Rotationally resolved spectra of jet-cooled RuSi

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We report the first gas-phase spectroscopic investigation of diatomic ruthenium silicide (RuSi). The molecules were produced by laser ablation of a Ru disk into a flow of helium carrier gas containing 0.5% SiH_4, and were cooled in a supersonic expansion. The RuSi molecules were then studied using resonant two-photon ionization spectroscopy. Investigations conducted in the spectral range from 18 800 to 23 800 cm^{-1} show a large number of excited vibronic levels that cannot readily be grouped into electronic band systems. The ground state is been demonstrated to be of $^3\Delta_3$ symmetry, deriving from the $2\delta^3 14\sigma^1$ electronic configuration. Correcting for the effects of the spin-uncoupling operator, the ground state bond length (r_0) is determined to be 2.0921±0.0004 Å (1σ error limit). Diatomic RuSi is shown to have strong $d\pi$-$p\pi$ bonds, unlike the isovalent AlCo molecule. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2761889]

I. INTRODUCTION

With the increasing number of potential industrial applications, transition metal silicides have been subject to increasing scientific scrutiny. Like the related transition metal carbides and nitrides, transition metal silicides possess many desirable physical properties, including high melting points, low densities, and low chemical reactivity.[1] Specific species such as nickel and platinum silicides have been found to have applications as protective coatings against high temperature oxidation[2] and in microelectronics as Schottky barrier detectors for IR-imaging arrays.[3] Ruthenium silicide species have shown promise in silicon based optical applications, particularly as light-emitting diodes.[4]

Because of these applications, there is new scientific interest in the properties of diatomic transition metal silicides. In past work, the bond energies of FeSi,[5] CoSi,[5] NiSi,[5] CuSi,[6] RuSi,[7] RhSi,[7] PdSi,[7] AgSi,[6] IrSi,[7] PtSi,[7] and AuSi (Refs. 7–9) have been measured by Knudsen effusion mass spectrometry. The isovalent diatomics VSi and NbSi have been studied by electron spin resonance spectroscopy in a matrix-isolated environment, where quenching of the orbital angular momentum of their $^2\Delta_r$ ground states by rare gas matrix interactions is observed.[10] Cavity ringdown laser absorption spectroscopy has been used to study CuSi,[11] AgSi,[12] AuSi,[13] and PtSi.[14] Platinum monosilicide has also been studied by resonant two-photon ionization (R2PI) spectroscopy.[15] An investigation of diatomic NiSi using both R2PI and dispersed fluorescence (DF) spectroscopies[16] provided the first measurement of its bond length, as well as confirmation of a closed shell $^1\Sigma^+$ ground state that was predicted by theoretical studies.[17,18] A laser-induced fluorescence investigation of RhSi, demonstrating it to have a $^2\Sigma^+$ ground state is also currently in preparation for publication.[19]

The work reported here, to our knowledge, provides the first spectroscopic investigation of RuSi in the gas phase, although the related molecule RuC has been extensively in-

vestigated by absorption, emission, R2PI, and DF spectroscopies.[20–26] The only previous experimental work on diatomic RuSi is a measurement of its bond energy using Knudsen effusion mass spectrometry.[7] The dissociation energy was determined to be $D_0''=4.08\pm0.22$ eV using a third-law analysis of the reaction

$$RuC(g) + Si_2C(g) \rightarrow RuSi(g) + SiC_2(g).$$
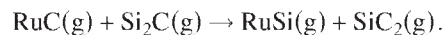
In the Knudsen effusion mass spectrometric study, the partition function of RuSi was evaluated assuming a ground electronic state of $^1\Sigma^+$. A recent theoretical study of all of the diatomic transition metal silicides predicts the ground state of RuSi to be the high spin $^3\Delta$ state,[27] unlike the $^1\Sigma^+$ ground state of the isovalent RuC molecule.[22] The calculated ground state of RuSi is similar to that of FeC, which has been spectroscopically determined to have $^3\Delta_3$ as its ground state.[28,29]

In this article, the visible spectra of jet-cooled diatomic RuSi are presented, as recorded by R2PI spectroscopy. The ground state is confirmed to be of $^3\Delta_3$ symmetry, adopting a high-spin electronic configuration similar to that of FeC, rather than a closed shell $^1\Sigma^+$ state like the isovalent RuC. Through this work, the bond lengths of the ground and excited states are provided. Also included is a discussion of chemical bonding, with comparisons to related molecules.

II. EXPERIMENT

The spectrum of diatomic RuSi was collected using the resonant two-photon ionization spectrometer that has been described in detail previously.[30,31] Diatomic RuSi was produced by pulsed laser ablation [Nd:YAG (yttrium aluminum garnet), 355 nm, and 5–10 mJ/pulse] of a metallic ruthenium sample disk in the throat of a supersonic expansion of helium seeded with 0.5% SiH_4. The ablation laser pulse was timed to coincide with the gas pulse, so that the metal atoms are entrained in the helium/silane gas flow. A series of gears and cams was used to rotate and translate the target metal disk in order to achieve uniform ablation and to avoid drilling holes in the sample. The resulting plasma is then allowed

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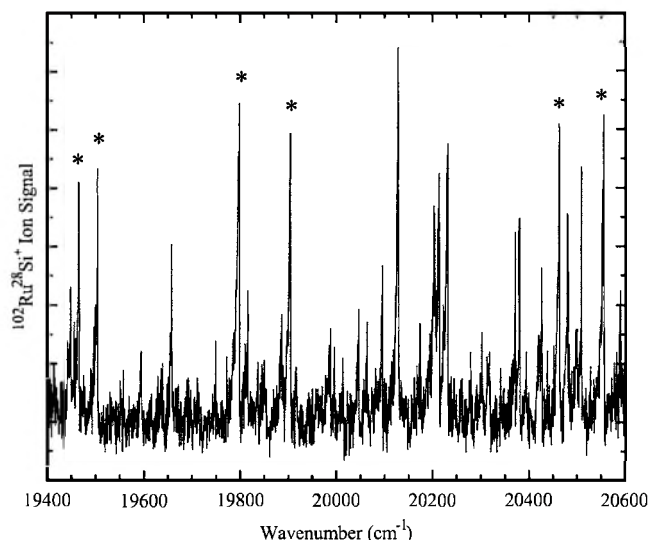
FIG. 1. Vibronic spectrum of $^{102}Ru^{28}Si$ recorded for the range of 19 400–20 600 cm^{-1}. Bands marked with asterisks were examined under higher resolution.

to supersonically expand into vacuum. Following expansion, the molecular beam is roughly collimated by a 1 cm aperture and passed into a second chamber, in which the molecules are interrogated by tunable radiation from a Nd:YAG-pumped dye laser. When the radiation from the dye laser is resonant with a molecular transition, the molecules are carried to the excited electronic state. The excited molecules are then exposed to ultraviolet radiation provided by an ArF (193 nm) excimer laser, which together with the dye laser photon provides sufficient energy for ionization. The resulting ions are detected in a Wiley-McLaren[32] reflectron-type[33] time-of-flight mass spectrometer equipped with a microchannel plate detector. The signal from the detector is amplified, digitized, and stored on a computer for later analysis.

The dye laser used for all measurements in this study is a Coherent (formerly Lambda-Physik) ScanMate Pro. Survey scans of the vibronic bands were performed by scanning the diffraction grating, providing a laser linewidth of 0.15 cm^{-1}. Rotationally resolved scans were recorded by narrowing the linewidth of dye laser to 0.04 cm^{-1} using an intracavity étalon. The laser was then pressure scanned using sulfur hexafluoride (SF_6). The absorption spectrum of isotopically pure $^{130}Te_2$ was simultaneously collected in order to calibrate the rotationally resolved spectrum by reference to the Te_2 spectral atlas.[34] A small correction to the spectrum was performed in order to compensate for the Doppler shift experienced by the RuSi molecules as they travel toward the excitation radiation source at the beam velocity of helium (1.77×10^{-5} cm/s).

III. RESULTS

The spectrum of diatomic RuSi was recorded from 18 800 to 23 800 cm^{-1}. Above 19 000 cm^{-1}, a large number of intense vibronic transitions were observed, as displayed in Fig. 1 for the 19 400–20 600 cm^{-1} range. The density of vibronic transitions was unfortunately too great to allow the bands to be grouped into vibronic progressions. Some of the

features examined under higher resolution, in particular, the features near 19 455 and 19 900 cm^{-1}, were found to contain two or more vibronic bands. In some isotopomers, these bands were well separated and could be rotationally analyzed; in others, overlap between bands or perturbations between the upper states were too severe to permit analysis. For some isotopomers, particularly $^{96}Ru^{28}Si$, the natural abundance was too low to permit analysis for many features. Table I provides a list of bands that were successfully analyzed for $^{96}Ru^{28}Si$ (5.09%), $^{99}Ru^{28}Si$ (11.7%), $^{100}Ru^{28}Si$ (11.6%), $^{101}Ru^{28}Si$ (15.7%), $^{102}Ru^{28}Si$ (29.1%), and $^{104}Ru^{28}Si$ (17.2%), along with the fitted spectroscopic constants.

The rotationally resolved bands all display structure that is similar to that shown in Fig. 2 for the 19 791 band of $^{102}Ru^{28}Si$. All of the recorded bands are red shaded, with an immediate bandhead in the R branch. The first R line is obscured in the R head in all bands, but all of the bands exhibit $Q(3)$ as the first Q line. Given that the only plausible candidates for the RuSi ground state are the $2\delta^4$, $^1\Sigma^+$ ($\Omega''=0^+$); $2\delta^3 14\sigma^1$, $^3\Delta_3$ ($\Omega''=3$); or $2\delta^2 14\sigma^2$, $^3\Sigma^-$ ($\Omega''=0^+$ or 1) states, the presence of $Q(3)$ as the first Q line in all of the examined bands proves that the ground level is $2\delta^3 14\sigma^1$, $^3\Delta_3$.

Given that the ground state is of $^3\Delta_3$ symmetry, the observation of $Q(3)$ as the first Q line implies that the upper levels of all of the investigated bands have $\Omega'=2$ or 3. The only remaining allowed value of Ω', $\Omega'=4$, would give a first Q line of $Q(4)$. Thus, all of the bands that were examined have $\Omega'=2$ or 3. To definitively distinguish between these possibilities, one must establish the presence ($\Omega'=2$) or absence ($\Omega'=3$) of the $P(3)$ line. In some of the measured spectra it is difficult to absolutely prove the presence or absence of $P(3)$ because of overlap with Q lines [generally $Q(6)$] or with lines of the returning R branch [generally $R(13)$, $R(14)$, or $R(15)$]. Based on a careful examination of the spectra of all of the isotopomers, including comparison of branch intensities to simulated spectra, the upper state assignments listed in Table I are thought to be correct. Most
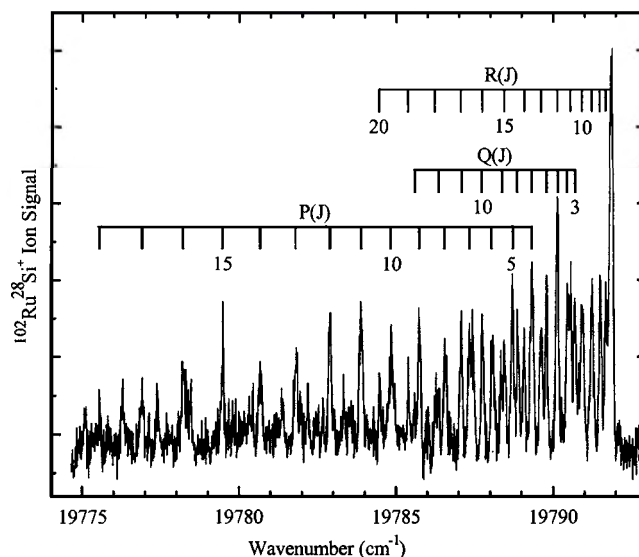

FIG. 2. Rotationally resolved spectrum of the 19 791 cm^{-1} $\Omega'=3 \leftarrow X\ ^3\Delta_3$ band of $^{102}Ru^{28}Si$.

TABLE I. Spectroscopic parameters of measured bands of RuSi isotopomers. The values of B', B'', r', and r'' reported here are uncorrected for any effects due to spin uncoupling. Such corrections (for the ground state) are discussed in the text. Error limits (1σ) are provided in parentheses in units of the last quoted digit. Spectroscopic constants (ν_0, B', and B'') are given in cm^{-1} units; bond length are reported in Å.

Ω'-Ω''		^{96}Ru ^{28}Si	^{99}Ru ^{28}Si	^{100}Ru ^{28}Si	^{101}Ru ^{28}Si	^{102}Ru ^{28}Si	^{104}Ru ^{28}Si
3–3	ν_0	Too weak to	19 450.0139(36)	19 447.4538(38)	Out of recorded	Out of recorded	Out of recorded
	B'	analyze	0.151 129(49)	0.150 809(58)	range	range	range
	r'		2.261 59(37)	2.261 50(44)			
3–3	ν_0	Too weak to	19 469.1547(40)	Perturbed	19 462.2241(28)	19 459.1293(25)	19 453.7284(25)
	B'	analyze	0.150 868(53)		0.150 652(43)	0.150 415(37)	0.149 378(36)
	r'		2.263 55(40)		2.260 22(32)	2.259 59(28)	2.262 71(27)
3–3	ν_0	Too weak to	19 506.4278(34)	19 503.3725(45)	19 500.4779(46)	19 497.7807(48)	19 492.8794(34)
	B'	analyze	0.147 425(49)	0.146 478(67)	0.146 088(55)	0.145 674(47)	0.144 505(34)
	r'		2.289 83(38)	2.294 69(53)	2.295 25(43)	2.296 06(37)	2.300 55(27)
3–3	ν_0	Too weak to	Perturbed	Perturbed	19 792.5750(36)	19 791.0538(27)	19 787.8370(31)
	B'	analyze			0.146 136(65)	0.144 864(55)	0.143 459(60)
	r'				2.294 88(51)	2.302 48(44)	2.308 92(48)
2–3	ν_0	Too weak to	19 896.5159(41)	19 891.9919(45)	Not recorded	Perturbed	19 892.2358(41)
	B'	analyze	0.142 984(49)	0.140 826(84)			0.143 646(70)
	r'		2.325 12(40)	2.340 28(70)			2.307 42(56)
3–3	ν_0	19 904.1594(52)	Out of recorded	19 902.8690(41)	19 899.3882(38)	Perturbed	19 898.1079(38)
	B'	0.145 660(135)	range	0.142 293(71)	0.143 247(65)		0.144 365(43)
	r'	2.311 59(107)		2.328 19(58)	2.317 90(53)		2.301 66(34)
3–3 or 2–3	ν_0	Too weak to	Too weak to	Too weak to	20 456.2065(39)	20 453.5730(31)	20 448.0087(45)
	B'	analyze	analyze	analyze	0.146 157(49)	0.145 878(63)	0.145 102(47)
	r'				2.294 71(39)	2.294 46(50)	2.295 81(37)
3–3	ν_0	Too weak to	20 553.0351(50)	20 550.4324(27)	20 547.9316(34)	20 545.4595(41)	20 540.6056(42)
	B'	analyze	0.147 878(53)	0.147 573(68)	0.147 266(40)	0.146 919(39)	0.146 932(50)
	r'		2.286 32(41)	2.286 16(53)	2.286 05(31)	2.286 32(30)	2.281 47(39)
$X\,^3\Delta_3$	B''	0.177 115(155)	0.176 239(61)	0.175 676(66)	0.175 360(47)	0.175 015(43)	0.174 253(51)
$v=0$	r''	2.096 30(92)	2.094 29(36)	2.095 34(39)	2.094 94(28)	2.094 78(26)	2.094 99(31)

of the observed bands are thought to be $\Omega'=3 \leftarrow \Omega''=3$ transitions, in which $P(3)$ is absent. Line positions for all of the interpretable isotopomers of RuSi have been deposited with the Electronic Physics Auxilliary Publication Service of the American Institute of Physics,[35] and are also available from Morse. The electronic document also contains spectra for all of the rotationally resolved bands.

The measured line positions were fit to the standard expression[36]

$$\nu = \nu_0 + B'J'(J'+1) - B''J''(J''+1). \qquad (3.1)$$

To obtain the most accurate values of the ground state rotational constant, B'', all of the measured bands were combined into a single rotational fit, thereby constraining all of the B'' values to be the same for the measured bands of a given isotopomer. These values are reported in Table I. Apart from the value of B'' determined for the ^{96}Ru^{28}Si isotopomer, which results from the measurement of a single band, the B'' values of all of the other isotopomers are consistent, providing a value of the ground state bond length of $r''_0 = 2.0949 \pm 0.0004$ Å (1σ error limit). This result, however, is based on neglecting the effects of the spin-uncoupling operator, which couples the $X\,^3\Delta_3$ and $^3\Delta_2$ levels. Assuming that the separation between the $X\,^3\Delta_3$ level and the corresponding

$^3\Delta_2$ level is the same as measured in the previously studied RuC molecule,[22] a correction can be made to account for the effects of the spin-uncoupling operator. Taking this operator into account, the true B value is related to the measured B value for the $\Omega=3$ component, via the equation[36]

$$B_{\text{eff}}(\Omega) = B_{\text{true}}\left(1 + \frac{2B_{\text{true}}\Sigma}{A\Lambda}\right). \qquad (3.2)$$

Solving for the true B value using the value $A=387$ cm^{-1} and converting to a bond length allows a more accurate value to be obtained, thereby providing $r_0 = 2.0921 \pm 0.0004$ Å (1σ error limit). This is our best estimate of the true bond length of the RuSi molecule, averaged over the $v=0$ vibrational wave function and corrected for spin-uncoupling effects.

IV. DISCUSSION

To a first approximation, the chemical bonding in diatomic RuSi may be considered using the molecular orbital diagram of Fig. 3. Here, the $3p$ orbitals of Si, and the $4d$ and $5s$ orbitals of Ru are the most important orbitals involved in the chemical bond. The 12σ orbital is largely nonbonding due to its $3s_{\text{Si}}$ character, combined with the minor tendency of silicon to undergo $3s$-$3p$ hybridization. The 13σ orbital is
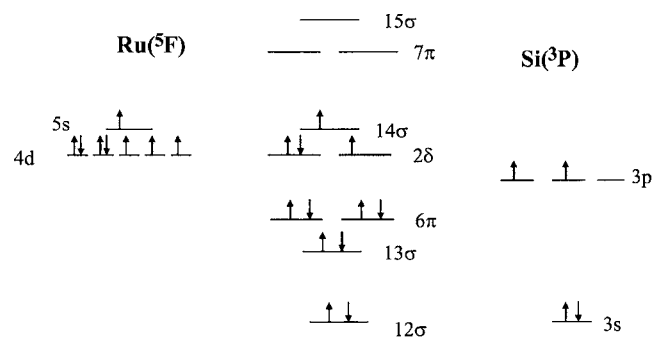
FIG. 3. Molecular orbital diagram of diatomic RuSi.

a bonding orbital formed by overlap between the $4d\sigma_{Ru}$ and $3p\sigma_{Si}$ atomic orbitals, with the 15σ orbital being its antibonding counterpart. Overlap between the $4d\pi_{Ru}$ and $3p\pi_{Si}$ atomic orbitals leads to the formation of the bonding 6π and antibonding 7π orbitals. The remaining $4d_{Ru}$ and $5s\sigma_{Ru}$ orbitals comprise the 2δ and 14σ orbitals, respectively, which are largely nonbonding in nature. Hyperfine analysis on the isovalent RuC molecule has determined the analogous nonbonding 12σ orbital to be 83% $5s_{Ru}$ in character. In the closely related RhC molecule ($X\,^2\Sigma^+$), hyperfine analysis shows the 12σ orbital to have approximately 69% $5s_{Rh}$ character.[37]

Similarly to NiSi and PtSi,[15,16] diatomic RuSi exhibits characteristics of strong $d\pi$-$p\pi$ bonding. The measured bond length ($r_0'' = 2.0921$ Å) and dissociation energy (4.08 ± 0.22 eV) (Ref. 7) both suggest that the $4d\pi$-$3p\pi$ bond is important in RuSi. Further evidence of the importance of π bonding in RuSi may be found by comparing to the isovalent AlCo molecule, which has been previously investigated in the Morse group.[38] Like RuSi, AlCo has an $\Omega'' = 3$ ground state that corresponds to the analogous $^3\Delta_3$ ground state. However, the bond length of AlCo ($r_0'' = 2.383$ Å) is about 0.29 Å longer than that of RuSi, despite the fact that Co is found in the $3d$ rather than the $4d$ period. Likewise, the bond energy of AlCo ($D_0 = 1.844$ eV) (Ref. 38) is far smaller than that of RuSi (4.08 ± 0.22 eV).[7] Based on a comparison of the $^3\Delta_3$ states of the isovalent FeC and RuC molecules, one would expect an increase in bond length of about 0.039 Å in moving from a $3d$ molecule such as AlCo to the isovalent $4d$ molecule, RuSi. Instead, in moving from AlCo to RuSi the bond length contracts by 0.29 Å. The reason for this discrepancy is the strong π bonding in RuSi, as opposed to negligible π bonding in AlCo. In AlCo a strong σ bond is formed by overlap of the $3p\sigma_{Al}$ orbital with the $4s\sigma_{Co}$ orbital. However, the $3p\pi$ orbital of the Al atom is empty. Therefore any electrons involved in $d\pi$-$p\pi$ bonding must come from the more electronegative Co atom, which is highly unfavorable. This situation is modified in RuSi in two ways. First, silicon is considerably more electronegative than aluminum, making it a much better electron acceptor. Second, silicon contributes one of the π electrons to the $d\pi$-$p\pi$ bond, allowing ordinary covalent bonding to occur, as opposed to dative covalent bonding.

The rotationally resolved studies reported here have revealed that RuSi has a high-spin $^3\Delta$ ground term rather than the closed shell $^1\Sigma^+$ ground term of the isovalent RuC mol-

ecule. The reason for the different ground states in these isovalent species ultimately derives from the greater intrinsic bond energy in RuC as compared to RuSi. The $^3\Delta$ term of both RuC and RuSi correlates to the ground separated atom limit of Ru $4d^75s^1$, ^{5}F + C (or Si) s^2p^2, ^{3}P. However, no singlet states arise from the ground separated atom limit of ^{5}F + ^{3}P, so the $^1\Sigma^+$ molecular term must correlate to an excited limit (specifically, Ru $4d^75s^1$, ^{3}F + C (or Si) s^2p^2, ^{3}P, which lies 6545 cm^{-1} above ground state atoms).[39] Thus, the only way the $^1\Sigma^+$ term can emerge as the ground state is if the bond energy is sufficient to overcome the 6545 cm^{-1} (0.81 eV) promotion energy penalty that is associated with formation of a singlet state. The high bond energy of RuC is sufficient to overcome this penalty; the somewhat weaker bond in RuSi is not. Extending this reasoning, one expects RuGe, RuSn, and RuPb to likewise have $^3\Delta_3$ ground terms.

V. CONCLUSION

Rotationally resolved investigations of RuSi have demonstrated that the molecule has a $2\delta^3\,14\sigma^1$, $^3\Delta_3$ ground state with $r_0 = 2.0921 \pm 0.0004$ Å. It is argued that strong $d\pi$-$p\pi$ bonds exist in this molecule, based on a comparison with the isovalent molecule AlCo. The difference between the $^3\Delta_3$ ground term of RuSi and the $^1\Sigma^+$ ground term of RuC is rationalized in terms of the greater promotion energy required to form the $^1\Sigma^+$ term, which correlates to an excited separated atom limit.

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