Circular Dichroism of an Optically Active Olefin Chromophore: (*R*)-3-Methylcyclopentene

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Abstract: The electronic circular dichroism and absorption spectra of (*R*)-3-methylcyclopentene have been measured in the gas phase down to 1400 Å. Four distinct bands with alternating sign are observed in the circular dichroism spectrum. Ab initio self-consistent field wave functions obtained for the ground and excited states of (*R*)-3-methylcyclopentene are used to calculate the optical rotational strengths of the lowest lying electronic excited states. The assignment of the measured spectra, based on the results of the calculations, shows that the first three observed bands can be identified with $\pi \rightarrow \pi^*$ and $\pi \rightarrow$Rydberg (R) type excitations of the olefin chromophore and $\sigma \rightarrow$R transitions of the skeletal frame. The first band is probably a combination of $\pi \rightarrow$R and $\sigma \rightarrow$R transitions.

Introduction

Natural circular dichroism (CD) is one of the methods widely used for the assignment of excited states in chromophores whose absorption spectra do not contain fine structure. The lack of fine structure occurs mainly at higher energies where processes such as photodissociation, predissociation, and ionization are significant and cause broadening of the absorption bands. It is therefore important to extend the wavelength limit of CD measurements to the vacuum ultraviolet.

Since the introduction of vacuum-UV CD instruments[2] the olefinic chromophore has been studied experimentally by two different groups.[3-5] Schnepp et al.[3] reported the vapor-phase absorption and CD spectra of *trans*-cyclooctene (a twisted olefin), α-pinene, and β-pinene and, later on, of several aliphatic olefins.[5] According to the general assignment proposed by Schnepp et al.[3] the order of the excited states in the olefinic chromophore is as follows: (1) a $\pi_x \rightarrow 3s$ Rydberg transition ($A_{1g} \rightarrow B_{3u}$) at ~210–230 nm; (2) a $\pi_x \rightarrow \pi_x^*$ transition ($A_{1g} \rightarrow B_{1u}$) peaking at ~190–200 nm; (3) a $\pi_x \rightarrow \pi_y^*$ transition ($A_{1g} \rightarrow B_{1g}$) which shows up around 180 nm (in chiral olefins such as the pinenes where the olefin chromophore has local planar symmetry) and whose CD band appears with opposite sign to that of the $\pi_x \rightarrow \pi_x^*$; (4) a $\sigma \rightarrow \pi_x^*$ ($A_{1g} \rightarrow B_{1g}$) peaking at about 150 nm. In *trans*-cyclooctene (a twisted olefin) the third transition appears to be missing in the CD spectrum and its weak rotatory strength was accounted for by theoretical calculations.[6]

Drake and Mason[4] measured the CD spectra of olefins in solution and were able to provide strong experimental support for the assignment of the first excited state in olefins as a $\pi \rightarrow 3s$ Rydberg transition. In addition, very large anisotropy factors, $g = \Delta\epsilon/\epsilon$, have been observed for the third transition in the planar chiral olefins.[5] This observation substantiates the assignment of this spectroscopic state as a magnetic dipole allowed, electric dipole forbidden transition of the type $\pi_x \rightarrow \pi_y^*$.

The guidelines for these assignments have generally been quantum-mechanical calculations of excitation energies, intensities, and rotational strength performed mainly for twisted chiral olefins.[6-10] The measured *g* values were also used to characterize the transitions. It is well known that transitions in the locally planar olefinic chromophore which are magnetic dipole allowed and electric dipole forbidden have larger *g* values as compared with transitions which are electric dipole allowed and magnetic dipole forbidden. Thus higher *g* values were measured[5] for transitions such as $\pi_x \rightarrow \pi_y^*$ and $\sigma \rightarrow \pi_x^*$ than for the $\pi_x \rightarrow 3s$ and $\pi_x \rightarrow \pi_x^*$ transitions. All the quantum-mechanical calculations of the rotational strength intensities and energies of the various excited states of the chiral olefins were performed on a model twisted ethylene.[6-10] The results have successfully accounted for the bands observed in the CD spectrum of *trans*-cyclooctene with respect to the measured parameters such as excitation energy, rotatory strength, and oscillator strength. No quantum-mechanical calculation has been carried out for the corresponding chiral planar olefins.

In this study we have measured the absorption and CD spectra of the chiral planar olefin (*R*)-3-methylcyclopentene and carried out ab initio SCF calculations for the excited states of this molecule. This olefin is the smallest studied so far down to 1450 Å. Although there has been a report of vacuum-UV CD measurements on (*S*)-3-methyl-1-pentene,[5] the molecule studied here has the advantage of having a rigid cyclic skeleton. The assignments of the various transitions observed in the spectra are based on the results of our ab initio calculations.

II. Experimental Section

The instrument for the measurement of CD in the vacuum UV has been described previously.[11] The monchromator used for the CD and absorption measurements in the vacuum-UV was a McPherson 225 equipped with a 600 lines/mm grating. The dispersion of this monochromator is 16 Å/mm. The vapor pressure of the samples was measured by a Celesco P7D capacitance manometer. The detailed synthesis of (*R*)-3-methylcyclopentene was reported elsewhere.[12] The sample was found to contain 61.5% of (*R*)-3-methylcyclopentene and 38.5% of the non-optically-active 4-methylcyclopentene.[17] The calculations of ϵ and $\Delta\epsilon$ have been corrected for the presence of 4-methylcyclopentene assuming the same composition in the gas and liquid phases. A solution of (*R*)-3-methylcyclopentene in perfluoro-*n*-hexane was prepared and the absorption of the solution was measured by a Cary 17 spectrophotometer down to 195 nm.

III. Results

Figure 1 shows the gas-phase absorption and CD spectra of (*R*)-3-methylcyclopentene. The main features observed in these spectra are as follows:

(a) A negative CD band centered at around 205 nm reveals two (or three) vibrational bands with a spacing of ~1200 cm^{-1}. This band has the largest *g* value in the molecule (about 4×10^{-3}).

(b) The strongest absorption band ($\epsilon \sim 8000$) peaks at ~185 nm and a corresponding positive CD band is observed in the same wavelength region. The *g* value calculated for this transition is

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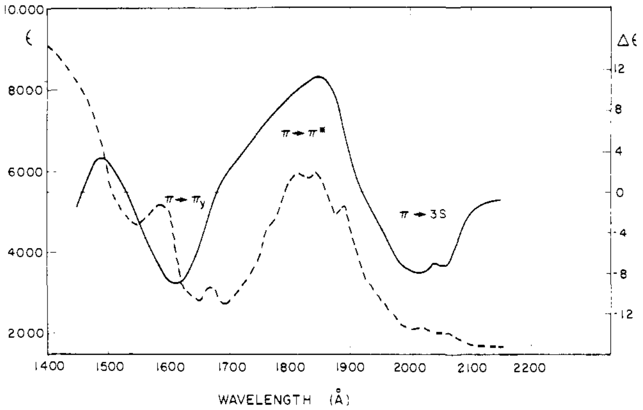

Figure 1. Absorption (- - -) and CD (—) spectra of MCP. The spectral resolution of the absorption spectrum is 0.8 nm and that of the CD spectrum is 3.2 nm.

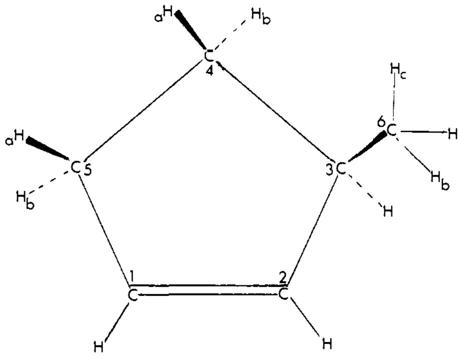

Figure 2. Molecular frame of MCP.

$\sim 2 \times 10^{-3}$. The CD band is asymmetrically broadened toward lower wavelength.

(c) A negative CD band is observed at 161 nm which has a corresponding absorption peak at 159 nm. The g value of this transition is $\sim 2 \times 10^{-3}$.

(d) A positive CD band with a peak at 149 nm is observed in the unstructured absorption spectrum shorter wavelength region.

We can summarize these observations by arguing that the general scheme of the four main transitions discussed above is repeated in (*R*)-3-methylcyclopentene. The absorption spectrum of the a solution of the (*R*)-3-methylcyclopentene in perfluoro-*n*-hexane did not show any peaks in the 215–195-nm region. This is a strong indication that the first transition is indeed a π–3s Rydberg transition which is expected to essentially disappear in a condensed-phase medium.

However, despite the similarity between these spectra and the results obtained for other chiral olefins there are two questions that these experimental results raise. In local planar symmetry the Rydberg transition is electric dipole allowed and magnetic dipole forbidden, and according to the criteria widely used in the assignment of excited states one would expect it to exhibit a smaller g value, while for the molecule studied it shows a relatively large g factor. A second problem is the asymmetric broadening of what can be immediately identified as a $\pi \rightarrow \pi^*$ transition suggesting the possibility of additional contributions to this band of a second excited state. Since all the quantum-mechanical calculations to date were restricted to the hypothetical twisted ethylene, we felt that an ab initio calculation on (*R*)-3-methylcyclopentene would help to point out the differences between the locally twisted and planar olefin chromophores and help clarify the interpretation of the methylcyclopentene spectra reported here.

IV. Theoretical Aspects

Ab initio self-consistent-field (SCF) calculations were carried out on the (*R*)-3-methylcyclopentene (MCP) molecule in order to obtain the transition energies and rotational strengths (RS) of the lowest lying excited electronic states. The same fixed geometric nuclear configuration was used for all the electronic states considered here with the atom Cartesian coordinates tabulated in Table I and coordinate axis system shown in Figure 2. The Cartesian frame's origin is located at the geometric center of the olefin double bond.

Table I. (*R*)-Methylcyclopentene

	z	y	x
C_1	−1.268	0	0
H_1	−2.916	−1.219	0
C_2	1.268	0	0
H_2	2.916	−1.219	0
C_3	2.296	2.680	0
H_3	3.317	3.492	−1.606
C_4	0	4.300	0.663
H_{4a}	0	5.563	2.302
H_{4b}	0	5.563	−0.9760
C_5	−2.296	2.680	0
H_{5a}	−3.317	3.492	1.606
H_{5b}	−3.317	3.492	−1.606
C_6	3.726	3.8176	2.247
H_{6a}	3.726	5.506	3.443
H_{6b}	3.726	2.1286	3.443
H_{6c}	5.4150	3.8176	1.0510

The Gaussian expansion basis set used here is a combination of valence and Rydberg-type orbitals. For each hydrogen atom a completely contracted four Gaussian primitive representation of the 1s orbital, $(4^s)/[1^s]$, was taken[13] with an exponent scale factor of $(1.2)^2$. The expansion basis for the carbon atoms consists of the $[3^s2^p]$ contraction of Huzinaga's (9^s5^p) atom optimized functions set,[14] augmented by a double set of s- (exponents = 0.0230 and 0.0055), a double set of p- (exponents = 0.021 and 0.0049), and a single set of d-type functions (exponent = 0.0150) centered at the origin of the molecular frame (Figure 2). These latter type functions should adequately represent the Rydberg-type excited-state orbitals. The final basis set is thus 198 Gaussian primitives contracted to 78 basis functions.

With regard to the calculation of electronic states and wave functions a formidable problem is encountered in trying to obtain a variational self-consistent-field (SCF) description of the excited states of MCP owing to the absence of any symmetry elements in the molecule. Consequently, among the electronic states of interest here only the lowest energy spin singlet (i.e., the ground state, N) and the spin triplet (T) states can be rigorously determined variationally within single-configuration (SC) SCF theory. On the other hand, it can be safely assumed that in these type olefins[8,15] the lowest energy excited electronic states belong essentially to the olefinic part of the molecule ($C_1{=}C_2$ in Figure 2). Thus, the local (higher) ethylenic symmetry should dominate and constrain the nature of the lower energy electronic states in MCP to be similar to those in ethylene itself, where the symmetry problem does not exist. On the other hand, however, σ skeletal strain[8,15,16] is expected to raise the occupied σ manifold of molecular orbitals with respect to the π level causing excitations from the σ levels to appear at relatively low frequencies.

From a practical point of view, the lowest energy open-shell spin singlet electronic state has a significantly different electronic configuration from the closed-shell ground state. Therefore, it is easily possible to calculate an electronic wave function for an open-shell singlet state that is reasonably close to the true variational (orthogonal) open shell singlet state wave function. Within this framework, respective higher energy open shell triplet and singlet electronic states can be obtained within a frozen core approximation where only the exciting or active electron changes orbital character relative to the lowest energy open shell state. This latter technique has been implemented in a form called the

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Table II. Total Energies

state	total energy, au	state	total energy, au
$^1A(N_1)$	−232.732376	$^1A(S)$	−232.510419
$^1A(N_2)$	−232.762971	^2A	−232.422663
$^3A(T)$	−232.607082		

improved virtual orbital (IVO) method[17] and has been used here to generate the higher open shell excited states arising out of a one-electron excitation from the olefinic π orbital.

It is now well documented that the $\pi \rightarrow \pi^*$ singlet excited state of olefins (the V state) cannot be corretly obtained within the framework of SC–SCF theory, which gives a pure Rydberg (R) for this essentially valence excited state.[18] Extensive configuration interaction (CI) is needed to bring the theoretical description of the V state in line with experiment. An alternative method for generating a reasonably accurate description of the spatial part of the V state within SC–SCF theory is to use the spatial part of the $\pi \rightarrow \pi^*$ triplet excited state wave function (the T state), which is calculated to be purely valence type within SC–SCF theory and, as will be shown, is the lowest energy triplet state in the molecule. The true V state is more spatially diffuse than the spatial part of the T state[19–21] and this difference must be kept in mind when using the T state wave function to obtain V state properties.

The single electronic configuration ground state of MCP can be described as

$$1a^2 2a^2 \ldots 23a^2 \qquad {}^1A(N_1) \tag{1}$$

The lowest energy open shell electronic configuration is then

$$1a^2 2a^2 \ldots 23a^1 24a^1 \qquad {}^3A(T),\ {}^1A(R) \tag{2}$$

giving rise to both triplet and singlet electronic states. The SC–SCF triplet calculation is found to describe the 23a molecular orbital (MO) as essentially (97.4%) centered on the $2p_x$ orbitals of the olefinic carbon atoms (the π orbital) and 24a is calculated to be primarily (98.9%) the antibonding $2p_x$ basis orbital combination of the olefinic carbon atoms (π^*). On the other hand, as expected, in the singlet state SCF calculation the 24a MO is almost pure Rydberg 3s in character while, again, 23a is calculated to have mainly π character. In both the positive ion

$$1a^2 2a^2 \ldots 23a^1 \qquad {}^2A \tag{3}$$

and in the optimum double configuration (DC) ground state[22]

$$1a^2 2a^2 \ldots [A(23a^2) + B(24a^2)] \qquad {}^1A(N_2) \tag{4}$$

the 23a MO is also found to be essentially the olefin π orbital. All these results support the arguments presented above about the expected nature of the relevant MOs as obtained from SC–SCF theory and confirm the expected π nature of the exciting orbital in the lowest excited states. The calculated total energies of the various state configurations are listed in Table II.

As mentioned above, the higher excited states of the open-shell triplet and singlet state configurations were obtained by using the IVO method[5] based on configuration (2). Thereby, for a given spin state all the higher MOs (from 24a and higher) are obtained by using a single Fock Hamiltonian which excludes any two-electron interaction terms which are dependent on the (singly) occupied 24a MO. These higher MOs are then determined in the field of $N - 1$ electrons (where N is the actual number of electrons in the molecule) and the energy of the higher electronic state (spin singlet or triplet) formed in going from, for example, configuration (2) to one in which the last electron is in the *na* MO ($n > 24$) is just $E_0 + \epsilon_{na} - \epsilon_{24a}$, where E_0 is the energy of (2) and ϵ is the orbital energy.

With the orbitals and energies obtained as described above the calculation of the rotational strength (RS) was carried out by using the formula described previously:[8]

$$\mathrm{RS}(\nabla) = (471.38/\Delta E)\langle 23a|\nabla|na\rangle \cdot \langle 23a|r \times \nabla|na\rangle \tag{5}$$

and the corresponding formula by using $\langle r \rangle$ in place of $\langle \nabla \rangle$.[10] The values of ΔE (au) appearing in (5) were calculated for the singlet states obtained from the open-shell triplet state manifold by using

$$E(^1A) = E(^3A) + 2K_{23a,na} \tag{6}$$

where only n = 24, 25 were considered. The values for the exchange integral were taken from known results[15] for the ethylene molecule; for the $^1(\pi,\pi^*)$ state $2K_{23a,24a} = 4.0$ eV and for the same polarization Rydberg state $2K_{23a,25a} = 0.5$ eV.

A summary of the results, as they are applied to the interpretation of the experimental CD spectrum reported here, is shown in Table III. At lowest energy in the singlet state manifold is the $\pi \rightarrow$R(3s) excitation with a negative sign rotation. Both the next electronic transition in the singlet set and the first excitation in the triplet manifold are $\pi \rightarrow n$p(x) excitations, both with positive sign rotations, except that in the triplet manifold n = 2 (a valence excited state) and in the singlet calculation n = 3 (a Rydberg excited state). Whether, in fact, these are the same excitations, with the different calculated upper-state characters between the S and T set calculations being just a reflection of deficiencies in the methods used here, is answered by the observation that the second excited state in the T manifold is also calculated to be mostly $\pi \rightarrow$3p(x) with a positive sign rotation. Thus two out-of-plane excitations are predicted both with the same sign rotation, but with one being valence and the other Rydberg. We thus identify the 23a→25a excitation in both the S and T sets as the same transition, $\pi \rightarrow$R(3p$_x$). The next excitation in the S manifold is a $\pi \rightarrow$R(3p$_{y,z}$) type with a negative sign rotation. The last of the $\pi \rightarrow$R(3p) transitions (23a→27a) in the S manifold is calculated to have a very small CD.

Until now this discussion has ignored possible $\sigma \rightarrow \sigma^*$ or $\sigma \rightarrow$R type transitions. Within the frozen orbital framework it is possible to calculate rotational strengths for the

$$1a^2 2a^2 \ldots 22a^1 23a^2 na^1 \qquad {}^1A \tag{7}$$

state configuration ($n > 24$) by using the ^{1}A SC–SCF wave functions calculated from (2). Alternatively, a SC–SCF calculation can be carried out directly on (7) forcing a maximum overlap criterion in the SCF iteration procedure to maintain 23a as the olefinic π orbital and the RS is then calculated by using only the MOs determined in (7). Neither of these procedures is variational in the sense that they both ignore orthogonality to lower excited states, but it is expected that the different orbital character of the various excited states will survive more rigorous treatment.

Interestingly enough, although there is over 2.7 eV relaxation energy difference between the two methods,[23] the results are very similar in the following sense. In both cases (a) the 22a molecular orbital is centered on C3, C4, and C6 (Figure 2) in the $2p_z$ orbital, (b) the 24a is the Rydberg 3s orbital, and (c) for an assumed ΔE = 7.0 eV the RS (∇) values for the 22a(σ)→24a(R) transition are -5.51×10^{-40} and -5.39×10^{-40} cgs for the SCF wave functions based on (2) and (7), respectively. As shown in Table III, a negative RS is calculated for the first [$\pi \rightarrow$R(3s)] and fourth [$\pi \rightarrow$R(3p$_{z,y}$)] transitions. The SCF energy based on (7) places the $\sigma \rightarrow$R(3s) transition in the same spectral region as the $\pi \rightarrow$R(3s) transition. Although nonorthogonality in the calculation may cause the excitation energy of the former to be underestimated, it is also unreasonable to assume that it will be pushed up as high as the fourth transition, beyond the $\pi \rightarrow \pi^*$ excitation. The frozen orbital results for the first four $\sigma \rightarrow$R transitions from the S manifold calculations are also shown in Table III.

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[22] Calculated $A = 0.975901$ and $B = -0.218213$.

[23] The SC–SCF calculation based on (7) was not fully converged for economy reasons. The total energy comes close to the energy [^{1}A(S) state in Table II] based on (2).

[24] $[\alpha]^{20}_{\mathrm{D}}$ +133°.

Table III. Calculated Electronic States

manifold[a]	$^1(ka,na)$ state k	n	ΔE[b]	RS(∇)[c]	RS($\mathbf{r}$)[c]	oscillator strengths $f(\nabla)$[d]	oscillator strengths $f(\mathbf{r})$[e]	orbital description
S	23	24	0.22196	−2.42	−1.64	0.032	0.006	$\pi \rightarrow R(3s)$
T	23	24	0.27230	2.16	3.31	0.339	0.748	$\pi \rightarrow \pi^*$
T	23	25	0.31843	1.41	1.52	0.008	0.011	$\pi \rightarrow R(3p_x)$
S	23	25	0.23835	3.31	3.03	0.006	0.006	$\pi \rightarrow R(3p_x)$
S	23	26	0.24094	−1.82	−0.89	0.006	0.006	$\pi \rightarrow R(3p_{y,z})$
S	23	27	0.24597	0.02	−0.30	0.004	0.008	$\pi \rightarrow R(3p_{y,z})$
S	22	24	(0.2573)[f]	−5.51	−6.51	0.006	0.006	$\sigma \rightarrow R(3s)$
S	22	25	(0.2756)[f]	1.18	0.57	0.004	0.008	$\sigma \rightarrow R(3p_x)$
S	22	26	(0.2940)[f]	0.15	−0.70	0.008	0.014	$\sigma \rightarrow R(3p_{y,z})$
S	22	27	(0.3124)[f]	−3.98	−4.50	0.004	0.008	$\sigma \rightarrow R(3p_{z,y})$

[a] S = singlet, T = triplet. [b] In au. [c] In 10^{-40} cgs. [d] $f_{kn}(\nabla) = (2/3\Delta E)|\langle\nabla\rangle|^2$. [e] $f_{kn}(\mathbf{r}) = (2\Delta E/3)|\langle\mathbf{r}\rangle|^2$. [f] Assumed for the purpose of calculating RS(∇), f(∇), and f($\mathbf{r}$).

Table IV. Assignment of the Observed Spectrum of MCP

band	description	energy[a]		RS[b]		f[d]	
		obsd	calcd	obsd	calcd[c]	obsd	calcd
1		6.05		−16		0.03	
	$\pi \rightarrow R(3s)$		6.04		−2.03		0.014
	$\sigma \rightarrow R(3s)$				−6.01		0.006
2		6.7		+26		0.16	
	$\pi \rightarrow \pi^*$		7.4		+2.74		0.504
3		7.0					
	$\pi \rightarrow R(3p_x)$				+3.17		0.006
	$\sigma \rightarrow R(3p_x)$				+0.75		0.006
4		7.7		−16		0.09	
	$\pi \rightarrow R(3p_{y,z})$				−1.36		0.005
	$\pi \rightarrow R(3p_{z,y})$				−4.24		0.007

[a] In eV. [b] In 10^{-40} cgs. [c] Average of RS(∇) and RS($\mathbf{r}$) in Table III. [d] $f = [f(\mathbf{r}) \cdot f(\nabla)]^{1/2}$.

The interleaving of the two different calculated manifolds of excited electronic states (S and T) arising out of one-electron excitations from the π orbital as shown in Table III was carried out in accord with the known and calculated spectroscopic properties of the olefin chromophore[8,15] and agrees with the experimental CD spectrum. However, the excitation energies of all the $\pi \rightarrow R(3p)$ singlet states in the S manifold are calculated to fall below the $^1(\pi,\pi^*)$ energy. The most probable explanation for the relatively low energies calculated for the $\pi \rightarrow R(3p)$ excitations in the S manifold is their lack of orthogonality to the $^1(\pi,\pi^*)$ state which is completely missing in the S manifold. As evidence for this we find in the T manifold that the ^{1}(23a,25a) state is calculated as over 2 eV above the corresponding state in the S manifold, although, as discussed above, they can be identified as representing the same spectroscopic state.

Configuration interaction among the various SCF excited states shown in Table III would be expected to be much less than that found previously[8] by using the virtual orbital approximation. In any event, the states among which mixing would be expected to be strongest are those that have the most similar spatial orientation, as, for example, ^{1}(23a,24a) and ^{1}(23a,25a) in the T manifold. In this latter case, although the two wave functions represent extreme situations, running from pure valence to pure Rydberg, they still have the same sign CD. Therefore, the sign of the CD for the spectroscopic $^1(\pi,\pi^*)$ state is not expected to be affected by the extent of diffuseness of the wave function, an aspect which is neglected in these calculations.

The calculated ionization potential for MCP from the data in Table II is 8.43 eV. If we add to this value the approximate pair correlation energy of the π bond as the difference between the N_1 and N_2 ground state calculations (0.82 eV) we get a value of 9.25 eV, which is probably very close to the experimental value.

V. Discussion and Conclusions

In Table IV we compare the measured excitation energies, rotational strengths, and oscillator strengths with the results obtained from the ab initio calculations. As far as the rotational strength is concerned the calculations predict the right sign for the various transitions, though the magnitude is systematically small by an order of magnitude. The calculations help to explain the broad asymmetry observed in the $\pi \rightarrow \pi^*$ energy region by assigning it to a $\pi \rightarrow R(3p_x)$ transition which has the same positive CD signal as the $\pi \rightarrow \pi^*$. The calculations provide support for the assignment proposed by Schnepp et al.[3] and Drake et al.[4] in which the band of opposite sign which appears to the blue of the $\pi_x \rightarrow \pi_x^*$ in planar olefins is attributed to a $\pi_x \rightarrow \pi_y^*$ transition. The calculations predict the existence of a negative sign Rydberg $3p_{y,z}$ transition where the 3p excited molecular orbital lies in the plane of the double bond.

It is still unclear why the magnitude of the rotational strength of this transition is drastically reduced in twisted olefins as calculated by Liskow and Segal.[6] Since the $\pi_x \rightarrow \pi_y^*$ transition is calculated as a pure Rydberg state the explanation proposed by Liskow and Segal, claiming that a moderate increase in valence character in planar olefins would increase the rotatory strength for the state, is insufficient.

The question of the unexpected large g factor measured for the CD band at 2020 Å which is assigned[3,4] the $\pi \rightarrow R(3s)$ Rydberg may also be solved based on the ab initio results. As it was shown above the $\sigma \rightarrow R(3s)$ transition might contribute appreciably to the rotational strength of the 2020 Å band. The transition (B_{3g} symmetry in ethylene) is electric dipole forbidden and magnetic dipole allowed from the ground state and should have therefore a larger g factor than the $\pi \rightarrow R(3s)$. The calculated RS for the $\sigma \rightarrow R(3s)$ has a negative sign and is indeed larger than the $\pi \rightarrow R(3s)$ (-5.4×10^{-40} as compared with -2.4×10^{-40}). As it was pointed out above we tend to believe that the energy of the $\sigma \rightarrow R(3s)$ transition is in the same spectral region as that of the $\pi \rightarrow R(3s)$ transition.

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