interest in studies of proteins. When applied to larger proteins of interest, comparison of backbone and side-chain dynamics in different kinds of secondary structure will be possible. Importantly, changes in dynamics accompanying transitions between functionally distinct states can be studied. This kind of information is required to characterize the internal dynamics of biopolymers and to ascertain whether or not these motions hinder, aid, or are irrelevant to function. Equally important is the possibility of using unbiased information on the internal dynamics of biopolymers during the generation and refinement of structures based upon the distance-geometry transform.[35]

The methodology presented here is experimentally simple and direct. In order to extend such work to proteins of significant size, isotopic enrichment can be used in conjunction with selective proton labeling of nitrogens by deuterium-hydrogen exchange. We have initiated such studies of human ubiquitin and cytochrome *c*.

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Structure of $(SiO)_2$: A Comparison between $(AlF)_2$, $(SiO)_2$, and $(PN)_2$. Matrix Infrared Investigation and ab Initio Calculation

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Abstract: The structure of dimeric SiO is reexamined by a study of the IR spectra of the matrix-isolated species. Spectra of isotopomers from experiments with ^{29}Si- and ^{18}O-enriched samples are discussed with the help of normal-coordinate analysis. The results are in line with data of the geometrical and electronic structure obtained by ab initio SCF calculations. The dimerization energy calculated by quantum chemical methods agrees well with experimental data, which have been recalculated. With the help of additional ab initio calculations on the isoelectronic species PN and AlF, interesting correlations between their tendency toward dimerization can be obtained. Structural data of SiO are compared with the analogous ones of similar molecules (e.g., BF).

1. Introduction

When quartz is heated above 1500 K monomeric SiO is by far the most favored species in the gas phase.[1] But during cocondensation of such a high-temperature molecule with an excess of argon on a helium-cooled surface, oligomers of SiO are formed. The composition of these oligomers strongly depends on the experimental conditions. By this method the molecules $(SiO)_2$ and $(SiO)_3$ have been detected with infrared spectroscopy some time ago.[2,3] As the results of these investigations are called in question in a recent study of dimeric SiO[4] and as there is an increased interest in the system Si/O in the last years, stimulated by surface reactions of silicon wafers, we took up this subject once more in the discussion presented here. New findings could be expected (1) by experiments with samples enriched in ^{29}Si, (2) by a detailed normal-coordinate analysis including the unsymmetrical species $^{28}Si_2{}^{16}O^{18}O$ and $^{29}Si^{28}Si^{16}O_2$, (3) by ab initio SCF calculations, (4) and by the recalculation of the dissociation energy of $(SiO)_2$. In order to understand structural data and bonding of SiO and its dimer, they are compared with those of similar molecules.

2. Technical Details

2.1. Starting Compounds, Matrix Isolation, and Spectroscopy. SiO is generated when O_2 is passed over heated Si (Wacker) at about 1500 K in an Al_2O_3 furnace. Experiments with ^{29}Si-enriched SiO have been performed in the following way: $^{29}SiO_2$ (Oak Ridge Laboratory) was first reduced with the help of Be in a Knudsen cell. Subsequently, ^{29}SiO was generated by passing O_2 over the heated mixture as described above. A mixture of Ar/SiO (with the composition 200:1) was condensed for about 2 h on a helium-cooled Cu surface. The setup with the flow cryostat has been described before.[5] The IR spectra were recorded using a Perkin-Elmer 225 spectrometer.

Normal-coordinate analysis was carried out using a modified version of the Shimanouchi program system.[6]

2.2. Details of Computation. Ab initio SCF computations were performed for the electronic ground states of BF, AlF, PN, SiO, $(SiO)_2$, $(AlF)_2$, and $(PN)_2$ by using the Karlsruhe version[7] of the Columbus system of programs.[8,9] A gradient program[10] was used for geometry optimization.

The following CGTO basis was used:[11] B, (9,5,1)/[5,3,1], $\eta(d) = 0.5$; O, (9,5,1)/[5,3,1], $\eta(d) = 1.0$; Al, (11,7,1)/[6,4,1], $\eta(d) = 0.3$; P,

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(1) As the dissociation energy of $(SiO)_2$ is about 200 kJ/mol (298 K) (section 3.4), the ratio in partial pressures of $SiO/(SiO)_2$ is on the order of 10000 at the conditions of our experiments.

(2) Anderson, J. S.; Ogden, J. S. *J. Chem. Phys.* **1969**, *51*, 4189.

(3) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *Inorg. Chim. Acta* **1969**, *3*, 601.

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(8) Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* **1976**, *65*, 111. Rys, J.; Dupuis, M.; King, H. F. *J. Comput. Chem.* **1983**, *4*, 154.

(9) Pitzer, R. M. *J. Chem. Phys.* **1973**, *58*, 3111.

(10) Schaefer, H. F.; Pitzer, R. M. Private communication to R. Ahlrichs.

(11) To obtain more accurate values for the dissociation energy of $(SiO)_2$, CPF calculations[12] have been performed with differrent basis sets: (1) Si, (11s,7p,2d)/[6,4,2], $\eta_1(d) = 0.7$, $\eta_2(d) = 0.23$; O, (10s,6p,2d)/[6,4,2], $\eta_1(d) = 1.5$, $\eta_2(d) = 0.5$; (2) Si, (11s,7p,2d,1f)/[6,4,2,1], $\eta_1(d) = 0.7$, $\eta_2(d) = 0.23$, $\eta(f) = 0.5$; O, (10s,6p,2d,1f)/[6,4,2,1], $\eta_1(d) = 1.5$, $\eta_2(d) = 0.5$, $\eta(f) = 1.1$.

(12) Ahlrichs, R.; Scharf, P.; Ehrhardt, C. *J. Chem. Phys.* **1985**, *82*, 890.

0002-7863/89/1511-4578$01.50/0

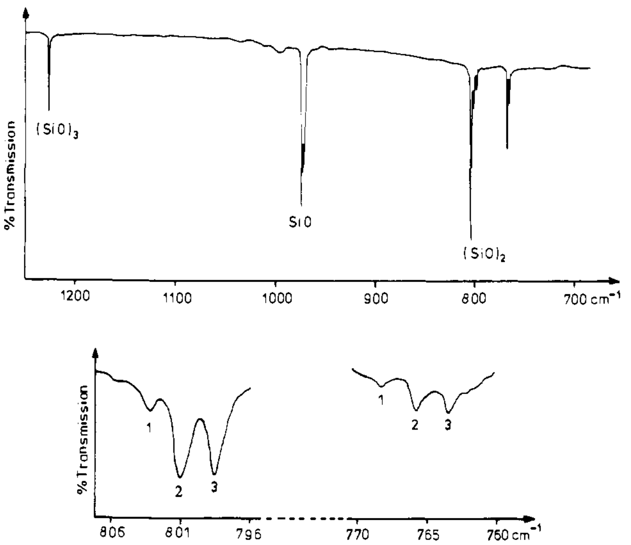

Figure 1. Infrared transmission spectrum of an Ar matrix containing SiO, $(SiO)_2$, and $(SiO)_3$: (1) $^{28}Si_2{}^{16}O_2$; (2) $^{28}Si^{29}Si^{16}O_2$; (3) $^{29}Si_2{}^{16}O_2$.

(11,7,1)/[6,4,1], η(d) = 0.4; N, (9,5,1)/[5,3,1], η(d) = 0.8; F, (9,5,1)/[5,3,1], η(d) = 1.3; Si, (11,7,1)/[6,4,1], η(d) = 0.4.

The parameters of s and p CGTO basis functions were taken from Huzinaga's tables.[13] The basis is of DZP quality, or better, which on the SCF level usually gives geometric structure constants with errors of about 1–2° or pm.

The electronic structure was visualized by means of a population analysis based on occupation numbers.[14-16] Within this approach the electronic structure is characterized by atomic net charges Q(A) for atom A and the shared electron number SEN(AB) for the AB bond.[17]

3. Results

3.1. IR Spectra of the Matrix-Isolated Species. When gaseous SiO, generated by the reaction of Si with O_2 at temperatures of about 1500 K, is deposited with an excess of Ar on a helium-cooled surface, the IR spectrum shown in Figure 1 is observed. Alongside the absorption of monomeric SiO at 1226 cm^{-1}, additional bands attributed to the dimer (803 and 768 cm^{-1}) and the trimer (972 cm^{-1}) can be seen. These results are in line with earlier investigations of matrix-isolated SiO species,[2,3] though in these cases SiO was produced in a different way at higher temperatures. Our method has an important advantage over the former ones, in that the concentration of SiO can be varied over a wide range in a highly reproducible way. Therefore, it can easily be shown that the dimerization of SiO in the matrix depends strongly on the SiO concentration: the concentration of $(SiO)_2$ grows by a factor of about 4 when the SiO production is doubled.[18] This experiment confirms the former assignment of the $(SiO)_2$ bands. But as there was some doubt about the structure of $(SiO)_2$,[2] we reexamined this subject.

On the experimental side we did some work with the different isotopomers produced by $^{16}O/^{18}O$ and $^{28}Si/^{29}Si$ substitution. The absorptions of $(SiO)_2$ enriched with ^{29}Si are shown in an expanded scale of the stretching region in Figure 1. The accurate frequencies of these species are listed together with the corresponding values of all $^{16}O/^{18}O$ isotopomers in Table I. These spectroscopic results (e.g., absorption pattern[19] clearly demonstrate that there are two identically bonded oxygen and silicon atoms in $(SiO)_2$. As the frequency of both vibrations is in the region typical for SiO single bonds, $(SiO)_2$ should have a ring structure as proposed by Ogden.[2]

Table I. Calculated[a] and Observed Frequencies of $(SiO)_2$

D_{2h} Symmetry

		A_g	A_g	B_{1g}	B_{2u}	B_{3u}
$(^{28}Si^{16}O)_2$ (1)	calcd	826.25	380.96	632.1	803.96	768.82
	obsd				803.2	768.2
$(^{29}Si^{16}O)_2$ (2)	calcd	821.57	376.46	628.56	798.90	763.98
	obsd				798.5	763.4
$(^{28}Si^{18}O)_2$ (3)	calcd	795.08	373.14	607.80	774.88	741.01
	obsd				774.7	740.5

C_{2v} Symmetry

		A_1	A_1	B_1	B_1	A_1
$^{28}Si_2{}^{18}O^{16}O$ (4)	calcd	814.25	377.07	618.91	790.46	751.34
	obsd				789.5	750.4

C_{2v} Symmetry

		A_1	A_1	B_1	A_1	B_1
$^{29}Si^{28}Si^{16}O_2$ (5)	calcd	824.16	378.71	630.30	801.18	766.43
	obsd				800.8	765.8

[a] Calculations have been performed with the following force constants (PEDs in parentheses, are given according to the frequencies listed above): f_{SiO} = 3.22 mdyn·Å^{-1} (76, 2, 137, 90, 83); f_{SiOSi} = 0.89 mdyn·Å (2, 65, 0, 0, 19); f_{OSiO} = 0.45 mdyn·Å (1, 33, 0, 7, 0); $f_{OSi/SiO}$ = 0.48 mdyn·Å^{-1} (11, 0, −20, 14,−12); $f_{SiO/OSi}$ = 0.44 mdyn·Å^{-1} (10, 0, −17, −11, 10).

3.2. Normal-Coordinate Analysis. Two of the main conditions to perform a normal-coordinate analysis are the knowledge of the geometry of the species under discussion and the proper assignment of the observed bands.

For $(SiO)_2$ a ringlike structure has been derived from the IR spectra.[2] A correct assignment of the two IR absorptions can only be made if the values of the bond angles SiOSi and OSiO are known. On the basis of spectroscopic data, Ogden postulated 87° for the OSiO angle.[2] We could confirm this geometry by ab initio calculations, which agree with data published recently.[20,21] The following structural parameters of planar $(SiO)_2$ have been obtained: $\angle(OSiO) = 86°$ and d_{SiO} = 168 pm. More details of these computations are presented in subsection 3.3.

In agreement with Ogden's work,[2] the two IR absorptions can be assigned as follows: 803 cm^{-1} (B_{2u}) and 768 cm^{-1} (B_{3u}).[22]

In $(SiO)_2$ with D_{2h} symmetry the two IR active modes belong to different symmetry classes with just a single entry. Then a symmetry force constant can easily be calculated, as usually has been done for molecules of this type.[23] If the symmetry does not change under isotopical substitution, isotopic frequency shifts can as well be calculated in this way.

On the basis of two bands only, it is of course not possible to get values for the individual types of restoring forces that constitute the symmetry force constant. But together with the spectra of isotopically substituted molecules, we could measure a total of 10 frequencies. These experimental data should then limit a proper force field, which also should be comparable with the force fields of other SiO compounds.

Ogden made the first attempt to calculate the five in plane vibrations of $(SiO)_2$ using a three-parameter force field (f_{SiO}, f_{SiOSi}, f_{OSiO}).[2] With the bond/bond interaction constants $f' = f_{OSi/SiO}$

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(13) Huzinaga, S. Approximate Atomic Functions. Technical Report: University of Alberta: Canada, 1971.

(14) Davidson, E. R. *J. Chem. Phys.* **1967**, *46*, 3320. Roby, K. R. *Mol. Phys.* **1974**, *27*, 81.

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(16) Erhardt, C.; Ahlrichs, R. *Theor. Chim. Acta* **1985**, *68*, 231.

(17) The SEN provides a reliable measure of the covalent bond strength. In order to give the idea of typical values found for SEN, we list some representative cases: strong bonds like C–C or C–H (SEN = 1.4); double bonds like C=C (SEN = 2.2); triple bonds like C≡C or N≡N (SEN = 3.3). A reduced SEN is found for polar bonds as in NaF (SEN = 0.3) and for weak bonds such as in Cl_2 (SEN) = 0.9) and in F_2 (SEN = 0.6).

(18) Within these experiments all other parameters (e.g., temperature of the matrix) have to be identical.

(19) Starting with mixtures of $^{16}O_2/^{18}O_2$ (1:1), concentration of $Si_2{}^{16}O^{18}O$ is twice as high as that of the "pure" species $Si_2{}^{16}O_2$ and $Si_2{}^{18}O_2$ (concluded from the intensity of their absorptions, which exhibit a nearly symmetrical triplet). A similar pattern is observed in the $^{28}Si/^{29}Si$ experiments (Figure 1).

(20) Snyder, L. C.; Raghavachari, K. *J. Chem. Phys.* **1984**, *80*, 5076.

(21) Steiger, T.; Walther, P. *Z. Chem.* **1985**, *25*, 257.

(22) When the symmetry is lowered to C_{2v} under $^{16}O/^{18}O$ [$^{28}Si/^{29}Si$] partial substitution, the five in-plane vibrations ($2A_g + B_{1g} + B_{2u} + B_{3u}$) fall into the symmetry classes A_1 [A_g and B_{3u} (A_g and B_{2u}) from D_{2h}] and B_1 [B_{1g} and B_{2u} (B_{1g} and B_{3u}) from D_{2h}].

(23) Ismail, Z. K.; Hauge, R. H.; Margrave, J. L. *J. Mol. Spectrosc.* **1975**, *54*, 402.

Table II. Physical Properties of SiO and $(SiO)_2$ Obtained by ab Initio SCF Computations

	total energy,[a] au	d_{SiO}, pm	SEN	Q(Si)
SiO	−363.794 25	149 (exp = 151.0[b])	2.47	0.34
$(SiO)_2$	−727.683 63	168	1.31	0.58
		∠(OSiO) = 86°	1.12 (SiSi)	

High-Lying Occupied MOs

	orbitals	energy, au
SiO	$7\sigma(3s)$	−0.434
	$2\pi(2p\ O)$	−0.475
	$6\sigma(2p\ O)$	−0.665
$(SiO)_2$	$5b_{1u}(3s)$	−0.347
	$7a_g(3s)$	−0.429
	$b_{1g}(2p\ O)$	−0.494

[a] 1 au = 2625.5 kJ/mol. [b] Reference 49.

and $f'' = f_{SiO/OSi}$, we introduced two additional parameters to perform normal-coordinate calculations for all in-plane vibrations of the symmetrically (D_{2h}) and unsymmetrically (C_{2v}) substituted species. As a consequence of the lower symmetry the frequencies of the latter species are also influenced by vibrations, which were not observed.[24] For the C_{2v} species force constants and isotopical shifts are strongly correlated. So values for the force constants and for the unobserved modes could be fixed within small limits. The final force constants are listed in Table I. They are justified by the following reasons:

(1) They reproduce the 10 vibrational frequencies measured very well.[25] Small discrepancies (Table I) may be due to Fermi resonances.[26]

(2) f_{SiO} has a value of 3.22 mdyn/Å. It is comparable with f_{SiO} in $Me_3SiOSiMe_3$ (4.27 mdyn/Å),[27] since in this molecule the SiO distance is much shorter (163 pm)[28] than that in $(SiO)_2$ (169 pm).

(3) The observed frequencies of the D_{2h} isotopomers can be reproduced by many force fields, which of course differ in the stretching (mdyn/Å) and deformation constants (mdyn·Å). E.g., $f_{SiO} = 3.0, f_{SiOSi} = 1.1, f_{OSiO} = 1.0$; $f_{SiO} = 3.22, f_{SiOSi} = 0.89, f_{OSiO} = 0.45$; $f_{SiO} = 3.55$, $f_{SiOSi} = 0.3$, $f_{OSiO} = 0.2$. The last set is comparable to that used by Ogden.[2]

But for the C_{2v} molecules no fit between the calculated and measured shifts can be obtained using values for $f_{SiO} = 3.0$ or 3.5 mdyn/Å. This can be best achieved by the second set of constants ($f_{SiO} = 3.22$ mdyn/Å).

(4) The value of f_{SiOSi} is not unexceptionally large or small, it has just the same value as in the molecule $Me_3SiOSiMe_3$.[27]

Table III. Total and Reaction Energies[a]

	MP4	SCF[c]	CPF[d]	CPF[e]
SiO	−364.102 65	−363.794 25	−364.128 48	−364.156 97
$(SiO)_2$	−728.275 01	−727.683 63	−728.336 92	−728.403 21
$(SiO)_2 \rightarrow 2SiO$	+182.7	+249.1	+209.5 (+261.9)[f]	+234.0
$\Delta_R H_{298}{}^{\circ}$[g]	+179.7	+246.2	+206.5	+231.1

[a] Total energies in hartrees and reaction energies in kilojoules per mole.[20] [b] Basis: 6-31G + 2d. [c] Basis according to section 2.2. [d] Basis with two additional d functions for O and Si.[11] [e] Basis with two additional d functions and one f function for O and Si.[11] [f] With the same basis but at the SCF level. [g] Recalculated experimental values: 192 and 202 kJ/mol (section 3.4).

Table IV. Physical Properties of PN and $(PN)_2$ Obtained by ab Initio SCF Computations

	total energy,[a] au	d_{PN}, pm	SEN	Q(P)
PN	−395.121 77	146.2	2.86	0.29
$(PN)_2$	−790.236 32	165.0	1.58	0.73
		∠(NPN) = 95.1°	0.48 (PP)	

High-Lying Occupied MOs

	orbitals	energy, au
PN	$2\pi(3p;\ 2p\ N)$	−0.447
	$7\sigma(3s;\ 2p\ N)$	−0.483
	$6\sigma(3s)$	−0.658
$(PN)_2$	$1b_{1g}(2p\ N)$	−0.373
	$5b_{1u}(2p\ N;\ 3p)$	−0.375
	$4b_{3u}(2p\ N)$	−0.402

[a] 1 au = 2625.5 kJ/mol.

(5) Equal changes of f' and f'' do not influence the frequency of the B_{2u} or B_{3u} modes of the D_{2h} species, but in the C_{2v} molecules f' and f'' influence indirectly and to a great extent the wave numbers calculated for the former (in D_{2h}) B_{2u} and B_{3u} modes. This occurs by coupling with the former (D_{2h}) A_{1g} and B_{1g} frequencies whose values strongly depend on these interaction constants. Values of $f' = 0.48$ and $f'' = 0.44$ mdyn/Å give the best fit between the measured and calculated isotopic shifts. A value of $f' = 0.44$ mdyn/Å seems to be high in comparison with $f_{SiO/OSi} = 0.11$ in $Me_3SiOSiMe_3$.[27] But interaction constants in ringlike molecules are expected to be different from those in simple siloxanes.

3.3. Ab Initio Calculations. In Table II we have collected the computed properties of monomeric and dimeric SiO. The results for SiO agree within the expected limits with those of former publication.[20,21,29]

The electronic structure of $(SiO)_2$ seems to be very complex, as there is a strong mixture of AOs in most of the high-lying MOs.[30] Thus a discussion of the MOs may not be fruitful. But bonding in this molecule is well described by the main structural parameters such as geometry, SEN, and charges (cf. Table II).

The total energy of SiO together with that of $(SiO)_2$ allows us to calculate the dissociation energy. $\Delta H_{diss}{}^{\circ}$ values obtained by different methods[11] are listed in Table III. The best results are expected with the CPF method[12] including two d functions and one f function at all atoms. As there are unexpected discrepancies between experimental and theoretical data, we recalculated $\Delta H_{diss}{}^{\circ}$ with the new geometry. The results are presented in the next subsection.

In order to judge the $\Delta H_{diss}{}^{\circ}$ value for $(SiO)_2$, we wanted to compare it with those of the isoelectronic molecules $(AlF)_2$ and $(PN)_2$. The required quantum chemical calculations on $AlF/(AlF)_2$ have been performed previously;[31] those on $PN/(PN)_2$ are presented in Table IV. The dissociation of $(PN)_2$ is studied in more detail in order to get a better understanding of the unexpected negative value of the dissociation energy. Therefore, we also performed ab initio SCF calculations for $(PN)_2$ species with different geometries. All results predict the D_{2h} molecule with four identical PN distances (Table IV) to be the most stable one.[32]

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(24) Especially, the totally symmetric breathing mode should be of nearly equal energy as the B_{2u} and B_{3u} vibrations.

(25) After correction of the experimental $\Delta\nu$ values as a consequence of anharmonicity: Becher, H. J. *Fortschritte der chemischen Forschung*; Springer: Berlin, 1968; Vol. 10.

(26) A value of $\Delta\nu$ of 2.4 cm^{-1} for the molecules 1 and 5 has been observed for the B_{2u} modes, whereas values between 2.6 and 2.8 cm^{-1} are calculated. We attribute this deviation to a Fermi resonance between the overtone of the A_1 deformation mode (2×378.7 cm^{-1}) with the vibration at 801.2 cm^{-1}; both are of the same symmetry (cf. Table I). There must be a very small Fermi interaction in the other C_{2v} molecule 4: The observed $\Delta\nu$ of the B_{3u} mode between the molecules 1 and 4 is 17.8 cm^{-1}. In our calculations $\Delta\nu$ varies between 17.0 and 17.5 cm^{-1}. This very small deviation may also be caused by a Fermi coupling between 2×377.1 cm^{-1} (ν_6, A_1) with the vibration at 751.3 cm^{-1} (A_1) (cf. Table I), which should lead to a larger shift than the calculated one.

(27) Bürger, H.; Goetze, U.; Sawodny, W. *Spectrochim. Acta* **1968**, *24*, 2003.

(28) Csákvári, B.; Wagner, Z.; Gömöry, P.; Mijlhoff, F. C.; Rozsondai, B.; Hargittai, I. *Organomet. Chem.* **1976**, *107*, 287.

(29) Pacansky, J.; Hermann, K. *J. Chem. Phys.* **1978**, *69*, 963.

(30) As expected, the mixture of the AOs decreases in the direction to more ionic bonding: $(PN)_2 \rightarrow (SiO)_2 \rightarrow (AlF)_2$.

(31) Ahlrichs, R.; Lin Z.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1984**, *519*, 155.

(32) (a) $(PN)_2$ in analogy to P_4 with distortion from D_{2h}: $E = -790.21295$ au; $d_{PP} = 211$ pm; $d_{NN} = 146$ pm; $d_{PN} = 176$ pm; $SEN_{NP} = 1.17$; $SEN_{NN} = 1.19$; $SEN_{PP} = 1.22$. (b) PNNP with $D_{\infty h}$ symmetry: $E = -790.17213$ au; $d_{PN} = 156$ pm; $d_{NN} = 118$ pm; $SEN_{NN} = 1.95$; $SEN_{NP} = 1.93$. (c) NPPN with $D_{\infty h}$ symmetry: $E = -789.98235$ au; $d_{PN} = 152$ pm; $d_{PP} = 191$ pm; $SEN_{PP} = 1.81$; $SEN_{NP} = 2.02$.

Additionally, we have calculated the energy of molecules with D_{2h} structure at different distances of the monomeric moieties. Approaching two monomers dipole–dipole interaction causes a small gain in energy at large distances. With further shortening of the monomer–monomer distance, we observe a potential barrier only for the dimerization of PN. On the other side, no activation energy is calculated for the reaction of two SiO monomers. This is in line with the results of Snyder and Raghavachari.[20]

The small positive energy for $(PN)_2$[33] and the large negative one for $(SiO)_2$ at the bottom of the steep potential curve will be discussed later on.

3.4. Thermodynamic Data. 3.4.1. The High-Temperature Equilibrium $SiO/(SiO)_2$. The equilibrium

$$(SiO)_2(g) \rightleftharpoons 2SiO(g) \qquad (1)$$

has been studied by means of mass spectrometric measurements.[34] At 1450 K the equilibrium constant is 3.47 atm. From this value $\Delta_R H°(1)$ can be determined if $\Delta_R S°(1)$ is known.

In the former work[34] $S°_T(Si_2O_2)$ has been calculated on the grounds of a linear structure (O–Si–Si–O) of the molecule $(SiO)_2$. We have recalculated $S°_T(Si_2O_2)$ including our results from ab initio and force constants calculations (section 3.3) and obtained a value of 393 J mol^{-1} K^{-1}.

With $\Delta_R S°_{1450} = 137$ J mol^{-1} K^{-1} we get a value of 184 kJ/mol for $\Delta_R H_{1450}°(1)$: this can be transformed[35] to 298 K to be $\Delta_R H°_{298}(1) = 192$ kJ/mol.

3.4.2. The High-Temperature Equilibrium over Li_2O/Si. In a later work $\Delta_R H°(1)$ was reinvestigated.[36] The following equilibrium gas has been studied by mass spectroscopy over a mixture of solid Li_2O and Si between 1400 and 1600 K:

$$LiSiO(g) + Li(g) \rightleftharpoons Li_2(g) + SiO(g) \qquad (2)$$

$$(SiO)_2(g) + Li(g) \rightleftharpoons SiO(g) + LiSiO(g) \qquad (3)$$

In contrast to the former considerations[36] we calculate $\Delta_R H°(1)$ without the unknown thermodynamic data of the molecule LiSiO by the following method:[37]

Addition of eq 2 and 3 results in

$$(SiO)_2(g) + 2Li(g) \rightleftharpoons 2SiO(g) + Li_2(g) \qquad (4)$$

with $K(4) = K(2) \times K(3)$.[38] Thus, with the help of the known values of $\Delta_f H°$ and $S°$ for SiO(g), Li(g), and $Li_2(g)$[39] and the calculated one for $S°$ of $(SiO)_2(g)$ (vs), $\Delta_f H°$ of $(SiO)_2$ can be determined to be 414 kJ/mol at 1490 K.[41]

From this a value of 194 kJ/mol results for $\Delta_R H°_{1490}(1)$, which can be transformed to be $\Delta_R H°_{298}(1) = 202$ kJ/mol.

Both results obtained by our recalculations (192 and 202 kJ/mol) agree much better than the original ones given in literature: $\Delta_R H°_{1463}(1) = 187$ kJ/mol[34] and $\Delta_R H°_0(1) = 256$ kJ/mol.[36]

It is not possible to report the uncertainty of our values because we have no detailed information about the experimental data from literature.[34,36] Anyhow the error of our $S°$ and C_p calculations are small compared with errors given for $\Delta_f H°$ of SiO(g), Li(g), and $Li_2(g)$.[42]

Table V. Properties of the Molecules $(AlF)_2$, $(SiO)_2$, and $(PN)_2$ Obtained by ab Initio SCF Computations

	$(AlF)_2$	$(SiO)_2$	$(PN)_2$
d_{xy}, pm	189.9	168.8	165.0
∠(FAlF) resp	73.8	85.5	93.3
f_{xy},[a] mdyn/Å	1.2[b]	3.3	c
ΔH_{diss}	55[b]	202[d]	−19
bond energy, kJ/mol	351	451	337
Q	0.22	0.58	0.73
SEN	0.78	1.31	1.58

[a] From vibrational frequencies determined experimentally. [b] Reference 31. [c] Reference 73. [d] From experimental data (section 3.4.2).

Even after this recalculation of $\Delta_R H°(1)$, there remains a discrepancy of about 30 kJ/mol for the best theoretical result (231.1–202 kJ/mol (or 192 kJ/mol)). As a certain error has also to be taken into account for experimental data (cf. discussion above and ref 42), one cannot decide whether theoretical or experimental data are more reliable. This is even more valid as theoretical results do not differ more among themselves (Table III) than the experimental data known as yet.[34,36]

4. Discussion

4.1. Monomeric Species. To understand formation and structure of $(SiO)_2$, it is reasonable to look first at bonding of monomeric SiO. This can be best explained by comparison with data of the isoelectronic species AlF and PN and their lighter homologues. In the following the SENs and charges of these molecules are listed:

$$^{-0.19}B{-}F^{+0.19},\ 2.04;^{43} \qquad ^{+0.06}C{=}O^{-0.06},\ 2.57;^{44}$$

$$N{\equiv}N,\ 2.94;^{45} \qquad ^{+0.11}Al{-}F^{-0.11},\ 1.63;^{46}$$

$$^{+0.34}Si{=}O^{-0.34},\ 2.47; \qquad ^{+0.29}P{\equiv}N^{-0.29},\ 2.8$$

The most remarkable molecule within this series is BF. Its unexpected distribution of charge and its high SEN can be visualized by the formula $^-B{=}F^+$. This description implies a double bond, which is weakened by a shift of electrons according to electronegativity.

Experimental results such as bond energy, force constant, and distance,[47] as well as the SEN value, confirm this picture of bonding in BF. The strong bond in BF can also be visualized by a comparison of structural data of BF and BF_3:[48]

	bond energy, kJ/mol	f, mdyn/Å	d, pm
B–F	755[39]	7.9[49]	126[49]
BF_3	645[39]	7.3[50]	131[51]

The molecule corresponding to BF in the second period is AlF. The higher difference in electronegativity and the smaller tendency to form double bonds (appropriate orbitals differ in energy) do not allow a description like $^-Al{=}F^+$.[52] But nevertheless for AlF,

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(33) More sophisticated calculations including correlation effects might cause a loss in energy for $(PN)_2$ relative to PN. But as this would not conflict with our conclusions, in which mainly trends in stability of the dimers are discussed, we have not performed these expensive computations.

(34) Zmbov, K. F.; Ames, L. L.; Margrave, J. L. *High Temp. Sci.* **1973**, *5*, 235.

(35) The following $\Delta_R C_p$ values have been used: for 298–600 K, −3.75 J mol^{-1} K^{-1}; for 600–1450 K, −7.93 J mol^{-1} K^{-1}.

(36) Wu, C. H.; Ihle, H. R.; Zmbov, K. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 447.

(37) We thank M. Binnewies for helpful discussions.

(38) $T = 1438$ K, 10 $K(2) = 1.6$, $K(3) = 2.13$, 10 $K(4) = 3.4$; $T = 1488$ K,, 10 $K(2) = 1.6$, $K(3) = 3.33$, 10 $K(4) = 5.3$; $T = 1538$ K, 10 $K(2) = 1.72$, $K(3) = 4.22$, 10 $K(4) = 7.3$.

(39) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R.; Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *Janaf. Thermochemical Tables*, 3rd ed.; American Chemical Society: Midland, 1985.

(40) Bond energies: $E_{SiO} = 800$ kJ/mol; $E_{PN} = 684$ kJ/mol.[39]

(41) This is the average value between $\Delta_f H°_{1438} = 412$ kJ/mol and $\Delta_f H°_{1538} = 416$ kJ/mol.

(42) $\Delta_f H_{298}°(SiO(g)) = -100.42 \pm 8.4$ kJ/mol,[39] $\Delta_f H_{298}°(Li(g)) = -159.3 \pm 1$ kJ/mol,[39] $\Delta_f H_{298}°(Li_2(g)) = -215 \pm 3$ kJ/mol.[39]

(43) Though the BF molecule has been studied extensively by quantum chemical methods,[44] we performed a further SCF calculation to obtain SEN and Q values, which are comparable with those of the other molecules. The results of these calculations are −124.143 38 au for the total energy and 124.9 pm for d_{BF}.

(44) Sutton, P.; Bertonici, P.; Das, G.; Gilbert, T. L.; Wahl, A. C.; Sinanoglu, O. *Int. J. Quantum Chem., Symp.* **1969/70**, *3*, 479. Sutton, P.; Bertonici, P.; Das, G.; Gilbert, T. L.; Wahl, A. C.; Sinanoglu, O. *Int. J. Quantum. Chem., Symp.* **1970**, *4*, 633.

(45) Ahlrichs, R.; Ehrhard, C. *Chem. Unserer Zeit* **1985**, *19*, 120.

(46) These results have been obtained by additional SCF computations, which are based on data of a former work.[31]

(47) Hoeft, F.; Lovas, F. J.; Tiemann, E.; Toerring, T. *J. Chem. Phys.* **1970**, *53*, 2736.

(48) In BF_3 the short bond distance and the low Lewis acidity is mostly explained by partial BF double bonds.

(49) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.

as for BF, there remains a bond stronger than a single bond, which is in line with the bond energy, the SEN, and the initially unexpected small polarity.

Comparison of structural data of AlF and AlF_3 shows that there are some remarkable differences between the boron and aluminum fluorides:

	bond energy, kJ/mol	*f*, mdyn/Å	*d*, pm
Al–F	675[39]	3.9[31]	165[49]
AlF_3	592[39]	4.8[56]	163[58]

In the pair BF/BF_3 the higher bond energy in BF corresponds, as expected, to a higher force constant and a smaller distance. In AlF, probably because of more ionic contributions, the force constant is smaller, the distance is longer, but the bond energy is higher than that in AlF_3.

In the pair CO/SiO differences in the covalent bond strengths (SEN) are smaller than in BF/AlF. This means that there is a formal triple bond in CO as well as in SiO, which is weakened by polarization according to electronegativity. This weakening is only slightly stronger in SiO than in CO. Therefore, the main difference between CO and SiO is polarity: whereas CO is nearly unpolar, SiO exhibits a certain amount of ionic character.

As expected, ionic contributions are smaller and the SENs are larger in the couple N_2/PN than in CO/SiO.

4.2. Dimeric Species. As expected, no stable dimers are known in the series N_2, CO,[59] and BF.[60,63] Therefore only the dimeric molecules $(AlF)_2$, $(SiO)_2$, and $(PN)_2$ are discussed in the following section. The results of ab initio and force constant calculations for these species are presented in Table V.

The bond angles are consistent with the size of the electropositive atoms, which increases in the direction P → Si → Al. The SENs and the calculated distances are confirmed by the force constants determined experimentally. The values for bond energies are obtained from those of the monomers[39,40] and the dissociation energy (sections 3.4.1 and 3.4.2). The charges, *Q*, are increased with respect to those of the monomers.[64]

According to polarity, dimerization energy should increase in the order AlF → PN → SiO, if only dipole–dipole interactions are taken into account (vs). But experimental investigations contradict this simple idea of bonding: with respect to the monomers, $(AlF)_2$ is more stable than $(PN)_2$. So $(AlF)_2$ is formed under matrix conditions,[31] whereas no $(PN)_2$ has been detected so far, though PN and $(PN)_3$ absorptions are present in matrix spectra.[65,66] On the other hand, $(SiO)_2$ is by far the "strongest" dimer. It can be detected even in the gas phase at high temperatures (section 3.4.1). Thus, all data obtained from ab initio calculations are well substantiated by experimental facts.

The increase in ΔH_{diss} going from $(AlF)_2$ to $(SiO)_2$ can be rationalized by dipole–dipole interactions. This model fails in the case of $(PN)_2$, demonstrating the difficulties in describing bonding situation by simple arguments as, e.g., ionic or covalent contributions. Though there are PN bonds stronger than single bonds with additional ionic contributions, this molecule is destabilized by other effects (vs), which cannot be deduced from values as SEN, *Q*, and geometry. Instability of $(PN)_2$ may be caused by repulsion of electron pairs within this small ring. The same argument is valid for small ring systems like $(N_2)_2$ or $(C_2H_2)_2$.

The remarkable stability of $(SiO)_2$ in comparison with that of $(PN)_2$ has been mentioned in section 3.3. It can be rationalized with some additional results of ab initio calculations:

There is a significant SEN of the Si–Si bond with a value of 1.12.[67] This is in line with the small Si–Si distance (247 pm), which is comparable to that found in stable compounds containing Si–Si bonds (Si_2H_6, $d_{SiSi} = 232$ pm).[71] Further hints for a certain amount of Si–Si bonding can be deduced from experiments with other carbene analogous compounds such as SiF_2 under cryochemical conditions.[72] The products obtained often contain Si–Si bonds, a fact that can be interpreted by the assumption that Si–Si bonds are formed in dimeric SiF_2.

Thus the high stability of $(SiO)_2$ in contrast to $(AlF)_2$ and especially to $(PN)_2$ can be interpreted as a gain of additional covalent bonds during dimerization. The sum of SEN values rises from about 5.0 for two SiO molecules to 6.4 in $(SiO)_2$.[63]

All explanations concerning stability of the dimers clearly touch on only the most important aspects. It turns out to be impossible to extract more convincing results from the ab initio calculations of these dimers than the data presented here (*Q*, SEN, energy, geometry). But as these values reflect the complicated balance between covalent and ionic contributions in bonding, their comparison helps to understand bonding in these molecules.

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(50) Sawodny, W. A.; Fadini, A.; Ballein, K. *Spectrochim. Acta* **1965**, *21*, 995.

(51) Ginn, S. G. W.; Kenney, K. J.; Overend, J. *J. Chem. Phys.* **1968**, *48*, 1571.

(52) The tendency of atoms in the second period to form "double bonds" with O decreases in the direction S → P → Si → Al. In comparison with single bonds double bonds are only favored in sulfur and phosphorus compounds. Thus, only molecules like SO_2 and $POCl_3$ are "stable" at ordinary conditions. This is in line with a significant decrease in (X = O) force constants (mdyn/Å):f_{SO} (SO_3) = 10.4,[53] f_{PO} (PO_2Cl) = 10.45,[54] f_{SiO} (SiO_2) = 8.8,[5] f_{AlO} (OAlF) = 6.6.[55]

(53) Siebert, H. *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*; Springer Verlag: Berlin, 1966.

(54) Ahlrichs, R.; Ehrhardt, C.; Lakenbrink, M.; Schunck, S.; Schnöckel, H. *J. Am. Chem. Soc.* **1986**, *108*, 3596.

(55) Schnöckel, H. *J. Mol. Struct.* **1978**, *50*, 267.

(56) Values obtained from calculations with data of the matrix-isolated species AlF_3[57] and OAlF.[55]

(57) Snelson, A. *J. Phys. Chem.* **1967**, *71*, 3202.

(58) Akishin, P. A.; Rambidi, N. G.; Zasorim, E. *Z. Kristallogr.* **1959**, *4*, 186.

(59) Molecules like $(N_2)_2$ and $(CO)_2$ are not of interest in this context as their dimerization energy is very small (mainly van der Waals forces). Monomeric species are favored in these reactions as a consequence of the high stability of their multiple bonds. The opposite situation is found in the higher homologues (P_4 is more stable than 2P2 (228 kJ/mol[39]).

(60) Though no stable dimers of BF are known in the gas phase, in the solid state BF should be able to form subhalides[61] in analogy to BCl: B_4Cl_4, B_8Cl_8, B_9Cl_9, and $B_{10}Cl_{10}$.[62]

(61) Theoretical and experimental investigations on this subject are under way: (cf. about B_4F_4: Swarson, D. J.; Ahlrichs, R. *Theor. Chim. Acta* **1989**, *75*, 163).

(62) Massey, A. G. *Adv. Inorg. Radiochem.* **1983**, *26*, 1–54.

(63) In this respect it would be interesting to know more about dimeric BF. As there are often similarities between boron and silicon compounds, it may be possible that an isomer with a B–B bond is more stable than a ring compound.[61]

(64) This is plausible: in the series $(NaCl)_1$ → $(NaCl)_2$ → solid NaCl, covalent contributions decrease, whereas charges reach a maximum in solid NaCl, with a coordination number of 6 for both ions.

(65) Atkins, R. M.; Timms, P. L. *Spectrochim. Acta* **1977**, *33A*, 853.

(66) Calculations on $(PN)_3$ show formation of this molecule to be exothermic with respect to the monomer. Ahlrichs, R., to be submitted for publication.

(67) In the corresponding molecules $(AlF)_2$ and $(PN)_2$ the values are 0.53 and 0.48 for SEN(Al/Al) and SEN(P/P), respectively. Bonding in other ring systems like $R_2SiO_2SiR_2$ with small Si–Si distances but without significant Si–Si bonding[68] is different from that in $(SiO)_2$, as here more electrons are available for bonding.[69,70]

(68) West, R. *Angew. Chem.* **1987**, *99*, 1231; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.

(69) In a recent work[70] bonding in cyclodisiloxanes is described as that of a "bibridged π-complex" and the bond between the silicons is most likely that of an "unsupported π-bond".

(70) Grev, R. S.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 6577.

(71) Bethke, G. W.; Wilson, M. K. *J. Chem. Phys.* **1957**, *26*, 1107.

(72) Timms, P. T. *Adv. Inorg. Radiochem.* **1972**, *14*, 121.

(73) $(PN)_2$ has not been detected experimentally so far.