Electronic states of ketene

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State of the art *ab initio* techniques of molecular electronic structure theory have been employed to investigate different structural aspects of the electronic states of ketene. Vertical excitation energies of more than 40 singlet and triplet states have been determined from equation-of-motion coupled cluster singles and doubles (EOM-CCSD) and configuration interaction singles (CIS) calculations employing extended basis sets. Most importantly, all singlet and triplet electronic states below 70 000 cm^{-1}, close to the first ionization potential of ketene, 77 500 cm^{-1} have been determined. Only four pure excited valence states have been identified: the $1\,^3A_1$, $2\,^3A_1$, $1\,^3A_2$, and $1\,^1A_2$ states. Vertical ionization energies have also been determined at the EOM-CCSD level. They are found to be in nice accord with the available experimental results. All lower-lying members of the Rydberg series of ketene terminating at 77 500 cm^{-1} are assigned based on theoretical data, symmetry considerations, and use of the Rydberg formula and the available experimental results. High-quality estimates are given for the possible occurrence of fluorescence emission from the first singlet state of ketene. © *1996 American Institute of Physics.* [S0021-9606(96)00927-0]

I. INTRODUCTION

Detailed experimental[1–30] and theoretical[31–49] studies of the electronic states of ketene, $H_2C{=}C{=}O$, are important as (a) the complicated single- and multiphoton photochemistry[14,16,19,21,26,27] of ketene is of considerable interest in its own right; (b) ketene has been a convenient photochemical source of both singlet and triplet methylene, systems which have great importance for unimolecular chemical kinetics and dynamics studies; (c) its unimolecular dissociation pathways depend on the excited state prepared,[36–38] thus studies on ketene afford highly interesting spectroscopic test studies of dynamical models such as phase space theory (PST),[50] statistical adiabatic channel models (SACM), separate statistical ensembles (SSE), and the variational form of the Rice–Ramsperger–Kassel–Marcus (RRKM) theory;[51] (d) it belongs to a series of well-studied[6] 16-valence-electron molecules, such as allene, diazomethane, hydrazoic acid, isocyanic acid, and linear symmetric azide anion; (e) the molecule is of astrophysical interest, observed[52] in the interstellar medium and in the upper-atmosphere; (f) ketene is a candidate for far infrared laser action when pumped with a CO_2 laser.[53]

Despite the fact that many experimental and theoretical papers dealt with properties of the low-lying electronic states of ketene, and thus ketene is probably one of the most studied 5-atomic molecule, there are still many important questions which await to be answered, including: (a) which are the pure valence and pure Rydberg states of ketene and how should one assign the latter states of recent experimental interest;[11] (b) can one clarify the assignment of the vertical and adiabatic (0–0) excitation energies observed by diverse sophisticated experimental techniques; (c) what are the equilibrium geometries of the low-lying states of ketene, which states have equilibrium geometries of C_{2v} symmetry and which of C_s^{I} and C_s^{II} symmetries, where the point group classification C_s^{I} and C_s^{II} is due to Allen and Schaefer,[36] exemplifying that in C_s^{I} and C_s^{II} the bending of the CCO angle is out of the plane and in the plane of the CH_2 unit, respectively; and (d) how to explain the lack of observation of fluorescence from the excited states of ketene.

The most useful approaches modern molecular electronic structure theory offers to answer most of the above questions are the so-called equation-of-motion (EOM)[54] or the related linear response (LR)[55] methods. The greatest promise of these methods is that they directly result in transition energies instead of obtaining them as differences of independently computed total energies, as in more traditional methods of electronic structure theory. The origin of the EOM methods can be traced back to works by Rowe[54] in nuclear spectroscopy and by McKoy[56] in electron spectroscopy in the late 60's and early 70's. (In fact, the first *ab initio* EOM calculation on the excited states of ketene was reported by Galasso and Fronzoni[42] more than a decade ago.) The suggestion[57] of the use of coupled-cluster-type (CC) wave functions for the EOM reference state was an important development. Strong features of the resulting EOM-CC methodology[57,58] include: (a) it can simultaneously describe a number of electronic states in a ''black box'' nature; (b) the reference state, from which CI-like excitations (all singles and doubles in the EOM-CCSD scheme) are made, is defined by the coupled cluster method employed successfully to describe ground states of a large number of diverse chemical species; (c) EOM-CC excitation energies scale properly in the noninteracting limit; and (d) the method can equally well be applied to obtain states that contain fewer or more electrons than the reference state. Several applications[59–62]

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proved the utility of a recent implementation[63] of the EOM-CC method at the EOM-CCSD level. In this method accurate excitation energies are obtained for excitations of single electron replacement character, while excitations of double electron replacement character seem to be less accurately described. Naturally, use of a single-determinant reference also limits the application range of the EOM-CCSD approach but none of these two limitations of the method are of concern for the present study. The computationally much simpler TDA (Tamm–Dancoff approximation[64,65]) or CIS (configuration interaction with singles[66]) method can be viewed as a zeroth-order approximation to EOM-CC. This method does not include electron correlation,[67] resulting in a deterioration of its predictive power.[62(b)] Note that the more accurate but computationally considerably more demanding EOM-CCSDT[68(a)] and EOM-CCSD(T)[68(b)] approaches have also been developed and implemented, but they are considered to be too expensive at present for detailed studies of the electronic states of molecules as large as ketene. In the present study the TDA(CIS) and the EOM-CCSD methods are employed.

This paper is organized as follows. After a short description of the theoretical methods applied the calculated and measured vertical excitation energies are compared in Sec. III. The ionization potentials and the Rydberg states of ketene are discussed in Sec. IV. Section V summarizes the structural aspects of the present research, giving geometries, harmonic frequencies, and one-dimensional cross sections of the potential energy surfaces of several electronic states of ketene. Section V also discusses fluorescence from the lowest singlet excited state of ketene.

II. THEORETICAL METHODS

Several basis sets of contracted Gaussian functions (CGFs) have been selected for this study. Most of them contain both polarization and diffuse functions, as the need for including these functions in basis sets employed for calculations on electronic states has long been recognized. The smallest basis sets employed are the DZP basis of Huzinaga and Dunning[69–71] and the polarized basis set (PBS) of Sadlej.[72] While the former basis cannot describe electronic states of diffuse character, the latter compact basis was designed for calculations on Rydberg-type electronic states. The correlation-consistent, polarized-valence (aug)-cc-pVDZ and (aug)-cc-pVTZ basis sets of Dunning and co-workers[73,74] have also been extensively used. (Note that only the augmented (aug) basis sets contain diffuse functions.) The extended basis of Widmark, Malmqvist, and Roos[75] (WMR) with a $6s5p3d2f$ contraction on C and O, and a $5s3p2d$ contraction on H has also been employed during calculations of vertical excitation energies. The DZP, aug-cc-pVDZ, PBS, cc-pVTZ, aug-cc-pVTZ, and WMR basis sets contain 55, 87, 90, 118, 184, and 196 CGFs for ketene, respectively. During the course of this study it became evident that characterization of the higher-lying electronic states of ketene requires basis sets with considerably more diffuse functions than present in basis sets just described. Therefore, the compact aug-cc-pVDZ basis was augmented with two sets of diffuse s, p, and d functions with exponents defined as geometric progressions of the lowest two related exponents. These basis sets are denoted in this paper as aug-{spd}-cc-pVDZ, e.g., aug-sp-cc-pVDZ if two sets of diffuse s and p functions have been added. Only the pure spherical harmonics of the d and f manifolds of the basis sets have been included.

The closed-shell ground electronic state of ketene has been described with coupled cluster (CC) methods including all single and double excitations (CCSD),[76] and in cases, additionally, a perturbative correction for contributions from connected triple excitations [CCSD(T)].[77,78] Most of the calculations on excited electronic states utilized the equation-of-motion (EOM) coupled cluster singles and doubles (EOM-CCSD)[63] and the TDA[64] (CIS)[66] methods. For accurate description of the lowest excited singlet and triplet states at non-C_{2v} geometries the two-determinant CC (TD-CC)[79,80] and the UHF-CCSD methods[81] were employed. For calculations on ionized states the EOMIP-CCSD method,[82,83] a special version of EOM-CCSD has been employed. Unless otherwise noted, no orbitals have been kept frozen in correlated-level calculations.

As mentioned in the Introduction, the accuracy of the EOM-CCSD method depends strongly on the excitation level of the electronic states: high accuracy can be expected only for singly excited states. To characterize the excitation level of electronic states Stanton and Bartlett[63] proposed a measure referred to as AEL, approximate excitation level. AEL values smaller than 1.14 were found for all states of ketene considered, therefore the mentioned limitation of the EOM-CCSD method is of no concern for the present study.

The geometrical structures of the different electronic states of ketene were optimized utilizing analytic gradient techniques at the CCSD,[84,85] CCSD(T),[86,87] TD-CCSD,[80] and EOM-CCSD[88,89] levels. The residual Cartesian gradients were in all cases less than 3×10^{-4} hartree/bohr. If in doubt that the optimized structure corresponds to a minimum on the respective potential energy surface of ketene, the appropriate quadratic force constants were determined at the optimized geometry by numerical differentiation of analytic first derivatives.

All electronic structure computations were performed with a local version of the program package ACES II.[90]

III. VERTICAL EXCITATION ENERGIES

While the earliest observations on the photochemical behavior and the ultraviolet absorption spectrum of ketene were reported by Lardy[1] and Norrish *et al.*,[2] the classic interpretation of the far-UV and vacuum-UV electronic spectrum of ketene is due to Price, Teegan, and Walsh.[3] They (a) proposed assignment of six observed transitions between 54 680 and 75 179 cm^{-1} as the $n=3$, 4, 5, 6, 7, and 8 members of a $ns\leftarrow\pi$ Rydberg series; (b) placed the limit of the series, corresponding to the first ionization energy, at 77 500 cm^{-1}, a result confirmed later by several different techniques;[10,11,20,28] (c) suggested that the 31 300 cm^{-1} system of ketene arises from the excitation of a nonbonding electron on the oxygen atom; and (d) proposed that the band system around 47 600 cm^{-1} may be interpreted as an excitation from the CO bonding π orbital to an antibonding π^* upper orbital. Herzberg, in his classic book on electronic spectra of polyatomics,[12] summarizes the early literature on the electronic states of ketene but, as it turns out, some of the assignments had to be revised later on. Dixon and Kirby[4] investigated the absorption spectrum of ketene in the visible and ultraviolet region and predicted, based on MO calculations carried out within the PPP approximation, that (a) the $1\,^3A_2$ and $1\,^1A_2$ states are the lowest excited states of ketene and they lie around 27 000 and 31 000 cm^{-1}, respectively; and (b) both the $1\,^3A_2$ and $1\,^1A_2$ states have equilibrium structures with in-plane bent CCO bonds, i.e., have C_s^{II} symmetry. In their reviewlike article Rabalais *et al.*[6] summarize the above and a few other experimental works. In addition, they (a) predicted a $1\,^3B_2 \leftarrow 1\,^1A_1$ transition around 27 000 cm^{-1}, and (b) assigned bands at 46 900 and 58 800 cm^{-1} to $^1B_1 \leftarrow 1\,^1A_1$ transitions of ketene. By analyzing the vibrational progression evident in the absorption spectrum Laufer and Keller[7] derived adiabatic excitation energies of less than 19 300 and 21 370 cm^{-1} for the lowest excited triplet and singlet levels of ketene, respectively. Frueholz *et al.*[8] in an investigation of the electron-impact energy-loss spectrum of ketene in the energy-loss range 0–15 eV, (a) were the first to observe and assign the $1\,^3A_1 \leftarrow 1\,^1A_1$ transition at 42 700 cm^{-1}; (b) observed a transition at 29 800 cm^{-1} and assigned it to the $1\,^1A_2 \leftarrow 1\,^1A_1$ transition; (c) assigned the $1\,^1B_1 \leftarrow 1\,^1A_1$ transitions to 47 300 cm^{-1}, and emphasized the Rydberg character of the transition based also on calculations of Harding and Goddard;[34] and (d) found no evidence of a triplet state with maximum intensity at 27 000 cm^{-1}, and thus challenged the experimental result of Dixon and Kirby[4] and indicated a small singlet–triplet separation for the first A_2 states. In the threshold electron impact excitation spectrum of ketene Vogt *et al.*,[9] based also on results from *ab initio* calculations, (a) assigned transitions at 30 600, 40 300, and 46 800 cm^{-1} to be due to $^3A_2$, $^3A_1$, and $^3B_1$ states of ketene; and (b) suggested that several Rydberg series start around 56 000 cm^{-1}. Ashfold *et al.*[11] used the resonance-enhanced multiphoton ionization (REMPI) technique to investigate the Rydberg spectrum of ketene, and found three Rydberg progressions attributable to ketene. They place the start of the $^1A_1$, $^1A_2$, and $^1B_1$ symmetry progressions at 54 683, 56 740, and 61 359 cm^{-1}, respectively.

As far as theoretical calculations are concerned, calculation of (mostly) vertical excitation energies of ketene have been performed at various levels of theory.[9,33,34,36,42] Dykstra and Schaefer[33] determined, from excited state single-configuration SCF calculations employing DZ, DZ+R, and DZ+P basis sets, excitation energies for 18 electronic states of ketene, but most of the results obtained proved to be unreliable, as was shown a decade later by Allen and Schaefer.[36] Vogt *et al.*[9] performed Hartree–Fock calculations, and described some singly excited states by solving the one-electron problem in the field of the ground state of the ketene cation. Harding and Goddard[34] and Galasso and Fronzoni[42] utilized the GVB-CI and EOM methods, respectively. Allen and Schaefer[36] employed various SCF and CISD methods with basis sets of at least DZP quality and obtained results for five electronic states of ketene, among them vertical and adiabatic excitation energies. Finally, Yoshimine,[39] in a study utilizing multiconfiguration self-consistent-field (MCSCF) and multireference configuration interaction (MR-CI) calculations, investigated the first excited $^1A''(C_s^{\mathrm{II}})$ potential energy surface and revealed the existence of a surface crossing with the ground state suggesting that this provides ‘‘an efficient mechanism for the fast internal conversion that explains no fluorescence being observed in photolysis of ketene.’’

In Table I vertical excitation energies of around forty singlet and triplet states of ketene are listed along with the available experimental results. The calculated values were obtained employing EOM-CCSD and CIS methods with basis sets of differing quality. The excitation energies are sorted according to symmetry instead of pure energy ordering.

There is only one state, the overall lowest energy $1\,^3A_2$ state, where CIS and EOM-CCSD give almost indistinguishable results. As expected,[62(b)] in almost all cases CIS overshoots the excitation energy by 2000–5000 cm^{-1} (0.2–0.6 eV) when compared to EOM-CCSD. Nevertheless, the number of states and their approximate energy order comes out mostly correctly from CIS calculations employing the same basis set as in complementary EOM-CCSD calculations.

It is instructive to note that changes in the excitation energies due to use of different basis sets in CIS or EOM-CCSD calculations are much greater than the direct effects of the change of the methods. This is due to the fact that most of the states described have considerable Rydberg character (*vide infra*), and therefore their description is faulty even with extended basis sets, such as cc-pVTZ, containing no diffuse functions. The results obtained indicate that diffuse functions are essential, while larger *sp* sets or higher angular momentum functions are somewhat less important in describing the electronic states of ketene considered. The smallest basis employed which contains the essential diffuse functions is the PBS basis of Sadlej,[72] thus the PBS EOM-CCSD calculations are the least expensive ones reported which can be considered reliable.

Identification of pure valence states can here be achieved by comparing the excitation energies obtained with different basis sets: their excitation energy should not change significantly after augmenting the basis with diffuse functions. The only pure valence excited states thus identified are: $1\,^3A_1$, $2\,^3A_1$, $1\,^3A_2$, and $1\,^1A_2$. Most importantly, no states of B_1 and B_2 symmetry are among the valence states. It has to be stressed, at the same time, that relatively high-lying Rydberg states, close to the ionization limit, might not be very well described even with the most extended basis sets employed in this study. This, however, does not cause significant problems during interpretation of the Rydberg series, as (a) those Rydberg states, especially if their lower-energy analogs are known, can usually be assigned by use of the simple Ryd-

TABLE I. Vertical excitation energies (in cm^{-1}) for $\widetilde{X}\,^1A_1$ ketene.[a]

	DZP (55)		PBS (90)		TZ[b] (118)	a-spd-DZ[b] (157)	a-TZ[b] (184)	WMR (196)		
State	CIS	EOM	CIS	EOM	CIS	CIS	CIS	CIS	EOM	Expt.
1 $^3A_1$			41 210	44 880	41 820	41 270	41 340			42 700[c], 40 300[d]
2 $^3A_1$			55 530	59 600	55 530	55 560	55 550			
3 $^3A_1$			62 520	60 370		60 420	62 240			
2 $^1A_1$	69 550		63 240	58 320	{69 310}	61 180	63 230	62 620	59 100	54 680[h]
3 $^1A_1$	{91 150}		68 980	65 610		67 040	68 720	68 650	66 220	
4 $^3A_1$			{74 550}	{71 120}		68 890	{73 960}			
4 $^1A_1$			{78 260}	{74 070}		70 010	{77 180}	75 200	72 430	
5 $^3A_1$						70 840				
5 $^1A_1$						71 910		{88 750}	{84 940}	
6 $^1A_1$						74 320				
1 $^3A_2$			31 020	30 920	31 340	31 100	31 180			27 000[e], 30 600[d]
1 $^1A_2$	35 290	32 520	34 790	32 090	35 210	34 860	35 010	35 000	32 080	29 800[c], 31 000[g], 31 200[f]
2 $^3A_2$			60 300	57 150	{71 630}	59 570	60 060			
2 $^1A_2$	{80 040}	{77 030}	60 930	57 490	{75 610}	60 100	60 660	60 920	59 290	
3 $^3A_2$			72 300	68 750		68 600	72 110			
3 $^1A_2$			73 320	68 780		68 700	72 970	71 990	69 460	
4 $^3A_2$			{73 780}	{71 640}		70 410	74 110			
4 $^1A_2$			{79 540}	{76 360}		70 720	{79 080}	{79 920}	{76 050}	
5 $^3A_2$						73 120	{79 480}			
5 $^1A_2$						73 700				
6 $^1A_2$						73 900				
1 $^3B_1$			49 160	46 160	57 390	48 850	49 100			46 800[d]
1 $^1B_1$	79 330	74 900	52 000	47 840	62 040	51 610	51 890	52 000	49 510	>46 500[f], 46 900[g], 47 300[c]
2 $^3B_1$			62 060	58 140	{78 160}	60 840	61 770			
2 $^1B_1$	{88 780}	{84 260}	63 060	58 550	{81 550}	61 420	62 490	62 030	59 730	58 800[g]
3 $^3B_1$			68 750	66 100		65 920	71 420			
3 $^1B_1$			71 070	66 810		66 890	72 260	70 820	68 020	
4 $^3B_1$			72 240	68 690		67 310	72 270			
4 $^1B_1$			75 310	71 060		68 180	74 120	75 250		
5 $^3B_1$						68 480	73 920			
5 $^1B_1$			{77 120}	{73 260}		68 950	{79 400}	{79 780}		
6 $^3B_1$						70 980	{84 260}			
6 $^1B_1$						71 160				
7 $^1B_1$						73 010				
8 $^1B_1$						73 650				
9 $^1B_1$						73 770				
1 $^3B_2$			72 620	70 520	{87 190}	67 420	82 090			
1 $^1B_2$	{98 190}		75 380	72 080		67 980	86 420	84 280	81 720	
2 $^3B_2$			{87 260}	{83 210}		73 310	{87 180}			
2 $^1B_2$			{94 080}	{85 860}		73 640	{93 970}	{93 990}		
3 $^3B_2$						74 530				
3 $^1B_2$						74 560				

[a] The ground state orbital occupancy of ketene is $\ldots 7a_1^2 1b_2^2 1b_1^2 2b_2^2 2b_1^2$. The calculations were carried out at the ground state cc-pVTZ CCSD(T) optimized geometry (see Table IV). The number of CGFs in each basis set is indicated in parentheses. The purely valence-type electronic states are printed in bold face. EOM=EOM-CCSD. In curly brackets the state next in energy within a given multiplicity and symmetry set is given; these states most likely do not correspond to the correct state order due to deficiences in the basis set. The 1*s* core orbitals on the C and O atoms have been kept frozen during TZ, a-spd-DZ, and a-TZ CIS calculations. Several higher-lying Rydberg-type triplet states are not reported, as the related singlet-triplet splittings are all quite small.

[b] To ease notation, in the designation of the correlation-consistent basis sets the prefix cc-pV was dropped and aug is abbreviated as a.

[c] From electron-impact energy-loss spectra (Ref. 8).

[d] From threshold electron-impact excitation spectrum (Ref. 9).

[e] From electronic spectra (Ref. 4).

[f] From absorption experiment (Ref. 3).

[g] Reference 6.

[h] Reference 12.

berg formula [see Eq. (1) below]; and (b) accuracy of even the most sophisticated calculation might not be sufficient to directly help the assignment of these states of low term values.

When comparing experimentally measured excitation energies to calculated vertical excitation energies, it should be kept in mind that there is an imprecise relationship between the absorption maximum and the vertical energy difference obtained in the calculation. Furthermore, it is possible to observe the 0–0 transition (the adiabatic separation) and these values are always reported when available.

As noted previously for a few states,[67] nice agreement can be found between EOM-CCSD results and experiments for the vertical excitation energies of ketene. For the valence states and for the Rydberg-type $2\,^1B_1$ state the errors are of the same magnitude as the discrepancies between the different experiments. In light of this nice agreement we are confident that the vertical excitation energies for most other electronic states of ketene obtained by the present calculations are accurate and should aid further experimental investigations on the electronic spectra of ketene.

As far as the previous *ab initio* calculations on vertical excitation energies of ketene are concerned, the early Hartree–Fock results of Dykstra and Schaefer[33] are mostly inadequate, as already pointed out by Allen and Schaefer.[36] The calculations of Vogt *et al.*[9] resulted in vertical excitation energies for 14 states up to an energy of 58 500 cm^{-1}. The order of the first five states below 50 000 cm^{-1} was obtained correctly, while order of the next states calculated seems to be unreliable as some low-lying states are missing (e.g., $3\,^1A_1$, $3\,^3B_1$, and $3\,^1B_1$), while order of some others differs significantly from that reported here. In an *ab initio* study constituting to an early application of the EOM method on ketene Galasso and Fronzoni[42] reported vertical excitation energies for 15 electronic states of energies up to 90 000 cm^{-1}. (This large value is simply due to deficiencies in the basis set applied, see also Table I). The states investigated are by no means those of lowest energy, as even the third state, $1\,^3A_1$, is missing from their compilation as results are reported for only two triplet states. Order of the singlet states is different, in a few occasions, from that reported here due again to considerable basis set limitations in the study of Galasso and Fronzoni (e.g., they interchange the $2\,^1A_2$ and $2\,^1B_1$ states, while calculate too high of an energy for the $4\,^1B_1$ state). The present systematic study of the electronic states of ketene reveals that even in the most detailed theoretical work on the low-lying electronic states of ketene prior to the present EOM-CCSD study the five excited states investigated by Allen and Schaefer,[36] $1\,^3A_2$, $1\,^1A_2$, $1\,^3A_1$, $1\,^1B_1$, and $2\,^1A_1$, are *not* of lowest energy. Thus, their Figs. 5 and 6 should significantly be altered to include the $1\,^3B_1$ state just below $1\,^1B_1$, and the states $2\,^3A_1$, $2\,^3A_2$, $2\,^1A_2$, $2\,^3B_1$, $2\,^1B_1$, and $3\,^3A_1$ between their states $1\,^1B_1$ and $2\,^1A_1$.

IV. RYDBERG STATES

The optical spectrum of ketene consists of weak diffuse bands between 21 100 and 27 030 cm^{-1}, another system of diffuse bands between 27 030 and 38 500 cm^{-1}, the maximum of the band located at 31 250 cm^{-1}, and a third band system between 46 500 and 51 300 cm^{-1}. These latter transitions belong to the first member of the formally B_1 symmetry Rydberg electronic states, as discussed below.

It is well known that Rydberg series terminate at a corresponding ionization energy. As mentioned in the Introduction, one principal advantage of the EOM-CC scheme is that calculations on systems having one more or less electrons than the reference state are straightforward. Thus, ionization energies, E_i, of ketene have been determined at the PBS EOMIP-CCSD level. They are presented in Table II together with the available experimental results.[20,30] Agreement between the measured and calculated values is very satisfactory.

TABLE II. Ionization energies, in cm^{-1}, of ketene.[a]

		VIE		AIE
Symm.	Order	PBS EOM	Expt.[b]	Expt.[c]
A_1	$\tilde{D}$	135 390	135 500	130 980
	$\tilde{E}$	147 790		145 900
	$\tilde{H}$	188 260		
A_2		219 830		
B_1	$\tilde{X}$	77 280	79 040	77 580
	$\tilde{B}$	124 220	120 980	117 830
	$\tilde{G}$	171 500		
B_2	$\tilde{A}$	115 700	114 530	111 280
	$\tilde{C}$	135 080	131 470	129 600
	$\tilde{F}$	156 230		

[a] VIE = vertical ionization energy; AIE = adiabatic ionization energy; EOM = EOMIP-CCSD.

[b] Reference 20.

[c] Reference 30.

The first two ionization energies of ketene, around 77 500 and 111 300 cm^{-1}, are well separated. Therefore, all Rydberg absorptions below the first ionization limit will originate at the highest occupied molecular orbital (HOMO) of the ground electronic state of ketene, which happens to be the $2b_1$ orbital having substantial $\pi_{\mathrm{C{=}C}}$ bonding character as opposed to $\pi_{\mathrm{C{=}O}}$ bonding character assumed by Price *et al.*[3] The low-lying Rydberg states should then belong to $ns \leftarrow 2b_1$, $np \leftarrow 2b_1$, and $nd \leftarrow 2b_1$ excitations. Symmetry considerations reveal that $ns \leftarrow 2b_1$, $np \leftarrow 2b_1$, and $nd \leftarrow 2b_1$ electronic promotions lead to electronic states of B_1, triads of $\{A_1, A_2, B_1\}$, and pentads of $\{A_1, A_2, B_1, B_1, B_2\}$ symmetry, respectively. Then, splitting caused by the aspherical core and energy ordering of the resulting states is of principal concern and constitutes a substantial part toward assignment of the lower-lying Rydberg polyads of ketene.

The first *vertical* singlet–singlet Rydberg-type transition, which can be ascribed to $ns \leftarrow 2b_1$ with $n=3$, is the $1\,^1B_1 \leftarrow 1\,^1A_1$ transition at around 47 000 cm^{-1}.[3,6,8] This assignment is supported by electron-impact energy-loss experiments in which a singlet–singlet vertical excitation at 47 300 cm^{-1} was assigned as $3s \leftarrow 2b_1$,[8] and by threshold electron spectroscopy.[9] However, geometry optimizations following the $1\,^1B_1$ state along the C_s^{I} path at the PBS EOM-CCSD level confirm a suggestion of Allen and Schaefer[38] concerning this second singlet excited state of ketene: the $1\,^1B_1$ state dissociates monotonically along the C_s^{I} path into $\tilde{b}\,^1B_1$ CH$_2$ and $X\,^1\Sigma^+$ CO. Therefore, it is not at all surprising that Ashfold *et al.*[11] were unable to observe the corresponding vibronic band system in their REMPI experiment. In fact, this important characteristic of the $1\,^1B_1$ state offers a complementary explanation to that presented by Ashfold and co-workers to rationalize their lack of observance of bands around 50 000 cm^{-1}. Nevertheless, employing the usual Rydberg formula

$$\nu_0^n = \mathrm{E_i} - \frac{R_\infty}{(n-\delta)^2} \tag{1}$$

with $\mathrm{E_i}$=77 500 cm^{-1} and R_∞=109 737 cm^{-1} gives, for $n=3$ and ν_0^3=47 000 cm^{-1}, a quantum defect of δ=1.1, a very reasonable value (e.g., Price *et al.*[3] used δ=1.07 for the ns series). These values result in an ns series (47 000, 64 500, 70 300, 72 900, 74 400, 75 200) cm^{-1} for $n=3-8$. Therefore, the states $1\,^1B_1$, $3\,^1B_1$, $7\,^1B_1$, and $11\,^1B_1$ could be assigned as the $n=3-6$ members of the lowest-lying ns Rydberg series of ketene. Note at the end that the assignment just presented is different from that given by Price *et al.*[3] for $n=3$ but seems to support their assignments for the $n=4-6$ members of the ns Rydberg series.

Using theoretical data alone, assignment of the np and nd Rydberg series can be based on (a) vertical excitation energy values; (b) the observation that only the nd Rydberg pentads contain states of B_2 symmetry; and (c) application of Madelung's empirical rules for atoms[91] to the Rydberg states of ketene, which predicts the following mean energy order for the Rydberg polyads of interest: $3s$, $3p$, $4s$, $3d$, $4p$, $5s$, $4d$, $5p$, and $6s$. Note, first of all, that the WMR EOM-CCSD data in Table I place the $1\,^1B_2$ state at about 80 000 cm^{-1}, at an energy considerably higher than the first $\mathrm{E_i}$ of ketene. This result points clearly to the inadequacy of the WMR basis to describe the B_2 members of the nd Rydberg pentads and to the subsequent need to include more diffuse functions in basis sets designed for computational studies of Rydberg states of molecules. The PBS EOM-CCSD result of 72 080 cm^{-1} is more reliable, due mostly to the fact that the most diffuse d functions in the PBS basis have exponents 0.0386 and 0.0639 on the C and O atoms, respectively, while the most diffuse d functions in the WMR basis have exponents of 0.0815 and 0.1608. Nevertheless, the aug-spd-cc-pVDZ CIS result, 67 980 cm^{-1}, suggests that the true excitation energy should be considerably lower, around 64 000 cm^{-1}. Since the aug-cc-pVDZ basis set was enlarged sequentially in the aug-{spd}-cc-pVDZ CIS calculations to include diffuse functions of higher and higher angular momenta, the results obtained and presented in Table III are very instructive during assignment of the Rydberg polyads. For example, inclusion of very diffuse s functions in the basis set does not change the vertical excitation energies of the singlet A_1 states as no s-type Rydberg or semi-Rydberg states belong to this symmetry species.

Careful examination of the entries of Table III suggests that the triad $\{2\,^1A_1, 2\,^1A_2, 2\,^1B_1\}$ is the perfect candidate for the first np, $n=3$, Rydberg triad of ketene. Use of the Rydberg formula with ν_0^3=55 000 cm^{-1} then gives a reasonable quantum defect of δ=0.8, which in turn results in an estimate of the np Rydberg series (54 800, 66 800, 71 300, 73 400) for $n=3-6$. Furthermore, simple electrostatic arguments suggest that splitting of np orbitals becomes smaller as n increases. Thus, the core splitting, about 2000 cm^{-1} at the PBS EOM-CCSD level, observed for the $n=3$ triad should be less for $n>3$. Note also that the core splitting of the $3p$ triad thus determined is very similar to that found in formaldehyde.[16] To proceed further it is noted that PBS EOM-CCSD 0–0 transition energy calculations place the first three $^1A_1$ excited states at around 55 000, 64 000, and 72 000 cm^{-1}, the last value being too high due to basis set deficiencies. Therefore, the 0–0 transition triads with $n=3$ and 4 are assigned to lie around 55 000 and ''72 000'' cm^{-1}, respectively, and the $4p$ triad is assigned as $\{4\,^1A_1, 4\,^1A_2, 6\,^1B_1\}$. This choice assigns $3\,^1A_1$ as a member of the first Rydberg pentad with $n=3$. This assignment is further supported by the use of δ=0.0 for the $3d$ pentad yielding 65 300 cm^{-1} as its mean energy, suggesting also that its true value should be somewhat lower. The present calculated values thus support an early assignment proposed by Robin,[16] in that the band at 54 680 cm^{-1} belongs to an np Rydberg series instead of to an ns series. Based on limited amount of data Robin[16] proposed two assignments for the bands observed around 62 000 cm^{-1}: they are either $4p \leftarrow 2b_1$ or $3d \leftarrow 2b_1$ Rydberg states split by the aspherical core. The present theoretical results support the view that the $3d$ and $4p$ Rydberg polyads are indeed close to each other in energy, separated by less than 2000 cm^{-1}. The proposed formal assignments of the $3d$, $4p$, and $4d$ Rydberg polyads are given in the last column of Table III.

In their detailed experimental study Ashfold and co-workers[11] measured several two-photon resonances of ketene in the energy range 54 000–71 000 cm^{-1} and proposed assignments for most observed bands. The assignments were based on (a) differences between REMPI spectra observed with linearly and circularly polarized laser radiation; and (b) the argument that no component of the electric dipole moment operator transforms as A_2, thus excited states of A_2 symmetry are unlikely to appear in the one-photon absorption spectrum while should be observable using REMPI. Assignment of the $2\,^1A_1 \leftarrow 1\,^1A_1$ transition at 54 683 cm^{-1} is based upon the former argument and is clearly supported by the EOM-CCSD calculations. Assignment of the electric dipole forbidden $2\,^1A_2 \leftarrow 1\,^1A_1$ transition at 56 740 cm^{-1} is based upon the latter argument and it seems to be supported by the EOM-CCSD calculations. The third, $^1B_1$, component of the $n=3$ triad was placed by Ashfold *et al.* to 61 359 cm^{-1}. This assignment, on the other hand, is clearly questioned based on all calculated results as this energy is more characteristic of the $3\,^1A_1$ state than of the $2\,^1B_1$ state. Therefore, the band observed at 61 359 cm^{-1} is tentatively assigned to $3\,^1A_1$, a state which is a member of the $3d$ pentad. Appearance of the transition corresponding to $2\,^1B_1$ is expected at around 55 000 cm^{-1}, at the edge of the spectrum observed and assigned by Ashfold *et al.* Assignment of the three $^1B_1$ transitions, given by Ashfold *et al.*, between 64 782 and 70 425 cm^{-1} is also questioned based on the aug-spd-cc-pVDZ CIS data, which suggest that two transitions to $^1B_1$ states remain unaccounted for in this energy range. Since both these states belong to the first Rydberg pentad ($3d$), elementary considerations suggest that they could indeed be missed in REMPI experiments.

In summary, the vertical and adiabatic excitation data obtained from high-quality EOM-CCSD and CIS calcula-

TABLE III. Singlet–singlet excitation energies, in cm^{-1}, for some Rydberg-type electronic states of ketene.[a]

			Vertical exc. en.					0–0 Trans.			
I.R.	State	Sym.	a-DZ	a-s-DZ	a-sp-DZ	a-spd-DZ	PBS	PBS EOM	Expt.[b]	Expt.[c]	Assign.[e]
A_1	$2\,^1A_1$	C_s^{I}	64 040	64 070	61 200	61 180	58 320	54 550	54 683	*54 680*	$3p$
	$3\,^1A_1$		69 440	69 480	67 130	67 040	65 610	[63 850]	*61 359*		$3d$
	$4\,^1A_1$		{79 850}	{79 830}	70 040	70 010	74 070	72 460[72 410]	66 206		$4p$
	$5\,^1A_1$				71 980	71 910	{85 390}				$4d$
	$6\,^1A_1$				74 350	74 320					$5p$
	$7\,^1A_1$				75 330	74 710					
	$8\,^1A_1$				77 280	75 420					
A_2	$2\,^1A_2$	C_{2v}	60 730	60 270	60 110	60 100	57 490	55 660	56 740		$3p$
	$3\,^1A_2$		74 610	70 920	68 730	68 700	68 780	[66 800]			$3d$
	$4\,^1A_2$		{79 850}	74 570	70 730	70 720	{76 360}				$4p$
	$5\,^1A_2$			{74 790}	73 890	73 700					$4d$
	$6\,^1A_2$				73 960	73 900					$5p$
	$7\,^1A_2$				74 750	74 730					
B_1	$1\,^1B_1$	$(C_s^{\mathrm{I}})^{\mathrm{d}}$	51 780	51 640	51 620	51 610	47 840				$3s$
	$2\,^1B_1$	C_{2v}	62 910	61 470	61 430	61 420	58 550	56 800			$3p$
	$3\,^1B_1$		{73 720}	67 530	67 200	66 890	66 810	[65 000]	64 782	64 760	$4s$
	$4\,^1B_1$			69 650	68 590	68 180	71 060				$3d$
	$5\,^1B_1$			71 330	69 090	68 950	73 260				$3d$
	$6\,^1B_1$			72 540	71 190	71 160	{84 130}		68 759		$4p$
	$7\,^1B_1$			73 710	73 120	73 010			70 425	70 371	$5s$
	$8\,^1B_1$			75 860	73 790	73 650					$4d$
	$9\,^1B_1$			76 500	74 120	73 770					$4d$
	$10\,^1B_1$			{79 180}	74 530	74 040					$5p$
	$11\,^1B_1$				75 050	74 470				72 983	$6s$
B_2	$1\,^1B_2$			{93 840}	68 830	67 980	72 080				$3d$
	$2\,^1B_2$				{74 360}	73 640	{85 860}				$4d$
	$3\,^1B_2$					74 560					

[a] I.R. = Irreducible representation. Sym. = True symmetry of the equilibrium configuration corresponding to this state. The values put in curly brackets are the first members within a given symmetry species and multiplicity set which are suspect of considerable error. The 0–0 transition values put in square brackets were obtained at the respective $2\,^1A_1(C_s^{\mathrm{I}})$, $2\,^1A_2(C_{2v})$, and $2\,^1B_1(C_{2v})$ equilibrium geometries of the $3p$ Rydberg triad determined at the PBS EOM-CCSD level. To ease notation, the cc-pV suffix of the correct basis set notation has been dropped, while aug is denoted as a. The resulting a-{spd}-DZ basis sets have been described in the text. All vertical excitation energies (exc. en.) have been obtained at the CIS level with variants of the DZ basis, whereas the PBS results were determined at the EOM-CCSD (EOM) level. The $1s$ core orbitals on the C and O atoms have been kept frozen during the CIS calculations.

[b] Reference 11, except for 61 359 cm^{-1}, which has been reassigned (see text).

[c] Reference 3. Obviously, the original assignation of the transition at 54 680 cm^{-1} to the $1\,^1B_1$ state is incorrect.

[d] Dissociates monotonically along the C_s^{I} path.

[e] Assign. = formal assignment of the state as a member of a particular Rydberg polyad.

tions of the present study suggest revision of some of the assignments of the Rydberg states reported by Ashfold *et al.*[11] and by Price *et al.*[3] as follows: (a) the core splitting and the energy ordering of the singlet members of the lowest Rydberg ‘‘$3p$ complex’’ given by Ashfold *et al.* is changed due to a new assignment of the $2\,^1B_1 \leftarrow 1\,^1A_1$ transition; (b) it now seems clear that experimental assignment[11] of the 61 359 cm^{-1} transition to the $3\,^1A_1$ state should be revised, while Ashfold *et al.*[11] correctly assigned the now $2\,^1A_1$ and $4\,^1A_1$ 0–0 transitions; (c) some $^1B_1$ states in the energy range 65 000–70 000 cm^{-1} remain unaccounted for experimentally; and (d) the assignment of the $n=4-6$ members of the ns Rydberg series presented by Price *et al.* seems to be correct, they assigned only the starting member, $n=3$, of the series incorrectly. All lower-lying Rydberg states are now believed to be correctly assigned based on theoretical data, symmetry considerations, and use of the Rydberg formula and the available experimental results.

V. STRUCTURES

Though there is a plethora of information available for the structure of the ground state of ketene,[49,92,93] including high-quality estimates of its equilibrium geometry,[49] structures of the excited states of ketene are much less well understood.

Modern electronic structure theories facilitate calculation of equilibrium geometries of excited states by gradient techniques available at the CCSD,[84,85] CCSD(T),[86,87] TD-CCSD,[80] and EOM-CCSD[88,89] levels of interest for this study. While vertical excitation energies are determined at a given geometry in a single EOM-CCSD or CIS run, determination of geometries of excited states is expensive as all states have to be considered separately. Therefore, it was decided that (a) equilibrium geometries are to be determined only for a few singlet states and the lowest triplet state; (b) geometries are to be determined only for the first members in the Rydberg series and the same geometry is assumed for the

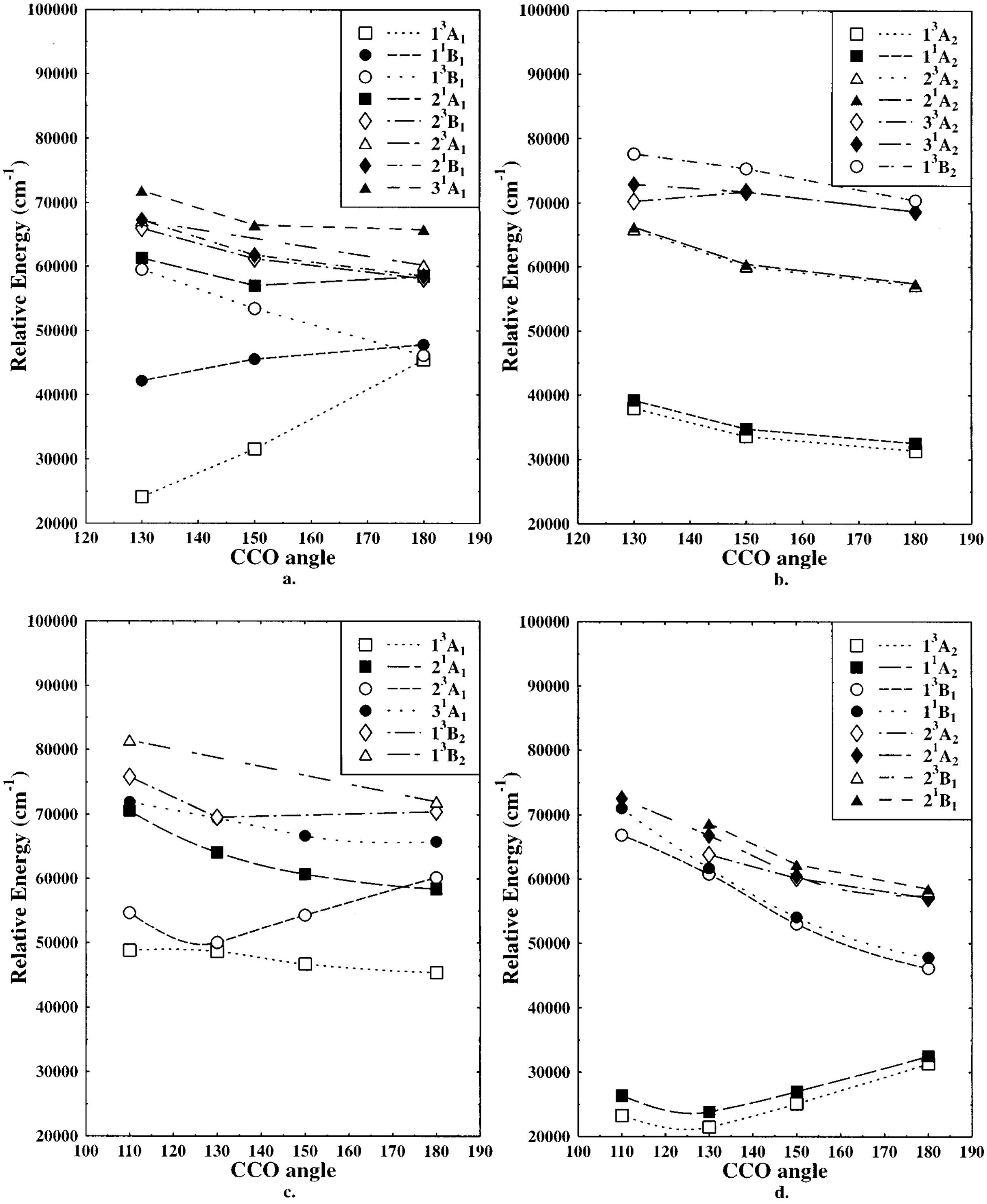

FIG. 1. Dependence of the excited electronic state energies of ketene on the CCO bending angle (all other geometric parameters are relaxed, see text for further details). States are labeled according to their C_{2v} designation: (a) A' states of C_s^{I} symmetry; (b) A'' states of C_s^{I} symmetry; (c) A' states of C_s^{II} symmetry; (d) A'' states of C_s^{II} symmetry.

higher-lying states, as the geometry in a given Rydberg series is not expected to change significantly; and (c) to describe relaxations which break the C_{2v} symmetry of the ground electronic state of ketene, behavior of the states is examined along selected internal coordinates, such as the two direction of bending of the CCO angle. The fact that ketene has its lowest excited states with equilibrium geometries of lower symmetry than the ground state C_{2v} structure is, of course, well known experimentally from the vibrational structure of the related rotationally diffuse electronic bands.

TABLE IV. Structural results for $\tilde{X}\ {}^1A_1$ ketene.[a]

Method	Energy	r(C═O)	r(C═C)	r(C–H)	∠(H–C═C)
DZP CCSD	−152.247 403	1.1717	1.3306	1.0850	119.0
cc-pVTZ CCSD	−152.376 793	1.1569	1.3083	1.0714	119.1
cc-pVTZ CCSD(T)	−152.403 000	1.1639	1.3128	1.0732	119.1
r_0 structure[b]		1.161(2)	1.316(2)	1.078(1)	119.0
r_e structure[c]		1.1603(3)	1.3121(3)	1.0758(1)	119.11(1)

[a] Bond distances in Å, bond angles in deg, and energies in hartrees.

[b] Reference 92.

[c] $r_e(I)$ of Table I of Ref. 49.

For example, Dixon and Kirby[4] noted that the mean spacing of the vibrational progression in the 21 000–26 000 cm^{-1} region is near 475 cm^{-1} indicating an excitation of the skeletal CCO bending motion of the excited state. All calculations reported in this section were performed with the PBS basis set, since this is the smallest basis set containing diffuse functions which is expected to yield reasonable geometries for electronic states of limited diffuseness.

A useful qualitative analysis of the shapes of the excited states of ketene can be based on restricted geometry optimizations, breaking the C_{2v} symmetry along the two possible CCO bending directions. The geometries of interest are produced by fixing the CCO bend at 150°, 130°, and 110° and optimizing all other geometry parameters of the ground electronic state. The total electronic energies obtained at these geometries for a few electronic states by the EOM-CCSD method are plotted on Fig. 1. The states are labelled according to their C_{2v} designation, regardless of their actual symmetry. In the C_s^{I} case the states $1\,{}^3A_1$ and $1\,{}^1B_1$ (the lowest singlet and triplet states of A' symmetry) are stabilized upon bending. (The pronounced energy lowering leads to a barrierless dissociation in the case of the $1\,{}^1B_1$ state, as discussed above.) In addition, a slight bending is favored for the $2\,{}^1A_1$ state, as well. No stabilization occurs for states of A'' symmetry. In the C_s^{II} case the lowest-energy $1\,{}^1A_2$ and $1\,{}^3A_2$ states will bend accompanied by a substantial energy lowering. Note that in the case of the $1\,{}^1A_2$ state this stabilization upon bending leads to changes in the position of the expected fluorescence, as discussed below. As far as states of A' symmetry are concerned, an interesting avoided crossing between the respective $1\,{}^3A_1$ and $2\,{}^3A_1$ states can be observed.

To gain further insight into the potential energy surfaces of the excited states of ketene the equilibrium geometries of some states of particular interest have been determined. *Ab initio* estimates of the equilibrium geometries of the ground and the ${}^1A''(1\,{}^1A_2)$ electronic states, the latter being of interest for the fluorescence of ketene, are given in Tables IV and V, respectively. As mentioned earlier, high-resolution spectroscopic experiments can often give precise values for the 0–0 transition energies, but the ''vertical'' excitations are less well defined. Geometry optimizations for states of considerable Rydberg character yielded the relevant 0–0 excitation energies if they were corrected for effects of zero-point vibrations. Structural results, including relative energies (T_e), geometry parameters, vibrational frequencies, and equilibrium rotational constants, are therefore reported in Table VI for several electronic states of ketene and for the ground state of its cation.

The states which possess equilibrium geometries of C_{2v} symmetry, $2\,{}^1A_2$ and $2\,{}^1B_1$, have rather similar geometries due perhaps to the fact that they belong to the same triplet of the first np Rydberg triad (see above). Furthermore, their geometries differ from that of the ground state the same way as the cationic ground state geometry differs from the geometry of the neutral ground state: the CO bond lengths are somewhat shorter, the CH bond lengths are slightly longer, while the CC bonds are considerably elongated. Interestingly, the third member of this triad, $2\,{}^1A_1$, does not have a C_{2v} equilibrium geometry but has C_s^{I}. In the C_s^{II} states, the CH bond lengths are again consistently elongated, and only a small change in the CCH angles accompany excitations. The longest CO and CC bonds are found for the pure valence $1\,{}^1A_2$ state. Its CCO angle of 130.3° also suggests that the binding situation for this state is substantially different from the others.

Though the S_1-S_0 fluorescence emission is spin-allowed and thus should be observable, all attempts[14(c),14(d),22–25] during the last 40 years failed in observing fluorescence of ketene. Apart from the extremely fast radiationless deexcitation processes operative in excited state ketene, the other difficulty confronting the experimentalist looking for ketene fluorescence is the varying estimates of the energy difference between the zero-point vibrational level in S_1 and

TABLE V. Structural results for $1\,{}^1A''$ (C_s^{II}) ketene.[a]

Method	r(CO)	r(CC)	r(CH$_c$)	r(CH$_t$)	∠(CCO)	∠(CCH$_c$)	∠(CCH$_t$)
DZP TD-CCSD	1.2066	1.4530	1.0928	1.0873	128.5	119.7	120.1
DZP EOM-CCSD	1.2059	1.4354	1.0871	1.0946	130.3	120.0	120.1
cc-pVTZ TD-CCSD	1.1825	1.4100	1.0722	1.0777	135.6	121.0	121.7

[a] Bond distances in Å and bond angles in deg.

TABLE VI. Molecular constants of some electronic states of ketene from PBS EOM-CCSD calculations.[a]

Param.	$1\,^1A_1$ (C_{2v})	$1\,^3A_2$ (C_s^{II})	$1\,^1A_2$ (C_s^{II})	$2\,^1A_1$ (C_s^{I})	$2\,^1A_2$ (C_{2v})	$2\,^1B_1$ (C_{2v})	$\tilde{X}\,^2B_1$[d] (C_{2v})
T_e	0	20 490	21 640	54 550	55 660	56 800	78 070
r(CO)	1.170	1.200	1.203	1.158	1.133	1.136	1.132
r(CC)	1.329	1.463	1.431	1.435	1.394	1.387	1.408
$r(\mathrm{CH}_t)$	1.091	1.094	1.093	1.109	1.101	1.105	1.100
$r(\mathrm{CH}_c)$		1.100	1.102				
$\angle(\mathrm{CCH}_t)$	118.7	119.9	120.3	116.7	116.1	120.0	117.6
$\angle(\mathrm{CCH}_c)$		119.3	118.9				
$\angle$(OCC)		127.5	131.0	158.3			
$\angle$(OCCH)				96.0			
ν_1	3300(3166)[b]		3257	3118	3146	3215	
ν_2	3179(3070)[b]		3082	2927	3096	3013	
ν_3	2215(2152)[b]		1809	2050	2275 (2319)[c]	2253	
ν_4	1415(1388)[b]		1434	1199	1388 (1468)[c]	1776	
ν_5	1156(1118)[b]		1134	1012	1060 (1121)[c]	1337	
ν_6	1000(977)[b]		1051	999 (827)[c]	1028	1063	
ν_7	619(588)[b]		1023	615	828	1017	
ν_8	522(528)[b]		610	501	469 (475)[c]	646	
ν_9	430(433)[b]		464	377	398	431	
ZPVE	6920		6932	6398	6840	7380	
A_e	9.1322	3.6011	3.8748	6.8783	8.5536	9.1234	8.8069
B_e	0.3372	0.3656	0.3630	0.3225	0.3318	0.3293	0.3274
C_e	0.3252	0.3319	0.3324	0.3138	0.3194	0.3178	0.3157

[a] Adiabatic excitation energies, T_e, vibrational frequencies, ν_i, $i=1-9$, zero-point vibrational energies, ZPVE, and equilibrium rotational constants, A_e, B_e, and C_e, are all given in cm^{-1}. The true symmetries of the electronic states are indicated, in parentheses, next to their designation based on the energy order of the corresponding vertically excited electronic states. In C_s^{II} symmetry H_c and H_t are the hydrogens cis and trans with respect to the bent CCO unit, respectively. The vibrational frequencies are not sorted according to symmetry but are given simply in descending order. Experimental vibrational frequencies, where available, are given in parentheses. Naturally, molecular constants of the $1\,^1A_1$ and the $\tilde{X}\,^2B_1$ states have been obtained from PBS CCSD calculations. The reference energy of the ground $1\,^1A_1$ state is $-152.277\,751$ a.u.

[b] References 49 and 93.

[c] Reference 11.

[d] Ground electronic state of the cation.

the zero-point and higher-lying vibrational levels in the ground singlet state. The present work offers a state of the art value for the 0–0 transition frequency based on the energy difference between the energy minima of the $1\,^1A''$ first excited state and of the $1\,^1A_1$ ground state. Another possible estimate is the difference of the potential energy at the calculated equilibrium geometry of the first excited singlet state and the potential energy of the ground state evaluated at a reference geometry equivalent to the equilibrium configuration of $1\,^1A''$. These values are 21 447 and 9824 cm^{-1}, respectively, using the cc-pVTZ basis and the TD-CCSD and CCSD methods for the excited and ground states, respectively. Note that the $1\,^1A''$ equilibrium geometry is obtained with the TD-CCSD method, and is given in Table V along with EOM-CC and TD-CCSD estimates using smaller basis sets, while the ground state geometry is provided in Table IV.

VI. SUMMARY

Extensive theoretical calculations employing state of the art *ab initio* methods of molecular electronic structure theory resulted in the following important conclusions, some about the methods themselves, some about salient features of the electronic states of ketene, and some about the experimental methods used to investigate the electronic states:

(1) Vertical excitation energies have been obtained, using both the CIS (TDA) and EOM-CCSD methods, for altogether more than 40 singlet and triplet electronic states of ketene, including all excited states below perhaps 70 000 cm^{-1}, close to the first $\mathrm{E_i}$ of ketene, 77 500 cm^{-1}. It is clearly demonstrated that the only pure excited valence states of ketene are the $1\,^3A_1$, $2\,^3A_1$, $1\,^3A_2$, and $1\,^1A_2$ states. All other excited states are either valence/Rydberg states or can clearly be identified as Rydberg states. After sorting the states according to their irreducible representation within C_{2v} symmetry, the triplet and singlet states come mostly in pairs with the triplets having the lower energy.

(2) Calculation of the vertical ionization energies (VIE) of ketene, at the PBS EOM-CCSD level, support all the values determined experimentally[20,30] and reveal that ionizations corresponding to the A_2 symmetry species are high in energy.

(3) It is evident from this study that even lower-lying Rydberg states of ketene cannot be properly characterized by standard basis sets. Addition of considerably more diffuse s, p, and (perhaps) d functions is necessary to the augmented correlation-consistent basis sets of Dunning[73] or the PBS basis of Sadlej.[72] Compared to its size the WMR basis[75] performs poorly when description of higher-lying states is sought, further emphasizing the need to the inclusion of

rather diffuse functions in the basis set before attempting to extend the core part of the basis. The aug-{spd}-cc-pVDZ basis defined and employed in this study seems to perform very well even close to the first ionization energy of ketene.

(4) The vertical and adiabatic excitation data obtained from high-quality EOM-CCSD and CIS calculations suggest revision of several assignments of the Rydberg states proposed by Ashfold *et al.*[11] and by Price *et al.*[3] as follows: (a) the core splitting and the energy ordering of the singlet members of the lowest Rydberg ''3*p* complex'' given by Ashfold *et al.* is changed due to a new assignment of the $2\,^1B_1 \leftarrow 1\,^1A_1$ transition; (b) assignment of the transition to the $3\,^1A_1$ state is also changed; (c) some $^1B_1$ states in the energy range 65 000–70 000 cm^{-1} remain unaccounted for experimentally; and (d) the assignment of the $n=4-6$ members of the *ns* Rydberg series presented by Price *et al.* seems to be correct, they assigned only the starting member, $n=3$, of the series incorrectly. All lower-lying Rydberg states are now believed to be correctly assigned based on theoretical data, symmetry considerations, and use of the Rydberg formula and the available experimental results.

(5) The second singlet excited state of ketene, formally $1\,^1B_1$, is shown to dissociate without barrier along the $C_s^{\rm I}$ path into $\tilde{b}\,^1B_1$ CH_2 and $X\,^1\Sigma^+$ CO. Therefore, while vertical excitations to this state have been observed around 47 000 cm^{-1}, the possibility to observe the related 0–0 transition should be ruled out. This second lowest energy singlet dissociation channel of ketene provides an ideal example of a unimolecular reaction without a barrier.[48]

(6) Detailed structural results, including adiabatic excitation energies, equilibrium geometry parameters, rotational constants, and vibrational frequencies are reported for the electronic states $1\,^1A_1(C_{2v})$, $2\,^1A_1(C_s^{\rm I})$, $1\,^3A_2(C_s^{\rm II})$, $1\,^1A_2(C_s^{\rm II})$, $2\,^1A_2(C_{2v})$, and $2\,^1B_1(C_{2v})$, as well as for the ground electronic state of the cation. These data should provide a good starting point to the further experimental exploration of these states.

(7) A lower estimate of the occurrence of fluorescence from the lowest excited singlet state of ketene is determined to be 9800 cm^{-1}. Therefore, signs of fluorescence of ketene should be searched for in the near-infrared region of the spectrum. However, the extremely fast radiationless deexcitation processes operative in excited state ketene hinder and might even prevent observation of ketene fluorescence.

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