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Electronically Excited States of Methylenecycloalkanes

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The vacuum UV spectra of methylenecyclopropane, methylenecyclobutane, methylenecyclopentane, and methylenecyclohexane have been obtained from 45 000 to 70 000 cm^{-1}. The transitions for methylenecyclopropane have been calculated at the EOM-CCSD/6-311(2+,2+)G** level. Using the equilibrium C═C bond lengths, the calculated transition energies are uniformly larger than observed, but increasing the bond length a small amount led to quite good agreement. Here, the transitions are found to originate from the two higher energy occupied cyclopropane ring orbitals in addition to the π orbital. The transitions for methylenecyclohexane are found to be linearly related to those for isobutene. CIS calculations for all of the methylenecycloalkanes using somewhat lengthened C═C bonds reproduced the lower energy transition energies fairly well.

1. Introduction

The excited states of alkenes have received much attention.[1] In many cases, the lowest energy transition is to a π−3s Rydberg state, which is followed by the relatively intense π−π* transition. The higher energy transitions are usually to Rydberg states that originate from the π-orbital. One group of alkenes that have been of interest to us is the methylenecycloalkanes. They have not received much previous study.[2] Methylenecyclopropane (**1**) presents the interesting possibility that the cyclopropane ring orbitals may be involved in one of the transitions. Methylenecyclohexane (**4**), on the other hand, should be similar to 1,1-dialkyl-substituted alkenes such as isobutene (**5**). An examination of a series of these compounds including methylenecyclobutane (**2**) and methylenecyclopentane (**3**) may provide useful information on the effect of ring size on the transition energies.

The present study is both experimental and computational. The VUV spectra were obtained from 45 000 to 70 000 cm^{-1}, and the transition energies were calculated using EOM-CCSD that is usually considered to be among the best of the single reference methods for such calculations.[3]

2. Methylenecyclopropane (1)

The spectrum is shown in Figure 1. There is little structure in any of the bands, and the intensity of the strong low energy band corresponds to an oscillator strength of 0.32.[4] It is clearly not possible to make assignments on the basis of the limited information in the spectrum. EOM-CCSD calculations were carried out using 6-311(2+,2+)G** that we have found to be particularly useful for excited-state calculations.[5,6] The structure of methylenecyclopropane was obtained by geometry optimization at the CCSD/6-311++G** level and gave r(C═C) = 1.3266 Å (Table 1). The effect of anharmonicity at the zero-point vibrational level was estimated via B3LYP/6-311+G* vibrational frequency calculations that included anharmonicity, and the change in C═C bond length was 0.0021 Å, making the final bond length = 1.3283 Å. This is in reasonable agreement with the structure derived from microwave spectroscopy (1.332 Å).[7]

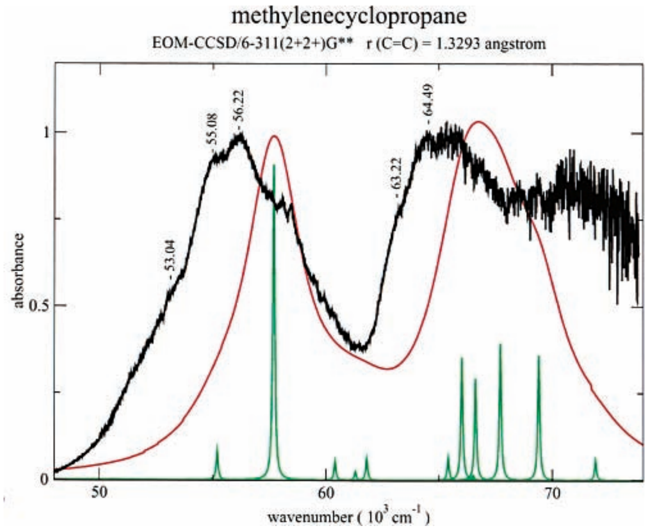

Figure 1. VUV spectrum of methylenecyclopropane. The red curve is a simulation of the spectrum using the EOM-CCSD calculated transition energies and oscillator strengths with r(C═C) = 1.329 Å. The individual calculated transitions are shown in green.

The transition energies calculated with r(C═C) = 1.329 Å are given in Table 2. It is difficult to appreciate the effect of overlapping bands with different oscillator strengths by just examining the numerical values. Therefore, each transition energy was replaced by a Lorentzian curve with an area proportional to the calculated oscillator strength. The result is shown as the green curve in Figure 1. It is clear that the calculated π−π* transition energy is significantly higher than the experimental value.

This is commonly found in calculations for alkenes. With ethene, the π−π* transition is observed at 7.65 eV, whereas a EOM-CCSD/6-311(2+,2+)G** calculation give 8.12 eV.[8] Higher level CASPT2[9] and MRSCF[10] calculations led to similar values. This transition is, of course, a vertical transition, and, following Condon,[11] the starting geometry for the above calculation was taken as the average geometry at the zero-point vibrational level. An earlier classical description of the process by Franck made use of the classical turning point for the

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TABLE 1: Calculated Structures of the Methylenecycloalkanes[a]

level	E	r(C═C)	r(═C−C)	CCC	ν(C═C)	μ(D)
		a. Methylenecyclopropane (C_{2v})				
B3LYP/6-311++G**	−156.01030	1.3195	1.4669	63.45	1826	0.45
anharmonic		1.3221	1.4719	63.70	1800	
MP2/6-311++G**		1.3283	1.4698	63.43	1835	0.35
CCSD(full)/6-311++G**	−155.62522	1.3266	1.4724	63.21		
expt[b]		1.332(2)	1.457(2)	63.9(1)	1743	0.40
radical cation:						
CCSD(full)/6-311++G**	−155.27902	1.4098	1.4512	64.03		
triplet:						
CCSD(full)/6-311++G**	−155.49604	1.5208	1.4545	64.42		
		b. Methylenecyclobutane				
B3LYP/6-311++G**	−195.25254	1.3267	1.5230	91.87	1735	0.60
anharmonic		1.3297	1.5295	92.17	1688	
MP2/6-311++G**	−194.72203	1.3359	1.5197	91.29	1738	0.51
expt.[c]		1.331(2)	1.524(4)	92.0(3)	1686	0.51
		c. Methylenecyclopentane				
B3LYP/6-311++G**	−234.70958	1.3314	1.5234	108.44	1712	0.69
MP2/6-311++G**	−233.95542	1.3406	1.5206	108.65	1709	0.56
expt.[d]					1709	0.60
		d. Methylenecyclohexane				
B3LYP/6-311++G**	−274.04218	1.3342	1.5112	114.26	1704	0.71
MP2/6-311++G**	−273.16290	1.3437	1.5065	114.48	1700[f]	0.58
expt.[e]					1654	0.61

[a] Unless otherwise specified, 6 Cartesian d orbitals were used in the calculations. [b] Reference 7 and Mitchell, R. W.; Merritt, J. A. *Spectrochim. Acta, Part A* **1971**, *27*, 1609. [c] Shen, Q; Dorofeeva, O. V.; Mastryukov, V. S.; Almeninngen, A. *J. Mol. Struct*. **1991**, *246*, 237. Scharpen, L. H.; Laurie, V. W. *J. Chem. Phys*. **1968**, *49*, 3041. [d] Durig, J. R.; Li, Y. S.; Carreira, L. A. *J. Chem. Phys*. **1972**, *57*, 1896. [e] Li, Y.-S. *J. Phys. Chem*. **1961**, *34*, 1516. [f] This calculation used 5d orbitals, the use of 6d's led to an imaginary frequency.

TABLE 2: Calculated Transition Energies for Methylenecyclopropane, EOM-CCSD/6-311(2+,2+)G**[a]

		r(C═C) = 1.329 Å			r(C═C) = 1.370 Å[b]				
state		eV	f	kK	ev	f	kK	orig MO	term MO
A_1	1	7.16	0.227	57.72	6.96	0.250	56.15	15	19
	2	7.98	0.000	64.38	7.94	0.057	64.04	13,14,15	16,17,19
	3	8.18	0.089	65.97	8.06	0.131	64.98	13,14,15	16,17,19
	4	8.26	0.073	66.59	8.20	0.037	66.16	14,15	17,19
	5	8.40	0.099	67.75	8.31	0.024	67.03	14,15	17,19
	6	8.81	0.001	71.02	8.80	0.005	71.00	13	16
	7	8.90	0.036	71.78	8.72	0.020	70.37	15	19
A_2	1	6.97	0.000	56.21	6.89	0.000	56.56	14	19
	2	7.40	0.000	59.68	7.24	0.000	58.42	15	17
	3	8.14	0.000	65.68	7.00	0.000	64.40	15	17
	4	8.53	0.000	68.81	8.52	0.000	68.66	14	19
	5	8.68	0.000	69.97	8.59	0.000	69.27	15	17
B_1	1	6.84	0.021	55.15	6.68	0.023	53.85	15	16
	2	7.49	0.014	60.43	7.33	0.014	59.58	15	16
	3	7.60	0.006	61.32	7.45	0.005	60.08	13	19
	4	8.11	0.016	65.41	7.94	0.016	64.05	15	16
	5	8.24	0.004	66.49	8.08	0.005	65.16	15	16
B_2	1	7.66	0.016	61.81	7.74	0.015	62.46	14	16
	2	8.30	0.000	66.97	8.23	0.000	66.40	14	16
	3	8.40	0.000	67.71	8.39	0.001	67.64	15	21
	4	8.60	0.090	69.38	8.60	0.088	69.39	13	17
	5	8.91	0.014	71.90	8.99	0.014	72.55	14	16

[a] 1 kK = 1000 cm^{-1}. [b] Calculations using 6-311(3+,3+)G** and r(C═C) = 1.37 Å gave transition energies that were insignificantly different from those given above, except for $5B_2$ shifting to 8.80 eV, and an additional A_1 transition at 8.57 eV (f = 0.030).

vibration rather than the average structure.[12] It would not be surprising to find that the "appropriate" C═C bond length for the transition is somewhat longer than the average bond length because it is known that $\pi-\pi^*$ transitions of alkenes lead to adiabatic geometries with considerably stretched C═C bonds.[13] In the case of **1**, an EOM-CCSD/6-311++G** geometry optimization for the $\pi-\pi^*$ excited state constrained to remain planar gave r(C═C) = 1.432 Å. Similarly, geometry optimization of the radical cation, which is the "core" for the Rydberg transitions, gives r(C═C) = 1.410 Å. There is no requirement that the "vertical" transition occurs at the average C═C bond length,[14] and it has been shown that, to reproduce the relative intensities of the vibrational components of the $\pi-\pi^*$ transition of ethylene, the effect of the methylene torsional mode must be included.[15]

To examine the bond length at the turning point, the displacement of the normal coordinate in the C═C stretching mode was calculated from[16]

$$\langle Q^2 \rangle_n = \frac{h}{4\pi^2 c\omega}\left(n + \frac{1}{2}\right)$$

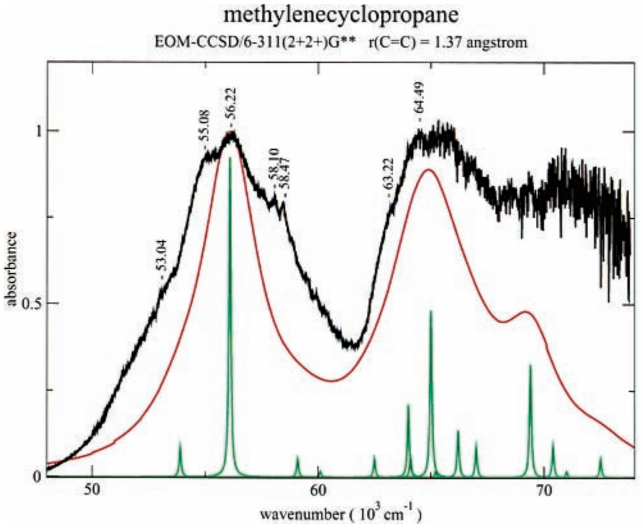

Figure 2. VUV spectrum of methylenecyclopropane. The red curve is a simulation of the spectrum using the EOM-CCSD calculated transition energies and oscillator strengths with r(C=C) = 1.37 Å. The individual components of the bands are also shown.

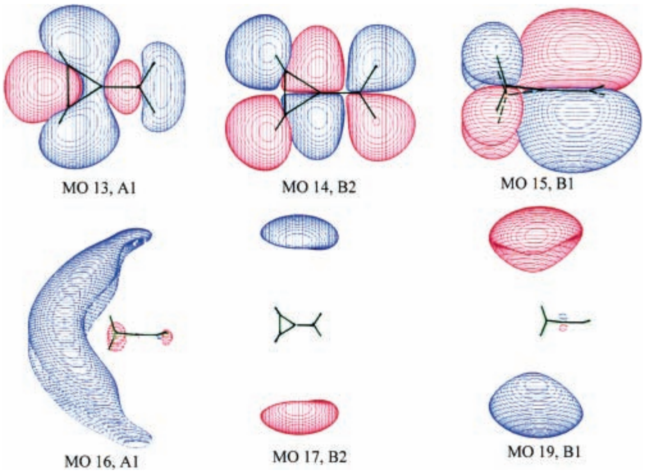

Figure 3. The three highest occupied and the three lowest virtual orbitals for methylenecyclopropane.

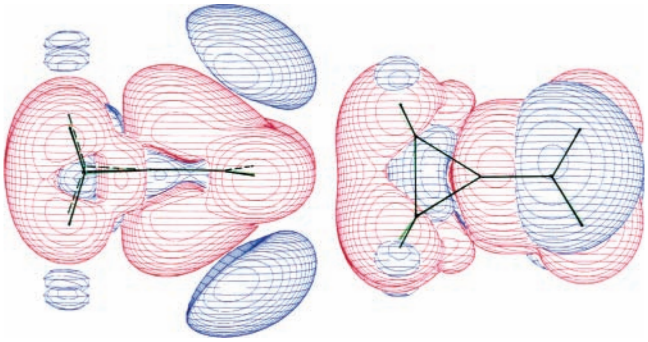

Figure 4. The EOM-CCSD difference density on going from the ground state to the $\pi-\pi^*$ transition for methylenecyclopropane. The regions that have lost electron density as a result of the transition are shown as red, and the blue regions gained electron density. Two views are shown, rotated by 90°.

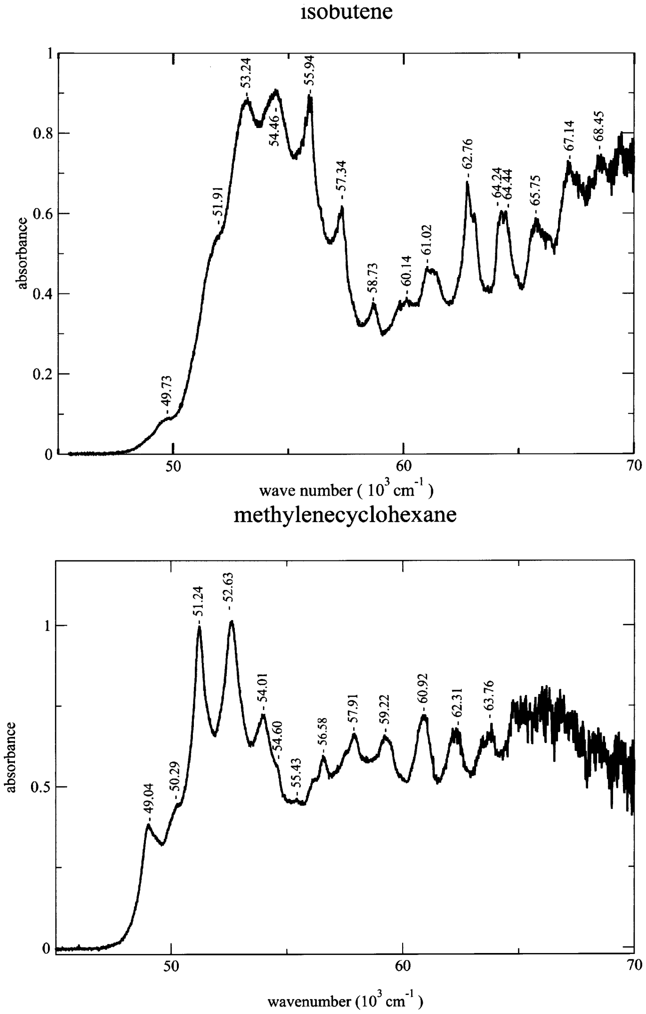

Figure 5. VUV spectra of methylenecyclohexane and isobutene.

and the rms displacement, ΔQ, is given by

$$\Delta Q_n = (\langle Q^2\rangle_n - \langle Q\rangle_n{}^2)^{1/2}$$

Here, $\langle Q\rangle_n{}^2$ will be zero for a normal mode. With the C=C stretch, only the zero-point mode need be considered and $n = 0$. Approximating ω by the calculated vibrational frequency, ν, in cm^{-1} and introducing the physical constants, one obtains[17]

$$\Delta Q = \pm(16.8576/\nu)^{1/2}$$

and the displacement in Cartesian coordinates is given by

$$\Delta x = \Delta Q/\mu^{1/2}$$

where μ is the reduced mass associated with the vibrational mode. The Cartesian displacements for the C=C stretching mode obtained as part of a vibrational frequency calculation (a unit vector) were multiplied by Δx to give the displacement in Å. The geometry for the C=C stretching mode at the positive turning point was derived from the above and the original molecular geometry and gave r(C=C) = 1.373 Å. This is significantly shorter than that found for the planar $\pi-\pi^*$ excited state or the radical cation (see above).

A satisfactory agreement with the observed spectrum was found using r(C=C) = 1.37 Å (Table 2, Figure 2). The figure also shows the contribution from each of the calculated transitions. It may be noted that both the $\pi-\pi^*$ and the Rydberg transitions are affected by the change in bond length. If that were not the case, one might suggest that the $\pi-\pi^*$ transition led to a somewhat twisted molecule, as has been suggested for ethene.[8] However, this would not be appropriate for the Rydberg states, and we prefer a common explanation for both the valence and the Rydberg states.

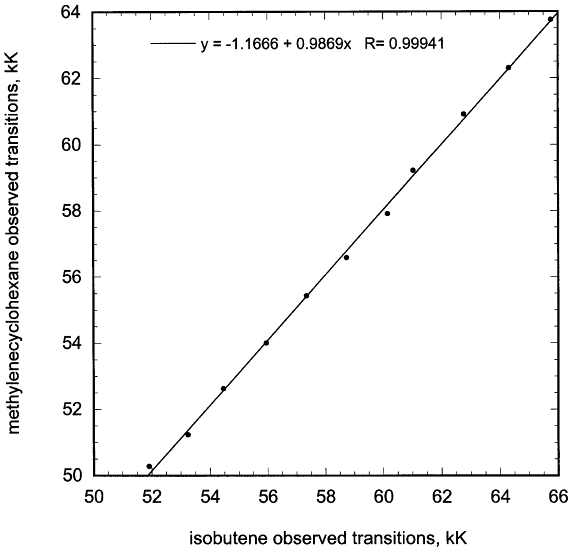

Figure 6. Correlation between the observed band positions of methylenecyclohexane and isobutene.

The EOM-CCSD calculation provides information on the occupied orbitals from which a given transition is derived, and the set of virtual orbitals into which the electron is transferred. This information is provided in Table 3. It can be seen that three of the occupied orbitals are involved in the transitions. The nature of the orbitals is shown in Figure 3 where MO 13, 14, and 15 are occupied, and MO 16, 17, and 19 are the first of the set of virtual orbitals of the given symmetry. The π* orbital is MO 23 with B_1 symmetry.

MO 13 and 14 are cyclopropane ring orbitals, and MO 13 is responsible for the strong interaction between a cyclopropane ring and an electron-deficient center.[18] MO 15 is the π orbital, and this type of orbital is the only one that is involved in the electronic transitions of the other methylenecycloalkanes, at least up to 9 eV.

MO 19 has the same symmetry as the π* orbital, but it is largely associated with the cyclopropane ring. MO 16 and 17 are also largely associated with the three-membered ring. In view of the types of virtual orbitals associated with the $\pi-\pi$* transition, it was of interest to examine the change in electron density distribution on going from the ground state to this excited state. The natural orbitals for the excited state were obtained, and the electron density distribution was calculated. The distribution for the ground state was subtracted from it, leading to the difference density shown in Figure 4. The regions that have lost electron density as a result of the transition are shown in red, and the regions that gain electron density are shown in blue. It can be seen that the CH bonds of the cyclopropane ring as well as the inner part of the double bond and the CH hydrogens lose electron density, whereas the central portion of the ring and the terminal end of the double bond

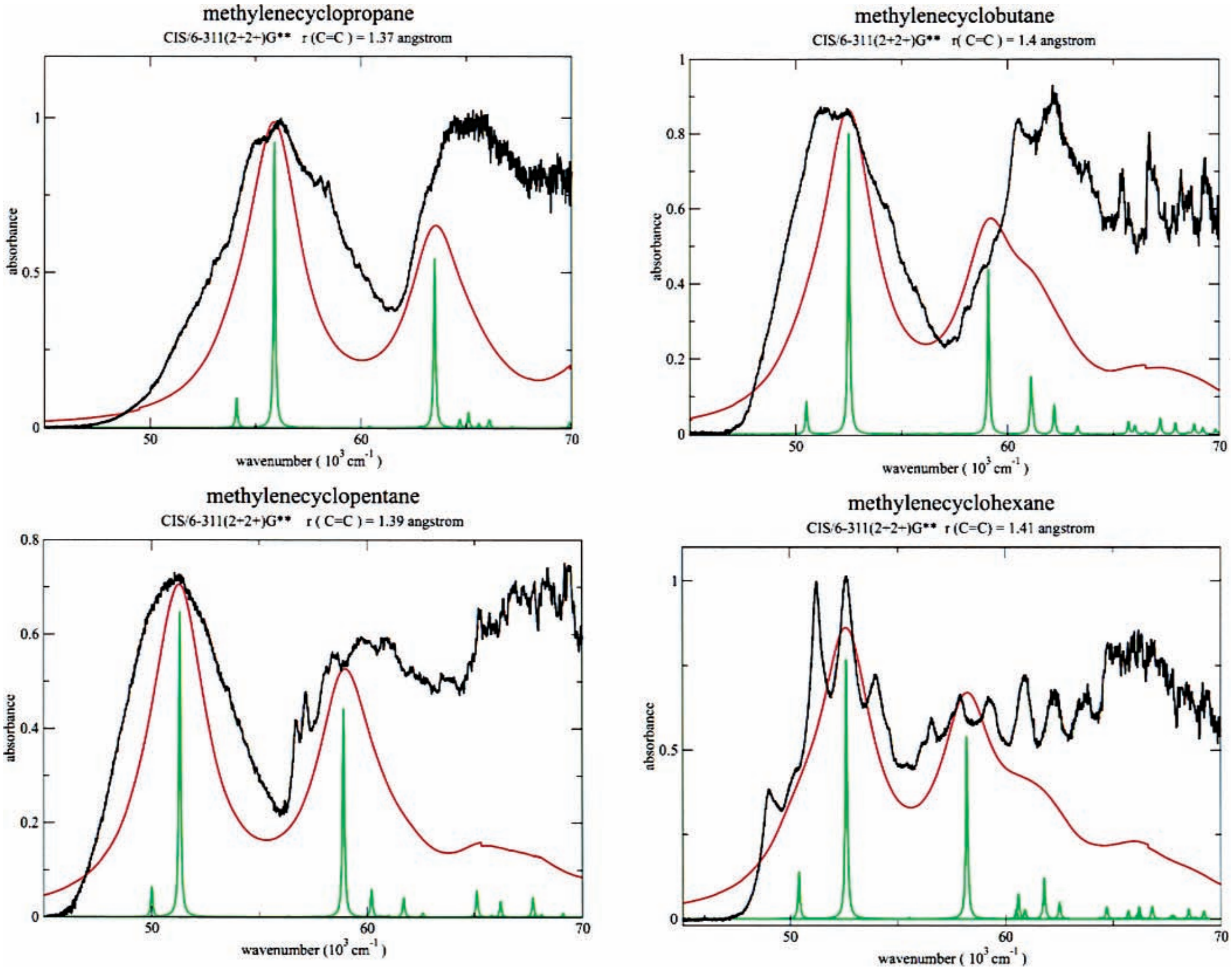

Figure 7. VUV spectra and CIS-derived simulated spectra for the four methylenecycloalkanes.

gain density. It is not surprising that the CH bonds are a source of electron density because we have shown that they generally participate to provide or release electron density to adjacent centers as needed.[19]

3. Methylenecyclohexane (4)

Methylenecyclohexane is too large for us to study using EOM-CCSD at this time. However, it may be noted that CIS[20] calculations find that all of the electronic transitions, at least through 9 eV, originate from the π orbital. Because the CIS results are used as the starting point for the ACES-II EOM-CCSD calculations, one may assume that the same origin would be found in the latter calculations. Thus, the electronic transitions of **4** are quite different from those for **1**.

It is interesting to compare the VUV spectra of **4** with the acyclic counterpart, isobutene (**5**) (Figure 5). It can be seen that there is a remarkable similarity. The experimental locations of the features of the spectra for the two compounds, except for the initial $\pi-3s$ transitions, are compared in Figure 6, and a very good linear relation is found. The main difference between **4** and **5** is a shift in the bands by about 1200 cm^{-1}. The spectrum of isobutene will be examined in some detail in another connection.

4. Methylenecyclobutane (2) and Methylenecyclopentane (3)

CIS calculations for **2** and **3** also find that all of the transitions are derived from the π-orbital. We have found that CIS, although not as effective as EOM-CCSD, does give a fairly good representation of the lower energy excited states of alkenes.[21] The CIS calculated transition energies are given in the Supporting Information. Those for **1** were calculated using $r(C{=}C) = 1.37$ Å corresponding to the second set of EOM-CCSD calculations. The C=C bond lengths for the other compounds were lengthened in a similar fashion: **2**, $r(C{=}C) = 1.40$ Å, **3**, $r(C{=}C) = 1.39$ Å, and **4**, $r(C{=}C) = 1.41$ Å. The results of these calculations are shown in Figure 7. The locations of the $\pi-\pi^*$ transitions are well reproduced, but the energies of the higher energy (Rydberg) transitions are underestimated.

The results of the CIS calculations clearly show that somewhat elongated C=C bonds are necessary to obtain satisfactory transition energies for these alkenes. The same has been found to be true for EOM-CCSD calculations for a series of C4 alkenes.[22]

5. Conclusions

In this group of structurally related compounds, the electronic transitions of methylenecyclopropane are unique in that they involve the occupied ring orbitals as well as the π-orbital. The transitions for the other compounds, at least through 9 eV, involve just the occupied π-orbital. The observed bands for methylenecyclohexane are linearly related to those of the acyclic analogue, isobutene.

In each case, the calculated transition energies at the equilibrium geometry are too large, but the use of a somewhat longer C=C bond length markedly improves the calculated transitions, leading to good agreement with the observed spectrum. The effect of the bond length change is found for both the $\pi-\pi^*$ transitions and the Rydberg transitions. Both of these types of transitions lead to excited states with significantly increased C=C bond lengths.

6. Experimental Section

Methylenecyclopropane was prepared by the procedure of Koster, Arora, and Binger.[23] The other compounds were commercial samples. The purity of all of the compounds was confirmed by NMR spectroscopy. The spectra were obtained using a 1 M vacuum spectrometer with a 1200 line/mm grating, and a deuterium lamp. The sample pressure was measured using a Baratron.

Calculations. The EOM-CCSD calculations were carried out using ACES-II.[24] Geometry optimizations and CIS calculations were carried out using Gaussian 03.[25] The difference density plot was prepared using CASGEN.[26]

Acknowledgment. This investigation was supported by NSF Grant CHE-0132678. A preliminary study of these compounds was carried out by G. Barney Ellison.[27] We thank Dr. Ajith Perera (University of Florida) for providing a modification of ACES-II that permitted the natural orbitals for an excited state to be accessed. We thank Prof. Patrick Vaccaro for helpful comments.

Supporting Information Available: Figure S1, comparison of the results of CIS, RPA, TDDFT, and EOM-CCSD calculations for methylenecyclopropane. Figures S2−S4, observed VUV spectra of methylenecyclobutane, methylenecyclopentane, and methylenecyclohexane. Tables S1−S6, calculated transition energies using different theoretical methods along with the effect of C=C bond length on the calculated transition energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) The broad band contains the relatively weak $1B_1$ and $2B_1$ transitions in addition to the strong $\pi-\pi^*$ transition, and the observed oscillator strength is the sum of the three.

(5) Wiberg, K. B.; Hadad, C. M.; Foresman, J. B.; Chupka, W. A. *J. Phys. Chem.* **1992**, *96*, 10756. They are derived from the standard 6-311++G** basis set by adding:

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C 0
sp 1 1.00
0.014600 1.0 1.0
sp 1 1.00
0.004867 1.0 1.0
****
H 0
s 1.
0.012000 1.0
s 1.0
0.004000 1.0
****
```

This gives the (3+,3+) set. The (2+,2+) set uses only the first of these coefficients.

(6) TDDFT using either B3LYP or B3P86 is much less successful then EOM-CCSD in reproducing the observed transitions. Of the simple methods, CIS was found to be the more successful in reproducing the experiments. The results for different levels of theory are compared in Figure S1 in the Supporting Information. Whereas CIS frequently gives fairly good estimates of the lower energy transitions for alkenes, it should be noted that this is not the case with carbonyl compound where TDDFT is more successful

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