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Theoretical Study on the Electronic States of Formylcarbene (HC·CHO) and Triplet Ketene (H_2 CCO) and the Ultraviolet Absorption Spectra Attributable to These Molecules

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The adiabatic energies, vibrational frequencies, and geometries of the ground and excited electronic states of formylcarbene and the triplet electronic states of ketene are calculated employing the state-of-the art ab initio methods. With the help of these calculations, certain ultraviolet (UV) absorption bands observed in the flash photolysis of oxazole and iso-oxazole are assigned to formylcarbene and triplet ketene.

I. Introduction

The ketene, $H_2C{=}C{=}O$, has been a subject of several experimental and theoretical investigations as it exhibits complicated single- and multiphoton photochemical behavior.[1] This molecule is of astrophysical interest and was observed in the interstellar medium and in the upper atmosphere.[2] The molecule has also been studied for its laser action in the far-infrared region, when pumped with a CO_2 laser.[3]

There is a plethora of information available for the ground and excited states of ketene and ketocarbene (HCCHO), including high-quality estimates of their equilibrium geometries, structures, and properties.[4−7] Unlike ketene, the ketocarbene or formylcarbene (HCCHO) is much less understood, though crossed molecular beam studies have revealed its existence.[8] The long-lived ^{3}HCCHO (triplet state) was postulated as an intermediate in the reaction of O(^{3}P) with acetylene (C_2H_2) and with higher alkynes.[5] In reaction with acetylene, the principle products are CO + CH_2 and HCCO + H, where the CO + CH_2 products are formed from a hydrogen shift following the initial formation of ^{3}HCCHO. The triplet ketocarbene was also expected to be formed in the flash photolysis (described below) of oxazole and iso-oxazole.

In the flash photolysis of oxazole and iso-oxazole, Krishnamachari and Venkatasubramanian observed three transient absorption band systems in the regions of 2500−3050 (system I), 3080−3400 (system II), and 3400−3670 Å (system III). In addition to these, the known absorption bands of CH (4300 and 3900 Å systems), HCO (bands in the region of 5200−6500 Å), and CN (3880 Å violet system) were also observed.[9] System I has been recently assigned to triplet HCN by Nayak et al.[10] Systems II and III were earlier assigned to the HCCO radical, in analogy with the HCCS radical observed in the flash photolysis of thiophene and thiazole.[11] However, the actual UV spectrum of HCCO was later observed in the region of 2630−2994 Å in the electrical discharge in a pulsed supersonic expansion of a mixture of acetylene, nitrous oxide, oxygen, and neon by Mordaunt et al.[12] In view of this, it has become necessary to reassign the band systems II and III to alternate carriers. In light of the theoretical work described in section III, the assignment of systems II and III to formylcarbene and triple ketene is considered in this paper.

II. Experimental Overview

The flash photolysis apparatus used in this work has been described elsewhere.[13] A path length of 16 m and a time delay of 5 μsec between the photolysis and monitoring flashes were used for recording the spectra, and the maximum intensity of the bands was observed when a mixture of 2 Torr of iso-oxazole and 50 Torr of argon was used.

System II consists of diffuse bands at 3395.64, 3390.95, 3338.34, 3288.44, 3241.03, 3229.24, and 3186.06 Å; each of these bands shows five or six diffuse sub-band heads characteristic of the K-structure of an asymmetric top molecule. The strong K-sub band of the 3338.34 Å (29946.4 cm^{-1}, 3.71 eV) band was chosen as the 0−0 band of the system, and with respect to this, the separations of the strong K-sub bands of the other bands were measured; a vibrational analysis with the help of these intervals was carried out, which yielded two lower state vibrational frequencies of 465 and 505 cm^{-1} and four excited-state vibrational frequencies of 454, 899, 1012, and 1431 cm^{-1}.

System III consists of bands at 3667.01, 3530.18, 3528.00, and 3400.38 Å. The strong band at 3667.01 Å (27262.4 cm^{-1}, 3.38 eV) was chosen as the 0−0 band of the system; the 0−0 band shows a sharp head and a diffuse rotational structure shaded toward the longer wavelength side; the remaining bands on the shorter wavelength side of the 0−0 band become progressively more and more diffuse. A vibrational analysis of the bands yielded two excited-state vibrational frequencies of 1052 and 1074 cm^{-1}.

Complete band data of systems II and III are given in the reference quoted earlier.[9] The absorption bands due to the ketene occur in the region of 3850−2600 Å;[14] however, no interference of these bands with the bands of systems II and III was observed. Apart from this, the bands of these systems, unlike those of ketene, are transient in nature, with lifetimes less than 50 μs.

III. Theoretical Methods

The coupled-cluster (CC)[15] based equation-of-motion (EOM)[16] method or the related linear response theory (LRT)[17] are the

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most widely used approaches for accurate electronic structure calculations. The greatest premise of these methods is that they are direct methods for energy difference calculations. The EOM-CC and CCLRT excitation energies scale properly in the noninteracting limit. In other words, these methods are size-extensive,[18] a property which is crucial for an accurate determination of state energies, bond cleavage energies, and related spectroscopic constants. Several applications proved the utility and strength of the EOM-CC/CCLRT method at the EOM-CCSD level (equation-of-motion coupled-cluster theory with single and double excitation). However, the use of single-determinant reference space limits its application to bond-breaking and curve-crossing regions as the SR-based approaches are incapable of providing accurate descriptions of the states of interest in these quasi-degenerate regions. Though the EOM-CCSD and its variants[19] are capable of providing accurate estimate of transition energies and related properties, these methods are computationally expensive, especially for large molecular systems.

Multireference (MR) generalizations of the SR theory describe the nondynamical electron correlation by using a reference space containing reference functions that can adequately describe the quasi-degeneracy, while the dynamical electron correlation is introduced using MR perturbation (MRPT) schemes. When applied to computing potential energy surfaces, some effective Hamiltonian-based MRPT methods are often plagued by ubiquitous intruder problems,[20] thereby seriously limiting their viability for global surfaces. Among several recent attempts at devising a chemically accurate MRPT approach [21−27] for computing smooth potential surfaces, the most promising MRPT methods include those based on the use of a zeroth-order multireference self-consistent field (MCSCF) or complete-active-space configuration interaction (CASCI) approximation, namely, the H^v,[21] MRMP,[22] MCQDPT,[23] CASPT2,[24] MRMP using APSG,[25] CIPSI,[26] an so forth methods.

Recently, we have proposed a computationally inexpensive version of MRMP/ MCQDPT in which the first-order reference functions are generated from the improved-virtual-orbital complete-active-space configuration interaction (IVO-CASCI) method[28−32] and then are used in subsequent MR perturbation calculations. The IVO-CASCI scheme is computationally simpler than CI-singles (CIS) and complete-active-space SCF (CASSCF) methods. The latter arises because the IVO-CASCI calculations do not involve iterations beyond those in the initial SCF calculation, nor do they possess features that create convergence difficulties with increasing size of the CAS in CASCI calculations. Since the IVO-CASCI approach contains both singly and doubly excited configurations in the CAS (in addition to higher order excitations), it provides descriptions of both singly and doubly excited states with comparable accuracy to CASSCF treatments. The latter contrasts with the CIS method, which cannot treat doubly excited states. Thus, the main computational advantages of our newly developed IVO-MCQDPT approach over the traditional MCQDPT method are (i) the absence of iterations beyond those in the initial SCF calculation and (ii) the lack of convergence difficulties from intruder states[20] that plague CASSCF calculations with increasing size of the CAS.

IV. Computational Details

The geometrical structures of ground and excited electronic states of ketene and formyl carbene were optimized at the complete-active-space self-consistent field (CASSCF) level with the correlation-consistent, polarized-valence triple-ζ (cc-pVTZ) Dunning basis set.[33] The basis set employed in these calculations is the same as that used by Szalay et al.[6] in their geometry optimization calculations for ketene. The structural parameters reported by Yarkony[5] and Harding et al.,[7] on the other hand, were computed using the double-ζ plus polarization (DZP)[34] basis set, C[9s5p1d]/(4s2p1d), O[955p1d]/(4s2p1d), and H[4s1p]/(2s1p). The CASSCF geometry optimizations in this work were performed with the Dalton[35] package.

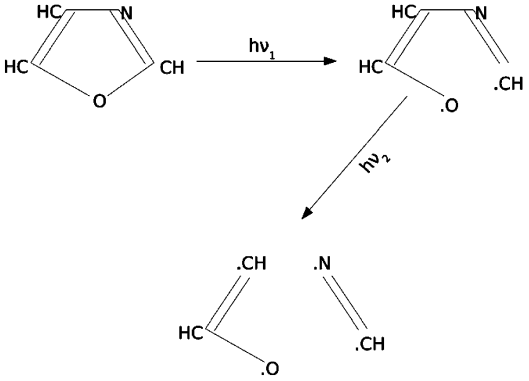

Figure 1. Photodecomposition of oxazole.

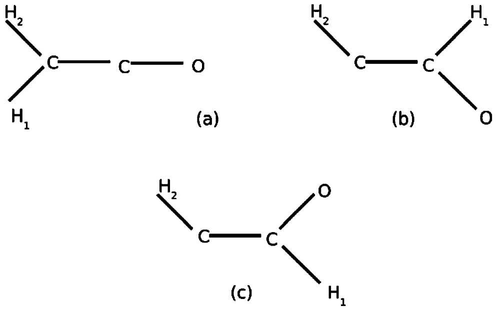

Figure 2. Geometrical structure of HCCHO isomers.

A. **Results and Discussion.** The excitation and ionization energies of ketene and its isomers were computed using the IVO-CASCI-based MCQDPT method (IVO-MCQDPT) with the augmented-cc-pVTZ (auc-cc-pVTZ) Dunning basis set.[33] The IVO-CASCI method is one portion of the latest generation of effective valence shell Hamiltonian computer codes that have been interfaced to the GAMESS package.[36] Unless otherwise mentioned, no orbitals have been kept frozen in these calculations.

The ground- and low-lying excited triplet state geometries and vibrational frequencies of ketene (see Figure 2a) determined using the CASSCF method are displayed in Table 1 and are compared in Table 2 with the experiment and with other correlated calculations. As can be seen in Table 2, the CASSCF-predicted C−O and C−C bond lengths are in excellent agreement with the state-of-the-art CCSD. The average discrepancies (with respect to CCSD) in the CASSCF bond lengths for C−O, C−C, and C−H are only 0.0015, 0.003, and 0.021 Å, respectively. It is worth mentioning that the CASSCF-predicted C−H bonds are shorter than the corresponding CCSD estimates. The average discrepancy in the CASSCF-predicted bond angle is 0.6°, with a maximum deviation of 0.9° for $\angle CCH_1$ in ketene (X^1A_1). The vibrational frequencies (harmonic) reported in this work for the ground state of ketene are also in excellent agreement with those from CCSD[6] and with those from the experiment.[4,37] The maximum (minimum) deviation in our computed vibrational frequency is 275 cm^{-1} (5 cm^{-1}) from the experiment and 104 cm^{-1} (10 cm^{-1}) from the CCSD.

TABLE 1: Ground- and Excited-State Spectroscopic Constants of H_2CCO (Figure 2a) (Bond Distances, Bond Angles, and Vibrational Frequencies Given in Å, Degrees, and cm^{-1}, Respectively)

	X^1A_1	$1^3A''$	$2^3A''$
r(C−O)	1.171	1.198	1.387
r(C−C)	1.325	1.465	1.423
r(C−H_1)	1.073	1.074	1.072
r(C−H_2)	1.073	1.069	1.069
∠CCH_1	119.62	120.28	121.22
∠CCH_2	119.62	119.73	118.61
∠CCO	180.00	128.04	127.44
ω_1	3404	3413	3412
ω_2	3275	3279	3296
ω_3	2147	1792	1647
ω_4	1478	1551	1523
ω_5	1146	1108	1116
ω_6	1026	963	956
ω_7	597	693	616
ω_8	449	486	437
ω_9	418	383	411

TABLE 2: Comparison of Ground- and Excited-State Spectroscopic Constants of H_2CCO with Other Theoretical and Experimental Data (Bond Distances, Bond Angles, and Vibrational Frequencies Given in Å, Degrees, and cm^{-1}, Respectively)

	X^1A_1			$1^3A''$	
	this work	Szalay et al.	expt.	this work	Szalay et al.
r(C−O)	1.171	1.170	1.160[44]	1.198	1.200
r(C−C)	1.325	1.329	1.315[44]	1.465	1.463
r(C−H_1)	1.073	1.091		1.074	1.100
r(C−H_2)	1.073	1.091		1.069	1.093
∠CCH_1	119.6	118.7	118.9[44]	120.3	119.9
∠CCH_2	119.6	118.7		119.7	119.3
∠CCO	180.0	180.0		128.0	127.5
ω_1	3404	3300	3166[4,37]		
ω_2	3275	3179	3070[4,37]		
ω_3	2147	2215	2152[4,37]		
ω_4	1478	1415	1388[4,37]		
ω_5	1146	1156	1118[4,37]		
ω_6	1026	1000	977[4,37]		
ω_7	597	619	588[4,37]		
ω_8	449	522	528[4,37]		
ω_9	418	430	430[4,37]		

The ultraviolet spectrum of ketene was first reported by Lardy[38] and Norrish[14] and was later interpreted by Price, Teegan, and Walsh et al.[39] They assigned six observed transitions between 54680 and 75179 cm^{-1} as the members of an $ns \leftarrow \pi$ Rydberg series. The band systems observed at 31300 and 47600 cm^{-1} were interpreted as a $\pi^*(CO) \leftarrow \pi(CO)$ transition. Later, Herzberg summarized the electronic spectra of ketene in his book on electronic spectra and electronic structure of polyatomic molecules, where some of the assignments were revised. An extensive survey on earlier theoretical and experimental work for ketene is given in ref 6.

The vertical excitation energies (VEEs) of ketene computed using the IVO-MCQDPT are compared with the experiment in Table 3. The VEEs calculated using the EOM-CCSD scheme with the polarized basis set (PBS) of Sadlej[40] and atomic natural orbital (ANO) basis set of Widmark et al.[41] are also listed in Table 3. Table 3 clearly demonstrates that the IVO-MCQDPT-estimated VEEs are lower than those of the experiment, while those obtained from the EOM-CCSD are higher than the experimental energy. The vertical ionization potential (reported in Table 4) also exhibits similar trends. The error in our estimated vertical ionization potentials (VIPs) for X^2B_1, 1^2B_2, and 2^2B_1 states are 0.13, 0.19, and 0.22 eV, respectively, while the corresponding EOMIP-CCSD[42,43] deviations are 0.18, 0.15, and 0.40 eV.

As the purpose of the present investigation is to identify/assign the (UV) absorption bands observed in the flash photolysis of oxazole, we only consider the first few excited and ionized states of ketene to access the accuracy of our computed/predicted quantities. The present study reveals that our reported spectroscopic constants, excitation, and ionization energies are in favorable agreement with the experimental values and with those from other correlated calculations, and hence, they are reliable.

We now discuss the numerical results for the formyl- or ketocarbene (see Figure 2b and c). The spectroscopic constants and geometrical parameters from CASSCF calculations for the ground and excited states of *cis*- and *trans*-HCCHO are listed in Tables 5and 6 and compared with earlier theoretical calculations of Yarkony[5] in Table 7. As can be seen in Table 7, the geometrical parameters reported in this work are in good agreement with the reference data. Since our predicted geometrical parameters and spectroscopic constants (vibrational frequencies, VEEs, and VIPs) for ketene are quite accurate and agree favorably with the far more expensive state-of-the-art EOM-CCSD geometries and energies, we believe that the our computed geometries and transition energies (see Table 8) for *cis*- and *trans*-HCCHO should be in accord with those form the experiment.

V. Assignment of Band Systems

A. Assignment of System II to Formylcarbene (HC•CHO). We are now in a position to assign the band systems observed in the flash photolysis of oxazole and iso-oxazole by Krishnamachari et al.[9]

The occurrence of triplet HCN (carrier for system I) as one of the photodecomposition products shows that the parent molecule (oxazole or iso-oxazole) undergoes photodecomposition by a two-step process that leaves the two fragments HCN and HCCHO with two unpaired electrons in each case, as shown in Figure 1. Since the HCN is formed in the triplet state, the formylcarbene, HCCHO, is thus expected to be formed in the triplet state. As HCCHO can exist in the cis and trans isomeric forms, the adiabatic excitation energies of both of these forms are calculated, which are shown in Table 8. Both the cis and trans isomer have $^3A''$ as their ground states at a height of 3 eV with respect to the ground state of H_2CCO and $1^3A'$ states around 1 eV, in agreement with the results reported by earlier workers. In the case of *trans*-HCCHO, states higher than 2.73 eV from its ground state were found to be repulsive. Since the energy of transition for the band system II is 3.71 eV, the *trans*-HCCHO does not explain the observed band system; the *cis*-HCCHO, however, has an excited state, $2^3A''$, at 3.93 eV from its ground state, which agrees well with the observed value of 3.71 eV. Thus, the band system II could be assigned to the $2^3A'' \leftarrow X^3A''$ transition of the *cis*-HCCHO. The calculated vibrational frequencies and geometries of the ground and excited states of *cis*-HCCHO are given in Table 5. The observed vibrational frequencies of the ground and excited states show very good agreement with the calculated values. The *cis*-HC•CHO is an asymmetric top molecule, and the transition moment for the transition $^3A''-^3A''$ lies in the plane of the molecule and would give rise to type-A and type-B bands with their accompanying K-sub bands; this explains the complex structure observed for the bands. The diffuseness of the bands could be ascribed to the predissociation of the excited $2^3A''$ state due to its interaction with the dissociation continuum of the ground state. The

TABLE 3: Vertical Excitation Energies (in eV) for X^1A_1 Ketene (H_2CCO)[a]

	PBS(90)		ANO(196)		ACCT[b] (184)		
state	CIS	EOM	CIS	EOM	EOM	IVO-MCQDPT	expt.
1^3A_2	3.846	3.834			3.750	3.413	3.348[45]; 3.794[46]
1^1A_2	4.313	4.065	4.340	3.968	3.890	3.488	3.695[47]; 3.844[48]; 3.868[39]
1^3A_1	5.109	5.565			5.421	5.354	5.294[47]; 4.997[46]
1^3B_1	6.095	5.723			5.885	5.681	5.803[46]
1^1B_1	6.447	5.931	6.447	6.139	6.095	5.743	5.765[46]; 5.815[48]; 5.865[47]
2^1A_1	7.841	7.231	7.764	7.328	7.314	7.054	6.780[44]
2^1B_1	7.819	7.259	7.691	7.406	7.415	7.178	7.290[48]

[a] The number of contracted Gaussian functions (CGFs) in the basis set is indicated in the parentheses. [b] aug-cc-pVTZ EOM=EOM-CCSD.

TABLE 4: Vertical Ionization Energies (in eV) of Ketene

state	EOMIP-CCSD[6]	Koopmann	IVO-MCQDPT	expt.[49]
$\tilde{X}^2B_1$	9.582	9.99	9.566	9.800
$\tilde{A}1^2B_2$	14.345	15.33	14.056	14.200
$\tilde{A}2^2B_1$	15.402	17.45	14.770	14.999

TABLE 5: Ground- and Excited-States Spectroscopic Constants of *cis*-HCCHO (Figure 2b) (Bond Distances, Bond Angles, and Vibrational Frequencies Given in Å, Degrees, and cm^{-1}, Respectively)

	X^3A''	$1^1A'$	$1^3A'$	$1^3A''$	$2^3A''$	$2^3A'$
r(C−O)	1.223	1.514	1.367	1.309	1.229	1.369
r(C−C)	1.447	1.262	1.334	1.432	1.433	1.321
$r(C-H_1)$	1.094	1.059	1.076	1.080	1.089	1.077
$r(C-H_2)$	1.073	1.059	1.065	1.091	1.070	1.066
$\angle CCH_1$	114.26	161.19	123.68	112.09	116.50	124.17
$\angle CCH_2$	129.19	161.19	133.21	105.24	129.72	132.35
∠CCO	124.51	65.36	124.72	116.33	123.79	124.46
ω_1	3346	3548	3425	3264	3372	3421
ω_2	3071	3481	3295	3156	3152	3287
ω_3	1659	1835	1596	1521	1611	1657
ω_4	1480	1115	1305	1489	1476	1322
ω_5	1186	1049	1090	1266	1201	1091
ω_6	1012	878	855	1212	980	884
ω_7	955	459	785	1078	932	688
ω_8	529	296	639	744	544	620
ω_9	453	231	512	678	476	516

TABLE 6: Ground- and Excited-State Spectroscopic Constants of *trans*- HCCCHO (Figure 2c) (Bond Distances, Bond Angles, and Vibrational Frequencies Given in Å, Degrees, and cm^{-1}, Respectively)

	X^3A''	$1^1A'$	$1^3A'$	$1^3A''$
r(C−O)	1.235	1.511	1.378	1.297
r(C−C)	1.454	1.280	1.333	1.418
$r(C-H_1)$	1.087	1.059	1.075	1.094
$r(C-H_2)$	1.072	1.059	1.066	1.087
$\angle CCH_1$	117.38	162.04	137.6	117.08
$\angle CCH_2$	128.08	162.04	122.6	109.99
∠CCO	121.31	64.95	110.2	138.48
ω_1	3356	3538	3417	3186
ω_2	3157	3479	3314	3095
ω_3	1590	1743	1579	1393
ω_4	1469	1120	1302	1221
ω_5	1124	1029	1011	1208
ω_6	1000	884	917	1172
ω_7	996	589	902	975
ω_8	606	452	615	762
ω_9	476	267	474	503

TABLE 7: Comparison of the Ground X^3A'' State Geometrical Parameters of Ketocarbenes (cis and trans) with Other Theoretical Data (Bond Distances, Bond Angles, and Vibrational Frequencies Given in Å, Degrees, and cm^{-1}, Respectively)

	trans-HCCHO		*cis*-HCCHO	
	this work	Yarkony[5]	this work	Yarkony[5]
r(C−O)	1.235	1.236	1.223	1.237
r(C−C)	1.454	1.449	1.447	1.401
$r(C-H_1)$	1.087	1.099	1.094	1.106
$r(C-H_2)$	1.072	1.084	1.073	1.085
$\angle CCH_1$	117.4	116.9	114.3	115.2
$\angle CCH_2$	128.1	129.8	129.2	131.2
∠CCO	121.3	121.6	124.5	124.5

TABLE 8: Adiabatic Excitation Energies (in eV) of HCCHO Isomers with Respect to X^1A_1 Ketene (H_2CCO)

state	adiabatic excitation energy
Ketene	
X^1A_1	0.00
$1^3A''$	2.17
$2^3A''$	5.46
cis-HCCHO	
X^3A''	3.04
$1^1A'$	3.21
$1^3A'$	3.79
$1^3A''$	4.82
$2^3A''$	6.97
$2^3A'$	7.40
trans-HCCHO	
X^3A''	2.98
$1^1A'$	3.20
$1^3A'$	3.89
$1^3A''$	5.05
$2^3A''$	5.71

calculated dissociation energy of the ground state to CH($X^2\Pi$) and HCO(X^2A') is 4.5 eV; thus, the dissociation limit lies close to the $2^3A''$ state. The CH and HCO radicals, whose absorption spectra are also observed in these experiments, would arise as a result of the dissociation of HCCHO from the $2^3A''$ state.

B. Assignment of System III to Triplet Ketene H_2CCO. Ketene, H_2CCO, represents the stable configuration for the HCCHO system. Harding and Wagner[7] and Yarkony[5] have theoretically studied the formylcarbene formed as a metastable complex in the reaction of atomic oxygen (O^3P) with acetylene and proposed that the formylcarbene would undergo an internal conversion to ketene in the region of the intersection of the potential energy surfaces of the two molecules.[5,7] The adiabatic excitation energies calculated for the first two triplet states of ketene are shown in Table 4. A schematic diagram of the energy levels of ketene and *cis*- and *trans*-HCCHO is shown in Figure 3. As could be seen from this figure, a crossing of the potential energy surfaces of the $1^3A'$ state of *cis*-HCCHO and the higher vibrational levels of the $1^3A''$ of ketene would occur, resulting in the formation of ketene in the $1^3A''$ state. Since both of these states are of the same multiplicity, triplet states, this transfer would be an efficient process compared to the formation of the ketene in the X^1A_1 state, which involves an intersystem crossing, which was studied by Yarkony.[5] The observed absorption band system III would correspond to the transition $2^3A'' \leftarrow 1^3A''$; the calculated energy for this transition, 3.29 eV, agrees well

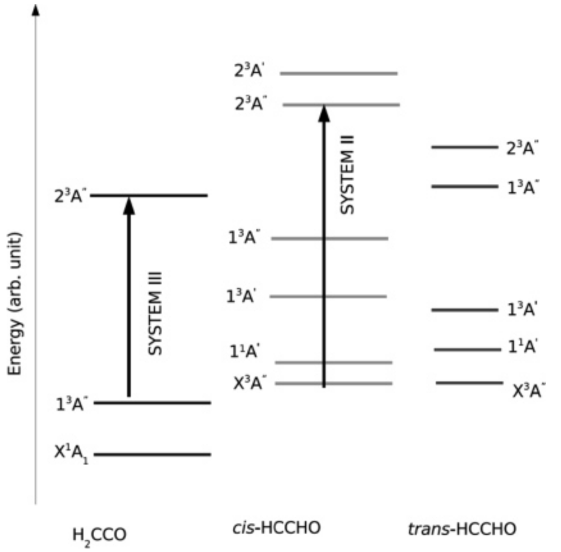

Figure 3. Energy level diagrams of ketene and formylcarbene.

with the observed value of 3.38 eV. The calculated vibrational frequencies and geometries for triplet ketene for the states discussed in this work are shown in Tables 1−6. The observed excited-state vibrational frequencies of 1059 and 1074 cm^{-1} could be correlated with the 977 and 1118 cm^{-1} fundamentals in the ground state, which represent the C−C stretching and C−H bending modes. The assignment of system II to formylcarbene, HC•CHO, and system III to triplet ketene thus satisfactorily explains all of the observed features of these two band systems. The present work constitutes the first experimental observation of the ultraviolet absorption spectra of formylcarbene and triplet ketene.

VI. Concluding Remarks

Extensive theoretical calculations using the CASSCF and our recently proposed IVO-CASCI-based MCQDPT method resulted in the following important conclusions:

(a) For band system II, the observed transition energy and the vibrational frequencies of the ground and excited states show very good agreement with the calculated values of the $2^3A'' \leftarrow X^3A''$.

(b) The observed absorption band system III would correspond to the transition $2^3A'' \leftarrow 1^3A''$ of ketene; the calculated energy for this transition, 3.29 eV, agrees well with the observed value of 3.38 eV.

(c) The present calculations further demonstrate that the IVO-MRMP method is capable of providing reliable energies even for complicated systems like ketene and formylcarbene. We further emphasize that IVO-CASCI and IVO-MRMP methods are highly cost-effective compared to other sophisticated electronic structure theories.

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