

# A THEORETICAL STUDY OF THE $A^2\Sigma^+ - X^2\Pi$ SYSTEM OF THE SiP MOLECULE<sup>1</sup>

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Received 1999 December 27; accepted 2000 February 24

## ABSTRACT

The  $A^2\Sigma^+$  and  $X^2\Pi$  electronic states of the SiP species have been investigated theoretically at a very high level of correlation treatment (CASSCF/MRSDCI). Very accurate potential energy curves are presented for both states, as well as the associated spectroscopic constants as derived from the vib-rotational energy levels determined by means of the numerical solution of the radial Schrödinger equation. Electronic transition moment function, oscillator strengths, Einstein coefficients for spontaneous emission, and Franck-Condon factors for the  $A^2\Sigma^+ - X^2\Pi$  system have been calculated. Dipole moment functions and radiative lifetimes for both states have also been determined. Spin-orbit coupling constants are also reported. The radiative lifetimes for the  $A^2\Sigma^+$  state, taking into account the spin-orbit diagonal correction to the  $X^2\Pi$  state, decrease from a value of 138 ms at  $v' = 0$  to 0.48 ms at  $v' = 8$ , and, for the  $X^2\Pi$  state, from 2.32 s at  $v'' = 1$  to 0.59 s at  $v'' = 5$ . Vibrational and rotational transitions are expected to be relatively strong.

*Subject headings:* ISM: molecules — molecular data — molecular processes

## 1. INTRODUCTION

Molecules containing phosphorous and silicon are expected to be present in detectable quantities in the interstellar/circumstellar gas, since these are cosmically reasonably abundant species ( $P/H = 3 \times 10^{-7}$ ,  $Si/H = 3 \times 10^{-5}$ ). However, astronomical searches in the interstellar medium for PO have been unfruitful (Matthews, Feldman, & Bernath 1987), in disagreement with the ion-molecule reactions models (Thorne et al. 1984), which predicted that this species would be the most abundant interstellar P compound. Also, the molecular species  $PH_3$  (Hollis et al. 1980), HCP (Hollis et al. 1981; Turner et al. 1990), PS (Ohishi et al. 1988), CP (Saito et al. 1989), and HPO (Turner et al. 1990) have been searched for unsuccessfully in the interstellar medium. Fortunately, Turner & Bally (1987) and Ziurys (1987) detected PN, the first P-bearing molecule in relatively warm molecular clouds, but not in cold clouds such as Taurus molecular cloud 1 (TMC-1; Turner et al. 1990). The observed abundance of the PN molecule is  $10^3$ – $10^4$  times higher than that predicted from the Thorne et al. (1984) scenario. In order to explain the observed results, the chemistry of phosphorous in dense molecular clouds has been discussed by Millar, Bennett, & Herbst (1987), Turner & Bally (1987), Millar (1991), and Charnley & Millar (1994). These studies showed that PN might be formed in space (by a combination of grain disruption and/or gas phase reactions), with the P atom being the most abundant species.

More recently, toward the expanding envelope of the late-type carbon star IRC + 10216, Guélin et al. (1990) have detected the CP free radical. According to these authors, HCP is photodissociated to CP but HCP has been

observed neither in interstellar sources, nor yet in IRC + 10216 (Hollis et al. 1981; Turner et al. 1990). In this context, the depletion into grains of P (HCP) is suggested, as was the case also for Si compounds. Depletion of P and Si elements are also found in molecular clouds (e.g., Martín-Pintado, Bachiller, & Fuente 1992; Turner et al. 1990). The Si element exhibits significant depletion in the diffuse interstellar medium, in contrast with P, which appears to be little depleted at low densities (Savage & Sembach 1996), but it is unclear what fraction of P and Si remains in the gas phase within more dense regions.

To date, eight silicon-containing molecules ( $SiC$ ,  $SiC_2$ ,  $SiC_4$ ,  $SiN$ ,  $SiO$ ,  $SiS$ ,  $SiH_2$ , and  $SiH_4$ ) have been detected in the circumstellar envelope around IRC + 10216 (e.g., Gensheimer, Likkell, & Snyder 1995; Turner 1992 and references therein). Observed abundances of  $SiO$  and  $SiS$ , detected in the inner part of the envelope, are much lower than those predicted by current models (Tsuji 1973; McCabe, Smith, & Clegg 1979; Lefont, Lucas, & Omont 1982; Cherchneff & Barker 1992). The relatively low abundances of these molecules have been interpreted as the result of incorporation of silicon into grains in warm, high-density gas close to the star. In addition, Glassgold, Lucas, & Omont (1986), Herbst et al. (1989), and Glassgold & Mamon (1992) have proposed that the  $SiC$ ,  $SiC_2$ ,  $SiC_4$ , and  $SiN$  abundances could be explained by ion-molecule reactions, in which Si and  $Si^+$  are the progenitors of these species (e.g., Gensheimer, Likkell, & Snyder 1995; Turner 1992). However,  $SiO$  and  $SiS$  are the only interstellar molecules observed.  $SiS$  has been detected in relatively warm molecular clouds (e.g., Ziurys 1988). On the other hand,  $SiO$  has been fairly extensively observed in peculiar circumstances, possibly associated with shocks chemistry or high-temperature chemistry (e.g., Downes et al. 1982; Ziurys, Friberg, & Irvine 1989). There are models that predict the observed abundances in

<sup>1</sup> In memory of Professor Patan Deen Singh, who died at the age of 56, on 1999 October 9, in São Paulo, Brazil.

high-temperature postshock conditions (e.g., Neufeld & Dalgarno 1989; Flower et al. 1996), in fast neutral winds of young stars (Glassgold, Mamon, & Huggins 1991), in dense molecular clouds (Herbst et al. 1989), and in hot molecular cores (Mackay 1995).

Further studies and detection of P and Si compounds could certainly yield useful information concerning the depletion of heavy elements in the interstellar/circumstellar gas and their recycling in astrophysical sources, and, in this particular, the formation of a diatomic molecule containing these two atomic species is a possibility worth exploring. Surprisingly, however, little is known about SiP.

The possibility of the existence of SiP was raised by Mulliken in his early work on SiN (Mulliken 1925); however, to the best of our knowledge, there are no experimentally reported studies on this radical, except for an estimate of its dissociation energy (Smoes, Depière, & Drowart 1972).

Theoretically, the first *ab initio* calculations on SiP were carried out by Bruna et al. (1983). Using the multireference single and double excitations configuration interaction (MRD-CI) approach, they reported equilibrium geometries and  $T_e$  values for the two lowest lying states of SiP. Later, Bruna, Dohmann, & Peyerimhoff (1984) extended the previous study to cover the three lowest lying states of this radical, in which potential energy curves, equilibrium geometries,  $T_e$  values, and dipole moments at the equilibrium bond lengths are presented. They also reported excitation energies and equilibrium geometries for the lowest excited quartet states of SiP.

Recently, McLean, Liu, & Chandler (1992) calculated equilibrium distances, zero-point energies, and the first vibrational energy separation for the  $X^2\Pi$  and  $A^2\Sigma^+$  states, as well as the excitation energy for  $A^2\Sigma^+$  and the dissociation energy at the singles and doubles configuration interaction level of theory, including Davidson's correction (CISD + Q) for higher excitations. Finally, the most recent *ab initio* studies on this radical were published by Boldyrev & Simons (1993) and Boldyrev, Gonzales, & Simons (1994). In the first work, equilibrium geometries and harmonic vibrational frequencies calculated at the self-consistent field (SCF), frozen-core second-order Møller-Plesset perturbation theory (MP2), and quadratic configuration interaction, including singles and doubles with approximate triples (QCISD - (T)), are reported for the ground state and the lowest excited states of SiP; in the latter work, the above properties were reevaluated within the CASSCF(3, 2, 2, 0)/MRCISD(Q) approach.

In this paper, as part of an ongoing investigation on silicon-containing diatomics, which has already characterized the species SiB (Ornellas & Iwata 1997), AlSi (Ornellas & Iwata 1998), and SiS (Ornellas & Adi 2000) at a very high level of correlation treatment and analyzed the formation of silicon-containing diatomics by radiative association (Andreazza, Singh, & Sanzovo 1995; Andreazza & Singh 1997; Singh et al. 1999), we present results of *ab initio* calculations on the  $X^2\Pi$  and  $A^2\Sigma^+$  states of SiP. Potential energy curves, vibrational frequencies, spectroscopic constants, dipole moment functions, oscillator strengths, and Franck-Condon factors for both states are reported, as well as the transition moment function and Einstein emission coefficients, between these electronic states, and radiative lifetimes. We hope that this information should prove valuable as an additional guide for future experimental investigations of the SiP radical in the laboratory, as well as helping in its search in space.

## 2. METHODS OF CALCULATION

In this work, our main concern is a high-level description of the potential energy curves of the ground ( $X^2\Pi$ ) and the first excited ( $A^2\Sigma^+$ ) electronic states of the SiP molecule, their dipole moments, and the transition dipole moment between them. To achieve this goal, a wave function based on the state-averaged complete active space self-consistent field (SA-CASSCF) methodology (Werner & Knowles 1985; Knowles & Werner 1985) is first constructed, which basically accounts for the static correlation effects. Next, the incorporation of dynamical correlation is effected by the configuration interaction approach, which essentially corresponds to the inclusion in the wave function of all configuration state functions (CSFs) generated as single and double excitations on top of a selected subset of CSFs of the zeroth-order space. The state-averaging process involved first a CASSCF calculation in which nine electrons were distributed in 11 active orbitals, denoted as (5, 3, 3, 0) in the  $C_{2v}$  point group symmetry. This space corresponds to the valence 3s and 3p orbitals of both Si and P, plus one additional correlating orbital for each of the  $A_1$ ,  $B_1$ , and  $B_2$  symmetries. Core and inner-shell orbitals were kept doubly occupied in all calculations. This procedure allows for the construction of a common set of molecular orbitals, to be used in the transition moment calculation, by the optimization of an average energy that included the two lowest states of  $A_1$  symmetry and one state of each of the  $B_1$  and  $B_2$  symmetries, with equal weights. The final zeroth-order space is then generated by the inclusion of only those CSFs with coefficients greater 0.025 in absolute magnitude, a threshold that was proved very reliable by Taylor (1991) and by Partridge, Langhoff, & Bauschlicher (1995). The CASSCF calculation generated sets of dimensions 19,234 ( $A_1$ ) and 19,070 ( $B_1$ ), which after the selection step reduced to about 80 and 40 CSFs for the  $A_1$  and  $B_1$  symmetries, respectively. The use of the internally contracted multireference configuration interaction approach (Werner & Knowles 1988; Knowles & Werner 1988), as implemented in the MOLPRO-98<sup>2</sup> suite of programs, reduced the dimension of the CSF space from about 7 ( $A_1$ ) and 5 ( $B_1$ ) million terms to about 700,000 and 500,000 contracted terms, respectively. Natural orbitals from a state-averaged density matrix were used in the expansion of the  $n$ -particle space, and the atomic bases employed in the expansion of the molecular orbitals are the correlation consistent valence-polarized quadruple-zeta sets (cc-pVQZ) developed by Woon & Dunning (1993) and symbolized as [6s, 5p, 3d, 2f, 1g], which generated a set of 118 contracted functions. For the calculation of the spin-orbit constants, the  $g$ -type functions were excluded from the above set and the remaining functions were used in an uncontracted form, as required by the present version of the computational code. Vibrational energies and wave functions and radiative transition probabilities were computed with the INTENSITY program (Zemke & Stwalley 1981) based on the Numerov-Cooley numerical solution of the Schrödinger equation. The stan-

<sup>2</sup> MOLPRO-98 is a package of *ab initio* programs written by Werner, H.-J., and Knowles, P. J., with contributions from Almlöf, J., Amos, R. D., Berning, A., Cooper, D. L., Deegan, M. J. O., Dobbyn, A. J., Eckert, F., Elbert, S. T., Hampel, C., Lindh, A., Lloyd, A. W., Meyer, W., Nicklass, A., Peterson, K., Pitzer, R., Stone, A. J., Taylor, P. R., Mura, M. E., Pulay, P., Schütz, M., Stoll, H., and Thorsteinsson, T.

standard fitting procedures used to compute the spectroscopic constants and the convention used to evaluate the radiative transition probabilities are discussed elsewhere (Herzberg 1950; Ornellas 1985; Machado & Ornellas 1991; Borin & Ornellas 1993) and will not be repeated here.

3. RESULTS AND DISCUSSION

The potential energy curves for the  $X^2\Pi$  ground and  $A^2\Sigma^+$  first excited states of SiP have been calculated in the 3.10–12.00  $a_0$  range of internuclear distances and are given in Table 1 and illustrated in Figure 1. An enlarged view of these curves showing the relative positions of the lowest lying vibrational levels is shown in Figure 2. Both curves display a well-defined minimum and exhibit a smooth shape. The  $X^2\Pi$  ground state correlates with the first dissociation limit  $\text{Si}(^3P) + \text{P}(^4S)$  and has a calculated dissociation energy ( $D_e$ ) of 3.64 eV. Experimentally, an estimate of  $D_0$  equal to 3.73 eV obtained by mass spectrometry has been found in the literature (Smoes et al. 1972), which turns out to be quite concordant with our theoretical result of 3.60 eV.

Around the equilibrium distance, the dominant contributions for the  $X^2\Pi$  and  $A^2\Sigma^+$  states can be represented by the electronic configurations  $\dots 7\sigma^2 8\sigma^2 3\pi^3 9\sigma^2$ , and  $\dots 7\sigma^2 8\sigma^2 3\pi^4 9\sigma^1$ , respectively. Equilibrium internuclear distances, 2.089 Å ( $X$ ) and 2.002 Å ( $A$ ), are in very good agreement with the results of Boldyrev & Simons (1993) (2.087 and 2.007 Å for the  $X$  and  $A$  states, respectively) at the QCISD(T) level of theory and of Boldyrev et al. (1994) (2.092 Å [ $X$ ] and 2.012 Å [ $A$ ]) at the CASSCF(3, 2, 2, 0)/MRCISD(Q) level of theory. The equilibrium bond lengths obtained with other methods differ sensibly from our results since they have employed lower levels of theory (see Table 3, below). For the sake of completeness, the total

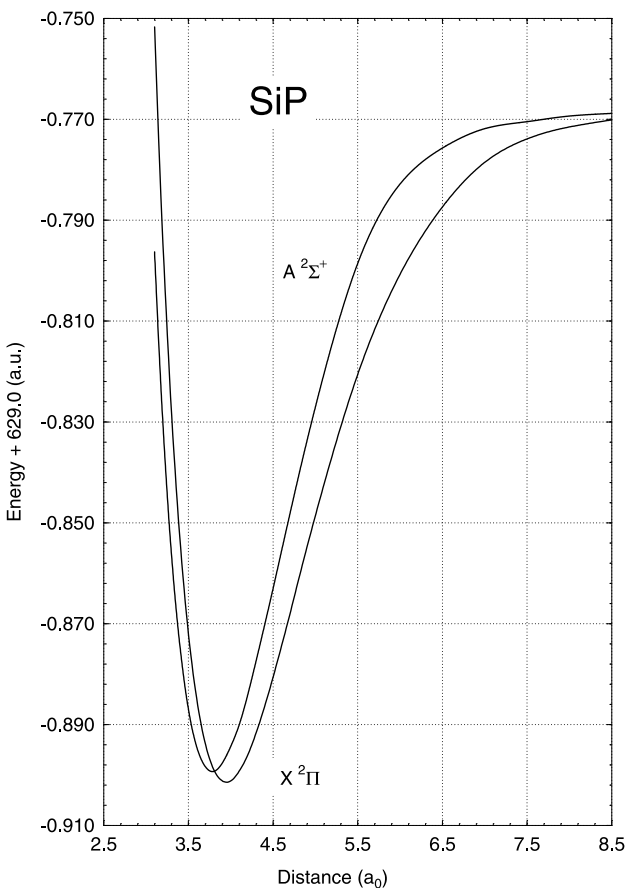


Fig. 1.—Calculated potential energy curves for SiP

TABLE 1  
ENERGIES (RELATIVE TO  $-629.0$  ATOMIC UNITS), DIPOLE MOMENTS, AND  
DIPOLE TRANSITION MOMENTS FOR THE  $X^2\Pi$  AND  $A^2\Sigma^+$   
STATES OF THE SiP MOLECULE

$R(a_0)$	$X^2\Pi$	$A^2\Sigma^+$	$\mu(X)$	$\mu(A)$	$\mu(X-A)$
3.10 .....	-0.751686	-0.796259	0.04256	-0.44048	0.32439
3.20 .....	-0.794731	-0.830616	0.00149	-0.45349	0.32171
3.30 .....	-0.827958	-0.856285	-0.04310	-0.46762	0.31705
3.40 .....	-0.853205	-0.874438	-0.08608	-0.47783	0.31111
3.50 .....	-0.871903	-0.886946	-0.12910	-0.48927	0.30396
3.60 .....	-0.885112	-0.894535	-0.17744	-0.49957	0.29582
3.70 .....	-0.893819	-0.898341	-0.22070	-0.50857	0.28674
3.80 .....	-0.898942	-0.899280	-0.26280	-0.51834	0.27666
3.90 .....	-0.901157	-0.897627	-0.30421	-0.52731	0.26602
4.00 .....	-0.901171	-0.894323	-0.34401	-0.53383	0.25611
4.10 .....	-0.899224	-0.890031	-0.38284	-0.54082	0.24665
4.30 .....	-0.891627	-0.877338	-0.44650	-0.55180	0.22200
4.50 .....	-0.880614	-0.863021	-0.50953	-0.55281	0.19731
4.70 .....	-0.868018	-0.848143	-0.56185	-0.54431	0.17351
5.00 .....	-0.848546	-0.827020	-0.62870	-0.50198	0.13852
5.50 .....	-0.820570	-0.798550	-0.67094	-0.29402	0.09071
6.00 .....	-0.800718	-0.782871	-0.57815	-0.00153	0.05221
7.00 .....	-0.778523	-0.771825	-0.25575	0.11958	0.02442
8.00 .....	-0.771509	-0.769346	-0.08999	0.06788	0.01536
9.00 .....	-0.769134	-0.768519	-0.02754	0.03808	0.01058
10.00 .....	-0.768328	-0.768194	-0.01097	0.02242	0.00735
12.00 .....	-0.767852	-0.767867	-0.00467	0.00953	0.00375

NOTE.—All quantities are in atomic units (a.u.).

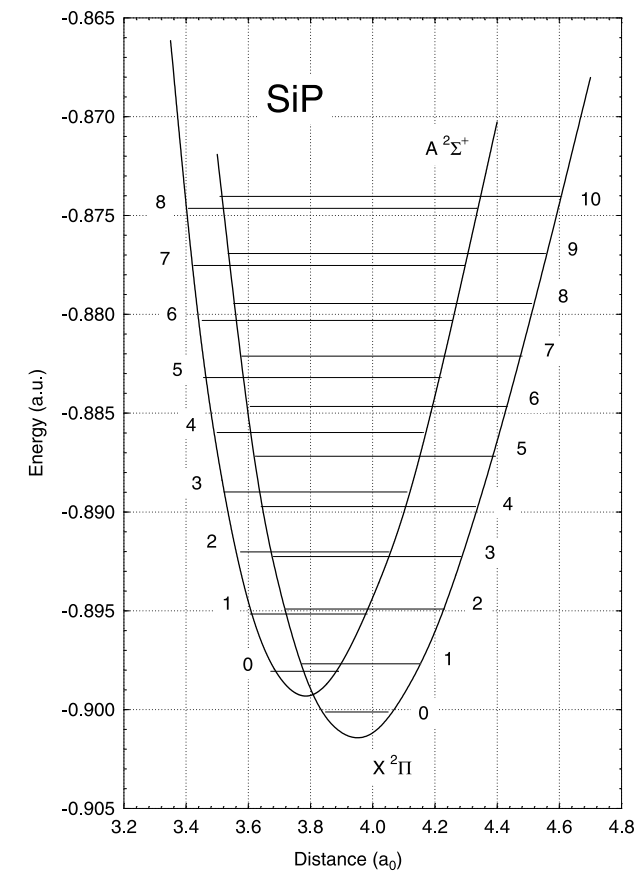


FIG. 2.—Enlarged view of calculated potential energy curves, showing the relative positions of the vibrational levels.

energies calculated at  $r_e$  are  $-629.901413$  and  $-629.899273$  a.u. for  $X^2\Pi$  and  $A^2\Sigma^+$  states, respectively. The  $A^2\Sigma^+$  electronic state also dissociates into the electronic ground states of the atoms  $\text{Si}(^3P) + \text{P}(^4S)$  and is deeply nested in the  $X^2\Pi$  ground state. The former is lying  $470\text{ cm}^{-1}$  ( $T_e$ ) higher than the latter. Of the theoretical results reported in the literature, the investigation of McLean et al. (1992), at the SDQ and SDCI levels of theory, predicted values of  $T_e$  of  $1659\text{ cm}^{-1}$  (SDQ) and  $2473\text{ cm}^{-1}$  (SDCI), which are considerably higher than the result of the

present investigation. These overestimated results are a reflection of the poor performance of the single-reference configuration interaction (CI) approach used in that work. On the other hand, the results of Bruna et al. (1984) by means of the MRD-CI method varies from  $403\text{ cm}^{-1}$ , with a canonical basis set, to  $585\text{ cm}^{-1}$ , with a natural orbital basis. If extrapolation to the full CI limit is carried out using natural orbitals,  $T_e$  values of  $484$  and  $645\text{ cm}^{-1}$  are obtained with basis sets with  $62$  and  $72$  contracted functions, respectively. From today's standpoint, despite its multireference zeroth-order function, these calculations still lack both saturation in the one-particle basis and an improved description of the  $n$ -particle space. As to the results of Boldyrev & Simons (1993), they failed to get a definitive answer to the ordering of these two states; their best projected MP4 calculation yielded the  $^2\Pi$  state higher than the  $^2\Sigma^+$  by  $1154\text{ cm}^{-1}$ , whereas with the QCISD(T) approach, the  $^2\Pi$  state was found to be  $315\text{ cm}^{-1}$  lower in energy than the  $^2\Sigma^+$ . However, in a more recent investigation at the CASSCF(3, 2, 2, 0)/MRSDCI(Q) level (Boldyrev et al. 1994), the  $^2\Sigma^+$  state was predicted to be  $770\text{ cm}^{-1}$  higher than the  $^2\Pi$ .

Since the determination of spectroscopic constants is dependent on the number of points used in the fitting procedure (Richards, Raftery, & Hinkley 1973), we have collected in Table 2 values of the first 10 vibrational spacings as well as the rotational constants  $B_v$ , computed as the average value  $\langle v | 16.8576/\mu R^2 | v \rangle$  over the vibrational levels  $|v\rangle$  for both  $X$  and  $A$  states. Vibrational and rotational constants were obtained from least-squares fits to standard expressions (Herzberg 1950; Machado & Ornellas 1991), employing the data in Table 2. These constants are summarized in Table 3, together with equilibrium distances ( $r_e$ ), dissociation energies ( $D_e$ ), electronic term ( $T_e$ ), and previous theoretical and experimental values. They are expected to represent the best set of constants reported so far for these two states of SiP. To the best of our knowledge, no experimental results were found in the literature.

The variation of the transition moment with internuclear distance is also displayed in Table 1 and illustrated in Figure 3. This function approaches zero at large internuclear distances since both electronic states dissociate into the electronic ground states of the atoms. The transition moment varies rather smoothly with respect to the inter-

TABLE 2						
VIBRATIONAL LEVELS SPACINGS $\Delta G_{v+1/2}$ , ROTATIONAL CONSTANTS $B_v$ , AND VIBRATIONALLY AVERAGED DIPOLE MOMENTS $\langle \mu_v \rangle$ FOR THE $X^2\Pi$ AND $A^2\Sigma^+$ STATES OF THE SiP MOLECULE						
$v$	$X^2\Pi$			$A^2\Sigma^+$		
	$\Delta G_{v+1/2}$ ( $\text{cm}^{-1}$ )	$B_v$ ( $\text{cm}^{-1}$ )	$\langle \mu_v \rangle$ ( $\text{e}\text{\AA}$ )	$\Delta G_{v+1/2}$ ( $\text{cm}^{-1}$ )	$B_v$ ( $\text{cm}^{-1}$ )	$\langle \mu_v \rangle$ ( $\text{e}\text{\AA}$ )
0.....	604	0.2622	$-0.1720$	656	0.2855	$-0.2736$
1.....	597	0.2608	$-0.1741$	654	0.2839	$-0.2741$
2.....	591	0.2594	$-0.1765$	650	0.2824	$-0.2746$
3.....	586	0.2579	$-0.1789$	644	0.2808	$-0.2751$
4.....	582	0.2564	$-0.1814$	638	0.2792	$-0.2756$
5.....	578	0.2550	$-0.1839$	632	0.2776	$-0.2761$
6.....	574	0.2536	$-0.1864$	626	0.2760	$-0.2765$
7.....	570	0.2522	$-0.1890$	620	0.2744	$-0.2768$
8.....	565	0.2507	$-0.1915$	615	0.2729	$-0.2771$
9.....	561	0.2493	$-0.1941$	609	0.2713	$-0.2774$

TABLE 3  
 CALCULATED SPECTROSCOPIC CONSTANTS OF THE SiP MOLECULE

Method	$\Delta G_{1/2}$	$r_e$	$T_e$	$w_e$	$w_e x_e$	$w_e y_e$	$B_e$	$\alpha_e$	$\gamma_e$	$D_e$
$A^2\Sigma^+$										
This work .....	656	2.002	470	661	2.003	-0.0440	0.2863	1.56E-03	-2.4E-06	3.58
MRCI <sup>a</sup> .....	...	2.032	...	...	...	...	...	...	...	...
MRCI <sup>b</sup> .....	...	2.027	...	...	...	...	...	...	...	...
SDCI <sup>c</sup> .....	615	1.972	2473	...	...	...	...	...	...	...
SDQ <sup>c</sup> .....	654	1.986	1659	...	...	...	...	...	...	...
SCF <sup>d</sup> .....	...	1.968	...	731	...	...	...	...	...	...
MP2/6-311+G <sup>d</sup> .....	...	1.987	...	694	...	...	...	...	...	...
QCISD(T) <sup>d</sup> .....	...	2.007	...	...	...	...	...	...	...	...
CASSCF/MRCISD(Q) <sup>e</sup> .....	...	2.012	...	629	...	...	...	...	...	...
$X^2\Pi$										
This work .....	604	2.089	0.0	608	2.886	0.0367	0.2630	1.47E-03	3.1E-06	3.64
MRCI <sup>a</sup> .....	...	2.111	...	...	...	...	...	...	...	...
MRCI <sup>b</sup> .....	...	2.106	...	...	...	...	...	...	...	...
SDCI <sup>c</sup> .....	655	2.061	...	...	...	...	...	...	...	2.68
SDQ <sup>c</sup> .....	627	2.077	...	...	...	...	...	...	...	3.15
SCF <sup>d</sup> .....	...	2.139	...	468	...	...	...	...	...	...
MP2/6-311+G <sup>d</sup> .....	...	1.991	...	754	...	...	...	...	...	...
QCISD(T) <sup>d</sup> .....	...	2.087	...	...	...	...	...	...	...	...
CASSCF/MRCISD(Q) <sup>e</sup> .....	...	2.092	...	608	...	...	...	...	...	...
Experimental ( $D_0$ ) .....	...	...	...	...	...	...	...	...	...	3.73

NOTE.—All units in  $\text{cm}^{-1}$ , except  $r_e$ , in Å, and  $D_e$ , in eV. Ten points have been used in the fitting of the vibrational and rotational constants.

<sup>a</sup> Bruna et al. 1983.

<sup>b</sup> Bruna et al. 1984.

<sup>c</sup> McLean et al. 1992.

<sup>d</sup> Boldyrev & Simons 1993.

<sup>e</sup> Boldyrev et al. 1994.

nuclear distance, that is, decreasing by only 0.094 a.u. between 3.5 and 4.4  $a_0$ . The slow variation of this function with geometry allows us to apply the Franck-Condon principle and check its validity for this case (Herzberg 1950).

Franck-Condon factors, given by the overlap integral of the two vibrational wave functions belonging to the two different electronic states, are an approximate way of determining the relative intensities of the various bands. Table 4 displays these results for the  $A^2\Sigma^+-X^2\Pi$  bands. Consistent

with the shift of about 0.16  $a_0$  between the two minima of the potential energy curves, larger values of the Franck-Condon factors also appear nondiagonally. For transitions from the two lowest levels ( $v' = 0-1$ ) of the  $A^2\Sigma^+$  state to the ground state levels  $v''$ , the Franck-Condon factors are seen to be relatively large, 0.35 and 0.40, respectively. In addition, large elements were also found for the ( $v' = 3, v'' = 1$ ), ( $v' = 4, v'' = 2$ ), ( $v' = 7, v'' = 4$ ), ( $v' = 6, v'' = 3$ ), and ( $v' = 8, v'' = 5$ ) bands.

 TABLE 4  
 CALCULATED VIBRATIONAL BAND ORIGINS, WITHOUT SPIN-ORBIT CORRECTION, OF THE  $A^2\Sigma^+-X^2\Pi$  TRANSITION BANDS, FRANCK-CONDON FACTORS  $q_{v'v''}$ , AND VIBRATIONALLY AVERAGED SPIN-ORBIT COUPLING CONSTANTS

$v''$	$v' = 0$ ( $\text{cm}^{-1}$ )	$v' = 1$ ( $\text{cm}^{-1}$ )	$v' = 2$ ( $\text{cm}^{-1}$ )	$v' = 3$ ( $\text{cm}^{-1}$ )	$v' = 4$ ( $\text{cm}^{-1}$ )	$v' = 5$ ( $\text{cm}^{-1}$ )	$v' = 6$ ( $\text{cm}^{-1}$ )	$v' = 7$ ( $\text{cm}^{-1}$ )	$v' = 8$ ( $\text{cm}^{-1}$ )	$A_{v''}$ ( $\text{cm}^{-1}$ )
0.....	494	1149	1803	2453	3097	3735	4367	4993	5613	-175.72
	.353	.400	.189	.049	.008	.001	0.0	0.0	0.0	...
1.....	...	545	1199	1849	2493	3131	3763	4389	5009	-175.44
	...	.001	.220	.286	.126	.028	.003	0.0	0.0	...
2.....	...	...	603	1252	1896	2535	3167	3793	4413	-175.14
	...	...	.100	.049	.266	.199	.061	.009	.001	...
3.....	...	...	12	662	1306	1944	2576	3202	3822	-174.84
	...	...	.008	.163	0.0	.184	.244	.102	.020	...
4.....	...	...	...	75	719	1358	1990	2615	3236	-174.52
	...	...	...	.017	.134	.034	.094	.255	.145	...
5.....	...	...	...	...	137	775	1407	2033	2653	-174.18
	...	...	...	...	.071	.068	.087	.030	.235	...
6.....	...	...	...	...	...	197	829	1455	2075	-173.84
	...	...	...	...	...	.106	.017	.121	.002	...
7.....	...	...	...	...	...	...	255	881	1501	-173.48
	...	...	...	...	...	...	.104	0.0	.125	...

NOTE.—Missing values for a given transition band ( $v', v''$ ) denote  $T_e + E(v') - E(v'') < 0$ , where  $E(v)$  is the vibrational energy. Franck-Condon factors less than  $10^{-3}$  are set equal to zero.

TABLE 5  
CALCULATED EINSTEIN COEFFICIENTS  $A_{v'v''}$  FOR THE SiP  $X^2\Pi-A^2\Sigma^+$  SYSTEM AND RELATED OSCILLATOR STRENGTHS  $f_{v'v''}$

$v''$	$v' = 0$ ( $s^{-1}$ )	$v' = 1$ ( $s^{-1}$ )	$v' = 2$ ( $s^{-1}$ )	$v' = 3$ ( $s^{-1}$ )	$v' = 4$ ( $s^{-1}$ )	$v' = 5$ ( $s^{-1}$ )	$v' = 6$ ( $s^{-1}$ )	$v' = 7$ ( $s^{-1}$ )	$v' = 8$ ( $s^{-1}$ )
0.....	1.25E01 3.84E-05	1.68E02 9.52E-05	2.86E02 6.58E-05	1.71E02 2.14E-05	4.80E01 3.74E-06	6.80E00 3.66E-07	4.66E-01 1.83E-08	1.29E-02 3.88E-09	3.52E-05 8.36E-13
1.....	...	2.70E-02 6.80E-08	1.03E02 5.40E-05	4.60E02 1.01E-04	4.56E02 5.50E-05	1.79E02 1.36E-05	3.24E01 1.70E-06	2.68E00 1.04E-07	8.30E-02 2.48E-09
2.....	...	...	6.48E00 1.33E-05	2.54E01 1.21E-05	4.56E02 9.50E-05	7.44E02 8.68E-05	4.00E02 2.96E-05	8.98E01 4.86E-06	8.78E00 3.38E-07
3.....	...	...	3.76E-06 1.99E-08	1.38E01 2.36E-05	9.94E-02 4.38E-08	3.32E02 6.60E-05	9.44E02 1.07E-04	6.76E02 4.94E-05	1.88E02 9.66E-06
4.....	...	...	...	2.26E-03 3.00E-07	1.43E01 2.08E-05	2.36E01 1.68E-05	1.78E02 3.36E-05	1.02E03 1.11E-04	9.80E02 7.02E-05
5.....	...	...	...	...	5.62E-02 2.24E-06	8.90E00 1.11E-05	6.62E01 2.50E-07	5.76E01 1.04E-05	9.60E02 1.02E-04
6.....	...	...	...	...	...	2.46E-01 4.76E-06	2.62E00 2.84E-06	1.00E02 5.56E-05	3.02E00 5.26E-07
7.....	...	...	...	...	...	...	5.18E-01 5.98E-05	1.37E-03 1.33E-09	1.12E02 3.74E-05

The computed Einstein spontaneous emission coefficients  $A_{v'v''}$  ( $s^{-1}$ ) between various vibrational levels  $v'$  of the upper electronic state and  $v''$  of the lower electronic state and the corresponding oscillator strengths ( $f_{v'v''}$ ), without the inclusion of spin-orbit perturbational effects, which we discuss later in this section, are given in Table 5. It is evident from this table that the infrared bands of the  $A-X$  system of SiP species are expected to be relatively weak ( $f_{v'v''} \simeq 10^{-5}$ ).

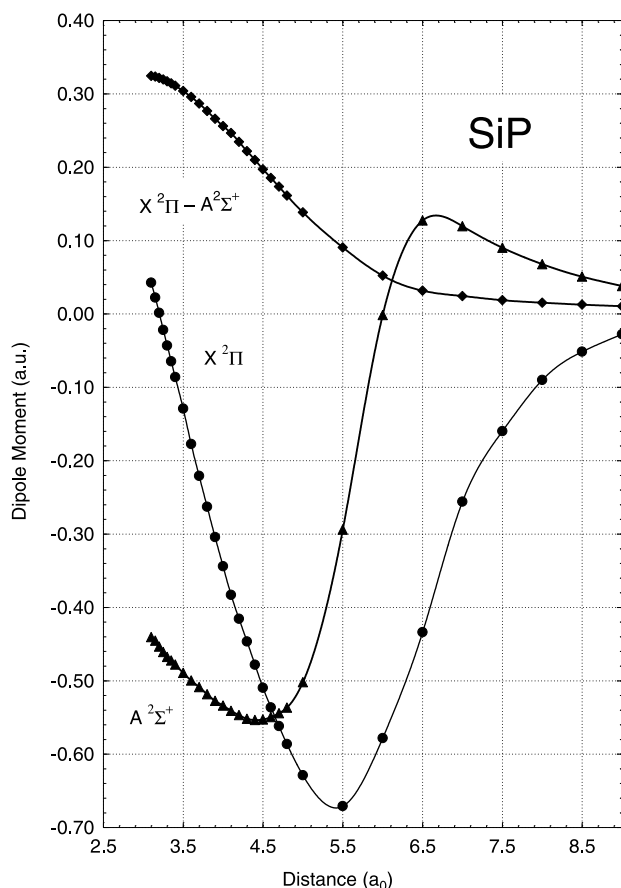


FIG. 3.—Calculated dipole moments and electronic transition moment of SiP as a function of the internuclear separation.

Values of radiative lifetimes ( $\tau_{v'}$ ) are displayed in Table 6. These lifetimes, defined as  $\tau_{v'}^{-1} = \sum_{v''} A_{v'v''}$ , decrease abruptly as  $v'$  increases from  $v' = 0$  to  $v' = 1$ , as expressed by the ratio  $\tau_1/\tau_0 = 0.074$ . It can also be rewritten as  $\tau_0^{-1} = A_{v',0}(1 + \sum_{v''=1} A_{v'v''}/A_{v',0})$ , and based on the  $A_{v'v''}$  data of Table 5, the ratio  $\tau_1/\tau_0$  can be reproduced by the product of the quotient  $A_{0,0}/A_{1,0} = 0.074$  and the ratio of terms written in brackets ( $=1$ ), so that the decrease of the radiative lifetime with increasing  $v'$  can be seen as essentially governed by the ratio  $A_{0,0}/A_{1,0}$ . Applying the Franck-Condon approximation  $A_{0,0}/A_{1,0} \simeq (v_{0,0}/v_{1,0})^3 \times (q_{0,0}/q_{1,0})$ , where  $v_{v',v''}$  is the energy difference and  $q_{v',v''}$  is the Franck-Condon factor, a ratio of  $A_{0,0}/A_{1,0} = 0.079 \times 0.88 = 0.070$  is obtained, in good agreement with the direct calculation of 0.074. These results show that the Franck-Condon factors and transition energies allow for a good estimation of the relative variation  $A_{0,0}/A_{1,0}$ , as well as of  $\tau_1/\tau_0$ . The latter parameter accounts for the 92% difference between the  $\tau_1$  and  $\tau_0$  lifetimes. For higher  $v'$ , this approximation turns out to be less reliable, and the proper ratio between the Einstein coefficients as given in Table 5 should be used as a measure of the relative intensities.

The computed Einstein spontaneous emission coefficients between various vibrational levels of the electronic ground state and the corresponding radiative lifetimes are contained in Table 7. The decrease of the lifetimes with an increase in  $v$  occurs more smoothly for the  $X^2\Pi$  state than

TABLE 6  
RADIATIVE LIFETIMES OF THE FIRST EXCITED STATE OF CN, CP, SiN, AND SiP

Lifetime	CN <sup>a</sup> (ms)	CP <sup>b</sup> (ms)	SiN <sup>c</sup> (ms)	SiP <sup>d</sup> (ms)
$\tau_0$ .....	$8.50 \times 10^{-3}$	$3.06 \times 10^{-2}$	1.4	80.0(138.4)
$\tau_1$ .....	$8.02 \times 10^{-3}$	$2.65 \times 10^{-2}$	0.63	6.0(7.4)
$\tau_2$ .....	$6.67 \times 10^{-3}$	$2.36 \times 10^{-2}$	0.40	2.6(3.0)
$\tau_3$ .....	$5.50 \times 10^{-3}$	$2.14 \times 10^{-2}$	0.029	1.5(1.7)

<sup>a</sup> Taherian & Slinger 1984.

<sup>b</sup> Gu et al. 1994.

<sup>c</sup> Borin & Ornellas 1997.

<sup>d</sup> This work. Values corrected for spin-orbit coupling are given in parentheses.

TABLE 7  
EINSTEIN COEFFICIENTS  $A_v^{v+k}$  AND RADIATIVE LIFETIMES  $\tau_v$  FOR THE VIBRATIONAL  
LEVELS OF THE  $X^2\Pi$  STATE OF SiP

$v$	$A_v^{v-1}$ ( $s^{-1}$ )	$A_v^{v-2}$ ( $s^{-1}$ )	$A_v^{v-3}$ ( $s^{-1}$ )	$A_v^{v-4}$ ( $s^{-1}$ )	$A_v^{v-5}$ ( $s^{-1}$ )	$\tau_v$ (s)
1.....	4.32E-01	...	...	...	...	2.32
2.....	2.74E-02	8.23E-01	...	...	...	1.18
3.....	8.27E-04	7.41E-02	1.19E-00	...	...	0.79
4.....	1.55E-04	4.72E-03	1.33E-01	1.54E-00	...	0.60
5.....	4.16E-06	2.13E-04	1.25E-02	2.06E-01	1.88E-00	0.48

for the  $A^2\Sigma^+$  one. Also, the lifetimes of the first excited electronic state are shorter than those of the ground state. This is partly due to the fact that the  $\Sigma \rightarrow \Pi$  transitions are statistically 2 times more probable than  $\Pi \rightarrow \Sigma$  transitions (Larsson 1983), so the decay of higher levels of the  $A^2\Sigma^+$  state into energetically lower lying vibrational levels of the  $X^2\Pi$  state are much more probable, in spite of the fact that the first vibrational level of the  $X^2\Pi$  state lies just  $111\text{ cm}^{-1}$  above the zeroth level of the  $A^2\Sigma^+$  state.

The calculated dipole moments as a function of the internuclear distance for the  $A^2\Pi$  and  $X^2\Sigma^+$  states are also listed in Table 1 and illustrated in Figure 3. As a general trend, the dipole moment for both states tends to zero at large internuclear distances, as is expected for neutral species. However, before reaching this limit, a significant change in the character of the dominant configuration state functions occurs, giving rise to the maximum and minima observed in Figure 3. The present study shows a charge polarity  $\text{Si}^+\text{P}^-$  in the ground state, except for distances smaller than  $3.20 a_0$ . The  $A^2\Pi$  state also possesses a  $\text{Si}^+\text{P}^-$  polarity, but for distances beyond  $5.9 a_0$  the polarity changes to  $\text{Si}^-\text{P}^+$ . Values of 1.12 D ( $\text{Si}^+\text{P}^-$ ) and 0.89 D ( $\text{Si}^+\text{P}^-$ ) calculated at the equilibrium bond lengths for the  $^2\Sigma^+$  and  $^2\Pi$  states, respectively, by Bruna et al. (1984), are about 20% overestimated relative to the results of this work. Between 3.0 and  $5.0 a_0$ , the dipole moment function for the ground state shows an almost linear behavior with a relatively steep slope compared with the corresponding function for the  $A^2\Pi$  state.

The intensity of rotational excitations is proportional to the square of the electric dipole moment. In the first excited state of SiP, the equilibrium dipole moment ( $-1.31$  D) is calculated to be larger than that of the ground state ( $-0.82$  D). For the  $A^2\Sigma^+$  state we predict that the line intensities are almost a factor of 3 larger. Based on these dipole moment values, both microwave and infrared spectra of the  $A^2\Sigma^+$  and  $X^2\Pi$  states should be of a moderate intensity. However, in the SiP ground state Franck-Condon region, the fundamental transitions should be quite strong as expected from the dipole moment function, which varies rather rapidly with the internuclear distance. In addition, the  $X^2\Pi$  state of SiP has an equilibrium dipole moment very similar in magnitude to that of the CP ground state ( $-0.86$  D) calculated by Rohlifing & Almlöf (1988), so that the astrophysical identification of this species via microwave spectroscopy may be possible. For the sake of completeness, we have also collected in Table 2 vibrationally averaged dipole moments for these two electronic states.

The results presented so far have been obtained within the Born-Oppenheimer approximation, but it would be elucidative also to take into account the effect of non-Born-Oppenheimer couplings on the energy and rates of

transition, since  $T_e$  is of the same order of magnitude as the vibrational spacings. Since in the context of this work spin-orbit couplings are expected to have a larger effect, we have displayed in Figure 4 the dependence of both diagonal and nondiagonal spin-orbit matrix elements on the internuclear distance and collected in Table 4 vibrationally averaged values of the spin-orbit coupling constant ( $A_v$ ). As in the limit of large internuclear distances the diagonal matrix element is equal to one-third the coupling constant of atomic silicon (Palmieri et al. 1998), and in the absence of any experimental result for comparison, it is comforting to verify that our first-order correction of  $62.78\text{ cm}^{-1}$  for this limit is in good agreement with the experimental value of  $77.15\text{ cm}^{-1}$  for Si (Moore 1971). As shown in Table 4, the spin-orbit coupling constant turns out to be negative, implying an inverted  $^2\Pi_i$  state with a positive shift in the energy of the  $\Omega = \frac{1}{2}$  component. Since only the  $^2\Pi$  state is affected, this coupling results in a decrease of the excitation energy, thus decreasing the emission rate, which depends on the third power of the excitation energy, with a consequent increase in the radiative lifetime. The effect of this coupling is very significant for  $v' = 0$  ( $\tau_0 = 138\text{ ms}$ ) but decreases as  $v'$  increases with values of 7.4, 3.0, 1.7, 1.2, 0.86, 0.68, 0.56, and 0.48 ms for  $v' = 1-8$ , respectively. From the experimental side, the long radiative lifetime, the small  $T_e$ , and the large difference in internuclear distance suggest that absorption

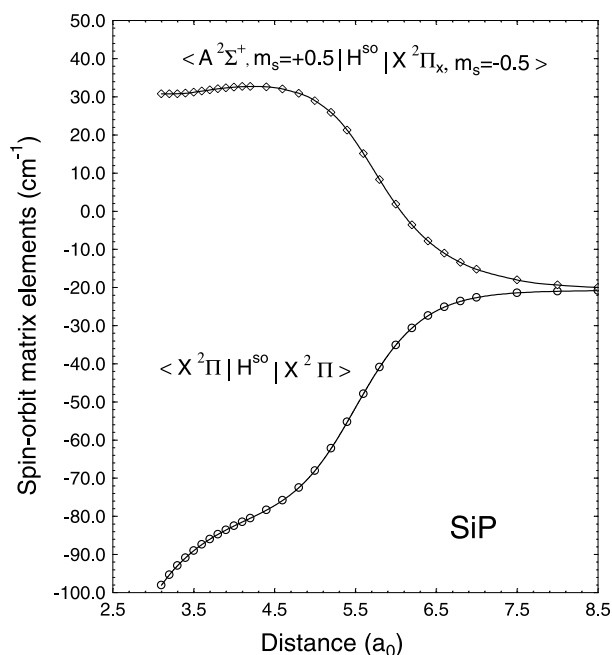


FIG. 4.—Spin-orbit matrix elements of SiP as a function of the internuclear separation.

studies would likely be more appropriate to characterize these two low-lying states. In fact, the anion  $\text{Si}_2^-$ , isoelectronic to SiP and with very similar potential energy curves, has been the subject of absorption studies (Liu & Davies 1996) and treated theoretically by Palmieri et al. (1998), but, to the best of our knowledge, no radiative lifetimes have been reported. For AIB, a system for which the  $A^2\Pi-X^2\Sigma^+$  separation has been calculated to be  $523\text{ cm}^{-1}$ , at a similar level of theory,  $\tau_0$  (within the Born-Oppenheimer approximation) has been estimated to be 210 ms (Bauschlicher & Langhoff 1994), a result comparable with our uncorrected value of 80 ms.

#### 4. COMPARISON WITH THE ISOVALENT MOLECULES CN, CP, AND SiN

In the absence of experimental data for SiP, it is of interest to compare the spectroscopic properties of this molecule with the isovalent CP, CN, and SiN species. These molecules contain nine valence electrons, but SiP has a  $^2\Pi$  ground electronic state instead of the expected  $^2\Sigma^+$  state, which is the ground state of CN, SiN, and CP. According to Bruna et al. (1984), the difference in ground-state configuration between first- and second-row diatomics is due to the relative stabilities of their  $\pi$  and  $\sigma$  orbitals and their respective electron occupation. Thus, for CN, SiN, and CP, the  $\pi$  orbital is preferred and fills first, resulting in a  $\dots\sigma\pi^4$  configuration. For higher row diatomics, the energetic order of the orbitals is reversed, the configuration with the  $\sigma$  orbital doubly occupied,  $\dots\sigma^2\pi^3$ , turns out to be more stable.

Experimentally, spectroscopic data are available for the  $X^2\Sigma^+$  and  $A^2\Pi$  states of the isovalent CN, CP, and SiN molecules (e.g., Huber & Herzberg 1979; Yamada et al. 1988; Ram, Tam, & Bernath 1992). Compared with the molecules CN ( $D_e = 7.89\text{ eV}$ ), CP ( $5.36\text{ eV}$ ), and SiN ( $4.57\text{ eV}$ ), the species SiP shows the weakest bond ( $D_e = 3.64\text{ eV}$ ) in its ground state.  $T_e$  values also follow a decreasing trend, i.e., CN ( $9245\text{ cm}^{-1}$ ), CP ( $6973\text{ cm}^{-1}$ ), SiN ( $2032\text{ cm}^{-1}$ ), and SiP ( $470\text{ cm}^{-1}$ ), as well as the harmonic frequencies for the ground state ( $w_e$ ), i.e., CN ( $2069\text{ cm}^{-1}$ ), CP ( $1240\text{ cm}^{-1}$ ), SiN ( $1151\text{ cm}^{-1}$ ), and SiP ( $608\text{ cm}^{-1}$ ). In the first excited state, there is a corresponding decrease in  $w_e$  of  $256\text{ cm}^{-1}$  in CN,  $177\text{ cm}^{-1}$  in CP, and  $120\text{ cm}^{-1}$  in SiN relative to the ground state values and a corresponding increase of  $53\text{ cm}^{-1}$  for SiP. The equilibrium internuclear distances clearly reflect the relative atomic radius, that is, CN ( $1.172\text{ \AA}$ ), CP

( $1.562\text{ \AA}$ ), SiN ( $1.572\text{ \AA}$ ), and SiP ( $2.089\text{ \AA}$ ). In the first excited state, the increase in  $r_e$  relative to that of the ground state is  $0.061\text{ \AA}$  in CN,  $0.092\text{ \AA}$  in CP, and  $0.064\text{ \AA}$  in SiN, except for SiP, in which  $r_e$  decreases by  $0.087\text{ \AA}$ .

In Table 6, we also compare radiative lifetimes for the CP, CN, and SiN molecules (Gu, Bunker, & Hirsch, 1994; Taherian & Slinger 1984; Borin & Ornellas 1997) with that of SiP obtained in the present work. We note that only for CN are the data determined experimentally and the calculated values for this species were found to be about 30% longer than those measured experimentally (e.g., Lu, Huang, & Halpern 1992). The radiative lifetimes for different vibrational levels of the first excited state of the SiP exhibited the same trend as those for the other molecules, decreasing with increasing vibrational levels, but does so much more rapidly. Clearly, vibrationally excited SiP molecules are predicted to live longer than the other isovalent species, a reflection of the much smaller excitation energy  $\nu_{0,0}$  of SiP ( $494\text{ cm}^{-1}$  for SiP vs.  $2057\text{ cm}^{-1}$  for SiN, for example).

#### 5. CONCLUSION

This work reports, for the first time, transition probabilities, Franck-Condon factors, oscillator strengths, and transition moments for the  $A^2\Sigma^+-X^2\Pi$  system, as well as electric dipole moment functions and radiative lifetimes for the ground  $X^2\Pi$  and excited  $A^2\Sigma^+$  states of SiP. The calculated radiative lifetimes for the  $A$  state lie between 138 ms at  $v' = 0$  and  $0.48\text{ ms}$  at  $v' = 8$ , with the spin-orbit correction, and for the  $X$  state, between  $2.32\text{ s}$  at  $v'' = 1$  and  $0.48\text{ s}$  at  $v'' = 5$ . It is found that the  $A^2\Sigma^+-X^2\Pi$  system has a very weak infrared spectrum, while the microwave and infrared spectra of each separate state should be of a moderate intensity. It is hoped that the present work will stimulate future experimental investigations on the SiP species.

C. M. A. is thankful to FAPESP for financial support under contracts Nos. 97/01648-2 and 98/01648-2. F. R. O. acknowledges the continuous academic support of Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). The authors are also grateful to the Laboratório de Computação Científica Avançada (LCCA) of the University of São Paulo for the computational facilities.

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