

Theoretical Study of the C³Π–X³Π Transition in CSi

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The radiative lifetimes of the C³Π–X³Π transition of the CSi radical have been calculated from highly correlated electronic wavefunctions and compared with available experimental data. For this transition, the Franck-Condon approximation fails due to the strong *R*-dependency of the transition moment function.

The CSi radical, which is of considerable astrophysical interest, was found in the circumstellar shell of the carbon star IRC + 10216 [1]. Theoretical investigation of the molecular evolution in interstellar matter predicted this species to be an abundant component in dense clouds [2]. During the last two decades the electronic structure of the low-lying states of CSi had been subject of several ab initio studies [3–13]. Its ground state was found to be X³Π, followed by A³Σ[–] and a¹Σ⁺. The first vibrational wavefunctions and Franck-Condon factors for the C³Π–X³Π transition were calculated by Larsson [7] using CASSCF-CI potentials. Langhoff et al. [13] reported the first dipole moment functions for the X³Π and A³Σ[–] states and the first transition moment function for the A³Σ[–]–X³Π transition. The first experimental observation of CSi was accomplished by Bernath et al. [10], who detected the d¹Σ⁺–b¹Π electronic transition. A detailed study of the X³Π ground state was reported by Cernicharo et al. [1], who measured the millimeter-wave spectrum. Mollaaghababa et al. [14] measured the rotational spectra of ¹³CSi and vibrationally excited CSi in the X³Π state. The A³Σ[–]–X³Π transition was observed by Brazier et al. [15]. The C³Π–X³Π transition was detected by Ebben et al. [16, 17]. They found that the *v*'-dependence of the measured transition probabilities cannot be explained by using the calculated Franck-Condon factors of Larsson [7]. Experimental spectroscopic constants of the X³Π and C³Π states have been reported by Butenhoff et al. [18], who also measured the C³Π–X³Π transition. The purpose of the present investigation was to investigate the *v*'-dependence of the radiative lifetimes of the C³Π state using the CASSCF-CI transition moment function.

The computations have been performed with the MOLPRO code [19]. For a detailed description of the computational procedures we refer to the previous works [20–25]. The basis set for carbon was the (13s8p) set of van Duijneveldt [26] contracted to [8s5p] and augmented by (3d2f1g) functions. For silicon we used a (17s12p) set of Partridge [27] contracted to [11s8p] and augmented by (4d2f1g) functions. The d function exponents were 1.848, 0.649 and 0.228 for carbon and 2.1, 0.9, 0.4 and 0.15 for silicon. The exponents of the f functions were 1.419 and 0.485 for carbon and 1.6 and 0.55 for silicon. The g function exponents were 1.011 for carbon and 1.1 for silicon. In the CASSCF calculations all valence orbitals were active, which led to CASSCF expansions of 592 CSFs. A state averaged procedure [28] was used in each spin symmetry in order to simplify the calculation of the electronic transition moment. In the CASSCF-CI procedure all single and double excitations of the valence MOs were taken into account. Only the configurations with two

Table 1. CASSCF and CASSCF-CI potential energy functions (all values in a.u.).

R	X ³ Π		C ³ Π	
	CASSCF	CASSCF-CI	CASSCF	CASSCF-CI
2.8	–326.662325	–326.824471	–326.540562	–326.702634
3.0	–326.700262	–326.859930	–326.582256	–326.740712
3.1	–326.709642	–326.868226	–326.594000	–326.750943
3.2	–326.714413	–326.872020	–326.601772	–326.757584
3.3	–326.715615	–326.872338	–326.606739	–326.761959
3.4	–326.714104	–326.870009	–326.609703	–326.764880
3.5	–326.710566	–326.865703	–326.611140	–326.766634
3.6	–326.705534	–326.859954	–326.611333	–326.767266
3.7	–326.699422	–326.853186	–326.610487	–326.766825
3.8	–326.692553	–326.845731	–326.608785	–326.765439
4.0	–326.677515	–326.829746	–326.603525	–326.760482
4.5	–326.639241	–326.790278	–326.586793	–326.742535
5.0	–326.607286	–326.757972	–326.575703	–326.727426

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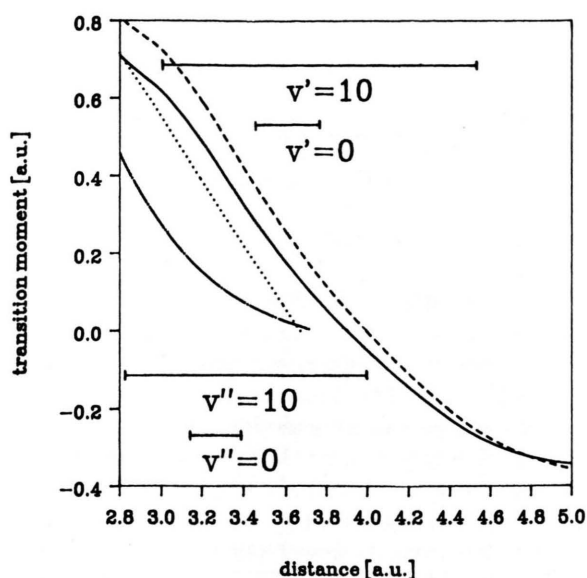


Fig. 1. CASSCF (broken line), CASSCF-CI (full line) and empirical transition moment functions for the $C^3\Pi-X^3\Pi$ transition of CSi. The linear and exponential forms used by Ebben *et al.* [17] are also depicted.

electrons in the external MO space were contracted. Vibrational wavefunctions and the radiative lifetimes were obtained from the CASSCF-CI potentials and the transition moment function using the Numerov approach [29].

The CASSCF-CI potentials and transition moment functions are listed in Tables 1 and 2. The dominating configuration in the $X^3\Pi$ wavefunction is $5\sigma^2 6\sigma^2 7\sigma 2\pi^3$. The $C^3\Pi$ state is a strong mixture of several configurations with nearly equal weight build up by different occupation of the 6σ , 7σ , 2π and 3π MOs [7]. In Table 3, the CASSCF-CI spectroscopic constants are compared with available experimental data. The CASSCF-CI equilibrium distances are too long by $0.006 \text{ \AA}$ for the ground state and too short by $0.100 \text{ \AA}$ for the excited state. In the calculations of the vibrationally averaged transition moments, the potential energy functions have been shifted to their experimental equilibrium distance. The T_e excitation energy has been calculated to be higher than the experimental value by 281 cm^{-1} . In the calculation of the radiative lifetimes the experimental T_e value was used.

The transition moment function of the $C^3\Pi-X^3\Pi$ transition decreases strongly with increasing R (Fig-

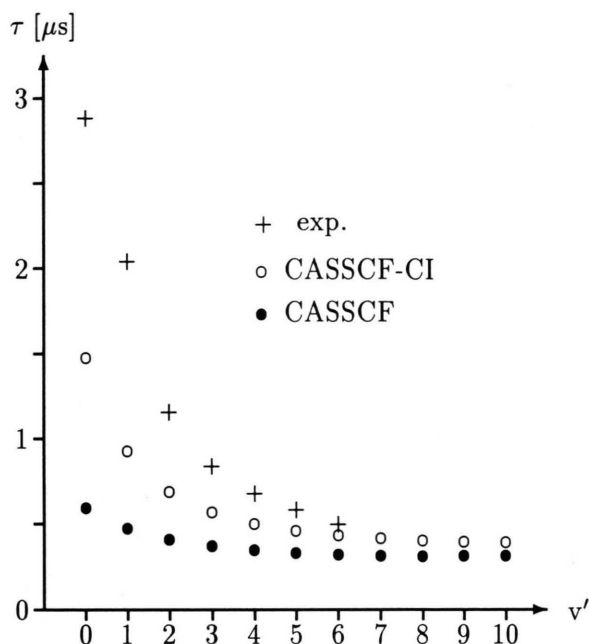


Fig. 2. Comparison of the theoretical and experimental radiative lifetimes.

R	CASSCF	CASSCF-CI
2.8	0.8087	0.7102
3.0	0.7234	0.6167
3.1	0.6635	0.5566
3.2	0.5907	0.4860
3.3	0.5073	0.4067
3.4	0.4191	0.3245
3.5	0.3330	0.2461
3.6	0.2532	0.1750
3.7	0.1806	0.1112
3.8	0.1142	0.0531
4.0	-0.0045	-0.0512
4.5	-0.2452	-0.2619
5.0	-0.3563	-0.3435

Table 2. CASSCF and CASSCF-CI transition moment functions of the $C^3\Pi-X^3\Pi$ transition (all values in a.u.).

Table 3. Comparison of theoretical and experimental spectroscopic constants.

State		Experiment		Theory
		Ref. [17]	Ref. [18]	This work
$X^3\Pi$	$R_e [\text{\AA}]$		1.7182	1.7248
	$\omega_e [\text{cm}^{-1}]$	964.6	965.16	962.2
$C^3\Pi$	$R_e [\text{\AA}]$		1.919	1.909
	$\omega_e [\text{cm}^{-1}]$	616.38	615.72	580.3
	$T_e [\text{cm}^{-1}]$	22 356.96	22 830.4	23 111

ure 1). This is the reason why the Franck-Condon factors alone cannot explain the observed relative intensities for this transition [17]. Ebben, Drabbles and ter Meulen [17] used a linear and exponential forms of the transition moment functions to describe the detected emission intensity ratios. Both functions are also displayed in Figure 1. Since they are valid only for the positive values of the transition moment, they do not cover the whole region of internuclear distances between the classical turning points of $v''=0$ and $v'=0$ (cf. Figure 1). A comparison of the CASSCF and CASSCF-CI transition moment functions shows that the electron correlation lowers the transition mo-

ment. Since the correlation contribution has not been completely accounted for in our best CASSCF-CI transition moment function, the calculated lifetimes are somewhat too small if compared with experiments (cf. Table 4 and Figure 2). Their dependence on v' , however, has been reproduced correctly. In independent calculations [30] we have shown that the emission into the $B^3\Sigma^+$ and $A^3\Sigma^-$ states is much weaker; the inclusion of these transitions in the calculations of the radiative lifetimes decreases the lifetimes of the vibrational states in the $C^3\Pi$ state by less than $0.07\ \mu\text{s}$. From these results we expect that the CASSCF-CI electronic transition moment function, which changes sign at about 4 bohr, has the correct shape for the region of internuclear distances of present interest, but the absolute values of the transition moment are probably too large by about 0.05 a.u. Values of the calculated Franck-Condon factors and rates of spontaneous emission for the $C^3\Pi-X^3\Pi$ transition are given in Table 5.

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Table 4. Radiative lifetimes of the $C^3\Pi-X^3\Pi$ -transition [μs].

v'	CASSCF	CASSCF-CI	Exp. values [17]
0	0.591	1.472	2.886
1	0.473	0.925	2.046
2	0.408	0.688	1.160
3	0.369	0.568	0.824
4	0.345	0.499	0.681
5	0.329	0.457	0.584
6	0.318	0.430	0.499
7	0.312	0.413	
8	0.309	0.401	
9	0.310	0.394	
10	0.312	0.390	

Table 5. Franck-Condon factors and Einstein coefficients for the $C^3\Pi-X^3\Pi$ transition.

v'	Franck-Condon factors Einstein coefficients [s^{-1}]									
	v''	0	1	2	3	4	5	6	7	8
0		5.27-2	1.49-1	2.23-1	2.27-1	1.72-1	1.02-1	4.81-2	1.84-2	5.75-3
		1.33+5	2.18+5	1.84+5	9.91+4	3.59+4	8.30+3	9.62+2	6.88+0	4.07+1
1		1.69-1	1.95-1	6.83-2	1.10-4	6.19-2	1.45-1	1.58-1	1.12-1	5.78-2
		5.69+5	3.82+5	7.43+4	2.47+2	2.19+4	2.25+4	8.50+3	1.03+3	1.99+1
2		2.56-1	5.69-2	1.86-2	1.10-1	7.16-2	1.60-3	4.08-2	1.23-1	1.43-1
		1.13+6	1.38+5	3.47+4	1.03+5	3.49+4	2.59+2	4.68+3	4.03+3	4.01+2
3		2.41-1	5.00-3	1.13-1	3.32-2	1.61-2	9.01-2	5.36-2	2.40-5	5.10-2
		1.39+6	2.63+4	2.47+5	3.79+4	1.39+4	3.60+4	9.69+3	9.79-2	9.02+2
4		1.59-1	9.94-2	5.63-2	2.01-2	8.36-2	1.09-2	3.06-2	8.40-2	2.95-2
		1.19+6	5.06+5	1.48+5	4.18+4	8.57+4	5.14+3	1.01+4	1.14+4	1.32+3
5		7.91-2	1.75-1	3.93-4	8.85-2	8.92-3	4.37-2	5.80-2	2.60-5	5.44-2
		7.70+5	1.12+6	5.59+3	2.10+5	9.32+3	3.91+4	2.53+4	4.97+0	5.39+3
6		3.06-2	1.59-1	6.53-2	4.06-2	3.09-2	5.52-2	1.49-3	6.29-2	2.53-2
		3.88+5	1.29+6	3.75+5	1.11+5	6.78+4	5.99+4	1.71+3	2.26+4	3.85+3
7		9.37-3	9.65-2	1.41-1	7.16-4	7.42-2	1.69-4	5.75-2	1.58-2	2.48-2
		1.56+5	1.01+6	9.84+5	9.22+3	1.88+5	1.15+1	5.47+4	6.97+3	7.46+3
8		2.26-3	4.37-2	1.43-1	5.63-2	2.64-2	4.10-2	2.80-2	1.90-2	4.83-2
		5.05+4	5.91+5	1.26+6	3.54+5	7.33+4	9.51+4	3.08+4	1.63+4	1.90+4

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