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Laser Vaporization of Silicon Carbide: Lifetime and Spectroscopy of SiC₂

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A pulsed YAG laser is used to vaporize silicon carbide. The vapors are studied by either trapping in a solid Ne matrix or direct probing by time-resolved, laser-induced fluorescence. SiC₂ and C₂ are the main species detected. The excitation and emission spectra of SiC₂ are recorded and analyzed and several vibrational frequencies reassigned. The lifetime of the $\tilde{A}^1\Pi$ state and its collisional relaxation are examined.

Introduction

Silicon is the second most abundant element in the earth's crust, and both carbon and silicon rank among the 10 most widespread elements in the universe. Rather surprisingly, in spite of the obvious importance of these elements and of their widespread occurrence, very little is known about binary compounds between them. Well-known is, of course, silicon carbide as colorless crystals with a hexagonal crystalline lattice resembling diamond. On the other hand, little information exists about discrete compounds and clusters of silicon and carbon. Although both the Si₂ and C₂ molecules are well-known and have been very thoroughly studied, no spectroscopic observations of the mixed SiC diatomic have been reported. Also, our knowledge of the larger binary clusters is only sketchy.

The major obstacle to studies of the silicon-carbon compounds is the very high temperatures which are needed to vaporize these elements. To complicate matters further, the equilibrium vapors above solid silicon carbide show an almost total absence of diatomic SiC and consist mainly of atomic Si, with SiC₂ and Si₂C being the major molecular species.¹ We have been recently developing in our laboratory techniques for obtaining molecular spectra by pulsed YAG laser vaporization of solids,^{2,3} followed by time-resolved, pulsed-laser-induced fluorescence study of the products.⁴ This technique was applied to the study of Pb₂, Sn₂, and numerous other metal clusters. The advantage of this approach is its generality and applicability even to highly refractory materials. In the present work we employ this technique to study the vaporization products of silicon carbide.

The initial intent of this work was the characterization of the elusive diatomic SiC molecule. We were, thus far, unsuccessful in this effort, and no spectra attributable to this species were observed. Several other molecular species were observed, however, including SiC₂, C₂, and Si₂.

The SiC₂ electronic absorption spectrum has been first observed in the atmospheres of carbon stars by several workers.^{5,6} The first laboratory observation and identification of the carrier of the spectrum is due to Kleman.⁷ Since then, the molecule was studied by a number of investigators, both in the gas phase⁸ and in cryogenic matrices.⁹ In spite of these several thorough studies, the

spectroscopy of SiC₂ is not well understood and there is considerable disagreement in the interpretation of its spectrum by different groups.

In the present manuscript, we report the result of our studies of laser vaporization of silicon carbide, with particular emphasis on the spectroscopy and dynamics of SiC₂. In addition to the gas-phase study, we also reexamine the SiC₂ spectrum in the matrix, both by absorption and by laser-induced fluorescence.

Experimental Section

The experimental setup was previously described.^{4,10} The silicon carbide is vaporized by pulses of a Q-switched YAG laser (10 ns, 100-300 mJ). The laser beam is loosely focused (focal spot diameter of 0.5-1 mm) on the surface of the silicon carbide sample and the resulting plume is swept by a flow of helium gas cooled by liquid nitrogen. The cold gas carrying the silicon carbide vapors effuses through a ~1-mm pinhole into an evacuated chamber. The species present in the effusing beam are then probed by laser-induced fluorescence, excited by a pulsed tunable dye laser, which is suitably delayed with respect to the YAG laser pulse. We might note that, in the present configuration, the conditions for supersonic cooling of the carrier gas are not fulfilled and the translational temperature of the effusing gas is somewhat above that of the liquid N₂ bath. However, by increasing the backing pressure and the pumping speed, the apparatus could readily be modified to provide additional cooling by adiabatic expansion.

The laser-induced fluorescence is collected perpendicular to both the gas flow and the probe laser and detected by a photomultiplier. The signal is then digitized by a fast waveform recorder (Biomation 8100) and averaged. In the present experiments, the fluorescence was not spectrally resolved, but colored or narrow band-pass interference filters were sometimes used to isolate the spectral region of interest or to reduce the chemiluminescent background and scattered laser light.

For the matrix experiments, the silicon carbide was again vaporized by the YAG laser operated at 10 Hz and codeposited with the matrix gas (Ne) on a metal substrate cooled to 4 K by liquid He. The fact that deposition of neon is continuous while that of the silicon carbide vapor is pulsed results in the sample consisting of layers richer in solute, separated, at the deposition rates and conditions used in our work, by ~20 Å layers of relatively pure matrix material. This, however, causes no serious problem and may, in fact, lead to enhanced production of molecular species in the matrix. The overall concentration of the trapped species is not known, but is lower than 1:5000.

Resolved emission spectra of the matrix fluorescence are obtained on a SPEX 14018 double monochromator with holographic gratings.

(1) J. Drowart, G. de Maria, and M. G. Ingram, *J. Chem. Phys.*, **29**, 1015 (1958).

(2) K. A. Lincoln, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 75 (1969).

(3) T. G. Dietz, M. A. Duncan, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.*, **74**, 6511 (1981).

(4) V. E. Bondybey and J. H. English, *J. Chem. Phys.*, **74**, 6978 (1981).

(5) P. W. Merrill, *Publ. Astron. Soc. Pac.*, **38**, 175 (1926).

(6) R. F. Sanford, *Astrophys. J.*, **111**, 262 (1950).

(7) B. Kleman, *Astrophys. J.*, **123**, 162 (1956).

(8) R. D. Verma and S. Nagaraj, *Can. J. Phys.*, **52**, 1938 (1974).

(9) W. Weltner and D. McLeod, *J. Chem. Phys.*, **41**, 235 (1964).

(10) V. E. Bondybey and J. H. English, *J. Chem. Phys.*, **76**, 2165 (1982).

TABLE I: SiC_2 , $\tilde{X}^1\Sigma \rightarrow \tilde{A}^1\Pi$ Vibronic Bands in Solid Ne

absorption			emission		
$\bar{\nu}$, cm^{-1}	$\Delta\nu$, cm^{-1}	assignment	$\bar{\nu}$, cm^{-1}	$\Delta\nu$, cm^{-1}	assignment
20 142		0_0^0	20 142		0_0^0
20 604	462	2_0^0	19 798	344	2_2^0
21 064	462 + 460	2_0^0	19 546		
21 153	1011	1_0^0	19 306	836	1_0^0
21 608	1466	3_0^0	18 473	836 + 833	1_0^0
22 079	1466 + 471	$3_0^0 2_0^0$	18 396	1746	3_0^0
22 650	1466 + 1042	$3_0^0 1_0^0$	18 082	1746 + 314	$3_0^0 2_0^0$
23 040	1466 + 1432	3_0^0	17 562	1746 + 834	$3_0^0 1_0^0$
23 512		$3_0^0 2_0^0$	16 734	1746 + 834 + 828	$3_0^0 1_0^0$
24 434		3_0^0	16 673	1746 + 1723 + 303	3_0^0
			16 370		$3_2^0 2_0^0$

Results and Discussion

Spectroscopy of SiC_2 and Its Fluorescence in Solid Neon. Triatomic molecules with 12–16 valence electrons are predicted by Walsh's rules to be linear in their ground state and in the low-lying excited electronic states.¹¹ This prediction is well established experimentally for numerous species in this category involving three first-row atoms. Linear geometry is also expected for isoelectronic molecules including second-row atoms, although for these much less detailed experimental data are available. The rigidity of the linear configuration appears to increase with the number of electrons in the highest occupied π orbital. In the ground state of C_3 with 12 valence electrons, this orbital is empty; the bottom of its bending potential function is very flat, with an uncommonly low value of vibrational frequency $\nu_2'' \sim 63 \text{ cm}^{-1}$.^{12,13}

If one considers the inclusion of a silicon atom into the isoelectronic SiC_2 molecule and takes into account the apparent reluctance of silicon to form multiple bonds, the linearity of SiC_2 is not a priori obvious. Nonetheless, we shall assume in our spectral analysis that SiC_2 is a linear Si-C-C molecule with $C_{\infty v}$ symmetry. Furthermore, in the absence of any evidence to the contrary, we shall retain the assumption of the previous investigators^{8,9} that the ground state of SiC_2 is $^1\Sigma^+$ and that, as in the isoelectronic C_3 molecule, the observed transition is $\tilde{X}^1\Sigma^+ \rightarrow \tilde{A}^1\Pi$.

While the focus of our present study is on the gas-phase fluorescence of SiC_2 , we have also reexamined its matrix emission. The gas-phase excitation spectrum at 77 K provides very little information about the ground-state vibrational structure; this is, on the other hand, easily obtained from the matrix emission spectrum. Spectra of SiC_2 in the matrix are rather strongly inhomogeneously broadened. One advantage of laser-induced fluorescence experiments is that one can selectively excite a particular site and remove thus the inhomogeneous broadening. The fluorescence of SiC_2 in solid Ne is shown for the lowest-energy site with origin at 19968 cm^{-1} in Figure 1. The structure in the spectrum appears to be independent of which of the upper-state vibrational levels was initially excited by the laser, and all of the observed emission originates from the vibrationless level. This observation that vibrational relaxation is fast compared with the radiative rate is not uncommon for polyatomic matrix isolated molecules.¹⁴

The progressions in the two ground-state stretching frequencies, $\nu_3'' = 1746 \text{ cm}^{-1}$ and $\nu_1'' = 836 \text{ cm}^{-1}$, are easily assigned in the spectrum, in good agreement with the

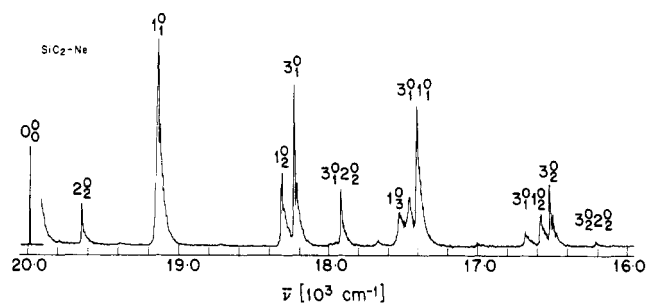


TABLE II: $\text{SiC}_2 \tilde{A}^1\Pi \rightarrow \tilde{X}^1\Sigma$ Vibronic Bands in the Gas Phase

$\bar{\nu}$, cm^{-1}	$\Delta\nu$, cm^{-1}	assignment	$\bar{\nu}$, cm^{-1}	$\Delta\nu$, cm^{-1}	assignment
19 716 ^{a,b}	-354	2 ₀ ⁰	22 009	1464 + 475	3 ₀ ¹ 2 ₀ ²
20 070	0	0 ₀ ⁰	22 467	(+458)	3 ₀ ¹ 2 ₀ ⁴
20 364 ^b	294		22 549	1464 + 1015	3 ₀ ¹ 1 ₀ ¹
20 525	455	2 ₀ ²	22 966	1464 + 1432	3 ₀ ²
20 698 ^b			23 454	(+488)	3 ₀ ² 2 ₀ ²
20 801 ^b			24 373	1464 + 1432 + 1407	3 ₀ ³
20 976	455 + 451	2 ₀ ⁴	24 864	(+491)	3 ₀ ³ 2 ₀ ²
21 049	979	1 ₀ ¹			
21 534	1464	3 ₀ ¹			

^a The wavenumbers of the strongest bandheads are given. Most of them agree well with the bands interpreted as "Q heads" in the higher-resolution study in ref 8. ^b These bands have no counterparts in the matrix spectra and are probably hot bands.

counterpart of the matrix emission band 2₀⁰, and it lends a strong support to the ν_2'' assignment discussed in the preceding section.

The most active progression forming mode is $\nu_3' = 1464 \text{ cm}^{-1}$, in agreement with previous investigators. This progression can be readily followed up to $\nu_3' = 3$, both in matrix absorption and in the gas-phase excitation spectrum, and shows a moderate anharmonicity with $x_{33}' \sim 15 \text{ cm}^{-1}$. Much less obvious is the assignment of the remaining bands in the spectrum. Each of the bands of the ν_3' progression is accompanied by a somewhat weaker band $\sim 455 \text{ cm}^{-1}$ higher in energy. Kleman assigned the 445- cm^{-1} interval to ν_1' in his original study. Weltner and McLeod reassigned this frequency to $2\nu_2'$, while Verma and Nagaraj reverted to the original ν_1' assignment. The latter workers assign the 2₀² transition to a moderately strong band near 20 378 cm^{-1} yielding a value of $\sim 292 \text{ cm}^{-1}$ for the $2\nu_2'$ interval.

This latest assignment, combined with our present value for the ground-state frequency $2\nu_2'' \sim 354 \text{ cm}^{-1}$, would require the bending frequency to decrease in the upper state. The electronic excitation in molecules of this type, however, places an electron into the unfilled π orbital, and this invariably results in increase of the ν_2 frequency in the excited state. Thus, in C_3 the ground-state frequency $\nu_2'' = 63 \text{ cm}^{-1}$ increases nearly by a factor of 4 in the excited $^1\Pi_u$ state. More importantly, the 20 378- cm^{-1} band (20 364 cm^{-1} in our work), which is prominent in the room-temperature spectrum, appears only weakly in our cooled-gas-phase spectrum in Figure 2 and is completely absent from the matrix excitation spectrum in Figure 3. We therefore conclude that it has to be attributed to a hot band and assign $2\nu_2'$ to the 455- cm^{-1} interval.

The remaining upper-state frequency, ν_1' , is then assigned to a rather strong band occurring at 21 049 cm^{-1} , 979 cm^{-1} above the origin. The corresponding interval appears at 1015 cm^{-1} both in the matrix absorption spectrum of Weltner and McLeod and in our laser excitation spectrum in Figure 3. Verma and Nagaraj attribute the 979- cm^{-1} interval to an overtone of the 455- cm^{-1} frequency. This, however, would require an uncommonly high "negative" anharmonicity for this frequency. Furthermore, this interpretation ignores a band appearing near the harmonic frequency in both the gas-phase and matrix spectra.

The $\sim 3\%$ increase of the ν_1' frequency in solid Ne when compared with the gas-phase value is somewhat larger than is usual for matrix shifts. We may note, however, that the individual vibronic transitions in the gas phase are relatively broad and different bands exhibit different rotational envelopes. In the absence of rotational analysis, the vibrational intervals given refer to the spacing of prominent bandheads, rather than of the band origins, and this may, at least in part, explain the discrepancy. We list the

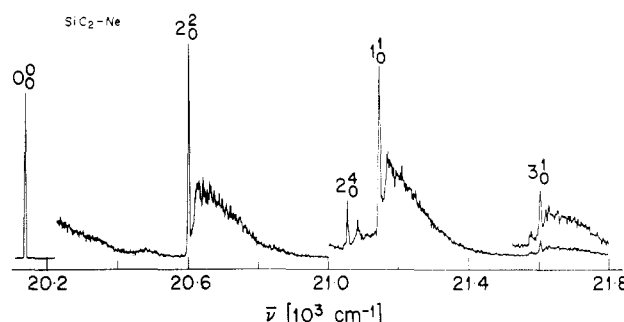


Figure 3. Laser excitation spectrum of SiC_2 in solid Ne. The 0₀⁰ fluorescence of the major site at 20 039 cm^{-1} was monitored.

TABLE III: Molecular Constants of SiC_2 ^a

ν_1 , cm^{-1}	ν_2 , cm^{-1}	ν_3 , cm^{-1}
852 ^c (836)	175 (172)	1742 ^c (1746)
$\tilde{A}^1\Pi$, $T_0 = 20070$ (20142) ^b		
979 (1011)	228 (231)	1464 (1462)

$\tau(\tilde{A}^1\Pi) = 370 \text{ ns}$ (310 ns)

^a The Ne matrix values are given in parentheses. ^b This T_0 value refers to the "major" site in solid Ne. ^c Gas-phase ν_1' and ν_3' values for the $\tilde{X}^1\Sigma$ state are from ref 8.

observed SiC_2 bands and their assignments in Table II and summarize the spectroscopic constants of the molecule in Table III.

Radiative Lifetime of SiC_2 and Nonradiative Relaxation. When the vibrationless level of the upper state is excited, the fluorescence exhibits an exponential decay with a 370-ns lifetime. This value appeared to be constant over a rather broad range of pressures from 0.5 to 10 torr. This indicates that collisional quenching of SiC_2 by helium is insignificant for the vibrationless level and the measured lifetime is radiative. This conclusion finds further support in the Ne matrix study, where we measure a lifetime of 310 ns for the same transition. The ratio of the two values, ~ 1.19 , is typical of lifetime shortening usually observed in solid Ne. It reflects an increase in the radiative rate due to the increased index of refraction of the solid medium. The vibrationless level of the excited electronic state thus apparently fluoresces with near unity quantum efficiency both in the gas phase in the range of He pressures studied, and in solid Ne.

The situation is quite different when the higher vibrational levels of the upper state are excited. Figure 4 shows an example of the fluorescence decay curve following excitation of the 3₀¹ transition at 21 534 cm^{-1} at a total pressure of ~ 0.5 torr. Under these circumstances, the decay is clearly doubly exponential, with a short component $\tau_s = 198 \text{ ns}$ and a longer lifetime $\tau_l \sim 1250 \text{ ns}$. With

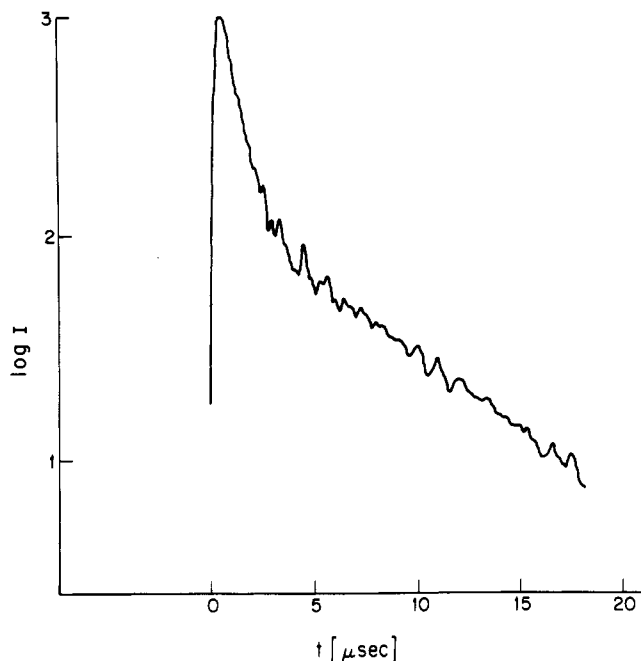


Figure 4. Typical decay curve of the SiC_2 $\tilde{A}^1\Pi$ fluorescence showing the double exponential behavior. The 2_0^2 band at $20\,525\text{ cm}^{-1}$ was excited. Pressure $P = 0.5$ torr.

increasing He pressure, both lifetimes shorten considerably and the amplitude of the short component decreases. At a constant pressure, the shorter lifetime decreases with increasing vibrational excitation. Thus, for 2_0^2 excitation, the lifetime shortening only becomes clearly observable at pressures above ~ 5 torr. On the other hand, for the 3_0^2 level, the fast component is shorter than our experimental resolution (~ 10 ns) for pressures above 1 torr.

Stern-Volmer plots for the short-lifetime component of all of the levels studied yield radiative lifetimes close to the ~ 370 -ns $v = 0$ value. A similar treatment of the long component extrapolates to a lifetime of $\sim 1.7\text{ }\mu\text{s}$ at zero pressure. The quenching cross sections exhibit a monotonic increase with increasing vibrational energy. It thus appears, that the excited levels of the $\tilde{A}^1\Pi$ state are collisionally quenched into vibrational levels of a nearby electronic state. One could furthermore argue that the origin of this state is located above the origin of the $\tilde{A}^1\Pi$ state, since no similar quenching is observed for the vibrationless $\tilde{A}^1\Pi$ level either by helium in the gas phase or in the more polarizable solid neon matrix.

Our data do not show unambiguously from what level the long-lived emission occurs. Since there is no evidence for this perturbing electronic state either in the matrix absorption or in the laser excitation spectrum, it would appear that it is not connected to the ground state by a strongly allowed electronic transition. The state involved could therefore be a nearby triplet, with the long-lived emission originating directly from this perturbing state. An alternative possibility may be that a reverse crossing from the low-lying levels of this state into the $\tilde{A}^1\Pi$ state takes place and that the long-lived emission occurs from the vibrationless $\tilde{A}^1\Pi$ state level. The observed decay

lifetime would then be mainly limited by the rate of this reverse crossing. These questions could be unambiguously answered by spectrally resolving the gas-phase emission. Crude tests using cutoff and band-pass filters seem to indicate that the spectral distribution of the long-lived emission does not differ drastically from that of the short-lived component.

The situation in the Ne matrix is also interesting. The only emission observed originates in the vibrationless $\tilde{A}^1\Pi$ state level. As noted before, it shows regardless of excitation wavelength a single exponential decay with ~ 305 -ns lifetime and no measureable risetime. On the other hand, the intensity of the higher vibrational levels in the excitation spectrum decreases much faster than the corresponding absorption intensities. Clearly, the quantum yield for relaxation into the $\tilde{A}^1\Pi$ vibrationless level decreases with vibrational excitation. This is apparently due to competition between vibrational relaxation within the $\tilde{A}^1\Pi$ state and irreversible intersystem crossing into some other electronic state. This may be the same state which is responsible for the SiC_2 relaxation behavior in the gas phase.

Other Species Present in the Vapor. Despite a rather extensive search, no fluorescence systems attributable to other silicon-carbon species were found. Weltner observed an absorption system with origin near $18\,860\text{ cm}^{-1}$ in solid Ne, which he assigned to the Si_2C molecule. In the present experiments, only a group of very strong bands near $19\,360\text{ cm}^{-1}$, which were clearly due to the $\Delta v = 0$ sequence of the Swan bands of C_2 , was found in this region. The observed lifetime of the emission, 130 ns, is also in good agreement with the literature value.

Si_2C is known from mass-spectroscopic studies to be a rather abundant component of silicon carbide vapor. The failure to observe its fluorescence in the present experiments may reflect a low emission quantum yield for this species.

Weak emission due to C_3 and Si_2 were also detected. On the other hand, no signal attributable to diatomic SiC was observed, even though one might expect allowed transitions of this molecule within the spectral range studied. It appears that appreciable concentrations of SiC are not formed in our system. It is possible that SiC is very efficiently removed by reactions of the type $2\text{SiC} \rightarrow \text{SiC}_2 + \text{Si}$ or $\text{SiC} + \text{C} \rightarrow \text{C}_2 + \text{Si}$. If this is the case, then solid matrix might be a better medium for searching for the SiC species.

Summary

Silicon carbide was vaporized by a pulsed YAG laser and the vapors, diluted by a cold helium gas, were studied by time-resolved, laser-induced fluorescence. C_2 , Si_2 , and SiC_2 are the major fluorescent molecular species found. No spectra are observed for either Si_2C or SiC . It is demonstrated that laser vaporization can be conveniently applied to preparation of matrix isolated samples. Fluorescence excitation and resolved emission spectra of SiC_2 both in the gas phase and in Ne matrix are recorded, and vibrational reassignment of the spectrum is proposed. Lifetimes and quenching of SiC_2 are also examined.