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Singlet−Triplet Gap, and the Electronic and Vibrational Spectra of Chlorophenylcarbene: A Combined Theoretical and Experimental Study

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Minimum energy structures of singlet and triplet chlorophenylcarbene, a prototypical carbene, were computed. The singlet−triplet energy separation was predicted to be 7.84 and 7.70 kcal/mol at the UCCSD(T)/6-31+G* and QCISD(T)/6-31+G** levels of theory, respectively, after zero-point correction. This is slightly larger than that predicted by the CAS(6,6) (4.5 kcal/mol), local spin density approximation (5.6 kcal/mol), and the BLYP (7.3 kcal/mol) methods with the 6-31G* basis set reported by Trindle et al. The UV−vis and IR spectra of chlorophenylcarbene were analyzed with the aid of the CASPT2/CASSCF(10,10) and the B3LYP/6-31G* levels of theory, respectively. The UV−vis and IR spectra of chlorophenylcarbene were assigned on the basis of these calculations. The *ab initio* calculations predicted the existence of strong absorption bands in the UV and a weak band in the visible in good agreement with published spectra. The long (750 nm) wavelength band corresponds to electron promotion from the lone pair σ (HOMO) to the π^* (LUMO). On the basis of the calculated harmonic frequencies, we cannot assign the 1244 and 1600 cm^{-1} IR bands observed in an argon matrix to chlorophenyl carbene. The most intense IR band (1225 cm^{-1}) corresponds to the symmetric C−C stretch of the carbene and aromatic carbon. The asymmetric and symmetric C−C−Cl stretches are assigned to the bands observed at 847 and 739 cm^{-1}, respectively.

I. Introduction

Knowledge of the kinetics and mechanisms of carbene reactions with various functional groups has advanced over the past 20 years. Laser flash photolysis (LFP) studies performed in several laboratories have played an important role in this field, and rate constants and activation thermodynamic properties have been reported.[1−16] These data were obtained by time-resolved absorption spectroscopy, which followed the rate of carbene decay as a function of concentration of various quenchers. Thus, the electronic spectrum of the carbenes is vitally important to correctly identify carbene intermediates and to determine their kinetics. In some situations the carbene does not present strong absorption bands and cannot be observed. In these cases the pyridine probe technique[17] has been utilized.[1−4,8,11] In addition to experimental studies, *ab initio* calculations have become an important tool to predict and understand carbene reactivity.[18−29]

Carbenes are usually generated in a closed shell singlet state upon photolysis of a photochemical precursor.[1,11,30,31] While many carbenes have singlet ground states, several others have triplet multiplicity in their lowest electronic state. In the latter case, fast intersystem crossing (ISC) of the singlet to the triplet state can take place.[32] Singlet and triplet carbenes have very different reactivity patterns and may generate distinct products upon reaction with the same compound.[33,34] For example, triplet carbenes react rapidly with oxygen and generate carbonyl oxides, while the singlet carbenes react slowly, if at all. In addition, when the singlet−triplet gap is small, both states may be in thermal equilibrium, which may result in the formation of products derived from both singlet and triplet states. Thus, the chemistry of a specific carbene is dependent on its singlet−triplet gap.[34]

Chlorophenylcarbene is one of the most thoroughly studied of all carbenes by experimental methods, and its spectroscopy[35] as well as its reaction kinetics with olefins,[36] carbonyl compounds,[37] alcohols,[16] and organic halides[38] have been reported. In the LFP studies, the rate of carbene decay was determined by monitoring the change in absorption around 320 nm. The attribution of this absorption band to this carbene was made by Turro et al.,[36a] upon photolysis of the corresponding diazirine at 77 K in a 3-methylpentane glass. Two persistent absorption maxima were observed in the low-temperature matrix at 282 and 308 nm, the latter being the most intense. Zuev and Sheridan discovered that this carbene has a weak broad absorption band between 600 and 850 nm ($\lambda_{max} = 750$ nm) in a nitrogen matrix.[39] Chlorophenylcarbene has also been prepared in an argon matrix at 10 K and its infrared spectrum has been recorded.[36b,39] The absence of an EPR signal from matrix-isolated samples indicated that this carbene has a singlet ground state, a conclusion corroborated by the stereospecificity of its reaction with olefins and by the fact that this carbene reacts slowly with oxygen.[36] Nevertheless, its singlet−triplet gap is unknown, and no reliable theoretical study of its electronic and vibrational spectra has yet been reported. In this work, we report new experimental results and high-level *ab initio* calculations of the electronic and vibrational spectra of chlorophenylcarbene. In addition, the

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singlet−triplet gap of chlorophenylcarbene has been predicted by advanced *ab initio* methodology.

II. Experimental Section

Matrix Isolation Spectroscopy. A gaseous mixture of chlorophenyldiazirine and argon was directly deposited on the surface of a CsI window of a closed-cycle cryogenic system cooled by helium (Air Products). The argon matrix formed was maintained at 14 K during the entire experiment. The UV/vis spectrum was measured with a Lambda 6 UV/vis spectrophotometer, and the IR spectrum was recorded with an FT-IR 2000 Perkin-Elmer spectrometer with 2 cm^{-1} resolution. Ray-o-Net 350 nm lamps were used to photolyze the sample and the resulting IR and UV/vis spectra were recorded at the same time in each step.

***Ab Initio* Calculations.** The geometries of the electronic states of chlorophenylcarbene were fully optimized at the HF, CASSCF(6,6), MP2,[40] and B3LYP[41] levels of theory using the 6-31G* basis set. For the triplet state, unrestricted UHF, UMP2, and UB3LYP methods were utilized. Planar C_s symmetry was maintained during the optimizations of both electronic states. The harmonic frequencies were calculated at the HF/6-31G*, MP2/6-31*, and B3LYP/6-31G* levels of theory and no imaginary frequencies were found. The restricted open shell MP2 (ROMP2) method[40] was employed with the single-point energy calculations of the triplet carbene due to high spin contamination of the UMP2 wave function ($\langle S^2 \rangle = 2.43$). Higher order coupled cluster with singles, doubles, and perturbative inclusion of triples excitations (UCCSD(T) and QCISD(T)), were performed with a more extended basis set of 6-31+G* and 6-31+G**. Additional basis set effects with 6-311G(2df,p) were performed with an additivity approximation for the correlation energy. The results are given in Table 1.

To study the electronic spectrum, we have used the CASSCF-(6,6) and MRMP2 method[42,43] in conjunction with the 6-31G* basis set, as well as CASSCF(10,10) and CASPT2 procedures using the ANO-S basis set, C and Cl with [4s3pld] and H[2slp]. The CASSCF calculations were performed by state-average orbital optimizations with equal weight for the three lowest states of each symmetry species. The multireference perturbations also were performed using these CASSCF wave functions. The results are given in Table 2. The MP2, B3LYP, QCISD(T), and CCSD(T) calculations were performed using the GAUSSIAN 94 program,[44] and for the CASSCF(6,6) and MRMP2 calculations, we have used the GAMESS program.[45] The CASSCF-(10,10) and CASPT2 calculations were performed with the MOLCAS program.[46]

III. Results and Discussion

Chlorophenylcarbene has been previously studied by *ab initio* methods by Trindle, Datta, and Mallik.[47] This group found that the singlet carbene is planar. The singlet−triplet energy gap was predicted to be 4−7 kcal/mol depending on the theoretical level, and the singlet state was the ground state at the CAS-(6,6)/6-31G*, LSDA/6-31G*, and BLYP/6-31G* methods.[47] Planar chlorophenylcarbene was calculated in this work with maintenance of C_s symmetry. The singlet state carbene is a minimum on the carbene potential energy surface as confirmed by the frequency calculations and has a lower energy than the triplet state. Figure 1 shows the structure and some geometrical parameters, which are not significantly affected by the levels of theory used in this work. The singlet is computed to have longer C(ring)−C(carbenic center) and C−Cl bond lengths than the triplet, while the C−C−Cl angle in the triplet carbene is greater by about 20° in our work. This pattern of geometric characteristics has been observed for other carbenes. For example, an MRSDCI/DZ+P(d) calculation[48] predicts that dichlorocarbene in the singlet state has $R(\mathrm{C-Cl}) = 1.716$ Å and $\theta(\mathrm{Cl-C-Cl}) = 109.5°$, while the triplet state has $R(\mathrm{C-Cl}) = 1.695$ Å and $\theta(\mathrm{Cl-C-Cl}) = 125.7°$. In the case of phenylcarbene, the BLYP/6-31G* method predicts a $\theta(\mathrm{C-C-H})$ angle of 105.9° and 134.9° for singlet and triplet states, respectively.[49] Because hydrogen is smaller than chlorine and is less electronegative,[50] singlet phenylcarbene can have a smaller bond angle than chlorophenyl carbene by 6°−7°.

TABLE 1: Triplet−Singlet Energy Gap of Phenylchlorocarbene[a]

	triplet−singlet energy gap, kcal/mol
At MP2/6-31G Geometry	
UMP2/6-31G	21.16
PMP2/6-31G	3.39
UCCSD(T)/6-31G	4.70
At MP2/6-31G* Geometry	
UMP2/6-31G*	25.34
PMP2/6-31G*	8.35
ROMP2/6-31G*	5.23
ROMP2/6-311G(2df,p)	7.17
UCCSD(T)/ 6-31G*	8.00
UCCSD(T)/6-311G(2df,p)[b]	9.94
AZPE[c]	1.51
Δ*E*[d]	11.45
At B3LYP/6-31G* Geometry	
UB3LPY/6-31G*	4.59
ROMP2/6-31G*	4.08
UB3LYP/6-311G(2df,p)	4.88
UB3LYP/6-311+G(2df,p)	5.18
UCCSD(T)/6-31G*	6.50
UCCSD(T)/6-31+G*	8.11
QCISD(T)/6-31+G**	7.97
UCCSD(T)/6-311G(2df,p)[e]	6.88
ΔZPE[c]	−0.27
Δ*E*[f]	6.61
At 6-31G* Basis Set[g]	
CASSCF(6,6)	4.5
LSDA	5.6
BLYP	7.3

[a] The geometries were obtained at the MP2/6-31G* and B3LYP/6-31G* levels of theory. [b] Obtained by additivity approximation: Δ*E*[UCCSD(T)/6-311G(2df,p)] = Δ*E*[UCCSD(T)/6-31G*] + Δ*E*[ROMP2/6-311G(2df,p)] − Δ*E*[ROMP2/6-31G*]. [c] Unscaled zero-point energy. [d] Δ*E*[UCCSD(T)/6-311G(2df,p)] + ΔZPE(UMP2/6-31G*). [e] Obtained by additivity approximation: Δ*E*[UCCSD(T)/6-311G(2df,p)] = Δ*E*[UCCSD(T)/6-31G*] + Δ*E*[UB3LYP/6-311G(2df,p)] − Δ*E*[UB3LYP/6-31G*]. [f] Δ*E*[UCCSD(T)/6-311G(2df,p)] + ΔZPE (UB3LYP/6-31G*). [g] Trindle, C.; Datta, S. N.; Mallik, B. *J. Am. Chem. Soc.* **1997**, *119*, 12947−12951.

The energy of singlet and triplet chlorophenylcarbene was calculated at the B3LYP/6-31G* level as a function of carbene bond angle. The bond lengths to the carbene center, along with the geometry within the phenyl ring, were kept constant. The results are shown in Figure 2. It indicates that the bond angle plays a very important role in the relative energies of singlet and triplet states. The singlet carbene is higher in energy than the triplet when the bond angle is greater than ~125°. When the bond angle is less than the 125°, the singlet is the ground state.

Triplet−Singlet Energy Gap. The results of triplet−singlet energy gap calculations of chlorophenylcarbene are given in Table 1. When the optimized geometry of MP2/6-31G* is employed, the energy values show a great dependence on the computational methods mainly due to the high spin contamina-

TABLE 2: Calculated IR Frequencies and Those Observed in an Argon Matrix

freq	predicted freq[a] (cm^{-1})	I^b	obsd freq (cm^{-1}) this work	obsd freq (cm^{-1}) ref 36c	
1	64	1.40			
2	193	0.09			
3	211	4.78			
4	344	9.64			
5	402	0.00			
6	451	0.00			
7	560	26.30	568(s)	563(m)	
8	603	4.19	608(w)		
9	668	23.40	676(s)	671(s)	
10	705	147.38	739(s)	744(s)	C−C−Cl sym str
11	760	39.50	765(s)	761(s)	
12	827	60.52	847(s)	840(s)	C−C−Cl asym str
13	840	0.02			
14	947	2.06			
15	967	0.12			
16	984	3.77	949(w)		
17	989	0.00			
18	1019	0.44			
19	1081	1.44			
20	1159	4.92	994(w)	995(w)	
21	1167	92.08	1170(s)	1168(s)	
22	1212	195.18	1225(s)	1222(s)	C(ring)−C (carbene) str
23	1299	18.79	1305(w)	1301(w)	
24	1332	16.06	1321(w)	1318(w)	
25	1441	23.06	1445(m)	1440(m)	
26	1475	7.73	1480(w)	1477(w)	
27	1570	0.26			
28	1596	73.12	1588(s)	1582(s)	phenyl ring deformation
29	3092	0.72			
30	3104	11.11			
31	3112	13.56			
32	3124	8.64			
33	3125	7.06			

[a] The calculated frequencies at B3LYP/6-31G* with scaled factor 0.97. [b] The calculated intensities.

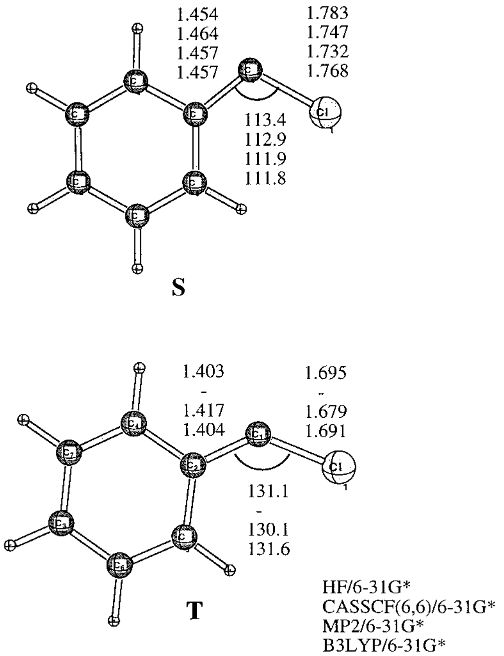

Figure 1. Geometries of chlorophenylcarbene in the lowest singlet and triplet electronic states. The geometric parameters and the level of theory used are indicated.

tion of the UMP2 wave function ($\langle S^2 \rangle = 2.43$) in the triplet case. Using the 6-31G* basis set, the UMP2 calculation predicts a triplet−singlet separation of 25.34 kcal/mol, while the projected MP2 (PMP2) calculation predicts a value of 8.35 kcal/mol, in agreement with the 5.23 kcal/mol value obtained using the restricted open shell ROMP2 method and 4.59 kcal/mol separation obtained at the B3LYP/6-31G* (positive numbers indicate that the singlet is the ground state).

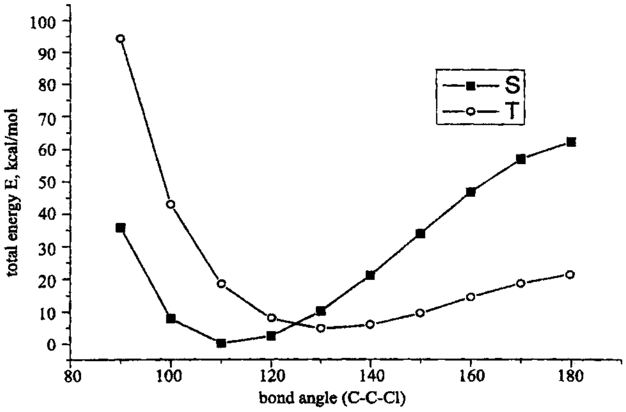

Figure 2. Total energy of singlet and triplet chlorophenylcarbene as a function of bond angle at the carbene center calculated at the B3LYP/6-31G* level. The carbene geometry was held constant except the bond angle of C−C−Cl.

In order to avoid the high spin contamination of the UMP2 wave function, the optimized B3LYP/6-31G* geometry was used to determine the energy gap (see Table 1). The triplet and singlet energy gap at the B3LYP level has no significant change with 6-31G*, 6-311G(2df,p), and 6-311+G(2df,p) basis sets. However, we found the energy gap has a large difference at the same theoretical level when the MP2/6-31G* and B3LYP/6-31G* geometries are used. The energy gap between the triplet and singlet carbene with the B3LYP/6-31G* geometry is 1.50 kcal/mol lower than that with the geometry of MP2/6-31G* at UCCSD(T)/6-31G* level while it is 1.15 kcal/mol smaller at the ROMP2/6-31G* level. This difference can be attributed to the high spin contamination of the UMP2 method which can overestimate the triplet energy.

The higher level UCCSD(T)/6-31G* calculation predicts a value of 8.00 kcal/mol using the MP2/6-31G* geometries. With the more extended 6-311G(2df,p) basis set and the additivity approximation, the gap increases to 9.94 kcal/mol. Zero-point energy correction increases the triplet energy by 1.51 kcal/mol in relation to the singlet, and the adiabatic triplet−singlet gap with the geometry of MP2/6-31G* becomes 11.45 kcal/mol.

Using the B3LYP/6-31G* geometries, the triplet and singlet energy gap with the more extended 6-311G(2df,p) basis set and the additivity approximation, plus zero-point energy correction, is 6.61 kcal/mol. When the double zeta basis sets including polarization and diffuse function were utilized, the QCISD(T) and CCSD(T) methods predicted a similar energy gap of 7.84 and 7.70 kcal/mol including the zero-point vibration energy correction of −0.27 kcal/mol. We consider this value of 7.84 kcal/mol to be our best prediction for triplet and singlet energy gap.

This value can be compared with other carbenes that contain phenyl and chlorine substituents such as HCCl, CCl_2, and PhCH; thus we can evaluate the effect of each substituent on the triplet−singlet gap. Methylene is the parent carbene, and its triplet−singlet gap is −9.1 kcal/mol (the negative sign denotes a triplet ground state).[51] The substitution of one H by Cl (HCCl) increases this value to 6.0 kcal/mol,[52] and substitution by two chlorines (CCl_2) results in a triplet−singlet gap of 20.9 kcal/mol.[52] On average, each chlorine atom increases the stability of the singlet in relation to the triplet by 15 kcal/mol. The phenyl group also preferentially stabilizes the singlet, but its effect is

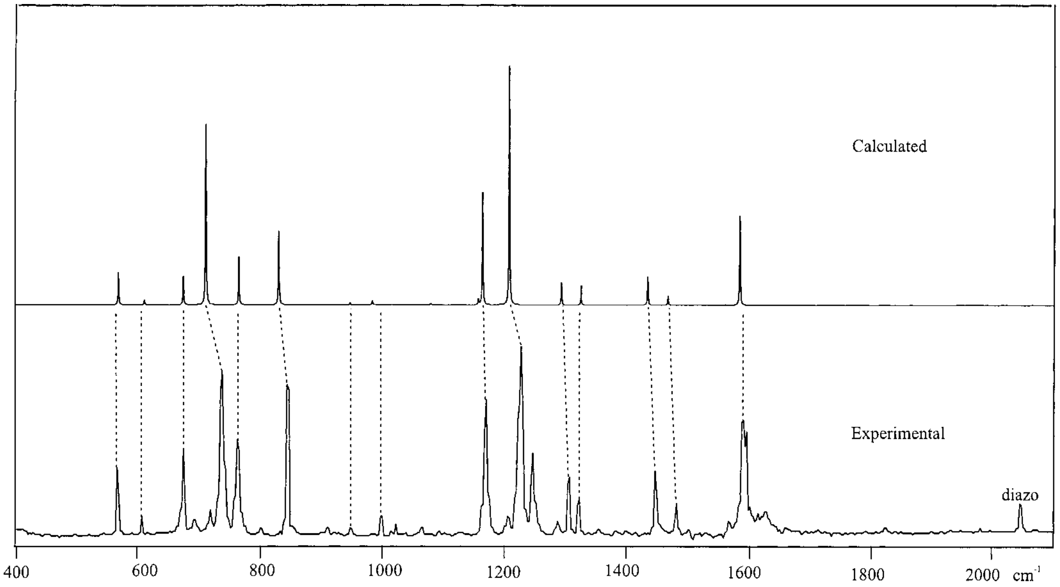

Figure 3. Observed IR spectrum of chlorophenylcarbene in argon at 14 K (bottom) and calculated (B3LYP/6-31G*) frequencies (top) with a scaling factor of 0.97.

smaller. For example, phenylcarbene has a computed triplet−singlet gap of −4 kcal/mol,[49] which corresponds to an increase of the singlet stability by 5 kcal/mol in relation to CH_2. If we consider the effect of the substituents as additive, we can predict that PhCCl has a triplet−singlet gap of about 11 kcal/mol, in reasonable agreement with our best *ab initio* value of 7.8 kcal/mol. The greater effect of Cl atoms on the triplet−singlet gap of carbenes is probably due its higher electron donation through π orbitals. The triplet−singlet gap of chlorophenylcarbene has not been determined by experimental methods. The stability of the singlet relative to the triplet explains why this carbene reacts slowly with oxygen and fails to produce a triplet EPR signal when studied by matrix spectroscopy.[36,39]

IR and UV/Vis Spectra of Chlorophenylcarbene. Irradiation of chlorophenyldiazirine in an argon matrix at 350 nm generated the well-known infrared and UV/vis spectra of the carbene shown in Figures 3 and 4, respectively. The IR spectrum is virtually identical to that reported by others.[36] From the IR spectrum, we can see a very small amount of diazo compound produced which has an absorption band at 2045 cm^{-1}. The simulated IR spectrum (insert, Figure 3) was calculated at the B3LYP/6-31G* level and scaled by 0.97 which yields values that are in good agreement with experiment.

Table 3 lists the calculated and observed frequencies. The most intense absorption band of 1225 cm^{-1} corresponds to the stretching mode of the C−C bond between the phenyl ring and the carbene center. The asymmetric and symmetric stretchings of the C−C−Cl bond in chlorophenylcarbene are at 847 and 739 cm^{-1}, respectively, which shifts to 745 and 726 cm^{-1} in dichlorocarbene.[53] The other intense band is at 1588 cm^{-1} which is related to a phenyl ring deformation mode. This is a very common absorption band in arylcarbenes.[49] The 1244 and 1600 cm^{-1} bands of chlorophenyl carbene observed by McMahon et al.[36c] are difficult to assign to chlorophenylcarbene based on a harmonic frequency calculation. Furthermore, the 1600 cm^{-1} band formed after 350 nm irradiation disappeared upon subsequent photolysis but the band at 1588 cm^{-1} remain unchanged. Thus, these two IR bands are not assigned at this time.

The UV−vis spectrum in Figure 4 has very intense bands at 282 and 300 nm and a weak absorption band around 700 nm which imparts a green color to the argon matrix. Figure 5 depicts the occupied and virtual molecular orbitals of chlorophenylcarbene involved in the electronic transitions. The 27a′ (HOMO) is the carbene nonbonded σ orbital, and the 6a″ (LUMO) is a π orbital with a great contribution of the p orbital located on the carbenic carbon. The 4a″ and 5a″ orbitals are π orbitals located on the aromatic ring. This transition was previously assigned to a σ−π transition on the basis of CIS calculations.[39]

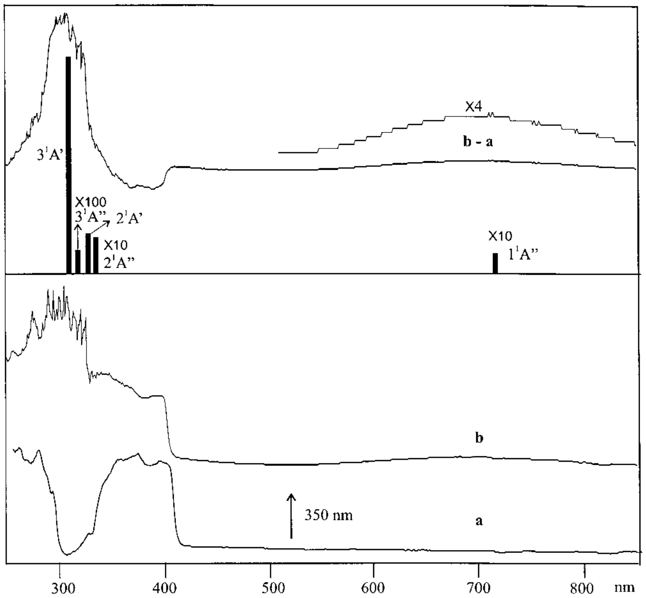

Figure 4. UV/vis spectra of chlorophenyldiazirine and chlorophenylcarbene in argon at 14 K (a) before photolysis and (b) after photolysis at 350 nm. The black bars are the calculated excited state energies and oscillator strengths of chlorophenylcarbene.

Utilizing the theoretical data, we can adequately analyze the experimental spectrum. The predicted excited state energies and oscillator strengths are listed in Table 2. The 1 $^1A''$ ← 1 $^1A'$ transition predicted by our best level of theory is at 716 nm and is of low intensity. It corresponds to the weak long-wavelength band centered at ∼750 nm. It consists predominantly of 86% electron promotion from 27a′ to 6a″ orbitals. This is a characteristic absorption of singlet carbenes which occurs, in general, in the visible region with low intensity. This transition in CCl_2 presents a weak band between 440 and 560 nm.[54] *Ab*

TABLE 3: Electronic Vertical Excited State Energies of Chlorophenylcarbene for the Singlet Ground State

	method[a]	λ (nm)	f[b]	configuration composition[d]
ground state (1 ^{1}A″)				87% $(5a'')^2\,(27a')^2\,(6a'')^0$
	CASSCF(6,6)	683		
$1\,^1A'' \leftarrow 1\,^1A'$	CASSCF(10,10)	569	0.0038	86% $(5a'')^2\,(27a')^1\,(6a'')^1$
	MRMP2	750		
	CASPT2	716		
	exp	~700		
	CASSCF(6,6)	263		
$2\,^1A'' \leftarrow 1\,^1A'$	CASSCF(10,10)	277[c]	0.007	46% $(4a'')^1\,(27a')^1\,(6a'')^2$ 31% $(5a'')^2\,(27a')^1\,(7a'')^1$
	MRMP2	370		
	CASPT2	338[c]		
	exp			
	CASSCF(6,6)	256		
$2\,^1A' \leftarrow 1\,^1A'$	CASSCF(10,10)	267	0.078	72% $(5a'')^1\,(27a')^2\,(6a'')^1$ 7% $(4a'')^1\,(27a')^2\,(8a'')^1$
	MRMP2	303		
	CASPT2	331		
	exp			
	CASSCF(6,6)	297		
$3\,^1A'' \leftarrow 1\,^1A'$	CASSCF(10,10)	258	0.00045	66% $(5a'')^1\,(27a')^1\,(6a'')^2$ 12% $(5a'')^2\,(27a')^1\,(8a'')^1$
	MRMP2	340		
	CASPT2	315		
	exp			
	CASSCF(6,6)	212		
$3\,^1A' \leftarrow 1\,^1A'$	CASSCF(10,10)	240	0.413	81% $(4a'')^1\,(27a')^2\,(6a'')^1$
	MRMP2	273		
	CASPT2	309		
	exp	~300		

[a] The CASSCF(6,6) and MRMP2 calculations performed using the 6-31G* basis set and MP2/6-31G* geometry. The CASSCF(10,10) and CASPT2 calculations performed on the B3LYP/6-31G* geometry and using the ANO-S basis set. [b] Oscillator strength. [c] The active space is (12,11) included four a′ and seven a″ orbitals due to the small weight of CASSCF wavefunction at CASSCF(10,10). [d] The contribution of the main electronic configuration calculated at CASSCF(10,10).

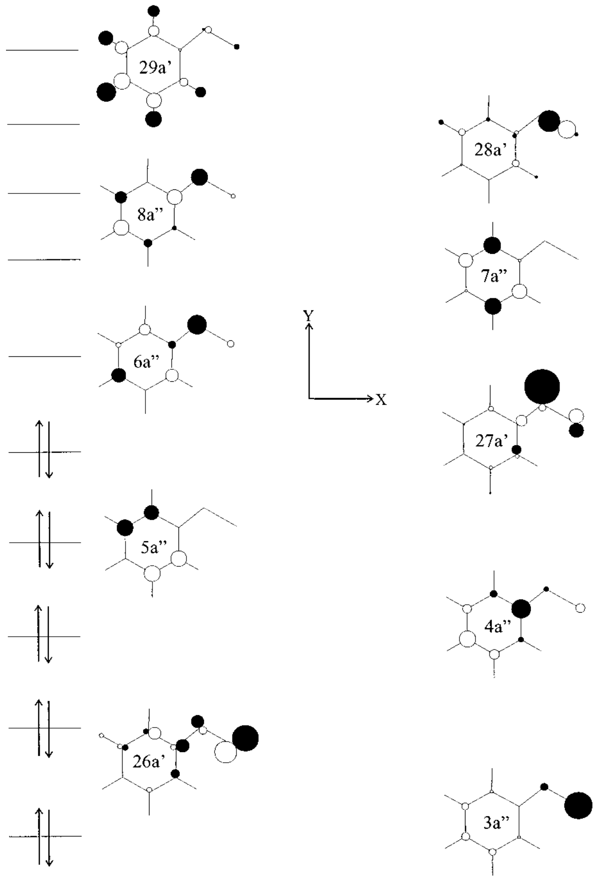

Figure 5. Orbitals of chlorophenylcarbene involved in the electronic transitions.

initio calculations by Kim et al.[53b] and Cai et al.[48] of CCl_2 indicate a vertical transition around 470 nm for this carbene. This absorption band has also been observed with adamantanylidene at 590 nm.[55]

The strong absorption band observed with $\lambda_{max} \approx 300$ nm is a mixture of the other four transitions predicted by theory. The $3\,^1A' \leftarrow 1\,^1A'$ transition corresponding to $\lambda = 309$ nm is the most intense absorption and is responsible for the most intense band in the observed spectrum. It is associated with the transition of $\pi(4a'')$ and $\pi^*(6a'')$. The second most intense absorption is the $2\,^1A'' \leftarrow 1\,^1A'$ transition with $\lambda = 331$ nm and the electronic configurations are 72% $\pi(5a'')-\pi^*(6a'')$ and 7% $\pi(4a'')-\pi^*(8a'')$. It has a relatively low oscillator strength, and it is not observed because it is hidden by the stronger absorption band. The remaining $2\,^1A'' \leftarrow 1\,^1A'$ transitions and $3\,^1A'' \leftarrow 1\,^1A'$ transitions are predicted to occur at 338 and 315 nm and have low intensity, and these two excited states are dominated by contributions from double excitations in the wave functions. They are also fully covered by the very high intensity $3\,^1A' \leftarrow 1\,^1A'$ transition.

IV. Conclusions

In this work, we have analyzed the UV/vis and IR spectra of chlorophenylcarbene using molecular orbital theory. This carbene was produced by photolysis of chlorophenyldiazirine in an argon matrix at 14 K. The 750 nm band of the carbene corresponds to electron promotion from the lone pair σ (HOMO) to the π^* (LUMO). On the basis of the calculated harmonic frequencies, we cannot assign the 1244 and 1600 cm^{-1} IR bands observed in the previous argon matrix study of McMahon et al.[36c] to chlorophenylcarbene. However, the most intense band in the spectrum (1225 cm^{-1}) corresponds to the C−C stretch of the carbene carbon and the phenyl carbon. The asymmetric and symmetric C−C−Cl vibrations are assigned to the IR bands at 847 and 739 cm^{-1}, respectively.

The energy difference between the triplet and singlet carbenes was calculated by *ab initio* and demitry functional theory methods. The best value is 7.84 and 7.70 kcal/mol which was computed at the UCCSD(T)/6-3l+G* and QCISD(T)/6-31+G** levels of theory including zero-point energy corrections. Our computed singlet−triplet splittings are slightly larger than that predicted by CAS(6,6) (4.5 kcal/mol), local spin density approximation (5.6 kcal/mol), and the BLYP (7.3 kcal/mol) methods reported by Trindle et al.[47]

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