

Vibrational spectra of disilenes. Normal coordinate analysis and identification of the $\nu(\text{Si}=\text{Si})$ stretching vibration¹

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Abstract

Experimental vibrational spectra are reported for three carbon-substituted disilenes along with data on normal coordinate analysis of several simplified disilene models. Calculations show that there is no normal mode in the disilene spectrum which is well-localized in the Si=Si bond. The Si=Si and Si–C stretching coordinates are heavily mixed. Their in-phase combination results in a normal mode with frequency in the region 450–550 cm⁻¹ which manifests itself as a Raman line of variable intensity (the so-called $\nu(\text{Si}=\text{Si})$). Their out-of-phase combination gives a mode in the region of about 700 cm⁻¹ which shows itself as an intense Raman line (the so-called $\nu^*(\text{Si}-\text{C})$). Vibrations of an aromatic ring, if present in a disilene molecule, can also couple with the $\nu(\text{Si}=\text{Si})$. Particular eigenvector elements of the two modes in question and thus their potential energy distributions strongly depend on the structure and symmetry of a given disilene molecule. However, the contribution of the Si=Si stretching coordinate to the normal coordinate with frequency in the region 450–550 cm⁻¹ is always significant, justifying the designation of this mode as the $\nu(\text{Si}=\text{Si})$. © 1997 Elsevier Science S.A.

Keywords: Silicon; Disilene; Raman and IR spectra; Normal coordinate analysis; Si=Si stretching vibration

1. Introduction

In spite of the fact that the first stable disilene, tetramesityldisilene (**I**) was synthesized in 1981 [1] and quite a number of other disilenes have been described since then (see the latest review [2] and references cited therein), their vibrational spectra have not yet been published. Only one Raman line near 530 cm⁻¹ was reported for **I** in Ref. [1] (along with a set of IR frequencies in a limited region) and assigned to the stretching vibration of the Si=Si bond, $\nu(\text{Si}=\text{Si})$. The Raman lines 539 cm⁻¹ for **I** and 525 cm⁻¹ for (*E*)-di-*tert*-butyldimesityldisilene (**II**) are also mentioned as the $\nu(\text{Si}=\text{Si})$ in the reviews of Raabe and Michl [3] with reference to unpublished results of West–Michl's team.

We have undertaken a systematic study of the vibrational spectra of disilenes in order to identify the $\nu(\text{Si}=\text{Si})$ mode, if it does exist, and to compare its spectral characteristics with those of the $\nu(\text{C}=\text{C})$.

It is well known that the $\nu(\text{C}=\text{C})$ frequency in the spectra of alkenes falls between 1600 and 1680 cm⁻¹, depending on the alkene structure, and that this mode manifests itself as an intense line in the Raman spectrum. Normal coordinate analysis (NCA) shows (see e.g. Refs. [4,5]) that this normal mode is not localized in the C=C bond, but is mixed with other vibrations. The contribution of the C=C coordinate to the potential energy of this normal mode (PED (%)) is 55–75, depending on the alkene substitution. The force constant of the C=C double bond is approximately double that of a C–C single bond [4,5].

It is of interest to obtain analogous data for the Si=Si bond. With this in mind, we report here vibrational (Raman and IR) spectra of three disilenes: R₂Si=SiR₂ with R = CH(SiMe₃)₂ (**III**) and Mes (**I**), as well as *trans*-Mes(*t*-Bu)Si=Si(*t*-Bu)Mes (**II**), Mes-2,4,6-trimethylphenyl. To properly assign the spectral bands observed, it was necessary to carry out NCA, that is, to calculate the frequencies and eigenvectors of normal modes in terms of molecular geometry and force field. However, complete NCA for the molecules **I–III**

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¹ Dedicated to the memory of Professor Yu.T. Struchkov.

would be rather complicated. For instance, formally the molecule **I** has 240 fundamentals. However, previous experience with the vibrational spectroscopy of organometallics shows that internal vibrations of carbon substituents do not interact kinematically through the heavier metal (silicon in our case) atoms, so that the frequencies of identical substituents coincide. This leads to a great simplification of the spectra. Therefore our NCA was restricted to several reasonable disilene models which were gradually made more complex. It should also be emphasized that our calculation was not intended to achieve strict agreement between observed and calculated frequencies by force field variation, because the latter procedure is not single-valued and is, to our minds, not of much use for molecules of any complexity. Our aim was to estimate the amount of mixing of vibrational modes and to analyse the effect of variation of some important parameters on the frequencies and intensities of the spectral features.

2. Results and discussion

2.1. NCA calculations for simplified disilene models

First, we tried to predict the spectrum of a simplified model $C_2Si=SiC_2$. For a hypothetical diatomic moiety $Si=Si$, with use of reasonable values of the force constant $F_{Si=Si}$, we obtained a $\nu(Si=Si)$ frequency lying within the limits $530\text{--}620\text{ cm}^{-1}$. This frequency is close to those for $\nu(Si-C)$ stretches [4,6,7]. It is evident that in the $C_2Si=SiC_2$ moiety, the oscillators of the neighbouring $Si-C$ and $Si=Si$ bonds, having similar frequencies, could strongly interact, and if so, the corresponding coordinates would be expected to mix to a greater or lesser degree. Our next approach was an approximate NCA of a planar model $Me_2Si=SiMe_2$ under symmetry point group D_{2h} (Fig. 1(a)). We treated methyl groups as single atoms of mass 15, took all the angles as 120° , and used the experimental $r_{Si=Si}$ 215 pm and r_{Si-C} 188 pm bond lengths from the X-ray data for disilenes summarized in Refs. [8,9]. Only in-plane vibrations were considered:

$$\Gamma(D_{2h}) = 3A_g + 2B_{1g} + 2B_{2u} + 2B_{3u}$$

A simplified force field was adopted from analogous calculation for $Me_3Si-SiMe_3$ [6] where methyl groups were also treated as point masses. However, the F_{Si-C} value was slightly increased from 2.5 to 2.6 mdyn \AA^{-1} to allow for the sp^2 hybridization of the Si atoms in disilene compared to sp^3 in disilane, by analogy with corresponding carbon compounds. In a first approximation, the force constant of the $Si=Si$ bond was taken as 3.4 mdyn \AA^{-1} , just double that of the ordinary $Si-Si$ bond [6], also by analogy with carbon compounds. However, we realize that this is an overestimate, be-

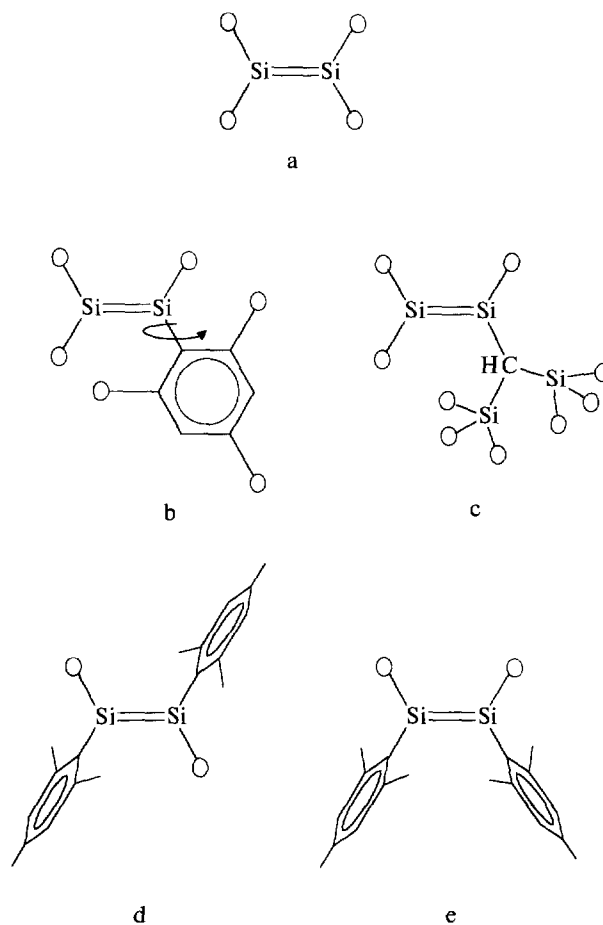


Fig. 1. Simplified disilene models for which normal coordinate analyses were performed.

cause the π component of the $Si=Si$ bond is known to be less than that of the $C=C$ bond [3]. Taking into account the data on σ and π components of the $Si=Si$ bond (74 and 25–30 kcal mol^{-1} respectively) given in Ref. [3], we varied the $F_{Si=Si}$ value from 3.4 to 2.5 mdyn \AA^{-1} in order to obtain the upper and the lower limits of the $\nu(Si=Si)$ frequency value. The results of the calculation for two A_g modes of hypothetical tetramethyldisilene are presented in Table 1. It is immediately seen that in the A_g modes, the $Si=Si$ and $Si-C$ stretching coordinates are, in fact, heavily mixed. Their in-phase combination, that is $(Si=Si) + (Si-C)$, results in a normal mode with frequency in the region $460\text{--}420\text{ cm}^{-1}$ (the interval depends on the $F_{Si=Si}$ value used), while their out-of-phase combination, $(Si=Si) - (Si-C)$, gives a mode in the region $760\text{--}710\text{ cm}^{-1}$. Such a phenomenon of repulsion of two close frequencies is usually called ‘intramolecular resonance’. Variation of the $F_{Si=Si}$ within the limits mentioned (Table 1) does not alter this general result but only moves the frequencies of both modes and changes the eigenvector elements and hence the potential energy distribution (PED). With the upper-limit $F_{Si=Si}$ value 3.4 mdyn \AA^{-1} ,

contributions of both Si=Si and Si–C stretching coordinates into PED of both 457 and 756 cm⁻¹ modes are approximately equal (Table 1). However, when we decrease the $F_{\text{Si=Si}}$ value to its lower-limit value 2.5 mdyne Å⁻¹, making it more realistic, the contributions of the Si=Si coordinate to the mode near 420 cm⁻¹ and of the Si–C coordinate to the mode near 700 cm⁻¹ become predominant, both values reaching approximately 62% in PED (Table 1). According to the data [6], analogous Si–Si and Si–C mode coupling takes place for hexamethyldisilane, but to a lesser extent. Our results show that in a disilene, the $\nu(\text{Si=Si})$ and $\nu(\text{Si–C})$ vibrations are mixed so extensively that the assignment of the lower-frequency mode to the $\nu(\text{Si=Si})$ stretch and of the higher-frequency mode to the totally symmetric $\nu(\text{Si–C})$ stretch is, in essence, arbitrary. However, we shall continue to designate them in this way for convenience, while keeping in mind their complex origin. In contrast, the antisymmetric $\nu(\text{Si–C})$ modes (those of the B_{1g}, B_{2u} and B_{3u} species), which cannot mix with the $\nu(\text{Si=Si})$ for symmetry reasons, are well-localized and situated in the region 620–720 cm⁻¹.

In some disilene molecules, the C₂Si=SiC₂ moiety is not planar but instead the two SiC₂ fragments are twisted about the Si–Si axis up to 12° [8,9]. We therefore investigated the kinematical effect of such twisting on the NCA results; this effect appeared to be small, the biggest frequency shift being only 10 cm⁻¹.

The above results suggest that the Raman frequency at 630 cm⁻¹ reported in Ref. [10] as a $\nu(\text{Si=Si})$ mode of a matrix-isolated Me₂Si=SiMe₂ is too high to belong to the $\nu(\text{Si=Si})$.

It is of interest to compare the NCA results obtained with those for the carbon counterpart tetramethylethylene [4,5]. In the latter, $\nu(\text{C=C})$ and $\nu(\text{C–C})$ vibrations are also mixed in the same manner but to a lesser degree. PED for the 1680 cm⁻¹ mode includes 72% C=C and 13% C–C, while PED for the 690 cm⁻¹ mode includes 15% C=C and 81% C–C.

In the molecules **I** and **II** mesityl groups are present, which themselves possess rich vibrational spectra. Detailed analysis of the vibrational spectrum of the non-substituted mesitylene molecule with its 57 fundamentals is available [5,11]. The next step of our NCA was that for a planar model R₂Si=SiR–Mes of C_s symmetry, shown in Fig. 1(b). Methyl groups in the mesityl substituent were also treated as point masses. All the parameters for the R₂Si=SiR moiety were the same as in the previous case, except that the force constant of the Si–C_{Mes} bond was slightly increased. The parameters for the mesityl group were transferred from the NCA of the non-substituted mesitylene [5] in accord with common practice. However, on going from a free to a substituted mesitylene moiety, its symmetry is lowered from C_{3h} to C_s, which should lead to a complication of its spectrum due to less strict selection rules and lifting of the degeneracy.

Two of the mesitylene normal modes are situated in the region 500 cm⁻¹ [5,11], that is, close to the so-called $\nu(\text{Si=Si})$. One of them is the aromatic ring breathing vibration of A' species which shows itself as an intense polarized Raman line at 578 cm⁻¹. The second is a ring deformation mode of E' species, occurring at 516 cm⁻¹ and also Raman active. The main aim of this step of calculation was to elucidate the behaviour of frequencies and eigenvectors of the modes in the region 450–750 cm⁻¹ when mesitylene is linked to a disilene fragment. The results for in-plane vibrations (Table 2) show that the $\nu(\text{Si=Si})$ frequency in this case must lie in the region 470–500 cm⁻¹, its exact value depending again on the $F_{\text{Si=Si}}$. This mode holds its complex eigenvector. It continues to be an in-phase combination of the Si=Si and Si–C coordinates but, what is very important, also becomes significantly mixed with mesityl group angle deformations. The out-of-phase combination of the Si=Si and Si–C coordinates now gives a normal mode in the interval 750–720 cm⁻¹ and is not at all coupled kinematically with the mesityl vibrations. Particular contributions of the Si=Si and Si–C coordinates to the

Table 1
NCA results for the A_g $\nu_{\text{Si=Si}}$ and $\nu_{\text{Si–C}}$ modes of a simplified Me₂Si=SiMe₂ model, illustrated in Fig. 1(a)

Normal mode designation	$F_{\text{Si=Si}}$ (mdyn Å ⁻¹)	Calc. frequency ν (cm ⁻¹)	Internal vibrational coordinates				
			Si=Si str.	Si–C str.	SiSiC def.	CSiC def.	
$\nu_{\text{Si=Si}}$	3.4	462	a ^a	48	50	1	1.5
			b ^b	0.11	0.17	-0.07	0.10
	2.5	423	a	62	33	2	3
			b	0.17	0.12	-0.09	0.12
$\nu_{\text{Si–C}}^s$	3.4	763	a	52	45	1	2
			b	0.24	-0.25	-0.12	0.17
	2.5	712	a	36	61	1	1.5
			b	0.22	-0.28	-0.11	0.16

^a a, PED (%).

^b b, Eigenvector elements, showing the extent to which each internal coordinate contributes to the normal coordinate.

potential energy of these two modes again strongly depend on the $F_{\text{Si}=\text{Si}}$ value, its decrease leading to their better localization (Table 2). It is notable that NCA predicts also a normal mode at about 320 cm^{-1} which has a complex eigenvector with notable participation of mesityl group angle deformations, as well as the Si=Si and Si–C coordinates. Thus, for the model in question, the Si=Si stretching coordinate participates appreciably in three normal modes, those at about 320, 500 and 730 cm^{-1} , its contribution to their PED being approximately 15, 40 and 20% respectively (with use of a more realistic $F_{\text{Si}=\text{Si}}$ value $2.5\text{ m dyn \AA}^{-1}$).

When a mesityl ring is attached to a disilene moiety, its breathing mode decreases in frequency from 578 cm^{-1} , that is, close to that of the $\nu(\text{Si}=\text{Si})$, but holds its localization in the aromatic ring. The frequency of the ring deformation mode moves from 516 to 503 cm^{-1} and becomes mixed with the Si=Si and Si–C stretches, but only slightly. Hence, among the four modes of our interest, occurring in the region $450\text{--}750\text{ cm}^{-1}$, three preserve their previous localization, two of them in the mesityl moiety and the third one in the disilene fragment. Only the $\nu(\text{Si}=\text{Si})$ mode becomes 'spread' over both fragments.

Thus, for the model in question with coplanar disilene and mesityl fragments, NCA predicts at least three Raman-active vibrational modes with frequencies in the

region $470\text{--}550\text{ cm}^{-1}$. Two of them are localized mostly in the mesityl ring while the third one is the so-called $\nu(\text{Si}=\text{Si})$.

The X-ray data for mesityl-containing disilene molecules [8,9] show that mesityl rings can be differently oriented in respect to the double bond plane. This fact prompted us to investigate the effect of the ring orientation on the frequencies and eigenvectors of the normal modes discussed above. It is very important that the frequencies appeared not to be sensitive to the kinematic effect of the mesityl group twist to orthogonality, while the eigenvectors do exhibit such a dependence (Table 2). When the ring is perpendicular to the plane of the Si=Si fragment, the contribution of the ring coordinates to the $\nu(\text{Si}=\text{Si})$ mode becomes much smaller. Hence, two mesityl-containing disilene molecules with different ring orientations would exhibit spectral bands with close frequencies but different intensities, the intensity being related to the mode eigenvector.

NCA of more complex models with larger numbers of mesityl groups attached to the disilene fragment will give other numerical results but will not change the main conclusions that the Si=Si stretching coordinate is coupled kinematically with the Si–C stretching and the mesityl ring deformation coordinates, and that it contributes to not less than three normal modes with fre-

Table 2

The results of NCA calculations (frequencies (cm^{-1}) and PED (%)) for the MesRSi=SiR₂ model (illustrated in Fig. 1(b)) with variation of the $F_{\text{Si}=\text{Si}}$ value and of the ring orientation

Normal mode assignment	$F_{\text{Si}=\text{Si}}$ used	Mes ring twist (°)	Frequency ν (cm^{-1})	PED (%) internal vibrational coordinates							
				Si=Si str.	Si–C str.	SiSiC def.	C–C str.	C–Me str.	internal CCC def.	mea ^a def.	
heavily mixed mode	3.4	0	318	8	34	11			19	19	
		90	318	9	34	11			19	18	
		2.5	0	316	14	31	11			18	19
$\nu_{\text{Si}=\text{Si}}$	2.5	90	315	15	30	11			17	18	
		3.4	0	490	25	24		8	29	10	
		90	492	38	35		5	17	5		
ring deformation	2.5	0	468	38	19			7	22	10	
		90	465	(0.15) ^b	(0.06) ^b						
		3.4	0	502	47	21		4	17	5	
ring breathing	3.4	90	500	7.5	13			10	37	29	
		90	500	1			13	49	36		
		2.5	0	501	1.5	3			46	36	
$\nu_{\text{Si}-\text{C}}^s$	2.5	90	500						49	36	
		3.4	0	535				28	52	15	5
		90	536				28	52	15	4	
$\nu_{\text{Si}-\text{C}}^s$	3.4	0	535				28	52	15	5	
		90	535				28	52	15	5	
		2.5	0	754	50	44					
ring breathing	3.4	90	749	52	45						
		2.5	0	721	16	79					
		90	713	(-0.15) ^b	(0.22) ^b						
ring breathing	3.4	90	713	20	78						

^a mea, Mesityl ring external angles.

^b Eigenvector elements.

Contributions less than 5% in PED are usually omitted.

quencies in the region below 730 cm^{-1} . One of them, the so-called $\nu(\text{Si}=\text{Si})$ stretching mode at about 500 cm^{-1} , has actually a complex eigenvector, whose particular elements depend on the $F_{\text{Si}=\text{Si}}$ value and on the mutual orientation of the disilene and mesityl moieties. The more coplanar these fragments, the more coupled their vibrations. The effect of this coupling would be mainly to lower the Si=Si eigenvector element for the so-called $\nu(\text{Si}=\text{Si})$ mode.

Thus, the results of NCA for tetra-carbon (alkyl and/or aryl) substituted simplified disilene models lead to the inference that, if a molecule of this type does contain an Si=Si bond, its Raman spectrum should exhibit a band in the region $450\text{--}550\text{ cm}^{-1}$, corresponding to a vibration of a complex eigenvector but with an appreciable participation of the Si=Si stretch. In other words, the normal mode assigned as $\nu(\text{Si}=\text{Si})$ has a characteristic frequency but is not well-localized in the Si=Si bond. The Si=Si stretching coordinate also noticeably contributes to a normal mode near 700 cm^{-1} , along with the Si–C stretches, but out-of-phase to them. Particular eigenvectors of both modes and contributions of the Si=Si coordinate to PED are determined by the particular substitution, structure, geometry and symmetry of a given disilene molecule. That is why the Raman intensity of the so-called $\nu(\text{Si}=\text{Si})$ mode can vary significantly. For disilenes with centrosymmetric structure, this mode should be IR-inactive.

Having in mind these results, it is time to discuss experimental disilene spectra beginning with a tetraalkyl-substituted one.

2.2. $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Si}=\text{Si}[\text{CH}(\text{SiMe}_3)_2]_2$ (III)

For this molecule no structural data are available. The Raman and IR spectra obtained for solid III are illustrated in Fig. 2. It is notable that in the region

below 750 cm^{-1} there are no Raman–IR coincidences, which points to a centrosymmetric structure for the disilene backbone. The most intense Raman lines are those at 454 , 579 , 649 and 733 cm^{-1} . To properly assign them, a model NCA calculation of a moiety $\text{C}_2\text{Si}=\text{SiC}[\text{CH}(\text{SiC}_3)_2]$ (Fig. 1(c)) was performed. The initial data were those used above for $\text{C}_2\text{Si}=\text{SiC}_2$ combined with the literature data for Me_4Si [4] and Me_3SiX [7]. The results show that in the normal vibration at 454 cm^{-1} , all the stretching coordinates: those of the Si=Si, =Si–C and SiC_4 bonds, participate but the contribution of the Si=Si is predominant (approximately 55% in PED), so that this mode may be readily assigned as the $\nu(\text{Si}=\text{Si})$ stretch. The lines at 579 and 649 cm^{-1} are mostly Si–C stretching vibrations, the frequency of the former being close to that of the $\nu^s(\text{Si}-\text{C})$ mode of tetramethylsilane, while the line at 733 cm^{-1} corresponds to the out-of-phase combination of the Si=Si and =Si–C stretching coordinates. It is notable that our simplified force field with the $F_{\text{Si}=\text{Si}} 2.5\text{ mdyn \AA}^{-1}$ has given a good fit of the experimental frequencies without any special refinement.

2.3. *trans-Mes(t-Bu)Si=Si(t-Bu)Mes* (II)

The Raman and IR data for this centrosymmetric molecule (in the solid) are presented in Fig. 3. The mutual exclusion rule does indeed hold for its vibrational spectrum in the region of skeletal vibrations. To assign the spectrum, a model NCA for a hypothetical *trans-MesMeSi=SiMeMes* molecule of C_{2h} symmetry (Fig. 1(d)) was carried out, treating Me as a point mass and using structural parameters from the X-ray data for II [12]. The main force constants used were as follows: $F_{\text{Si}=\text{Si}}, 2.5$; $F_{\text{Si}-\text{C}(\text{Mes})}, 2.6$; $F_{\text{Si}-\text{C}(\text{Alk})}, 2.5\text{ mdyn \AA}^{-1}$ (to account for the positive inductive effect of the t-Bu group): all others as in previous calculations. The calcu-

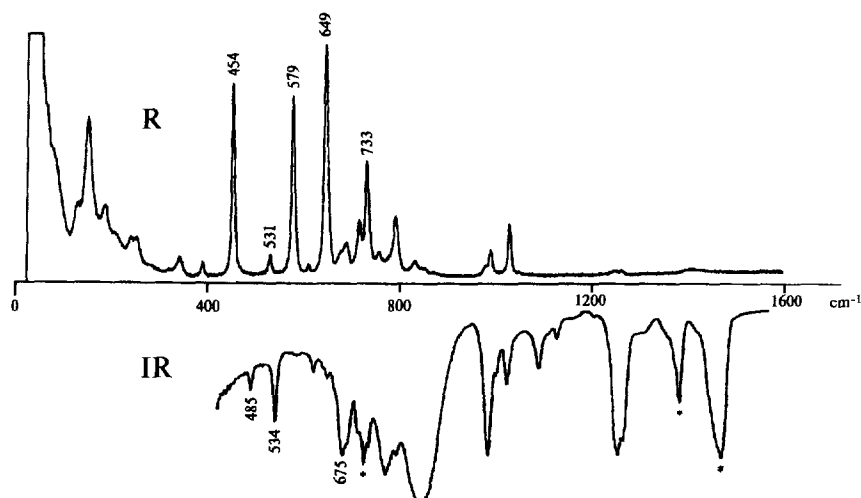


Fig. 2. The Raman and IR spectra of solid $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Si}=\text{Si}[\text{CH}(\text{SiMe}_3)_2]_2$. The IR bands of apiezon are marked by asterisks.

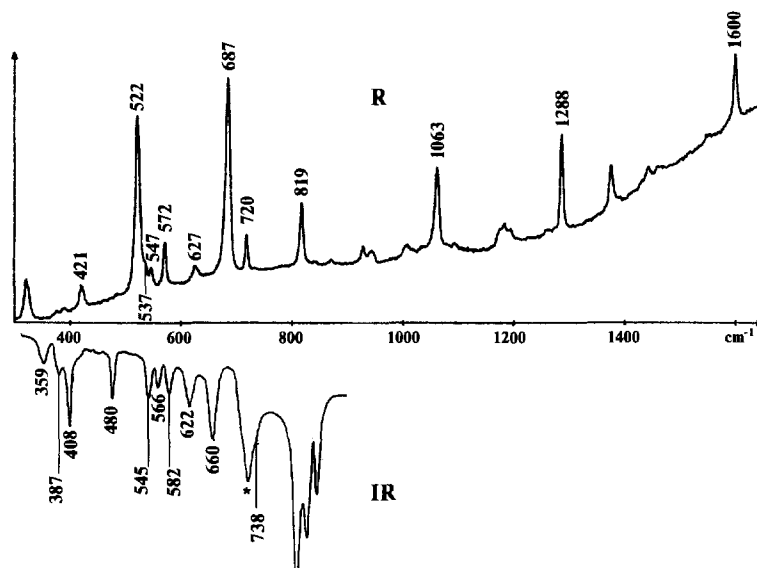


Fig. 3. The Raman and IR spectra of solid *trans*-Mes(t-Bu)Si=Si(t-Bu)Mes. The IR band of nujol is marked by an asterisk.

lated mode frequencies are in satisfactory agreement with the main features of the observed spectrum (Table 3).

An intense Raman line at 522 cm^{-1} , having no counterpart in the IR spectrum, is readily assigned to the A_g $\nu(\text{Si}=\text{Si})$ mode. This mode has a complex eigenvector with a significant participation of deformations of internal angles in the mesityl rings and with a moderate contribution from the $\text{Si}-\text{C}_{\text{Alk}}$ stretches, but the contribution of the $\text{Si}=\text{Si}$ stretch is substantial (about 40% in PED). There are two weak features in the same region of the Raman spectrum at 537 and 547 cm^{-1} . It is reasonable to assign them to mesityl deformation and

breathing modes respectively. Their Raman intensity is low because the aromatic rings in **II** are not π -conjugated with the $\text{Si}=\text{Si}$ bond, being perpendicular to the plane of the $\text{Si}=\text{Si}$ fragment [12]. NCA suggests that the $\text{Si}=\text{Si}$ stretching coordinate should also contribute significantly to three other A_g modes and approximately predicts their frequencies at about 300 , 630 and 715 cm^{-1} . A Raman line at 323 cm^{-1} of medium intensity can be unambiguously assigned to the former mode, which has a very complicated eigenvector with participation of both disilene and mesityl moieties, the $\text{Si}=\text{Si}$ contribution in PED being 16%. The assignment of the latter modes is not straightforward. We assign an in-

Table 3

Experimental and calculated mode frequencies (in the region $300\text{--}720\text{ cm}^{-1}$) and potential energy distribution for a *trans*-MesRSi=SiRMes model of C_{2h} symmetry, illustrated in Fig. 1(d)

Symmetry species	Frequency ν (cm^{-1})		Activity and intensity observed	PED (%)	Mode approximate assignment
	Calc.	Exp.			
A_g	299	323	R, m	16 Si=Si, 7 Si-C _R , 20 Si-C _{Mes} , 18 SiSiC, 12 CCC, 22 mea ^a	mixed
B_u	347	359	IR, w	32 Si-C _{Mes} , 33 CCC, 17 mea	mixed
B_g	444	421	R, w	10 CCC, 83 mea	ring deformation
A_u		408	IR, m	10 CCC, 83 mea	
A_g	490	522	R, v s	39 Si=Si, 9 Si-C _R , 28 CCC, 9 mea	$\nu\text{Si}=\text{Si}$ mixed
B_g	500	537	R, w	14 C-Me, 49 CCC, 36 mea	ring deformation
A_u			—		
A_g	536	547	R, w	27 C-C, 52 C-Me, 16 CCC, 5 mea	ring breathing
B_u		547	IR, w		
B_u	581	583	IR, w	7 Si-C _R , 30 Si-C _{Mes} , 11 C-C, 15 C-Me, 25 CCC, 11 mea	$\nu^{\text{as}}\text{Si}-\text{C}_{\text{Mes}}$ mixed
A_g	629	687	R, v s	22 Si=Si, 34 Si-C _{Mes} , 11 C-C, 9 C-Mes, 11 CCC	$\nu^{\text{s}}\text{Si}-\text{C}_{\text{Mes}}$ mixed
B_u	682	660	IR, m	90 Si-C _R	$\nu^{\text{as}}\text{Si}-\text{C}_{\text{R}}$
A_g	717	720	R, m	19 Si=Si, 77 Si-C _{R}}	$\nu^{\text{s}}\text{Si}-\text{C}_{\text{R}}$

^a mea, Mesityl ring external angle deformation.

tense Raman line at 687 cm^{-1} to the second mode which is of a complex origin and involves 22% of the Si=Si, 34% of the Si-C_{Mes}, 11% of the C-C stretches in mesityl rings and also ring angle deformations. We believe that the third mode, which is a purely stretching vibration and involves the Si-C_{Alk} stretch (77% in PED) out-of-phase to the Si=Si stretch (19%), corresponds to a Raman line of moderate intensity at 720 cm^{-1} . It should be emphasized again that particular contributions of the Si=Si coordinate to PED are significantly dependent on the $F_{\text{Si=Si}}$ value. The PED data presented above and in Table 3 were obtained with $F_{\text{Si=Si}} = 2.5\text{ m dyn \AA}^{-1}$. Meanwhile, it is seen from Table 3 that the observed frequency values for all modes with the Si=Si participation are somewhat higher than the calculated ones. We could easily make the fit better by increasing the $F_{\text{Si=Si}}$ value, which would inevitably lead to a change (numerical, not principal) in PED values, but we did not pursue this goal for the reasons given above.

The only salient spectral feature which characterizes t-Bu groups in **II** is an intense Raman line at 819 cm^{-1} (C-C stretch [4,5]).

Thus, in **II** the Si=Si stretching coordinate participates in four normal modes, but its contribution to the 522 cm^{-1} mode is predominant.

It was shown [13] that **II** undergoes *trans-cis* isomerisation under UV illumination. To elucidate the kinematic effect of this isomerisation on the vibrational spectrum, we carried out a corresponding NCA calculation for the *cis* isomer of MesMeSi=SiMeMes (Fig. 1(e)). The results have shown that the biggest frequency shift (15 cm^{-1}) is exhibited by a $\nu(\text{Si-C})$ mode. This means that it is in this spectral region that an admixture of the *cis* isomer in **II** could be detected.

2.4. Mes₂Si=SiMes₂ (**I**)

This molecule can exist in several modifications [8,9,14], differing in the molecular geometry and orientation of the aromatic rings. The UV, Raman, resonance Raman and IR spectra of all modifications of solid **I** will be presented and compared in detail in a later paper [14]. Here we report only the Raman spectrum in the region $400\text{--}750\text{ cm}^{-1}$ for the orange modification of **I** in the solid state (Fig. 4). According to its X-ray data [9], the mesityl groups in this molecule are in a propeller-like configuration which leaves some possibility for conjugation of the aromatic rings with the Si=Si bond. In the Raman spectrum of **I**, three lines are observed in the region near 500 cm^{-1} , in accordance with the NCA results presented above (Section 2.1), those at 520 , 530 and 540 cm^{-1} . In contrast to **II**, peak intensities in this triplet with 514.5 nm excitation are almost equal. The pattern observed can be rationalized as an overlap of three lines with close frequencies, one

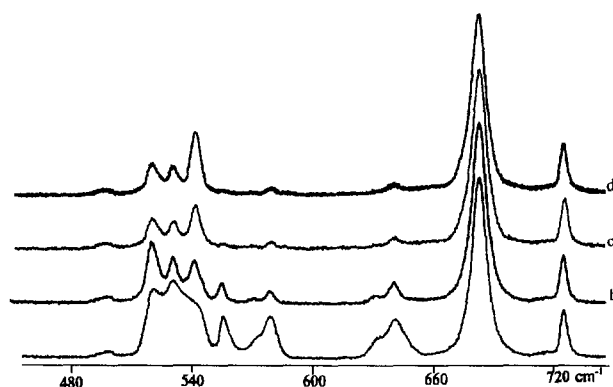


Fig. 4. The Raman spectra of solid Mes₂Si=SiMes₂ (orange modification) obtained using different exciting wavelengths $\lambda = 1064\text{ nm}$ (a); 632.8 nm (b); 514.5 nm (c); 457.9 nm (d).

corresponding to the so-called $\nu(\text{Si=Si})$ and two others to the ring breathing and deformation modes. An intensity redistribution in this triplet observed for **I** compared to **II** can be explained by two factors: (i) a change in eigenvector elements of these modes due to a different orientation of the rings (see Section 2.1) and (ii) partial π -conjugation of the aromatic rings with the Si=Si bond.

To identify the line corresponding to the so-called $\nu(\text{Si=Si})$ among the triplet observed, we have studied the exciting wavelength dependence of the Raman spectrum. The orange modification of **I** absorbs in the visible region at 460 nm [14], this absorption being due to a transition localized in the Si=Si bond [3]. When approaching resonance, the line at 540 cm^{-1} of the Raman triplet appeared to be mostly enhanced (Fig. 4), which is in accord with the unpublished data cited in Ref. [3]. This fact points to a noticeable Si=Si contribution to this mode. An observed decrease in intensity of the $\nu(\text{Si=Si})$ line at 540 cm^{-1} in the Raman spectrum of **I**, compared to that at 522 cm^{-1} for **II**, is evidently explained by a smaller contribution of the Si=Si coordinate into this mode in **I** due to the non-orthogonal orientation of the rings in this molecule.

3. Summary

Experimental data along with the results of NCA for several disilenes led to the following conclusions. There is no normal mode in the vibrational spectrum of a disilene which is well-localized in the Si=Si bond. For a disilene molecule with four carbon (alkyl or/and aryl) substituents one should observe in the Raman spectrum a line in the region $450\text{--}550\text{ cm}^{-1}$ which corresponds to a normal mode of a complex eigenvector. This mode is an in-phase combination of the Si=Si and Si-C stretching coordinates, and can also couple with the vibrations of aromatic rings, if present. The particular

contribution of the Si=Si stretch into this normal mode strongly depends on the structure, geometry and symmetry of a given disilene molecule. Hence, the intensity of the corresponding Raman line can vary from high to moderate. However, the contribution of the Si=Si coordinate remains still substantial, which makes it reasonable to designate this mode as 'the $\nu(\text{Si}=\text{Si})$ '. The second normal mode with significant Si=Si participation is an out-of-phase combination of the Si=Si and Si-C stretches. It occurs in the region 700 cm^{-1} and manifests itself as an intense Raman line. Depending on the disilene substituents and structure, there may be other normal modes with a smaller but still noticeable contribution from the Si=Si stretch.

4. Experimental

The synthesis of the compounds **I–III** studied was accomplished according to the methods reported previously in Refs. [1,12,15]. Because the disilenes react rapidly with oxygen of the air, special care was taken to prevent sample decomposition. All experiments were carried out in high vacuum or in an inert atmosphere. For Raman studies, the samples were sealed in capillaries in vacuo, for the IR measurements prepared as mulls in purified nujol and apiezon in an inert atmosphere.

The Raman spectra were recorded using laser Raman spectrometers Jobin-Yvon HG2S and U-1000. Various exciting lines in the visible region were used, those of an Ar^+ laser ILA-120 and a He-Ne laser SP-124. The Raman spectra presented in Figs. 2 and 3 were excited by a 514.5 nm line. A Fourier-transform Raman spectrum of **I** was also obtained using a Bruker-88 spectrometer equipped with FRA106 FT Raman module. The IR spectra were obtained using a Carl Zeiss M-80, a Nicolet and an IFS 113 V Bruker FT spectrometers.

Normal coordinate calculations were performed using a set of computer programs elaborated by Gribov and Dement'ev and described in Ref. [5].

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