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Abstract: The potential energy surfaces for the insertion reactions of silylene into NH₂, HOH, HF, PH₃, HS, and HCl have been characterized in detail by using ab initio molecular orbital theory, including electron correlation and zero-point corrections. All the interactions involve the initial formation of a donor–acceptor complex followed by a proton shift via an unsymmetrical high-energy transition state. The binding energies of the complexes as well as the rearrangement barriers for the hydrogen migration of these complexes to give the normal valent compounds have been calculated in all cases. The case between SiH₂ and NH₂ exists in a deep minimum with a high barrier for rearrangement (38 kcal/mol) to be a suitable candidate for spectroscopic observation. The silylene complex with PH₃ also involves a fairly deep minimum, but the overall insertion barrier is small. The interaction between SiH₂ and HOH, widely studied experimentally, involves a complex with a fairly high rearrangement barrier (22 kcal/mol). The interactions with H₂S, HF, and HCl are fairly weak with calculated rearrangement barriers (13, 10, and 8 kcal/mol, respectively). Detailed comparison is made between the structure and bonding of the silylene addition complexes with those of their carbon analogues. Significant differences, particularly in the multiple bond character of the central bond, are found.

Electron-deficient reactive intermediates like carbenes, nitrenes, and vinylidenes have long been the subject of intense experimental and theoretical investigation. The structures and reactivity of the corresponding divalent silicon species, silylenes, are gaining increasing attention in recent years. Thus, gas-phase and matrix-isolation spectroscopic studies have resulted in the structural characterization of the parent silylene, SiH₂, as well as numerous derivatives, while the study of the chemical reactivity of silylenes has led to the synthesis of several organic and inorganic molecules.

A recurring theme in the above studies is the degree to which silylenes resemble carbenes. Both similarities and differences have been noted. For example, silylenes, like carbenes, readily undergo reaction of silicon atoms with excess water, has indeed been observed recently with the aid of infrared spectroscopy by Margrave and his co-workers.

In order to examine the generality of the above results, we have undertaken a systematic investigation of the insertion reactions of the parent silylene into six first- and second-row halides (eq 1) at sophisticated levels of theory. Since the ground state of SiH₂ is a singlet, only the singlet surface was considered. All the reactions involve the initial formation of a donor–acceptor complex followed by a rearrangement (12, 14, 15, and 24 kcal/mol) and is predicted to be a suitable candidate for spectroscopic observation. Significant differences, particularly in the multiple bond character of the central bond, are found.

SiH₂ + XHₙ → SiHₓ – XHₓ – XHₓ – XHₓ

(1)

X = N, P, O, S, F, Cl

n = 3, 3, 2, 1, 1

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Experimentally, silylene insertions into N-H, O-H, F-H, P-H, S-H, and Cl-H bonds have all been observed. However, with the exception of the studies of Weber et al. involving O-H bonds, few mechanistic details are available. The present calculations provide comprehensive energetic information on the insertion potential energy surface for all the reactions.

The energetics involving the donor–acceptor complexes are of particular interest. As is well-known, divalent Sn and Pb salts readily form adducts with donor solvents like water, acetone, pyridine, etc. The calculated complexation energies for the different intermediates in eq 1 quantify the ability of divalent silicon to form such adducts.

The thermodynamic stability of a complex does not assure its experimental observation. The structure should also be separated from the more stable normal valent product by a sizable barrier. The calculated rearrangement barriers indicate the most favorable candidates for experimental study.

We have also compared the structure and bonding of the silylene addition complexes with those of their carbon analogues, the ylides. Significant differences, particularly in the bond character of the central bond, are found.

**Theoretical Methods**

The geometries for all the stationary points were completely optimized at the Hartree–Fock level with the 6-31G* basis set\(^{20}\) (split-valence plus d-type polarization functions on heavy atoms). This level of theory is denoted by HF/6-31G*.

Previous experience\(^{2}\) has shown that reoptimization of the geometries with the inclusion of electron correlation effects might change some of the geometrical parameters significantly, especially those parameters involving small force constants. However, since the potential energy surface is extremely flat for such parameters, the errors introduced in the calculation of the relative energies of the different species involved by the use of these HF/6-31G* geometries is usually very small. Some of the interesting geometrical parameters are listed in Table I along with the symmetry constraints under which the optimizations were performed. Complete geometry specifications are available as supplementary material.

The complete set of harmonic force constants was also evaluated\(^{21}\) for each stationary point. These can then be used to characterize the nature of the stationary point, a minimum being characterized by all positive eigenvalues.

Electronic correlation effects were included by means of Möller–Plesset perturbation theory\(^{22}\) by using the HF/6-31G* geometries. The calculations were performed in two stages. In the first stage, fourth-order Möller–Plesset perturbation theory (MP4) theory calculations in the space of single, double, and quadruple (SDQ) substitutions\(^{22b}\) were performed with the larger 6-31G** basis\(^{23b}\) (including p-type polarization functions on H).

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In the next stage, the effect of triple (T) substitutions\(^{26e}\) on the correlation energy was computed, again using fourth-order theory but only with the smaller 6-31G* basis set. Such effects of triple substitutions have been previously shown to be important for similar reactions involving first-row elements, especially for the calculation of activation barriers. The various correlation energy contributions are listed in Table II along with the zero-point energy corrections. All of these effects are used to calculate the final relative energies listed in the last column of Table II.

**Results and Discussion**

The results are divided into three sections, discussing the silylene insertion into NH₃ and PH₃, H₂O and H₂S, and HF and HCl, respectively. In each case, we point out the essential features of the reaction of a first-row hydride, along with the modifications that result in the reaction involving the second-row analogue. The results are also compared with available theoretical results on the corresponding carbene reactions. In the final section, the molecular and electronic structures of the silylene addition complexes are compared with those of ylides.

**Insertion into N-H and P-H Bonds**

The calculated reaction profiles for silylene insertion into NH₃ and PH₃ are shown in Figures 1 and 2, respectively. The interaction between the empty p orbital in singlet SiH₂ and the lone pair in NH₃ leads to the adduct 2, which has the largest binding energy (25 kcal/mol) of all the complexes considered in this study. This interaction energy is quite similar to that calculated for the analogous complex...
The donor-acceptor interaction leads to a calculated interaction holding 2 together is evident from its geometry involving singlet CH$_2$ and NH$_3$ (28 kcal/mol). The nature of the interaction holding 2 together is evident from its geometry involving singlet CH$_2$ and NH$_3$ (28 kcal/mol). The nature of the interaction holding 2 together is evident from its geometry involving singlet CH$_2$ and NH$_3$ (28 kcal/mol). The nature of the interaction holding 2 together is evident from its geometry involving singlet CH$_2$ and NH$_3$ (28 kcal/mol). The nature of the interaction holding 2 together is evident from its geometry involving singlet CH$_2$ and NH$_3$ (28 kcal/mol). The nature of the interaction holding 2 together is evident from its geometry involving singlet CH$_2$ and NH$_3$ (28 kcal/mol). The nature of the interaction holding 2 together is evident from its geometry involving singlet CH$_2$ and NH$_3$ (28 kcal/mol). The nature of the interaction holding 2 together is evident from its geometry involving singlet CH$_2$ and NH$_3$ (28 kcal/mol). The nature of the interaction holding 2 together is evident from its geometry involving singlet CH$_2$ and NH$_3$ (28 kcal/mol).
 considerably longer than in silanethiol, a sufficient lifetime for spectroscopic observation. The features as above but with uniformly reduced energy differences from the complex (Figure 3). The overall activation barrier is only 5 kcal/mol. The barrier for the hydrogen shift in the complex is also quite small, 13 kcal/mol.

**Insertion into F-H and Cl-H Bonds.** The insertion of SiH₂ into HF has a large thermodynamic driving force in view of the strength of the Si-F bond (calculated exothermicity = 84 kcal/mol, Table II, Figure 5). Since the reaction is indicated to be readily observable (calculated activation barrier is only 3 kcal/mol), experimental detection of the intermediate formed during the reaction is unlikely. The adduct formed by the interaction of a fluorine lone pair with the LUMO of the silylene involves only a weak bond (r_{Si-F} = 2.38 Å compared to 1.59 Å in H₃SiF, 13), with a complexation energy of only 7 kcal/mol.

Figure 3. Energy profile for the insertion reaction of silylene into H₂O (kcal/mol).

Figure 4. Energy profile for the insertion reaction of silylene into H₂S (kcal/mol).

The insertion of SiH₂ into H₂S state with an intermediate Si-S bond length of 2.53 Å has a C₁ structure similar to 9. The overall activation barrier is only 5 kcal/mol. The barrier for the hydrogen shift in the complex is also quite small, 13 kcal/mol.

The insertion of SiH₂ into H₂S shows essentially the same features as above but with uniformly reduced energy differences (Figure 4). The addition complex 11 has a geometry similar to 8, but the complexation energy is smaller, 9 kcal/mol. This is also reflected in the calculated Si-S bond length, 2.61 Å, considerably longer than in silanethiol, 10 (2.15 Å). The transition state with an intermediate Si-S bond length of 2.53 Å has a C₁ structure similar to 9. The overall activation barrier is only 5 kcal/mol. The barrier for the hydrogen shift in the complex is also quite small, 13 kcal/mol.

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![Figure 3](image-url)  
**Table 1.** HF/6-31G* Energies and Structural Information*  

<table>
<thead>
<tr>
<th>structure</th>
<th>point group</th>
<th>bond lengths, Å</th>
<th>HF/6-31G*</th>
<th>Hessian Index*</th>
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<td>-750.063</td>
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</tbody>
</table>

*Not all structural parameters are listed. The structures were, however, completely optimized within the given symmetry constraint. The complete structural information is available as supplementary material. *H denotes position intermediate between nonhydrogen atoms. 4 The other heavy atom in the molecule is denoted by A. 5 Bond lengths between the heavy atoms and the migrating hydrogen. Only bonded and partially bonded distances are shown. The number of negative eigenvalues of the matrix of energy second derivatives.
studies available on the analogous carbene complexes, viz., the
understood by comparing the present results with the detailed
The nature of the addition complexes involving silicon is best
studied. Again, we did not attempt to calculate the rearrangement
and 20 has the smallest binding energy of all the complexes
barrier for 20 going over to silyl chloride, 17.

The hydrogen-bonded minimum 20 with
is very similar to the previous case with the interactions being even
weaker. The complex 18 where silylene is the acceptor has a
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binding energy of only 2 kcal/mol with a long
bond length in 20,

Silylene forms a loose complex 16 with HF where the
is involved in a hydrogen bond type of interaction. The
structure has planar C$_2$ symmetry with a long Si–H distance, 2.79
Å. The complexion energy is only 2 kcal/mol, indicating that it is only a weak interaction. Analytical force constant evaluations show that this complex is indeed a local minimum. We have not, however, attempted to study the pathway for rearrangement of this structure to SiH$_3$F.

The calculated reaction profile of the insertion of SiH$_2$ into HCl is very similar to the previous case with the interactions being even weaker. The complex 18 where silylene is the acceptor has a
binding energy of only 2 kcal/mol with a long Si–Cl bond, 3.13
Å (Si–Cl bond length of SiH$_2$Cl, 17, is 2.07 Å). The rearrangement transition state, 19, again has C$_2$ symmetry with a fairly low overall barrier, 6 kcal/mol. More significantly, 18, with a rearrangement barrier of only 8 kcal/mol, is the shallowest minimum of all the complexes studied in this paper (Figure 6).

The hydrogen-bonded minimum 20 with SiH$_2$ acting as a σ
donor is again calculated to be a minimum. The interaction Si–H bond length in 20, 3.02 Å, is longer than that of the HF complex, and 20 has the smallest binding energy of all the complexes studied. Again, we did not attempt to calculate the rearrangement barrier for 20 going over to silyl chloride, 17.

**Comparison of the Addition Complexes of Silylene and Carbene.**

The nature of the addition complexes involving silicon is best understood by comparing the present results with the detailed studies available on the analogous carbene complexes, viz., the

![Figure 5. Energy profile for the insertion reaction of silylene into HF (kcal/mol).](image)

Figure 5. Energy profile for the insertion reaction of silylene into HF (kcal/mol).

Table II. Total and Relative Energies for Stationary Points

| Structure | HF | E$^{(1)}$ | E$^{(2)}$ | E$^{(3)}$ | E$^{(4)}$ | E$^{(5)}$ | E$^{(6)}$ | E$^{(7)}$ | E$^{(8)}$ | E$^{(9)}$ | E$^{(10)}$ | E$^{(11)}$ | E$^{(12)}$ | E$^{(13)}$ | E$^{(14)}$ | E$^{(15)}$ | E$^{(16)}$ | E$^{(17)}$ | E$^{(18)}$ | E$^{(19)}$ | E$^{(20)}$ |
|-----------|----|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| H$_2$Si + NH$_3$ | -346.19816 | -268.15 | -31.01 | -6.68 | -3.20 | 31.1 | 0.0 |
| H$_2$Si+NH$_3$ (1) | -346.29646 | -275.98 | -25.01 | -5.09 | -4.57 | 33.8 | -60.0 |
| H$_2$Si+NH$_3$ (2) | -346.23920 | -278.02 | -28.08 | -5.72 | -4.51 | 36.3 | -25.1 |
| H$_2$Si(H)NH$_3$ (3) | -346.15207 | -298.30 | -22.78 | -6.18 | -7.40 | 31.6 | +13.2 |
| H$_2$Si + PH$_3$ | -632.45680 | -205.11 | -39.60 | -8.40 | -2.86 | 24.3 | 0.0 |
| H$_2$Si-PH$_3$ (4) | -632.54362 | -214.99 | -35.52 | -5.98 | -4.24 | 28.7 | -53.1 |
| H$_2$Si-PH$_3$ (5) | -632.48203 | -217.60 | -36.89 | -6.47 | -4.50 | 28.6 | -17.5 |
| H$_2$Si(H)PH$_3$ (6) | -632.42777 | -235.59 | -36.67 | -6.18 | -6.66 | 26.6 | +2.2 |
| H$_2$Si + OH$_2$ | -360.02620 | -276.54 | -24.67 | -6.92 | -2.71 | 22.3 | 0.0 |
| H$_2$Si-OH$_2$ (7) | -366.14188 | -284.36 | -17.78 | -6.33 | -4.37 | 25.9 | -70.2 |
| H$_2$Si-OH$_2$ (8) | -366.05041 | -280.11 | -21.91 | -6.67 | -3.85 | 26.5 | -13.3 |
| H$_2$Si(OH)$_2$ (9) | -365.98502 | -309.21 | -14.63 | -8.44 | -7.46 | 23.3 | +8.7 |
| H$_2$Si + SH$_2$ | -688.71676 | -215.80 | -36.99 | -9.99 | -3.11 | 18.2 | 0.0 |
| H$_2$Si-SH$_2$ (10) | -688.77903 | -224.11 | -31.94 | -4.64 | -4.55 | 23.1 | -60.2 |
| H$_2$Si-SiH$_2$ (11) | -688.69031 | -224.39 | -35.34 | -5.92 | -4.19 | 22.0 | -8.6 |
| H$_2$Si(H)SH$_2$ (12) | -688.64687 | -244.64 | -32.07 | -4.94 | -7.35 | 20.1 | +4.8 |
| H$_2$Si + FH | -390.01418 | -263.71 | -20.02 | -7.32 | -2.77 | 14.1 | 0.0 |
| H$_2$Si-F (13) | -390.15284 | -271.34 | -13.05 | -7.68 | -4.55 | 18.6 | -84.3 |
| H$_2$Si-F (14) | -390.02494 | -269.13 | -18.13 | -7.65 | -3.50 | 16.8 | -7.0 |
| H$_2$Si(H)F (15) | -389.98211 | -294.99 | -10.34 | -10.43 | -7.59 | 15.2 | +2.7 |
| H$_2$Si-HF (16) | -390.01984 | -264.58 | -19.61 | -7.07 | -2.90 | 15.8 | -2.1 |
| H$_2$Si + ClH | -750.06884 | -219.98 | -33.40 | -5.72 | -2.88 | 12.5 | 0.0 |
| H$_2$Si-Cl (17) | -750.18774 | -225.33 | -28.10 | -3.65 | -4.16 | 17.8 | -68.8 |
| H$_2$Si-Cl (18) | -750.07224 | -222.83 | -32.94 | -5.42 | -3.20 | 14.3 | -1.8 |
| H$_2$Si(H)Cl (19) | -750.04155 | -241.75 | -28.80 | -4.50 | -6.54 | 13.6 | +5.9 |
| H$_2$Si-Cl (20) | -750.07251 | -220.94 | -33.03 | -5.44 | -3.01 | 13.7 | -1.4 |

*Total energies in hartrees, correlation energies in millihartrees, vibrational and relative energies in kcal/mol. * Obtained with the 6-31G** basis. * Obtained with the 6-31G* basis.

**Comparison of the Addition Complexes of Silylene and Carbene.**

The nature of the addition complexes involving silicon is best understood by comparing the present results with the detailed studies available on the analogous carbene complexes, viz., the

![Figure 6. (a) Silylene insertion into H bonds.](image)

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considerable attention. While most of the experimental structural investigations have utilized highly stabilized derivatives, theoretical calculations have been performed on model systems similar to those considered here. The available structures, complexion energies, proton-transfer energies, and the barriers to the proton transfer provide a firm basis for comparison of ylides with their silicon analogues.

A major conclusion from the study of carbene complexes is that second-row ylides differ significantly from their first-row coun-
terparts in structure and stability. Experimentally, the "C-X" bond lengths in ylides are consistently longer than C-X bonds in the stable tautomeric form when X is a first-row group. The opposite is true for structures involving second-row elements.

Theoretical calculations on model ylides yield the same result. Thus, C-N and C-O bonds are longer in ylides than in CH<sub>2</sub> NH<sub>2</sub> and CH<sub>2</sub> OH, respectively. On the other hand, C-P and C-S bonds are shorter in CH<sub>2</sub> PH<sub>3</sub> and CH<sub>2</sub> SH<sub>2</sub> than in CH<sub>2</sub> PH<sub>2</sub> and CH<sub>2</sub> SH, respectively. Therefore, first-row ylides are generally thought of as complexes between C=H and neutral bases, while multiple bond character is attributed to second-row ylides. All of the zwitterionic structures involving silicon considered in this study are similar to first-row ylides. At the calculated HF/6-31G* level, the Si-X bond length in the silylene addition complex is always longer than that in the more stable tautomer (Table I). Furthermore, the SiH<sub>2</sub> group in all these complexes is consistently aligned for maximizing the interaction between the vacant p orbital of silylene and the donor orbital of the base. Although geometry optimization with larger basis sets and electron correlation effects may change the calculated bond lengths somewhat, the qualitative features are not likely to change. A remarkable parallel to the calculated silylene addition complexes is provided by the nature of the complex between triphenylphosphine and GeC<sub>2</sub>l, which has a strongly pyramidal germanium center. A similar coordination is found in the calculated structures of ammonium and oxonium ylides, phosphonium and sulfonium ylides have nearly planar coordination around carbon.

The calculated interaction energies for the zwitterionic structures of Si and C reveal the same trends. The complexation energies of SiH<sub>2</sub> with NH<sub>3</sub> and OH<sub>2</sub> are similar to those of CH=H. However, the complexation energies with PH<sub>3</sub> differ significantly. The value calculated for the interaction between CH=H and PH<sub>3</sub> (36 kcal/mol, after zero-point corrections) indicates a much stronger bond in the ylide than that between Si and P in 5 (complexation energy = 18 kcal/mol). It is evident that the nature of bonding in the first- and second-row addition complexes of silicon does not differ appreciably.

As a criterion of hypervalency in ylides, Eades et al. have examined proton-transfer energies, i.e., the energy differences between the addition complexes and the stable tautomers. The rearrangement process is visualized as deprotonating a C=H bond and protonating the heteroatom. Since the former energy should be fairly constant, the proton-transfer energy should parallel the proton affinities of the heteroatomic bases. Deviations from the expected values, noted for P and S ylides, were attributed to additional stabilizing effects like hypervalency in the ylides. In the silicon systems, the calculated proton-transfer energies of 35, 36, 52, 57, 67, and 77 kcal/mol for 2, 5, 11, 8, 18, and 14, respectively, qualitatively follow the trends in the proton affinities of NH<sub>3</sub>, H<sub>2</sub> S, CH<sub>2</sub> OH, H<sub>2</sub> S, and H<sub>2</sub> Cl. This simple-minded analysis does not reveal any unusual stability for the second-row complexes. The large increase in the proton-transfer energies along the series H<sub>2</sub> Si-XH<sub>3</sub>, H<sub>2</sub> Si-XH<sub>2</sub>, and H<sub>2</sub> Si-XH is just a reflection of the increased destabilization of the addition complexes with increasing number of lone pairs as well as of the increased strength of the Si-X bond in the normal valent tautomers as X becomes more electronegative. The same trends within first- and second-row complexes were observed with carbene complexes also.

The differences in the bonding of first- and second-row ylides have been discussed repeatedly. The lone pair on the carbon of a first-row ylide is highly destabilized. When an adjacent second-row atom is present, a p<sup>-</sup>H bonding or donation into low-lying σ<sup>*</sup> orbitals is possible. Second-row complexes thus have considerable multiple-bond character. As is well-known, silicon differs from carbon in preferring to retain its atomic configuration (3s<sup>2</sup> 3p<sup>2</sup>) in its bonding instead of forming multiple bonds. The nearly equal stability calculated for silaethylene and methylsilylene provides a dramatic illustration. In all the silylene addition complex structures considered in this study, silicon is essentially unhybridized with bond angles close to 90°, in spite of being tricoordinate. The lone pair on silicon has considerable σ character and is relatively stabilized. There is little evidence for multiple-bond formation in these complexes even when second-row groups are present, since silicon does not gain much from the resulting rehybridization.

The reluctance of Si to rehybridize is also the reason for the significant barriers to hydrogen migration in these complexes. The rearrangement necessitates considerable electronic reorganization since the bonding in the addition complexes and in the stable tautomers differs considerably. However, the corresponding rehybridization is quite efficient with carbon derivatives, due to the smaller s-p gap associated with carbon. Therefore, the first-row ylides, if at all they are true minima, readily rearrange to the more stable tautomeric forms.

**Conclusions**

The addition complexes formed between SiH<sub>2</sub> and NH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub> O, H<sub>2</sub> S, HF, and HCl have been studied. The rearrangement barriers obtained for the hydrogen migration of these complexes to give the normal valent compounds have been calculated in all cases. The complex between SiH<sub>2</sub> and NH<sub>3</sub> exists in a deep minimum with a high barrier for rearrangement (38 kcal/mol). This addition complex is predicted to be a suitable candidate for spectroscopic observation. The complex between SiH<sub>2</sub> and PH<sub>3</sub> also exists in a fairly deep minimum (18 kcal/mol), but the overall activation energy for the insertion reaction is small. The complex formed between SiH<sub>2</sub> and H<sub>2</sub> O again exists in a fairly deep minimum, the rearrangement barrier being fairly significant (22 kcal/mol). This interaction has already been widely studied in experimental studies. The interaction between SiH<sub>2</sub> and H<sub>2</sub> S is weaker still with a smaller barrier for rearrangement (13 kcal/mol). In the case of both HF and HCl the interaction is extremely weak with very low rearrangement barriers (<10 kcal/mol). Both HF and HCl give loosely bound hydrogen-bonded complexes. Detailed comparison is made between the structure and bonding of the silylene addition complexes with those of their carbene analogues, the ylides. Significant differences, particularly in the multiple-bond character of the central bond, are found.

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Experimental Determination of the Bond Density of Molecular Hydrogen in Momentum-Space by Binary (e,2e) Spectroscopy

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Abstract: The spherically averaged bond density of molecular hydrogen in momentum-space has been derived by using the momentum distribution of the H\textsubscript{2} 1s orbital determined by binary (e,2e) spectroscopy and the exact solution of the Schrödinger equation for the 1s orbital of the H atom. Theoretical bond densities calculated by using different quality wave functions ranging from minimal basis set to extended Hartree-Fock are given for comparison. In addition, the orbital momentum moments of the H\textsubscript{2} 1s orbital are estimated from the measured orbital momentum distribution (Leung, K. T.; Brion, C. E. Chem. Phys. 1983, 82, 113.) and are found to be in good agreement with those calculated by using theoretical wave functions. Moreover, the dependence of the bond density on the quality of the wave function is discussed by using density difference maps in both position and momentum-space. The formation of the bond in momentum-space is also examined topographically in the critical range of internuclear separation between 2 and 1 \textmu\text{d}.

The bonding picture in momentum-space complements traditional position-space bonding concepts and further extends present understanding of momentum-space chemistry.

I. Introduction

The ground-state electronic wave function of molecular hydrogen has been the subject of many experimental investigations including binary (e,2e) spectroscopy\textsuperscript{1-4} and Compton scattering.\textsuperscript{5} Compton scattering experiments in general sample the momentum density due to all the electrons of the target. Binary (e,2e) spectroscopy\textsuperscript{1-2} on the other hand, samples selectively the momentum density of individual orbitals and provides a direct and sensitive experimental evaluation of molecular orbital wave functions. In the case of H\textsubscript{2}, the total momentum density is to a very good approximation that of the 1s orbital. The generally good agreement of the momentum distribution of molecular hydrogen observed by the two different techniques has been demonstrated in our recent study using binary (e,2e) spectroscopy.\textsuperscript{2}

The ground-state wave function of H\textsubscript{2} has also been investigated by many elaborate theoretical ab initio calculations, and H\textsubscript{2} is also the simplest test molecule for configurational interaction effects. Moreover, the hydrogen molecule involves the simplest (covalent) chemical bond and is thus suitable for the most fundamental studies of chemical bonding and electronic structural properties. Earlier works by Berlin,\textsuperscript{5} Roux et al.,\textsuperscript{6} Bader et al.\textsuperscript{7,8} involvement of position (charge) density difference (bond density) maps and the force concept. Other works by Bader and Preston\textsuperscript{9} and by Feinberg et al.\textsuperscript{10,11} examined the behavior of the kinetic and potential energy upon bond formation and the role of the Virial theorem in bond formation.

The bond density in either position or momentum space is defined in the present study to be the density difference between the molecular density (\rho_{\text{H}_2}) and the density due to independent atoms (the independent atom model density, \rho_{\text{IAM}}) at positions corresponding to the molecular nuclear geometry, i.e.

\[
\Delta \rho = 2 \rho_{\text{H}_2} - \rho_{\text{IAM}} \quad (1a)
\]

\[
\rho_{\text{IAM}} = \rho_{\text{H}_1} + \rho_{\text{H}_1} \quad (1b)
\]

both at R, where R is the internuclear separation and \rho denotes the single electron density. It is possible to obtain the "experimental" (spherically averaged) momentum-space bond density using the experimental momentum distributions of the H\textsubscript{2} 1s orbital and either the experimental or the exact theoretical momentum distribution of the 1s orbital for the H atom. The momentum distribution for the 1s orbital of atomic hydrogen has been determined recently in an elegant experiment by Lohmann and Weigold\textsuperscript{12} using binary (e,2e) spectroscopy. The measured result is found to reproduce the square of the exact solution of the Schrödinger equation in momentum-space. The only difficulty involved in obtaining the bond density is the normalization of the measured spherically averaged momentum density of H\textsubscript{2} 1s, because the noncoplanar symmetric (e,2e) experiment in most cases measures only relative cross sections.\textsuperscript{4} In the present study, this problem is solved by employing a numerical procedure. The "experimental" momentum-space bond density thus obtained is compared with theoretical calculations by using H\textsubscript{2} wave functions of different quality including extended Hartree-Fock (Ext-HF).\textsuperscript{13}