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The Ultraviolet Spectrum of Dimethylsilylene

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Abstract: The equilibrium geometries, vibrational frequencies, and infrared intensities of the three lowest lying states of dimethylsilylene have been predicted via a priori quantum mechanical methods. Our results agree with the recently disputed spectroscopic studies of West, Michl, and co-workers, and we confirm that the observed 450-nm absorption is due to ground-state dimethylsilylene.

The methyl substituent, CH_3, has played a major role in the development of silicon chemistry. Unlike the silicon hydrides, permethylated silicon rings and chains are relatively inert, and in the last few decades a rich chemistry of catenated silicon compounds has emerged which, in many ways, resembles the traditional organic chemistry of carbon and hydrogen.[1] Thus, in a sense, the methyl group is the "hydrogen" of silicon chemistry.

Silylenes, R_2Si, are often postulated as reactive intermediates in organosilicon chemistry,[2] and a great deal of effort, both theoretical[3-18] and experimental,[2] has been expanded to characterize these species. Silylene, SiH_2, has been most extensively studied. Both its electronic[19,20] and matrix isolation infrared spectra[21,22] have been observed, and theoretical studies of its ground $\tilde{X}\ {}^1A_1$[5,12,13,15,17,18] and excited state $\tilde{A}\ {}^1B_1$[12,13,17,18] properties are in essential agreement with experiment. The only experimental information available on the $\tilde{a}\ {}^3B_1$ state is Lineberger's determination, from the photoelectron spectrum of SiH_2^-, that $T_0 \leq 14$ kcal/mol.[23] Extensive ab initio studies suggest that a value near 20 kcal/mol is more likely.[5,12,17,18]

Dimethylsilylene, $Si(CH_3)_2$, was first observed spectroscopically by Drahnak, Michl, and West[24] and has since been the object of IR, UV, and fluorescence studies in inert matrices.[24-26] Its spectroscopic fingerprint has been a UV absorption maximum at 450 nm (presumably corresponding to the same $\tilde{X}\ {}^1A_1$–$\tilde{A}\ {}^1B_1$ transition as that found in SiH_2) and an IR absorption at 1220 cm^{-1}.[24,26] A recent report, however, has questioned this assignment. In particular Griller et al.[27,28] find that flash photolysis of known precursors of $Si(CH_3)_2$ produces species absorbing at 350 nm in hydrocarbon solution and 300 nm in tetrahydrofuran which yield insertion products expected of dimethylsilylene when appropriate scavengers were added to the solution. No absorption at 450 nm was observed. Griller et al. concluded that either the UV–vis spectrum has been incorrectly assigned or that there is a large (~100 nm) shift in its absorption maximum in going from matrices to solution.[27,29] West, Michl, and co-workers have stood firm on their original assignment of the UV–vis spectra and have offered alternative suggestions as to the possible identity of the species observed by Griller. They note that the 350-nm species may be a minor byproduct with a high extinction coefficient or, of more interest, it could be an intermediate in the production of ground-state dimethylsilylene, such as the triplet state of $Si(CH_3)_2$.[29]

A recent theoretical study of substituent effects on the $\tilde{X}\ {}^1A_1$–$\tilde{A}\ {}^1B_1$ type transitions in silylenes suggests that the 450-nm value of West, Michl, et al. is most likely correct.[30] This study was inconclusive, however, in that it used small basis sets for the geometrical optimization of the ground-state singlet and did not include the effects of electron correlation on the excitation energy. Others have employed theoretical methods in the study of this species but have concentrated their efforts on the $\tilde{X}\ {}^1A_1$–$\tilde{A}\ {}^3B_1$ energy splitting[14,15] and the energy of ground-state dimethylsilylene relative to other SiC_2H_6 isomers.[7]

Given the extreme importance of the methyl group as a substituent in organosilicon chemistry, the ubiquitous nature of silylenes, and the recent controversy on the UV–vis spectra of dimethylsilylene, we have undertaken a theoretical study of $Si(CH_3)_2$ including complete geometrical optimization of the ground and first excited singlet and triplet states. Inclusion of electron correlation effects with use of configuration interaction (CI) methods show the $\tilde{A}\ {}^1B_1$ state to lie 54.2 kcal/mol above ground-state $Si(CH_3)_2$ and yields a vertical excitation energy of 62.7 kcal/mol (=456 nm) which strongly suggests that the original assignment of West, Michl, and co-workers is correct.

Theoretical Approach

In this research we have employed Dunning's[31,32] standard double-ζ (DZ) contraction of Huzinaga's[33] primitive Gaussian basis sets. These

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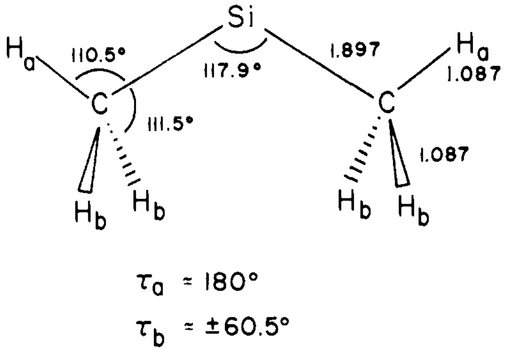

Figure 1. Optimized SCF geometry of the $^3B_1$ state of dimethylsilylene with a double-ζ plus d (DZ+d) basis set. Bond lengths are given in angstroms.

basis sets are technically labeled Si(11s 7p/6s 4p), C(9s 5p/4s 2p), and H(4s/2s). To this we add a single set of Cartesian d-functions (DZ+d) to both silicon and carbon with orbital exponents α_d(Si) = 0.5, α_d(C) = 0.75. The hydrogen s-functions are scaled by the standard factor 1.2. Selected studies are performed with use of a fully polarized DZP basis which adds a set of p-functions to each hydrogen in the DZ+d basis set. For our final energetic predictions we use McLean and Chandler's[34] triple-ζ (TZ) contraction of Huzinaga's 12s 9p primitive silicon basis augmented with two sets of d-functions with orbital exponents α_d(Si) = 0.63, 0.19. The carbon basis set is Dunning's TZ quality contraction of the same 9s 5p primitive set used above with the same d-function as in the DZ+d basis set. The hydrogen basis set is the same one used in our DZP basis set. This final basis set is labeled TZP in the text and should give results within a few kcal/mol for relative energies of the three states studied. Its technical designation is Si(12s 9p 2d/6s 5p 2d), C(9s 5p 1d/5s 3p 1d), and H(4s 1p/2s 1p).

While the triplet and open-shell singlet states are qualitatively described by a single electron configuration, it is well-known that closed shell singlet silylenes are best described by a two-configuration SCF (TCSCF) wave function in zeroth order.[5] Thus for the closed shell singlet we employ both TCSF and, for comparison, SCF techniques. The valence electron configurations for the different states of dimethylsilylene, considered in C_{2v} symmetry, are

$$\ldots 5a_1^2\, 3b_2^2\, 6a_1^2\, 7a_1^2\, 2b_1^2\, 4b_2^2\, 1a_2^2\, 5b_2^2\, 8a_1^2 \qquad {}^1A_1(\text{SCF})$$

$$C_1 \ldots 5a_1^2\, 3b_2^2\, 6a_1^2\, 7a_1^2\, 2b_1^2\, 4b_2^2\, 1a_2^2\, 5b_2^2\, 8a_1^2 +$$
$$C_2 \ldots 5a_1^2\, 3b_2^2\, 6a_1^2\, 7a_1^2\, 2b_1^2\, 4b_2^2\, 1a_2^2\, 5b_2^2\, 3b_1^2 \qquad {}^1A_1\ (\text{TCSCF})$$

$$\ldots 5a_1^2\, 3b_2^2\, 6a_1^2\, 7a_1^2\, 2b_1^2\, 4b_2^2\, 1a_2^2 5b_2^2\, 8a_1\, 3b_1 \qquad {}^3B_1,\ {}^1B_1$$

We will find it necessary to consider geometries in C_2 symmetry for which the orbital occupations and state labels may be found by using the decomposition a_1, a_2 → a and b_1, b_2 → b. Thus the states of interest become ^1A, ^3B, and ^1B.

All the structures have been precisely optimized with use of analytical SCF[35,36] and TCSCF[37] gradient techniques. The nature of the symmetry constrained structures was tested via the determination, using analytic second derivative methods,[38] of all quadratic force constants and harmonic frequencies. The infrared intensities have also been determined analytically.[39]

The effects of electron correlation have been included by the method of configuration interaction (CI).[40] Only the valence electrons have been included in the CI, i.e., all corelike (Si 1s, 2s, 2p; C 1s) orbitals and their virtual counterparts have been omitted from the CI. Otherwise, all singly and doubly excited configurations relative to the SCF or TCSCF reference have been included (CISD). The effects of unlinked quadruple excitations are included in an approximate manner with use of Davidson's formula[41] (CISD-Q).

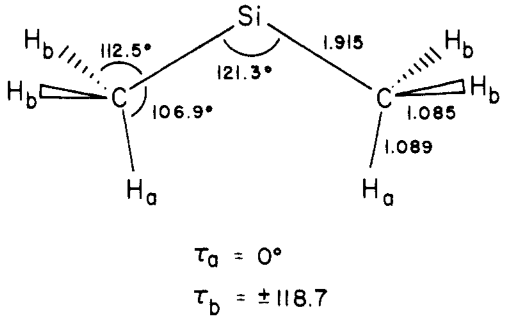

Figure 2. Optimized SCF geometry of the $^1B_1$ state of dimethylsilylene with a double-ζ plus d (DZ+d) basis set. Bond lengths are given in angstroms.

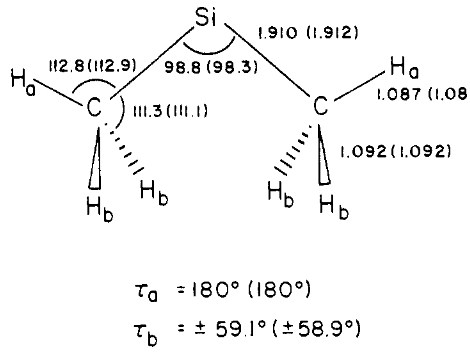

Figure 3. Optimized geometry of the C_{2v} symmetry $^1A_1$ state of dimethylsilylene with a double-ζ plus d (DZ+d) basis set in conjunction with two-configuration SCF and one-configuration SCF (in parentheses) methods. Using a fully polarized (DZP) basis set and SCF techniques one obtains r(Si–C) = 1.909 Å, r(C–H$_a$) = 1.087 Å, r(C–H$_b$) = 1.092 Å, Θ(Si–C–H$_a$) = 112.7°, Θ(Si–C–H$_b$) = 110.9°, ϕ(C–Si–C) = 98.5°, and τ_b = 58.8°. Bond lengths are given in angstroms.

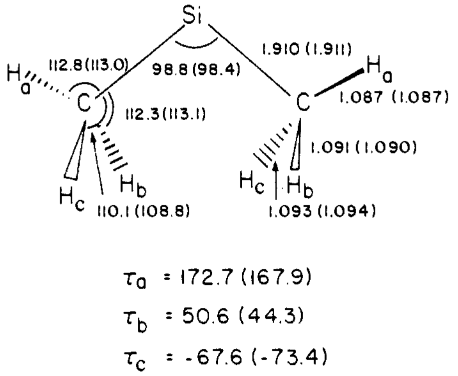

Figure 4. Optimized geometry of the C_2 symmetry ^1A state of dimethylsilylene with a double-ζ plus d (DZ+d) basis set in conjunction with TCSCF and SCF (in parentheses) methods. Bond lengths are given in angstroms.

Optimized Geometries

In the initial stage of geometry optimization we adopted a conformation of the methyl group which placed the unique in-plane hydrogen trans to the opposite Si–C bond (staggered conformation). Of the three states only the $^3B_1$ is found to be a minimum in this configuration (Figure 1). The $^1B_1$ state has two imaginary frequencies of 70i and 80i cm^{-1} in the staggered configuration (not shown) and is found, instead, to be a minimum with the in-plane hydrogen cis to the Si–C bond in an eclipsed configuration (Figure

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Table I. Total and Relative Energies of the C_2 Symmetry ^1A and C_{2v} Symmetry $^1A_1$ Optimized Structures[a]

state	description	DZ+d SCF	DZ+d CISD	DZ+d CISD-Q
^1A	SCF	−0.107 06 (−0.04)	−0.439 85 (−0.14)	−0.479 98 (−0.16)
^1A	TCSCF	−0.125 71$_2$ (−0.004)	−0.446 65 (−0.06)	−0.482 78 (−0.07)
$^1A_1$	SCF	−0.107 00 (0.0)	−0.439 63 (0.0)	−0.479 73 (0.0)
$^1A_1$	TCSCF	−0.125 70$_6$ (0.0)	−0.446 56 (0.0)	−0.482 67 (0.0)

[a] Total energies are given in hartrees, relative to −368 hartrees. Relative energies (in parentheses) are in kcal/mol.

Table II. Total and Relative Energies of the C_{2v} Symmetry $^1A_1$, $^3B_1$, and $^1B_1$ Optimized Structures[a]

state	description	DZ+d SCF	TZP SCF	DZ+d CISD	TZP CISD	DZ+d CISD-Q	TZP CISD-Q
$^1A_1$	SCF	−0.107 00		−0.439 63		−0.479 73	
$^1A_1$	TCSCF	−0.125 71 (0.0)	−0.159 28 (0.0)	−0.446 56 (0.0)	−0.535 59 (0.0)	−0.482 67 (0.0)	−0.580 71 (0.0)
$^3B_1$	SCF	−0.090 01 (22.4)	−0.121 34 (25.0)	−0.408 51 (23.9)	−0.495 82 (25.0)	−0.444 11 (24.2)	−0.540 67 (25.1)
$^3B_1$	vertical	−0.080 77 (28.2)	−0.112 17 (29.6)	−0.399 99 (29.2)	−0.487 06 (30.5)	−0.435 93 (29.3)	−0.532 17 (30.5)
$^1B_1$	SCF	−0.025 00 (63.2)	−0.060 21 (62.2)	−0.353 48 (58.4)	−0.445 46 (56.6)	−0.392 50 (56.6)	−0.494 40 (54.2)
$^1B_1$	vertical	−0.010 99 (72.0)	−0.043 82 (72.5)	−0.341 69 (65.8)	−0.431 11 (65.6)	−0.381 47 (63.5)	−0.480 75 (62.7)

[a] Total energies are given in hartrees, relative to −368 hartrees. Relative energies (in parentheses) are in kcal/mol. Vertical refers to energies determined at the $^1A_1$ optimized geometry.

2). The closed shell $^1A_1$ state (Figure 3) has a single imaginary frequency of 39i cm^{-1} (69i cm^{-1}) in the staggered configuration using the TCSCF (SCF) wave function. This mode is of a_2 symmetry, corresponding to a conrotatory motion of the two methyl groups, and leads to a ground-state minimum-energy structure of C_2 symmetry labeled ^1A (Figure 4). These differences in methyl group orientation are quantified by consideration of the dihydral angle, τ, between the planes H–C–Si and C–Si–C, with $-\pi < \tau < \pi$. Hence $\pi = 180°$ for the in-plane hydrogen of the staggered configuration and $\tau = 0°$ for the same in the eclipsed geometry. For tetrahedral carbon the dihedral angles of the hydrogens will be 120° apart, and we find only a slight (1–4°) variation from ideality. The only real difference in the methyl group geometry from state to state is the rotation by $\Delta\tau \sim 10°$ and 60° from the triplet to the closed-shell and open-shell singlets, respectively. Otherwise all C–H bond distances are in the range 1.090 ± 0.004 Å and all Si–C–H bond angles are within $110 \pm 3.1°$.

The principal difference between the optimized geometries is in the C–Si–C angle, ϕ, as is the case in SiH_2, SiHF, and SiF_2.[12] In particular, we find $\phi = 98.8°$ (98.4°) using the TCSCF (SCF) wave function for ^1A, $\phi = 117.9°$ for $^3B_1$, and $\phi = 121.3°$ for $^1B_1$. The results for the ground state and triplet state are nearly identical with those in previous theoretical studies of $Si(CH_3)_2$[7,14] and should be compared with values of 93.9°, 118.1°, and 122.6° obtained in a similar study on SiH_2.[12] Thus we find, as do others,[7,14] a ~5° increase in ϕ upon replacement of hydrogens by methyl groups in SiH_2. The Si–C bond distances show moderate differences between the states, ranging from a low of 1.897 Å in $^3B_1$, to 1.910 Å in ^1A, and to 1.915 Å in the open shell $^1B_1$.

Essentially the only geometrical difference between the SCF and TCSCF descriptions of ground-state $Si(CH_3)_2$ is that the methyl group in the SCF structure has a torsional angle ~5° farther from the staggered conformation than is the TCSCF structure. This correlates well with the higher imaginary frequency found in the SCF $^1A_1$ transition state (68i cm^{-1} vs. 39i cm^{-1}). This result is probably not significant, however, as the energy difference between the C_{2v} and C_2 symmetry structure is, for the SCF structures, only 0.16 kcal/mol, and for the TCSCF structures, 0.07 kcal/mol, using the DZ+d Davidson Corrected CISD energies in Table I. Inclusion of zero point vibrational energy corrections reduces these barriers to 0.03 and −0.03 kcal/mol, respectively. Thus the methyl groups are essentially free rotors, and, to simplify the wave functions, we obtain our final energetic differences using the TZP basis set in C_{2v} symmetry.

Relative Energies and Vibrational Frequencies

From the energies in Table II we see that the TCSCF method provides a very balanced treatment of the closed shell singlet and triplet states. That is, the $^1A_1$ (TCSCF)–$^3B_1$ (SCF) energy difference changes by only 1.8 kcal/mol, from 22.4 to 24.2 kcal/mol, after inclusion of correlation effects. Single point CI's using the larger TZP basis set at the DZ+d C_{2v} symmetry optimized geometries increase our final $^1A_1$–$^3B_1$ energy splitting to 25.1 kcal/mol. This compares with a best estimate of the singlet triplet splitting in SiH_2 of ~20 kcal/mol.[12,17]

The open-shell $^1B_1$ state is found to lie 56.6 kcal/mol above the ground-state $^1A_1$ with use of DZ+d CISD-Q energies. This is reduced to 54.2 kcal/mol with use of the larger basis set. A similar trend was found in SiH_2 where DZP CISD-Q methods found a singlet–singlet splitting of 50.0 kcal/mol, and larger basis sets of TZ + double polarization quality find 45.8 kcal/mol.[18] This may be compared to an experimental value of 44.4 kcal/mol in SiH_2.[19,20]

To resolve the experimental controversy over the UV–vis spectra of ground-state dimethylsilylene, we have determined the energies of the open shell singlet and, for completeness, triplet states at the DZ+d TCSCF $^1A_1$ optimized geometry. The DZ+d CISD-Q $\tilde{X}\ ^1A_1$–$\tilde{A}\ ^1B_1$ vertical excitation energy is predicted to be 63.5 kcal/mol, and this is lowered to 62.7 kcal/mol with the TZP basis set. Thus we would predict λ_{max} = 456 nm, in substantial agreement with West and Michl's results. The inescapable conclusion is that the original assignment of the spectra of dimethylsilylene is correct and that the absorptions at 300 or 350 nm observed by Griller et al. do not belong to the $\tilde{X}\ ^1A_1$–$\tilde{A}\ ^1B_1$ system unless there is a substantial shift in its absorption spectra on going from matrices to solution. Our final prediction for the $\tilde{X}\ ^1A_1$–$\tilde{A}\ ^3B_1$ vertical excitation energy is 30.5 kcal/mol.

In Tables III–V we list the harmonic frequencies and absolute IR intensities for the $^1A_1$ (Table III), ^1A (Table IV), $^3B_1$, and $^1B_1$ (Table V) optimized structures. As we might have expected from the small differences in the SCF and TCSCF structures, the frequencies obtained by these methods are very similar. With the exception of the low-frequency torsional modes, all the TCSCF $^1A_1$ frequencies are within 9 cm^{-1} of those obtained with use of SCF methods (13 cm^{-1} in the case of ^1A). Furthermore, the difference between the $^1A_1$ and ^1A frequencies is small with a few notable exceptions. In particular, those modes of a_1 and a_2 (b_1 and b_2) symmetry which are nearly degenerate in C_{2v} are allowed to mix and repel each other upon reduction to C_2 symmetry. This is most obvious in the case of ν_6 and ν_{10} for $^1A_1$ which become ν_8 and ν_9 of ^1A. The SCF $^1A_1$ frequencies are ν_6 = 680 cm^{-1} and ν_{10} = 694 cm^{-1}, and these become ν_8 = 710 cm^{-1} and ν_9 = 658 cm^{-1} in C_2 symmetry. We also note that the sum of the intensities of ν_8 and ν_9 is approximately that of $\nu_6(^1A_1)$ as one might expect (ν_{10} is IR inactive in C_{2v} symmetry).

It has been previously noted that infrared intensities are often qualitatively incorrect when basis sets of less than DZP quality are used. Too, it is possible that addition of hydrogen p-functions to the DZ+d basis set could significantly change the (essentially nonexistent) $^1A_1$–^1A barrier. To test these ideas we have reoptimized the $^1A_1$ SCF structure using a fully polarized DZP basis set and determined its vibrational frequencies and intensities. Generally speaking, the DZP frequencies (Table III) are 0–30

Table III. Harmonic Vibrational Frequencies (in cm^{-1}) and Absolute Intensities (in km/mol) Obtained for the $^1A_1$ State Using the DZ+d SCF and TCSCF and DZP SCF Wave Functions[a]

		SCF $^1A_1$	TCSCF $^1A_1$	DZP SCF $^1A_1$	exptl	assignment
A_1	ν_1	3267 (13.4)	3261 (14.9)	3252 (11.4)		CH_3 str
	ν_2	3160 (24.8)	3162 (22.8)	3143 (19.7)		CH_3 str
	ν_3	1584 (3.2)	1583 (4.4)	1558 (2.4)		CH_3 def
	ν_4	1433 (38.9)	1436 (39.3)	1401 (41.4)	1220 s (1222 s)	CH_3 def
	ν_5	966 (54.7)	959 (48.4)	949 (52.4)	850 s (844 vs)	CH_3 rock
	ν_6	680 (30.6)	681 (27.6)	680 (30.3)	690? m (690? w)	Si–C str
	ν_7	271 (4.0)	267 (3.6)	272 (3.8)		C–Si–C bend
A_2	ν_8	3215	3219	3199		CH_3 str
	ν_9	1587	1583	1562		CH_3 def
	ν_{10}	694	686	671		CH_3 rock
	ν_{11}	68i	39i	80i		torsion
B_1	ν_{12}	3224 (58.9)	3227 (57.6)	3208 (51.8)		CH_3 str
	ν_{13}	1606 (25.8)	1601 (27.0)	1581 (24.5)	1435	CH_3 def
	ν_{14}	627 (11.9)	636 (7.8)	599 (13.0)		CH_3 rock
	ν_{15}	103 (0.2)	125 (0.0)	95 (0.4)		torsion
B_2	ν_{16}	3267 (39.6)	3261 (40.5)	3252 (34.4)		CH_3 str
	ν_{17}	3156 (16.3)	3158 (18.6)	3138 (12.6)		CH_3 str
	ν_{18}	1568 (8.7)	1570 (9.2)	1542 (9.4)		CH_3 str
	ν_{19}	1423 (19.4)	1426 (22.6)	1390 (20.8)	1210 m (1212 s)	CH_3 def
	ν_{20}	809 (12.8)	802 (16.7)	795 (15.8)	806 vs (803 w)	CH_3 def
	ν_{21}	682 (49.7)	686 (48.6)	679 (47.2)	735? m (690? w)	Si–C str

[a] The experimental values are from ref 26 and 42 (in parentheses).

Table IV. Harmonic Vibrational Frequencies (in cm^{-1}) and Absolute Intensities (in km/mol) of the C_2 Symmetry ^1A State Using DZ+d SCF and TCSCF Methods

		SCF ^1A	TCSCF ^1A
A	ν_1	3268 (15.8)	3261 (15.7)
	ν_2	3218 (6.2)	3219 (1.8)
	ν_3	3153 (17.9)	3160 (20.8)
	ν_4	1592 (0.2)	1586 (1.1)
	ν_5	1578 (2.6)	1580 (3.0)
	ν_6	1432 (35.6)	1436 (38.2)
	ν_7	963 (56.9)	958 (49.1)
	ν_8	710 (14.3)	697 (12.6)
	ν_9	658 (15.5)	670 (14.8)
	ν_{10}	268 (3.9)	266 (3.5)
	ν_{11}	92 (0.0)	55 (0.0)
B	ν_{12}	3268 (35.3)	3261 (39.0)
	ν_{13}	3225 (55.3)	3227 (56.9)
	ν_{14}	3150 (19.5)	3156 (19.4)
	ν_{15}	1603 (24.6)	1600 (26.2)
	ν_{16}	1570 (10.6)	1570 (10.0)
	ν_{17}	1423 (23.5)	1426 (23.8)
	ν_{18}	811 (8.9)	803 (14.8)
	ν_{19}	696 (51.7)	690 (49.4)
	ν_{20}	624 (12.6)	635 (8.4)
	ν_{21}	108 (0.2)	124 (0.0)

Table V. Harmonic Vibrational Frequencies (in cm^{-1}) and Absolute Intensities (in km/mol) of the First Excited $^3B_1$ and $^1B_1$ States of Dimethylsilylene Using DZ+d SCF Methods

		$^3B_1$	$^1B_1$
A_1	ν_1	3278 (28.6)	3280 (10.9)
	ν_2	3193 (16.9)	3195 (20.5)
	ν_3	1602 (1.6)	1617 (5.3)
	ν_4	1441 (2.1)	1430 (0.3)
	ν_5	959 (56.9)	935 (25.3)
	ν_6	655 (1.9)	618 (0.0)
	ν_7	206 (1.1)	218 (0.4)
A_2	ν_8	3270	3290
	ν_9	1589	1573
	ν_{10}	835	929
	ν_{11}	88	108
B_1	ν_{12}	3270 (31.2)	3291 (25.6)
	ν_{13}	1595 (15.1)	1577 (7.5)
	ν_{14}	901 (17.6)	905 (18.3)
	ν_{15}	103 (0.1)	121 (0.4)
B_2	ν_{16}	3278 (8.6)	3278 (35.5)
	ν_{17}	3192 (50.5)	3191 (59.9)
	ν_{18}	1596 (14.2)	1606 (1.1)
	ν_{19}	1429 (4.3)	1401 (29.2)
	ν_{20}	804 (15.3)	808 (8.4)
	ν_{21}	765 (18.3)	714 (1.5)

cm^{-1} below the DZ+d results and, although minor variations are found, the intensities are in qualitative agreement as well. The a_2 symmetry imaginary mode increases from 68i to 80i cm^{-1}, suggesting only a very slight increase in the $^1A_1$–^1A barrier height with this basis set. Since the DZP results are generally more reliable, and since the $^1A_1$ and ^1A results are so similar, we use the DZP SCF $^1A_1$ frequencies for comparison with experiment.

Some features of West and Michl's IR spectra are immediately explicable. For example, the frequencies found experimentally at 1220 cm^{-1} (strong) and 1210 cm^{-1} (medium) are most assuredly the CH_3 deformations ν_4 and ν_{19} which we determine to be at 1401 and 1390 cm^{-1}, respectively, with a relative intensity of approximately 2:1. In a similar fashion, the modes at 850 cm^{-1} (strong) and 1435 cm^{-1} (medium) can be readily identified as ν_5, the a_1 symmetry methyl rock (found here at 949 cm^{-1}), and ν_{13}, the b_1 symmetry CH_3 deformation, the latter prediction being based solely on the relative intensities of the modes in that region. All of the above assignments agree with those of ref 26. Assignment of the bands found at 806 (vs), 690 (m), and 735 (m) cm^{-1} was less obvious. Particularly puzzling to us was the very strong absorption listed at 806 cm^{-1}. We found only one likely candidate in this region, i.e., ν_{20} (b_2) = 795 cm^{-1}, but its intensity is predicted to be only about one-third that of the most intense band, ν_5. It is particularly gratifying in this regard that a new matrix IR study of dimethylsilylene by Raabe, Vancik, West, and Michl (RVWM) finds this to be a weak absorption at 803 cm^{-1}.[42] (We should note here that the experimental designation of intensities as "strong" or "weak" refers to peak intensities while our calculations are for integrated intensities. Differences in line widths are definitely observed, so the comparison is not straightforward.) This unpublished study also finds the band at 735 cm^{-1} to be absent, and RVWM suggest that it may not belong to dimethylsilylene. Our data are inconclusive in this regard. Usually we find theoretical stretching frequencies to be ~10% above experimental values, but here we predict three different modes (ν_6, ν_{10}, and ν_{21}) within 10 cm^{-1} of each other, and the dynamical situation may be considerably more complex than the simple harmonic oscillator treatment implies (recall that ν_6 and ν_{10} split significantly upon reduction to C_2 symmetry). We will note that a similar situation exists in SiH_2, i.e., the symmetric and assymmetric stretch frequencies are predicted to be very close, and the assignment of its

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[42] Raabe, G.; Vancik, H.; West, R.; Michl, J. *J. Am. Chem. Soc.*, in press.

vibrational spectrum has recently been questioned.[22]

The vibrational frequencies of $^3B_1$ and $^1B_1$ dimethylsilylene are listed in Table V. One interesting feature of these is the intensity pattern for the two modes occurring near 1400 cm^{-1} which, by analogy with $^1A_1$, should be observed experimentally near 1200 cm^{-1}. In $^1A_1$ these were both observable with moderate to strong intensity; for $^3B_1$ they are predicted to both be very weak, and for $^1B_1$ only the lower mode has appreciable intensity. Another striking feature is that the out-of-plane CH_3 rocking modes ν_{10} and ν_{14} have been shifted up several hundred wavenumbers. Finally, we note that the symmetric and asymmetric Si–C stretches, ν_6 and ν_{21}, are now split by about 100 cm^{-1} instead of being nearly degenerate. We hope these data will be of use to experimentalists.

Finally, to determine whether the species observed by Griller and co-workers[27,28] could possibly be the triplet state of dimethylsilylene, we have determined CISD-Q energies of various triplet states at the $^3B_1$ optimized geometry with the DZ+d basis set. Specifically, we have examined the $^3A_2$, $^3A_1$, and $^3B_2$ states which arise from the configurations $5b_2 8a_1^2 3b_1$ ($^3A_2$), $5b_2^2 8a_1 9a_1$ ($^3A_1$), and $5b_2^2 8a_1 6b_2$ ($^3B_1$). These states are analogous to the lowest energy triplet states of SiH_2 found by Rice and Handy.[13] The energy of $^3A_2$ is 127.5, 116.0, and 111.4 kcal/mol above $^3B_1$ at the SCF, CISD, and CISD-Q levels of theory, respectively. The corresponding values for $^3A_1$ are 128.5, 119.7, and 116.7 kcal/mol, and for $^3B_2$ we find 115.3, 113.3, and 112.3 kcal/mol. Thus we predict that excitations from $^3B_1$ to these higher lying triplets lie approximately 15–20 kcal/mol above the highest energy transitions observed by Griller (300 nm = 95.3 kcal/mol). While this suggests that the species observed by Griller is not $^3B_1$ dimethylsilylene, it is possible that larger basis sets and more highly correlated wave functions could reduce the splitting significantly.[13] Of course, the minima on the excited triplet state surfaces will be below the vertical excitation energies given above. Our results, in this regard, are therefore inconclusive.

Conclusions

The first excited $^3B_1$ and $^1B_1$ states of dimethylsilylene are predicted to lie 25 and 54 kcal/mol above the ground state, respectively. We find a vertical excitation energy of 63 kcal/mol for the $^1A_1$–$^1B_1$ transition. This agrees very well with the spectroscopic observations of West, Michl, and co-workers who find the absorption maximum at 450 nm (62.7 kcal/mol = 456 nm). Thus we concur that the species observed by these researchers is due to ground-state dimethylsilylene and that the recent objections of Griller and co-workers to the earlier spectroscopic assignment are unfounded.

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Donor–Acceptor Interaction and the Peculiar Structures of Dications

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Abstract: The geometries and stabilities of dications are explained by the donor–acceptor interaction of a (neutral) donor and an (doubly charged) acceptor molecule, respectively. The bonding in these donor–acceptor complexes is analyzed by means of one-electron density analysis. A simple model is presented to rationalize the bonding features of dications CH_2X^{2+} and CH_4X^{2+}. Depending on the type and number of donor molecules, three cases of donor–acceptor complexes can be distinguished. Type I complexes comprise dications where the electron acceptor CH_2^{2+} is bound to molecule X which donates electronic charge via a lone-pair orbital. The second class (type II complexes) consists of species where electron donation of X arises from a bonding σ-MO, and type III complexes occur when two donor molecules, such as H_2 and X in CH_4X^{2+}, donate electronic charge into CH_2^{2+}. It is found that the geometries and stabilities of the three classes of dications can be explained by the strength and type of orbital interaction between donor and acceptor, respectively. The stabilization due to electron donation from two donors X and H_2 in type III dications is not simply additive but rather depends on the actual orbitals being involved in the interaction. The model presented here can be used to predict stable structures for unknown dications.

I. Introduction

In the last couple of years the experimental and theoretical study of doubly charged cations has become a very active field of chemical and physical research reflected in recent reviews on dications in solution[2] and in the gas phase.[3] Although doubly charged cations have been known since 1930,[4] only in the last 10 years has this field become a topic of broad interest. This is largely due to the development of new experimental techniques in gas-phase ion chemistry such as charge-stripping mass spectrometry, PIPICO (photoion–photoion coincidence), and IKES (ion kinetic energy spectroscopy), to mention only a few in this rapidly developing field. In solution, the use of superacids and "magic acids" facilitates the investigation of dications.[2] The interest in dications also arises from the finding that they exhibit some highly unusual structures: doubly charged methane is planar,[5] ethylene dication

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