interesting to compare the MH₃ and MH₂ bending force constants reported for the silicon and carbon analogues of H₃MMH₃ and H₃MMH₂I. For ethane, Schachtschneider and Snyder⁴² report values of 0.540 and 0.637 mdyn Å/rad² for

(42) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

H_α and H_β , respectively. Values for the corresponding force constants in ethyl iodide of 0.535 and 0.647 mdyne Å/rad² have been reported by Durig et al.⁴¹ On comparison of these force constants, a slight decrease is observed in the value of H_α for ethyl iodide whereas the value of H_β increases by 0.01 mdyne Å/rad². This trend is basically the same as the one observed for the analogous force constants of the silicon compounds, but the magnitude of the shift in the force constant values is not as great for the carbon compounds.

Conclusions

The microwave, infrared, and Raman spectra of disilyl iodide and disilyl-*d*₅ iodide have been recorded. The refined structural parameters obtained from the diagnostic least-squares analysis of the rotational constants are consistent with the corresponding parameters reported for other silyl and disilyl compounds. Of special interest is the value of 2.40 ± 0.009 Å obtained for the Si-I bond distance, which is statistically the same as the Si-I bond distance reported for silyl iodide. This agreement indicates that there is no detectable $p_\pi \rightarrow d_\pi$ back-bonding between the silicon and iodine atoms as suggested by the early NMR study.⁷ If this proposed back-bonding existed, one would also anticipate a shortening of the Si-Si bond distance; no shortening in this bond distance was observed in disilyl iodide. As it turned out, the Si-Si bond distance was found to be the most invariant of all of the disilyl structural parameters during the least-squares adjustment process. The value of 2.336 Å obtained for this bond distance in disilyl iodide is very consistent with the Si-Si bond distance

of 2.332 Å found in elemental silicon.⁴³ The results of the normal-coordinate analysis of disilyl iodide also yield considerable information about the Si-I bond. Comparison of the value of 1.57 mdyne/Å obtained for the Si-I stretching force constant of disilyl iodide to the value of 1.95 mdyne/Å reported for the corresponding bond in silyl iodide³⁴ suggests that the Si-I bond of disilyl iodide is weaker and has less single-bond character than the Si-I bond of silyl iodide. The force field obtained for disilyl iodide was in general very consistent with the force fields reported for several other silyl and disilyl compounds.¹² The major differences were found in the values reported for the SiH₃ and SiH₂ bending force constants. These differences, however, were found to follow the trend observed for the corresponding force constants of ethane⁴² and ethyl iodide.⁴¹ Considerable mixing was found between the SiH₃ and SiH₂ bending modes while the Si-H stretching modes and skeletal motions were found to be fairly pure. No information on the barrier to internal rotation of the SiH₃ group was obtained as the low vapor pressure and limited stability of the compound prevented the recording of Raman data for the gas phase with a good signal-to-noise ratio.

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Electronic Spectra and Structure of Bis(ethylene-1,2-dithiolato)nickel and Bis(propene-3-thione-1-thiolato)nickel

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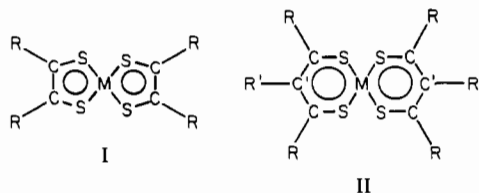
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The electronic ground states and spectra of Ni(S₂C₂H₂)₂ [bis(ethylene-1,2-dithiolato)Ni] and Ni(S₂C₃H₃)₂ [bis(propene-3-thione-1-thiolato)Ni] have been calculated with an INDO-type LCAO-MO CI program recently developed for treating systems containing transition-metal atoms. The ground-state descriptions obtained for these two compounds are consistent with the greater stability of Ni(S₂C₂H₂)₂ relative to Ni(S₂C₃H₃)₂ and also with the existence of mono- and dianions of the former. The electronic spectra of these compounds were assigned with utilization of extensive configuration interaction to describe the ground and excited states. The calculated transitions agree reasonably well with the energies and nature of the experimentally observed ones. In particular, low-energy transitions are found for Ni(S₂C₂H₂)₂, consistent with the observed spectra of Ni(S₂C₂R₂)₂-type compounds. These transitions are not found for Ni(S₂C₃R₃)₂, which is also in agreement with experiment.

Introduction

Square-planar complexes of Ni, Pd, and Pt with sulfur-containing conjugated ligands are interesting examples of complexes in which highly delocalized covalent bonding determines their observed properties.¹⁻⁴ Two characteristic types of such complexes are the bis(ethylene-1,2-dithiolato) complexes, M(S₂C₂R₂)₂ (I), and their bis(propene-3-thione-1-thiolato) analogues, M(S₂C₃R₃)₂ (II).

The parent compounds of type I with R = H are formed as a dianion from disodium salts of *cis*-dimercaptoethylene and the salts MCl₂, and two one-electron oxidations lead to the neutral species.⁵⁻⁸ The exact nature of the bonding in these



complexes has been somewhat uncertain. Several bonding pictures are possible for the neutral complexes (I), the most

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