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Wavenumbers and intensities of the fundamental vibrational modes of HNSi and DNSi from quantum-chemical computations¹

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Abstract

By means of ab initio quantum-chemical computations with large basis sets and extensive treatment of electronic correlation effects, we have calculated the transition wavenumbers and absolute intensities of the fundamental vibrational modes of ${}^{1}\mathrm{H}^{14}\mathrm{N}^{28}\mathrm{Si}$ and ${}^{2}\mathrm{H}^{14}\mathrm{N}^{28}\mathrm{Si}$ and other molecular properties. The available experimental data were used to test the nature of the basis sets and the extent of correlation needed to reproduce the observed properties. General features of these computations are discussed in relation to the cancellation of errors due to the incomplete basis set with errors due to the incomplete treatment of electronic correlation.

Introduction

The triatomic species iminosilicon (HNSi) is the first polyatomic molecule to be discovered [1] that contains what chemists consider to constitute a multiple bond [2] between silicon and another atomic centre, in this case nitrogen. The species was identified on the basis of a set of three lines in the infrared spectrum of the products formed after photodecomposition of azidosilane (H₃SiNNN) in solid argon near 4K and another set of three spectral lines produced similarly after photolysis of D₃SiNNN [1]. According to these six wavenumbers associated with the three fundamental vibrational modes of vibration of each of ${}^{1}H^{14}N^{28}Si$ (hereafter HNSi) and ${}^{2}H^{14}N^{28}Si$ (DNSi), a geometric structure was

deduced that has a central nitrogen atom: the nuclear conformation was concluded to be linear with bond lengths/ 10^{-10} m $R_{\rm NH} \approx 1.005$ and $R_{\rm NSi} \approx 1.54$ [1]. During the succeeding 25 years the only other experimental observations [3] on this species were essentially repetitions of the preceding experiment on H₃SiNNN in solid argon, although some microwave transitions in interstellar spectra were tentatively attributed to the isomeric species HSiN [4]. A measured vibrationrotational band centred near 3588 cm⁻¹ was attributed [5] to HNSi on the basis of the similarity of $\nu_1 \approx 3583 \,\mathrm{cm}^{-1}$ for HNSi trapped in solid Ar and the rotational parameter $B_{00^00} = 0.6344 \,\mathrm{cm}^{-1}$ [5] compared with the value 0.6436 cm^{-1} based on the estimated structure [1]. Later, several lines in the pure rotational spectrum of each of ${}^{1}H^{14}N^{28}Si$, ${}^{1}H^{14}N^{29}Si$ and ${}^{1}H^{14}N^{30}Si$ were reported [6]; the rotational parameter $B_{00^00} = 0.6344 \,\mathrm{cm}^{-1}$ of ¹H¹⁴N²⁸Si agreed with the preceding value.

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As in both cases the rotational parameters from experiment pertain to the state of zero-point energy, the values are hence undoubtedly significantly smaller than the equilibrium value B_e to which the value based on the estimated structure pertains by the nature of its derivation; in these circumstances, the agreement between the value of $B_{\rm e}$, still to be determined, and the value $0.6436 \,\mathrm{cm}^{-1}$ would be much better than between the latter and $0.6344 \,\mathrm{cm}^{-1}$. The combination of the experimental rotational parameter B_{0000} for the state of zero-point energy and the vibrational data allows us to make the best current estimate of the equilibrium structure with its (correlated) standard errors, $R_{\rm NH}/10^{-10} \,\mathrm{m} \approx 1.000 \pm 0.005$ and $R_{\rm SiN}/10^{-10} \,\mathrm{m} \approx 1.550 \pm 0.004$, with the corresponding estimate $B_{\rm e}/{\rm cm}^{-1} \approx 0.6364 \pm 0.0025$. The definitive structure from B_e must await the results of experiments that yield rotational parameters both for isotopic variants of H or N and for all the first vibrationally excited states of the three fundamental modes. In summary all available experimental data are consistent with a structure near that deduced originally [1]. There are still no reports of other properties of HNSi measured in the gaseous phase, such as the dipole moment, the bands associated with the fundamental vibrational modes ν_2 and ν_3 or any overtones and combinations of HNSi, any bands at all of DNSi, intensities of any vibration-rotational bands, etc.

During this same quarter century there were a few quantum computations of the molecular properties of HNSi. Following the proposed assignments of microwave lines in interstellar spectra to HSiN [4], a principal concern in these calculations [7-10] was the relative stability of HNSi and HSiN; all results concurred to the effect that HNSi was more stable than HSiN by 230-315 kJ mol⁻¹. This conclusion is consistent with the original production of HNSi [1] in that the order HSiN of atoms in the precursor became altered in the final relatively stable product HNSi; the electronic ground state of the latter molecule is likely to be $X^{1}\Sigma$ because HNSi lacks a tendency to react with H₂ and N₂ molecules constrained to remain adjacent within the site of production in solid argon [1]. For this reason the tentative assignments [4] of the lines in interstellar spectra to HSiN are unlikely to be correct. A further computation was closely related to the analysis of the pure rotational transitions in the sub-millimetre region [11].

These experimental data on HNSi and DNSi make possible both a test of computational methods and the prediction of molecular properties to guide further experiments. In designing the ab initio calculations, we must be aware of errors that inevitably appear in results therefrom. In any currently practicable quantum-chemical calculations on a molecule containing more than a few electrons, any fortuitously good agreement between experimental and calculated geometries and wavenumbers would arise from the cancellation of errors due to the use of an incomplete set of basis functions with errors due to incomplete calculation of the electronic correlation energy. For this reason it is impossible to make predictions a priori of the accuracy of an untested theoretical model. To test theoretical models for HNSi and DNSi, we have made calculations of their spectral properties for comparison with available experimental data. We particularly endeavoured to apply a basis set and electronic correlation method that had a quality sufficient to yield results of accuracy comparable with that of experimental quantities. Our results demonstrate some success towards that objective.

Basis sets and procedures

The notation of our basis sets is explained by Hehre et al. [12]. For our calculations the basis sets consisted of split valence plus polarisation 6-31G(d,p) [13] (single-zeta core, double-zeta valence and polarisation functions on all atoms), double zeta plus polarisation DZP [14] (CADPAC notation of Dunning basis set), and triple split valence plus polarisation 6-311G(d,p) [15]. The latter basis involves five d orbitals on both Si and N and the McLean-Chandler (12s, 9p) \rightarrow [6s, 5p] basis sets [16] for Si. We calculated the molecular properties at the single-configuration Hartree-Fock (HF) level and at correlated levels of theory, namely Moller-Plesset (MP) perturbation theory [17] to second (MP2), third (MP3), partial fourth (MP4DQ) and complete fourth (MP4SDTQ) order, and coupled-cluster theory [18] including all double substitutions (CCD). The bond lengths of HNSi were fully optimised at each level of theory; the criterion of convergence was that the maximum force was invariably less than 0.0001 atomic units, as implemented in CADPAC 4.2 [19] and the GAUSSIAN 90 and GAUSSIAN 92 [20] programs. The harmonic wavenumbers were calculated from analytical second derivatives at the HF and MP2 levels of theory, and from numerical derivatives of analytical gradients in CCD calculations. The computations were done on a workstation (80486 microprocessor at 33 MHz) or on IBM RS/6000 (model 320H) and 3090 (model 170J) computers.

Results and discussion

Because quantum-chemical calculations yield directly the harmonic wavenumbers of the fundamental vibrational modes, to facilitate comparison with the experimental data we converted the latter values for the stretching of the N-H or N-D (ν_1) and N-Si (ν_3) bonds to the harmonic wavenumbers by means of the empirical factors previously derived from data for diatomic molecules [21]; these results appear in the Tables beside the calculated values. These corrections take into account directly only the diagonal anharmonic terms. For the wavenumbers associated with the deformation vibrations ν_2 no such adjustment is possible because for a (supposed) linear molecule the symmetry precludes a finite value of terms of odd power in the angular coordinate, and most contributions to the observed harmonic correction would arise from off-diagonal terms [22]. For this reason and the undoubted existence of shifts of all measured wavenumbers (except ν_1 of HNSi from the gaseous phase) due to the matrix environment 245

of the absorbing molecules, all the harmonic wavenumbers are uncertain $\pm 10 \text{ cm}^{-1}$. As a basis of evaluation of the computed geometry, we take the approximate structure and the corresponding value of B_e from the analysis of the vibrational spectra of both HNSi and DNSi as described in the Introduction.

Before a comparison with the computed intensities, we assess the experimental results [1,3]. The three spectral lines of HNSi were originally recorded under necessarily varied conditions of resolution [1], due to the optical operation of the particular spectrometer. Nevertheless, the important feature of the results is that the peak absorbances and the corresponding integrated intensities of the sets of all three lines of each of HNSi and DNSi separately were comparable; i.e. the maximum range of the intensities was much less than an order of magnitude. Explicitly, for HNSi, the apparent relative intensities decreased in the order I_1 for ν_1 (3583 cm⁻¹) > I₂ for ν_2 (523 cm⁻¹) > I₃ for ν_3 (1198 cm⁻¹), whereas for DNSi, I_1 for ν_1 $(2669 \text{ cm}^{-1}) \sim I_3$ for ν_3 (1166 cm⁻¹) > I₂ for ν_2 $(395 \,\mathrm{cm}^{-1})$ [1]. In contrast, in the later spectrum [3], which was obviously affected by other products of photodecomposition of H₃SiNNN, the order of intensities for only HNSi appears to be $I_2 > I_3 \sim I_1$. These observed intensities of HNSi or DNSi molecules subject to the perturbing influences of adjacent atoms and molecules, whether N_2 , H_2 or Ar in the matrix environment, may inaccurately reflect the intrinsic intensities of the free molecules (in the gaseous phase at small densities). Despite these experimental results being somewhat inconsistent, probably due to varied conditions of temperature of the matrix, wavelength of ultraviolet irradiation, concentrations, spectral interference by other absorbing species etc., we endeavour to use them as a basis of comparison. In the Tables, the relative magnitudes of the experimental intensities are indicated qualitatively by the number of plus signs for each mode [1,3].

We evaluated our results in the light of related experience of previous computations. Errors in cal-

culated wavenumbers arise from inherent imprecision in the differentiation technique, from an incorrect equilibrium geometry and from inaccurate curvature of the potential-energy hypersurface at the energy minimum. For diatomic molecules with few exceptions all wavenumbers calculated with the basis set denoted HF/6-31G(d) were found to exceed the corresponding harmonic experimental quantities [12]; the mean relative magnitude of the deviation of the calculated wavenumbers from the experimental values after harmonic correction was 11%. With improved account of electron correlation in a MP2/6-31G(d) treatment, the calculated wavenumbers are nearer the experimental values, deviating about 5% or half the previous level, but for some hydrides the deviations according to either level of treatment were appreciably smaller. The effects of electronic correlation on calculated wavenumbers were largest for molecules with multiple bonds, as demonstrated for instance for the CC-stretching mode in ethane, ethene and ethyne [12].

Concerning the structures, some pertinent experience is that the HF/6-31G(d) treatments of CO, N₂, C₂H₂, HCO⁺, N₂H⁺, HCN and HNC [23] yielded bond lengths smaller than experimental values, but inclusion of electronic correlation by means of the MP2 treatment made them exceed

experimental values. The DZP and 6-31G(d) results for molecular geometries attained comparable qualities. From a DZP basis set the bonds were too short, but became too long after correlation was included. The use of 6-311G(d,p)basis sets led to shorter bonds than from 6-31G(d)or DZP treatments at the Hartree-Fock level of theory, thereby to poorer agreement with experiment, but inclusion of correlation improved agreement with experiment. In terms of mean error, the most accurate treatments with the 6-311G(d,p) basis are denoted MP4DQ, CCD, MP3 and CISD in order of decreasing accuracy. For uncorrected rotational frequencies derived directly from theoretical values of B_e — which means the errors in the rotational frequencies parallel those in the geometries — the best levels of theory are MP4DQ/6-311G(d,p) and CCD/6-311G(d,p) [23].

HNSi

The HF results in Table 1 are similar from one basis set to another among the sets tested; the geometry varied little as the quality of the basis set was increased. Both the SiN and NH bonds are too short and the wavenumbers associated with the stretching modes are too large relative to the experimental results. These observations agree

Table 1

HF results for HNSi; dependence of total energy/hartree, bond lengths/ 10^{-10} m, dipole moment/ 10^{-30} C m, wavenumbers ν_j/cm^{-1} and the corresponding intensities $I_j/10^{-19}$ m molecule⁻¹ on the basis set with experimentally derived data for comparison. Relative magnitudes of experimental intensities are indicated qualitatively by the number of plus signs (+) for each mode

Basis set	Energy	SiN length	NH length	Dipole moment	$\nu_1(I_1)$	$\nu_2 (I_2)$	$ u_3(I_3)$
6-31G(d,p)	-343.92268	1.528	0.987	0.54	4026 (2.1)	636 (4.0)	1372 (1.4)
DZP	-343.94009	1.529	0.989	1.8	4036 (2.4)	616 (4.0)	1365 (1.6)
6-311G(d6,p) ^a	-343.95491	1.528	0.987	1.2	4001 (2.3)	621 (3.8)	1366 (1.5)
Experiment ^b Intensity ^b Intensity ^c		1.550	1.000		3752 + + + + +	523 + + + + +	1214 + + +

^a CADPAC calculations with six d orbitals (6d); the exponent of d orbitals on Si is 0.388.

^bWavenumbers from ref. 1.

^c Ref. 3.

Correlation method	Energy	SiN length	NH length	Be			
MP4SDTQ	-344.24741	1.577	1.006	0.6160			
MP2	-344.21927	1.567	1.005	0.6235			
Full-MP2	-344.36262	1.566	1.005	0.6241			
MP2 ^b	-344.22721	1.561	1.005	0.6279			
MP2 ^c	-344.24178	1.565	1.004	0.6252			
MP3	-344.22187	1.545	0.999	0.6408			
CCD ^d	-344.21678	1.549	1.001	0.6369			
Experiment		1.550	1.000	0.6364			

Dependence of energy/hartree, bond lengths/ 10^{-10} m and rotational parameter B_e/cm^{-1} of HNSi on the correlation method^a with experimentally derived data for comparison

^a Default: frozen-core approximation, G92 calculations with 6-311G(d,p) basis set.

^b Basis set: 6-311G(2d(0.9, 0.225),d,p) two d orbitals only on Si.

^c Basis set: 6-311G (2d,p).

^d Basis set: 6-311G(d).

Table 2

with preceding experience: HF/6-31G(d) wavefunctions yield too steep a potential energy in the vicinity of the equilibrium geometry [12] and likewise for better basis sets [23]. As the use of the 6-311G(d) basis set with the McLean-Chandler functions on Si led to insignificant decrease of bond length relative to 6-31G(d) results, we scarcely improved agreement with experiment in this case; this behaviour contradicts the trends observed for molecules containing elements of the first row (Li-F) [13]. Being relatively small, the dipole moment is particularly sensitive to the nature of the basis set, whereas the intensities are less sensitive; the calculated intensity of the bending mode ν_2 seems somewhat too large by comparison with experiment [1].

Table 2 indicates the effect of various post-Hartree–Fock methods on the calculated geometry when the triple-split-valence basis set was used with various polarisation functions. MP4SDTQ is known to tend to produce bonds that are too long if they have multiple order [13] as in HNSi [2]; consistent with this trend, our MP4SDTQ calculation produced the longest SiN bond. That the MP2, MP3 and MP4DQ results are much better supports the view that a cancellation of errors due to incomplete calculation of the electronic correlation energy with errors due to the use of an incomplete set of basis functions is required to obtain good results. The bonds calculated according to the MP2 method are shorter, hence nearer the experimental values. Whether the full MP2 or an approximation with the core frozen was used is immaterial because the geometry altered only slightly, unlike the total energy. The exponent and numbers of polarisation functions on Si had a considerable influence on the geometry. When two d polarisation functions were placed exclusively on Si the length of the SiN bond decreased 0.06×10^{-10} m whereas when two d functions were used on both atoms the bond shortening was much less, 0.02×10^{-10} m. This result shows that in the former case the basis set became unbalanced, as reflected in other calculated properties.

The MP3 and CCD results agree well with the experimental geometry and with the calculations of Botschwina et al. [11]. The MP4DQ calculations yielded $(1.550 \pm 0.001) \times 10^{-10}$ m for the length of the SiN bond and $(1.001 \pm 0.001) \times 10^{-10}$ m for the NH bond. In the CCD calculation we placed no polarisation function on H because the results showed that it has only a slight effect on the calculated properties (Table 3).

Basis set	Energy	Bond length		Dipole moment		Be
		SiN	NH	HF	MP2	
6-311G(d6,p) ^a	-344.36708	1.570	1.005	1.7	1.2	0.6209
6-311G(d6) ^b	-344.35862	1.565	1.004	1.6	1.5	0.6248
6-311G(d6,p) ^b	-344.36794	1.566	1.005	1.7	1.1	0.6242
6-311G(2d6 d6)°	-344.37720	1.557	1.005	1.5	1.6	0.6304
6-311G(2d6d6,p) ^d	-344.38399	1.559	1.006		1.3	0.6292

Dependence of total energy/hartree, bond lengths/ 10^{-10} m, HF and MP2 dipole moment/ 10^{-30} C m and rotational parameter B_e/cm^{-1} of HNSi on the basis set with full MP2

^a The exponent of d orbitals on Si is 0.388.

^b The exponent of d orbitals on Si is 0.45.

^c Two d orbitals exclusively on Si have exponents 0.225 and 0.9. ^d Two d orbitals exclusively on Si have exponents 0.25 and 0.75.

Table 3 presents the MP2 results calculated with the same triple-split basis set and with various polarisation functions. The length of the SiN bond is sensitive to the polarisation functions on Si; the range extends over 0.013×10^{-10} m. When a single polarisation function was used, the larger exponent (0.45) gave a better result. When no polarisation function was placed on H, the changes in the equili-





Fig. 1. Surface of CCD-fc/6-311G(d) energy/hartree for HNSi as a function of SiN internuclear distance/10⁻¹⁰ m (from 1.540 to 1.554 in steps of 0.002) and NH internuclear distance/10⁻¹⁰ m (from 0.998 to 1.006 in steps of 0.002).

Table 3

brium bond lengths were -0.0005×10^{-10} m for SiN and -0.012×10^{-10} m for NH. The dipole moment was more sensitive to the polarisation function on H: the dipole moment from the HF wavefunction decreased whereas the value from the MP2 wavefunction increased when the polarisation function was omitted. When two polarisation functions were used the difference became less important as the flexibility of the polarised basis increased; the larger split (0.225 and 0.9) gave a slightly shorter (better) SiN bond. The polarisation function on H played a negligible role in the geometry but a more important role in the dipole moment. These results indicate that the d functions on Si are important in reproducing the molecular structure of HNSi whereas the p functions on H have less influence on the geometry but an important effect on the computed dipole moment.

The hypersurfaces of potential energy from the best methods are depicted in the Figures; for a collinear nuclear conformation, the SiN and NH distances are represented on the horizontal axes and energy on the vertical axis. The CCD (Fig. 1) and MP4DQ (Fig. 2) surfaces are similar in the position of the point of minimum energy, but the curvatures differ slightly; the MP3 surface in Fig. 3 is perceptibly different.

Table 4 presents the calculated zero-point energies and harmonic wavenumbers. The results of the double-zeta (MP2/631G(d,p) and DZP) calculations indicate that these basis sets are less suitable than the triple-split basis sets. The harmonic wavenumber ν_1 is well reproduced from all these basis sets, but the triple-split results are clearly superior to those from the MP2/6-31G(d,p) and DZP methods. The use of p polarisation on H influenced only



MP4DQ

Fig. 2. Surface of MP4DQ-fc/6-311G(d) energy/hartree for HNSi as a function of SiN internuclear distance/10⁻¹⁰ m (from 1.540 to 1.554 in steps of 0.002) and NH internuclear distance/10⁻¹⁰ m (from 0.998 to 1.006 in steps of 0.002).





Fig. 3. Surface of MP3-fc/6-311G(d) energy/hartree for HNSi as a function of SiN internuclear distance/10⁻¹⁰ m (from 1.540 to 1.554 in steps of 0.002) and NH internuclear distance/10⁻¹⁰ m (from 0.998 to 1.006 in steps of 0.002).

slightly the calculated results. The more precise CCD calculation reproduced well the experimental geometry, but yielded larger wavenumbers.

The wavenumber ν_2 is poorly reproduced from only the 6-31G(d,p) basis set, but is otherwise reasonably near the experimental result except when two d orbitals were placed exclusively on Si. Although the latter basis resulted in the best geometry, the basis set became unbalanced, reflected in the strongly underestimated wavenumber of the bending mode; the wavenumbers of ν_1 and ν_3 were well reproduced in this case.

The harmonic wavenumber ν_3 was consistently underestimated in the MP2 computations; likewise the intensity I_3 was relatively much too small in comparison with experimental observations. All intensities from the MP2 computation are smaller than those from the HF calculations; the differences are minor for ν_1 and ν_2 but large for ν_3 . Whether full MP2 or a frozen-core approximation was used is almost immaterial, as the vibrational wavenumbers and geometry altered only slightly. The exponent of the d function on Si strongly influenced mostly the harmonic wavenumber ν_3 ; compared with 0.388, the value 0.45 of this exponent improved both the geometry and the magnitude of ν_3 . In the CCD calculation this frequency is overestimated and the intensity is several times as large as the corresponding MP2 intensities.

The presence of a p polarisation function on H decreased the ν_1 and ν_3 wavenumbers slightly (~ 4 cm⁻¹), but had a larger effect (+15 cm⁻¹) on ν_2 ; an explanation is the weaker effect of H–N–Si delocalisation. The best MP2 wavenumbers agree well with experiment; the errors are +0.3, +0.4 and

Table 4

Full MP2 and CCD-fc (frozen-core) results for HNSi; zero-point energy/kJ mol⁻¹, wavenumbers ν_j/cm^{-1} and the corresponding intensities/ 10^{-19} m molecule⁻¹ with experimentally derived data for comparison. Relative magnitudes of experimental intensities are represented qualitatively by the number of plus signs (+) for each mode

Basis set	Zero-point energy	$ u_{l}$	Ii	ν_2	I ₂	$ u_3$	I ₃
6-31G(d,p)		3804		577		1183	
DZP		3800	1.8	524	3.3	1184	0.17
6-311G(d6,p) ^a	36.0	3756		531		1183	
fc/6-311G(d,p) ^b	36.1	3761	1.6	546	3.2	1190	0.12
6-311G(d6,p) ^b	36.1	3759	1.6	540	3.2	1192	0.12
6-311G(d6) ^b	36.1	3764	1.6	525	3.2	1196	0.12
6-311G(2d 6)°		3750	1.5	417	3.5	1198	0.15
CCD-fc/6-311G(d) ^b	36.9	3796	1.2	545	3.6	1279	0.50
Experiment ^d	36.1	3752	+ + +	523	+ +	1214	+
Experiment ^e			+ +		+ + +		+ +

^a The exponent of the d orbitals on Si is 0.388.

^b The exponent of the d orbitals on Si is 0.45.

^cTwo d orbitals exclusively on Si have exponents 0.225 and 0.9.

^d Ref. 1.

^e Ref. 3.

1.5% for ν_1 , ν_2 and ν_3 respectively, whereas the CCD computation produced errors of +1.1, +4.2and +5.4%. The cancellation of errors due to the use of an incomplete set of basis functions and errors due to incomplete calculation of the electronic correlation energy made the MP2 triple-split basis with polarisation functions on the heavy atoms suitable for calculations of vibrational wavenumbers. Unlike the position of the minimum energy, the curvature of the energy hypersurface was described correctly near the equilibrium geometry. For this reason the calculated wavenumbers agree better with experiment, as expected, unlike the molecular geometry and infrared intensities. For the latter two properties the CCD calculations seem superior. In agreement with experimental results, the molecular geometry is described consistently according to CCD, MP4DQ and MP3 calculations with the specified basis set. All calculations are consistent in that the relative intensities decrease in the order $I_2 > I_1 > I_3$, in partial agreement with experimental results; the latter intensities may not fairly reflect the properties of the free molecules for the reason already stated.

DNSi

Table 5 presents these results. As we learned that for HNSi the correlation energy plays an important role, we performed only MP2 calculations, using the DZP and 6-311G basis sets with various polarisation functions. We found the former to yield a good prediction of ν_2 but the latter to provide a superior result for ν_1 . The third basis set with no polarisation function on H produced the best agreement with experiment, consistent with the tendencies discerned for HNSi. When in the fourth calculation two d functions were placed on Si, ν_2 decreased as for HNSi. In all cases the harmonic wavenumber ν_3 was significantly underestimated, again like the results for HNSi. The intensities vary little with the basis set, with the same trends as for HNSi. As expected, the intensities of DNSi are smaller than the corresponding ones of HNSi, but of the same order of magnitude.

Conclusions

The main findings of this work are as follows. The experimental geometry is reproduced best by

Table 5

Harmonic wavenumbers and full MP2 results of DNSi; dependences of wavenumbers ν_j/cm^{-1} and the corresponding intensities $I_j/10^{-19}$ m molecule⁻¹ on the basis set, with experimentally derived data for comparison

Basis set	ν_1	I_1	ν ₂	I ₂	ν ₃	I ₃
DZP	2809	1.1	403	2.0	1150	0.15
fc/6-311G(d,p) ^a	2776	1.0	416	1.8	1155	0.10
6-311G(d6) ^b	2784	0.88	403	2.1	1161	0.083
6-311G(2d6,d6)°	2774	1.0	320	1.8	1163	0.10
Experiment ^d	2761	+ + +	395	+ +	1181	+ + +

^a The exponent of the d orbitals on Si is 0.45.

^bTwo d orbitals exclusively on Si have exponents of 0.225 and 0.9.

^c Ref. 1.

the CCD-fc (frozen-core) and MP4DQ-fc/6-311G(d) calculations. The MP3 treatment yielded slightly shorter bonds whereas the results from the MP2 and MP4SDTO treatments contained bond lengths that were too large. The geometry calculated at the MP2 level of theory is sensitive to the exponent of the d polarisation function on Si; a value 0.45 for this exponent gave better results than 0.388. Introduction of two d functions on Si yielded the shortest (best) bond, but the basis set became unbalanced; consequently ν_2 was poorly reproduced. Use of polarisation functions on H is unnecessary. The results from the correlated double-zeta basis are worse than those from the triple-split basis set, and the HF treatment was unable to reproduce satisfactorily the molecular geometry. The experimental harmonic wavenumbers are produced best from the MP2/6-311G(d)calculations because of the (partial) cancellation of errors due to the use of an incomplete set of basis functions with errors due to incomplete calculation of the electronic correlation energy. The HF treatment produced much larger errors. The calculated intensities decrease in the order $I_2 > I_1 > I_3$ in partial agreement with the experimental results. The order of intensities is independent of the method and the same for both HNSi and DNSi, in apparent inconsistency with the experimental results.

According to both our present results and published reports for molecules of modest size, one can achieve agreement of calculated properties of bond lengths and vibrational wavenumbers with an accuracy near that of the experimental measurements, at least in this case of HNSi for which, as it is an unstable or reactive species, the chemical properties have so far prevented extensive and accurate spectral data from being collected. In order to secure this achievement, one must rely, even within an ab initio framework, on not only large basis sets and massive calculations of the effects of electron correlation but also on cancellation of errors, as we have already described. At least as a result of our tests on HNSi we have gained a well founded impression of the nature of quantum-chemical computations required to produce this agreement. Although semi-empirical methods or other highly approximate techniques such as the use of density functionals - or even just HF methods without inclusion of electronic correlation — may produce estimates of molecular properties, as either tests of the methods or accurate predictors of many properties concurrently, these approaches clearly have extremely limited value because of their more or less gross approximations; our own preliminary tests with these methods have proved this inaccuracy. Despite the ability of such computer programs to generate extensive Tables of values, such as for energies of numerous vibrationally excited states and intensities of overtone and combination transitions, the value of these results is at best questionable because of the fundamental deficiencies of the algorithms. Even with our extensive computations for HNSi, we found difficulty in

predicting accurately the molecular dipole moment; our best estimate takes the form of the range $(1.2 - 1.6) \times 10^{-30}$ Cm, but even with that extent of uncertainty the estimate will be helpful to experimenters in their measurement of this property.

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