Excited Electronic States of Optically Active Substituted Ethylene Oxides: (−)-(*S*)-2-Methyloxirane and (−)-(*S*,*S*)-2,3-Dimethyloxirane

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Abstract: The excited electronic states of (−)-(*S*,*S*)-2,3-dimethyloxirane (DMO) and (−)-(*S*)-2-methyloxirane (MO) are discussed in light of the vacuum UV optical absorption and circular dichroism spectra and ab initio self-consistent field calculated excitation energies, oscillator strengths, and rotational strengths. The first three observed bands in MO and DMO are assigned as n(O) → Rydberg transitions. The possible location of a valence $\sigma \rightarrow \sigma^*$ transition in the region of the second and third bands in DMO is also examined.

Introduction

The excited electronic states of the three-membered ring molecules have recently been the subject of extensive experimental and theoretical study.[1-3] Natural circular dichroism (CD) is used in this study as a spectroscopic means of providing additional information about the excited electronic states of ethylene oxide. By its ability to measure both a positive or negative signal, the CD technique enables the uncovering of transitions that are not resolved in straight optical absorption measurements. Another advantage of the CD method is the identification of magnetic dipole allowed electric dipole forbidden transitions via a measurement of the anisotropy factor $g = \Delta\epsilon/\epsilon$.[4] Basch et al. measured the absorption spectrum of ethylene oxide in the gas and solid phases.[2] According to their assignment, which was aided by contracted Gaussian-type orbital calculations, Rydberg transitions, terminating in *n*s, *n*p, and *n*d (*n* = 3–6) orbitals, as well as valence transitions, were identified in the absorption spectrum.

Rauk[3] recently used ab initio SCF–CI methods to study the electronic states and their oscillator and rotatory strengths in 12 three-membered ring molecules. The results relevant to our study are those given for oxirane and (−)-(*S*)-2-methyloxirane. The lower transitions in these molecules were found to originate from nonbounding electrons on the oxygen atom and to terminate in diffuse orbitals of Rydberg nature, with some contribution of valence character. As far as the rotatory strength is concerned, Rauk's results disagree with the measured sign of the first two bands of (−)-(*S*)-2-methyloxirane. This discrepancy was attributed to the level of the CI which was not able to describe substantial reorganization of the "unexcited" electrons.

Although CD measurements of aliphatic ethers have been reported in the literature,[5] no CD measurements of molecules having ethylene oxide as their sole chromophore have yet been reported.

In this study, of which partial preliminary experimental results were reported elsewhere,[6] we have measured the absorption and CD spectra of (−)-(*S*)-2-methyloxirane and (−)-(*S*,*S*)-2,3-dimethyloxirane down to 1450 Å and carried out ab initio SCF calculations for the energies and oscillator and rotational strengths of the various excited electronic states. The assignment of the absorption and CD bands observed in the spectra is based on the results of these calculations.

Experimental Section

The VUVCD instrument used in this study has been described previously.[7] Since the instrument was recently modified by the introduction of a MgF_2 Wollastone prism (replacing the Biotite reflecting plate) as a linear polarizer, the measurements were repeated in the new mode and identical results were obtained. The monochromator used for these measurements is a McPherson 225 equipped with a 1200 lines/mm grating yielding a spectral resolution of 8 Å/mm. The vapor pressure of the samples was measured by a Clesco P7D capacitance manometer. The synthesis of MO was carried out as described in the literature[8] and the enantiomeric purity was found to be 98.2%. The DMO whose synthesis was reported elsewhere[6] was found to contain 98% of the (*S*,*S*) enantiomer $[\alpha]_{6328} = -37.4$ (neat). All the measurements were carried out in a 5-cm optical path cell.

Results

a. Absorption and CD of DMO. Figure 1 shows the gas phase absorption and CD spectra of (−)-(*S*,*S*)-2,3-dimethyloxirane (DMO). Four alternating sign transitions are observed in the CD spectrum of DMO (maxima at 1755, 1665, 1602, and 1510 Å) one of which (the 1665 Å negative signal) does not have a corresponding peak in the absorption spectrum. A comparison of the absorption spectra of DMO and ethylene oxide shows a great similarity between the first transition in those molecules, where the DMO transition is red shifted by 1400 cm^{-1} upon substitution. The vibrational structure observed for this first band in DMO is 1100 ± 50 cm^{-1}, which corresponds well with the 1120-cm^{-1} intervals observed for ethylene oxide. On the basis of this similarity and a term value[9] of 23 500 cm^{-1}, we assign this transition as the n(O) → 3s Rydberg transition. The nature of the active vibration was discussed by Basch et al.,[2] while Liu and Duncan[10] assigned the 1120-cm^{-1} upper state vibrational intervals to the totally symmetric ring breathing mode (ν_3) in ethylene oxide. The possibility of assigning this vibration as the ν_2 totally symmetric CH_2 scissors motion was also raised. We believe that the small change in the frequency of this vibration upon substitution indicates in favor of a ring breathing assignment.

The positive sign CD band at 1602 Å can be assigned as an n(O) → 3p Rydberg transition on the basis of its 18 100-cm^{-1} term value.[9] The vibrational structure observed for n(O) → 3p in ethylene oxide is smeared out in DMO. The negative CD band at 1510 Å cannot be unambiguously assigned on the basis of term values. An n(O) → 3d or n(O) → 4s or even a valence transition corresponding to the 1440 Å in solid ethylene oxide are all possible assignments. The most interesting feature is the negative CD band at 1655 Å which seems not to have any corresponding resolved absorption band in DMO. This band seems to relate to the

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[1] M. B. Robin and N. A. Keubler, *J. Chem. Phys.*, **69**, 860 (1978).
[2] H. Basch, M. B. Robin, N. A. Keubler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, **51**, 52 (1969).
[3] A. Rauk, *J. Am. Chem. Soc.*, **103**, 1023 (1981).
[4] S. F. Mason, *Mol. Phys.*, **5**, 343 (1962).
[5] E. H. Sherman, O. Schnepp, P. Salvadori, C. Bertucci, and L. Lardicci, *J. Chem. Soc., Chem. Commun.*, 1000 (1979).
[6] M. Levi, R. Arad-Yellin, B. S. Green, and A. Gedanken, *J. Chem. Soc., Chem. Commun.*, 847 (1980).
[7] M. Levi and A. Gedanken, *Rev. Sci. Instrum. 48*, 1661 (1977).
[8] V. Schurig, B. Koppenhölen, and W. Bürkle, *Angeuw. Chem., Int. Ed. Engl.*, **17**, 937 (1978).
[9] E. J. McAlduff and K. N. Houk, *Can. J. Chem.*, **55**, 318 (1977).
[10] T. K. Liu and A. B. F. Duncan, *J. Chem. Phys.*, **17**, 241 (1949).

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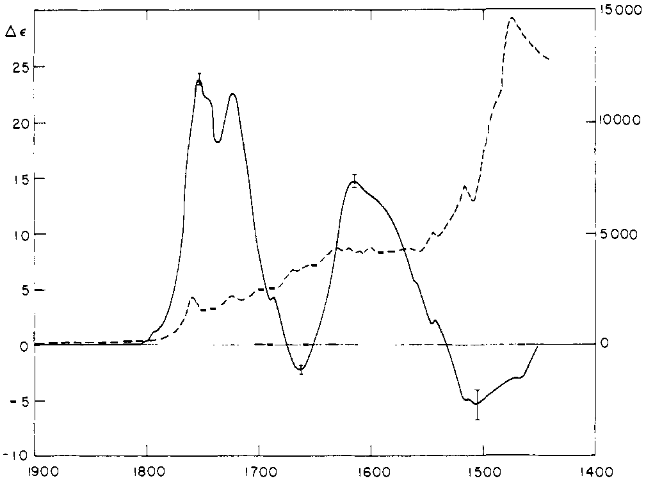

Figure 1. Absorption (---) and CD (—) spectra of (−)-(*S*,*S*)-2,3-dimethyloxirane. The spectral resolution of the absorption and of the CD spectrum is 16 Å.

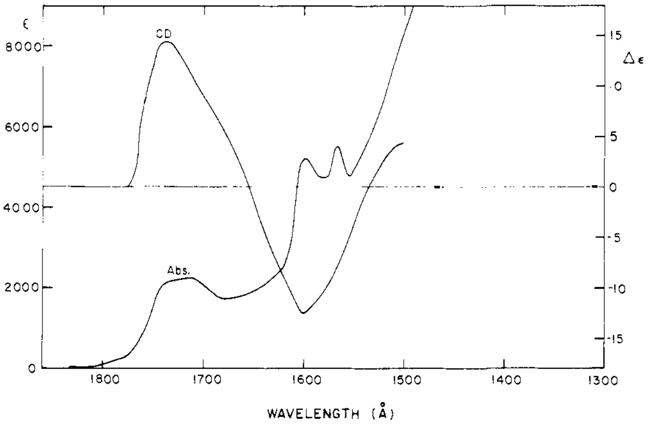

Figure 2. Absorption and cd spectra of (−)-(S)-2-methyloxirane. The spectral resolution of the absorption and cd spectrum is 16 Å.

63 000-cm^{-1} shoulder in the absorption of solid ethylene oxide which then leads to an n(O) → σ^* valence transition. However our ab initio calculations suggest that another component of the n(O) → 3p Rydberg transition appears in this energy range having a negative CD signal. The assignment of this band will be discussed later in this paper.

b. Absorption and CD of MO. Figure 2 shows the gas-phase absorption and CD spectra of (−)-(*S*)-2-methyloxirane. The CD spectrum of MO is simpler than that of DMO. It shows two strong bands peaked at ~1740 and 1600 Å. The third peak at higher energies is positive; however, its peak is not well established. These transitions are logically assigned as n(O) → 3s, n(O) → 3p and n(O) → 3d, respectively. The sign of the n(O) → 3s transition in MO and DMO is the same. The small negative CD band which appears at ~1655 Å in DMO is not observed in MO. This is apparently due to the change in the sign of the CD in going from the first to the second transition in MO which would overlap the "1665-Å" band. While previous[3] attempts to calculate the sign of the n(O) → 3s transition in MO yielded a negative sign, our calculations succeed in reproducing the experimental results, and we are able to account for the right sign for the n(O) → 3s transition in MO. In Table VII we compare the calculated and measured energies, oscillator strengths, and rotational strengths of the various electronic transitions in MO.

Table I. Coordinates of DMO[a,b]

	x	*y*	*z*
C_1	0.0	0.0	1.3854
C_2	0.0	0.0	−1.3854
H_1	−0.3775	1.7405	2.3894
H_2	−0.3775	−1.7405	−2.3897
C_A	−0.5383	−2.4822	2.8176
C_B	−0.5383	2.4822	−2.8176
O	2.3334	0.0	0.0
H_{1A}	−0.8650	−3.9884	1.4740
H_{1B}	−0.8650	3.9884	−1.4740
H_{2A}	1.0662	−2.9532	3.9940
H_{2B}	1.0662	2.9532	−3.9940
H_{3A}	−2.1938	−2.2461	3.9940
H_{3B}	−2.1938	2.2461	−3.9940

[a] These are the coordinates of the (*R*,*R*)-DMO enantiomer on which the calculations were performed. [b] In au.

Table II. Coordinates of MO[a,b]

	x	*y*	*z*
C_1	0.0	0.0	1.3854
C_2	0.0	0.0	−1.3854
H_1	−0.3775	1.7405	2.3897
C_A	−0.5383	−2.4822	2.8176
O	2.3334	0.0	0.00
H_{1A}	−0.8650	−0.39884	1.4740
H_{2A}	1.0662	−2.9532	3.9940
H_{3A}	−2.1938	−2.2461	3.9940
H_2	−0.41077	1.7422	−2.3868
H_3	−0.41077	−1.7422	−2.3868

[a] These are the coordinates of the (*R*) enantiomer on which the calculations were performed. [b] In au.

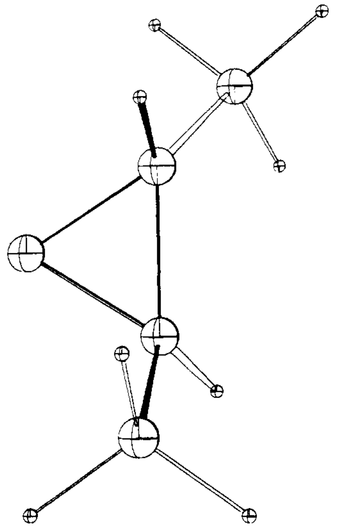

Figure 3. Molecular frame of DMO; (*R*,*R*) enantiomer.

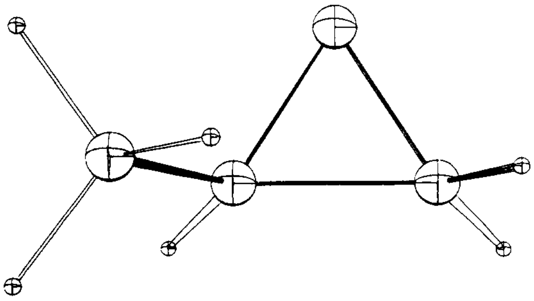

Figure 4. Molecular frame of MO; (*R*) enantiomer.

c. Calculational Details. Ab initio (spin-restricted) self-consistent field (SCF) calculations were carried out on the ground and excited states of (−)-(*R*,*R*)-2,3-dimethyloxirane (DMO) and (−)-(*R*)-2-methyloxirane in order to obtain electronic excitation transition energies and rotational strengths (RS). Since the experiments were carried out on the mirror image enantiomer in both cases, the signs of the calculated RS values were changed for comparison with experimental results. The fixed nuclear

Table III. Gross and Net Spin-Orbital Populations on DMO (*R,R*) Enantiomer

	^{1}A(GS)	^{1}A(AA)	^{1}B(AB)	^{1}A(BB)	^{1}B(BA)	^{3}B(BA)	^{2}B	^{2}A
total energy[a]	−0.85939	−0.57945	−0.56585	−0.61535	−0.62568	−0.62620	−0.53543	−0.48605
ΔE, eV	0.0	7.62	7.99	6.64	6.36	6.34	8.81	10.16
				Gross Population[b]				
Rydberg	0.01	0.99	0.97	0.97	0.99	0.99	−0.04	−0.04
C-H	6.76	6.55	6.56	6.67	6.67	6.66	6.70	6.59
C-H(3)	9.00	8.81	8.82	8.84	8.83	8.84	8.83	8.80
oxygen	8.47	8.28	8.25	8.00	8.01	8.01	7.99	8.25
				Spin Population[b]				
Rydberg		1.02	1.01	1.01	1.02	1.02	0.00	0.00
C-H		0.28	0.29	0.02	0.01	0.01	0.02	0.28
C-H(3)		0.03	0.02	0.01	0.01	0.01	0.01	0.03
oxygen		0.36	0.38	0.94	0.93	0.93	0.94	0.38

[a] Relative to −230 au. [b] Sum of all basis functions located on each group.

geometry used for all the states is shown in Tables I and II and Figures 3 and 4. The origin of the Rydberg basis functions is located, in each case, at the calculated molecular center of mass which, for example, in DMO is $\sim$0.25 Å from the ring carbon axis in the $+X$ direction.

The double-ζ atomic and Rydberg basis set used is the same as described previously for methycyclopentene[11] with the addition of the valence oxygen atom basis functions.[12] The final basis set in DMO, for example, is 166 primitive Gaussians contracted to 72 basis functions.

DMO has a single twofold rotation axis and therefore all the SCF orbitals and electronic states can be classified as either symmetric (a) or antisymmetric (b) with respect to this rotation. The electronic ground state of DMO can therefore be written as $(1a)^2(2a)^2...(11a)^2\ (1b)^2(2b)^2...(9b)^2$ or

$$\{\text{core}\}\ (11a)^2(9b)^2 \qquad {}^1\text{A(GS)} \tag{1}$$

A priori, there are four types of single-excitation (single configuration) open-shell excited states that can be formed here, depending on the symmetries of the originating and terminating orbitals.

$$\{\text{core}\}\quad (11a)^1(9b)^2(12a)^1 \qquad {}^1\text{A(AA)} \tag{2}$$

$$\{\text{core}\}\quad (11a)^1(9b)^2(10b)^1 \qquad {}^1\text{B(AB)} \tag{3}$$

$$\{\text{core}\}\quad (11a)^2(9b)^1(10b)^1 \qquad {}^1\text{A(BB)} \tag{4}$$

$$\{\text{core}\}\quad (11a)^2(9b)^1(12a)^1 \qquad {}^1\text{B(BA)} \tag{5}$$

Clearly, though, only the lowest energy ^{1}A and ^{1}B single-configuration SCF states can be variationally correct. However, each of these configurations is a distinctly different distribution, in numbers of electrons and type (single or double occupancy), between the two symmetries a and b. Therefore, there is no practical difficulty in converging separate SCF solutions (including the {core}'s which were not held frozen) for each of these states and no indication of variational collapse. The accuracy of the excited-state single-configuration wave function description will then depend on the overlap and extent of configuration interaction (CI) between the various energy states of the same symmetry.

An idea of the orbital makeup of the single configuration ground and excited states of DMO can be obtained from Table III, where in the first five columns of numbers the total group and net spin populations are compared for state-configurations (1)–(5). This table clearly shows that the open-shell excited states are all pure Rydberg in character. In this respect, there is no calculated difference here between the corresponding triplet- and singlet-state configurations of DMO, in contrast to what is found for the $\pi \rightarrow \pi^*$ type transition in olefins,[13] where the triplet is a pure valence state but the singlet is diffuse (in the SCF approximation). The near identity of the space parts of the corresponding triplet and singlet open-shell states in DMO is demonstrated by comparing columns 5 and 6 in Table III, the latter referring to the ^{3}B(BA) analogue of (2).

This lack of difference between the corresponding triplet and singlet open-shell SCF-state configurations of DMO is important for the ^{1}A states as evidence to rule out the possibility that the open shell SCF is still trying to represent the ground ^{1}A state, as has been found in some cases by Davidson and Nitzsche.[14] In the case of DMO, the pure Rydberg character of the calculated open-shell SCF states guarantees that the overlap with the ground state will be small.

The net change in orbital population in going from state to state can be obtained by comparing the gross populations for the two states, as shown in Table III. Thus, excited states (4) and (5), arising from a one-electron excitation from the 11a molecular orbital (MO), differ from the ground state by the redistribution of an electron which goes from being located almost uniformly on all the heavy atom groups in the ground state into a pure Rydberg orbital in the excited state. On the other hand, in those excited states formed by a one-electron excitation from the 9b MO, an electron of heavily (46%) oxygen character is promoted into a Rydberg orbital, although in the excited state itself the 9b orbital is $\sim$93% oxygen in character as shown by the net spin populations. As can also be seen from Table III where the SCF total energies are also tabulated, these latter are the calculated lowest energy excited states.

The total group and net spin populations for the two positive ions

$$\{\text{core}\}\quad (11a)^2(9b)^1 \qquad {}^2\text{B} \tag{6}$$

and

$$\{\text{core}\}\quad (11a)^1(9b)^2 \qquad {}^2\text{A} \tag{7}$$

are also shown in Table III in the last two columns. An examination of the numbers in Table III comparing the ^{2}B with the ^{1}B(BA) state, for example, shows that, except for the occupation of the Rydberg orbital in the latter state, the charge and spin distributions of these two states are essentially identical. This similarity in properties is just another example of the positive ion nature of the non-Rydberg part of the molecule in Rydberg excited states.[2]

An immediate results of this comparison is that any energy error in the ion state should be directly reflected in the calculated energies of the Rydberg states. The first ionization potential of DMO has been reported to be 9.98 eV,[9] for which the calculated value from Table III is 8.81 eV, an error of 1.17 eV. Correspondingly, the first Rydberg excited state in the optical absorption spectrum has been assigned to a band at 7.06 eV in the vacuum ultraviolet spectrum,[6] while the (Table III) calculated lowest

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(11) M. Levi, D. Cohen, V. Schurig, H. Basch, and A. Gedanken, *J. Am. Chem. Soc.*, **102**, 6972 (1980).

(12) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).

(13) H. Basch and V. Mckoy, *J. Chem. Phys.*, **53**, 1628 (1970).

(14) E. R. Davidson and L. E. Nitzsche, *J. Am. Chem. Soc.*, **101**, 6524 (1979).

Table IV. Orbital Energies of DMO[a]

molec orbital	state			
	$^1B(BA)$	$^1B(AB)$	$^1A(AA)$	$^1A(BB)$
9a	−0.6412	−0.6469	−0.6362	−0.6490
10a	−0.6153	−0.6321	−0.6257	−0.6179
11a	−0.5639	−0.6314	−0.6250	−0.5672
12a	−0.0909		−0.0953	
13a	−0.0643		−0.0608	
14a	−0.0478		−0.0483	
15a	−0.0476		−0.0472	
16a	−0.0469		−0.0471	
17a	−0.0453		−0.0455	
18a	−0.0410		−0.0377	
7b	−0.6399	−0.6571	−0.6486	−0.6457
8b	−0.6193	−0.6251	−0.6143	−0.6260
9b	−0.8098	−0.5975	−0.5919	−0.4110
10b		−0.0804		−0.0804
11b		−0.0684		−0.0607
12b		−0.0472		−0.0491
13b		−0.0444		−0.0456
14b		−0.0406		−0.0403
15b		−0.0331		−0.0398

[a] In au.

energy excitation, $^1A(GS) \rightarrow {}^1B(BA)$, is at 6.36 eV, an error of 0.70 eV. The smaller energy error for the lowest energy Rydberg state is undoubtedly due to the additional correlation energy error in the first Rydberg excited singlet state which should diminish in climbing the Rydberg ladder until complete ionization is reached.

Of particular interest in the SCF calculations of these single configuration electronic wave functions is the use of Fock operators for the open-shell orbitals that do not contain any self-interaction terms. Thus the higher energy improved virtual orbitals (IVOs)[15] should give a good single-configuration representation of excited state MOs, although CI could still substantially mix states of the same symmetry arising from different electronic configurations.

Table IV shows the IVO orbital energies for each of the SCF calculated excited states. The energy of the excited electronic state formed by promoting the highest orbital energy electron is one of state-configurations (2)–(5) into a higher MO is just the energy of the lower state plus the orbital energy difference between originating and terminating orbitals. This procedure, of course, assumes that the "passive" electrons are unchanged in the excitation process, which is not a bad assumption here considering the constant positive ion character of the non-Rydberg part of these wave functions (Table III). The specific Rydberg orbital character (s, p, or d) is taken from the majority basis Rydberg orbital character of that molecular orbital.

The orthogonality of the single-configuration SCF wave functions (1)–(5) was tested directly by calculating the determinant of the overlap matrix between the respective wave functions. The accuracy of the calculated overlap quantities is $\sim 2 \times 10^{-6}$ as obtained from an evaluation of the determinant of the self-overlap for the $^1A(GS)$ state. Thus, $\langle {}^1A(BB) | {}^1A(GS) \rangle$ was found to be -4.63×10^{-3} and $\langle {}^1B(AB) | {}^1B(BA) \rangle < 1 \times 10^{-6}$. These overlap numbers are very small and the wave functions are thus essentially orthogonal.

The CI mixing among the low energy manifold of A and B symmetry states separately was also examined to a limited extent. Using the lowest energy open-shell singlet-state MOs for each symmetry the CI calculations involved the interaction of all states arising from the distribution of four electrons among 12 spin-orbitals of both a and b symmetries. The results showed a negligible amount of configuration mixing, as would be expected for essentially pure Rydberg states.

In summary, then, the energies of the singlet excited states can be taken from the single-configuration results, with higher energy excited states of a given type parent configuration obtained using the IVOs of the respective parent configuration SCF calculation. The resultant energy ladder of states is shown in Table VI. The intensity calculations for the electronic transition and rotational strengths (RS), also shown in Table VI for both the length and velocity forms, were carried out using the orbitals obtained in the excited-state wave functions only, the same procedure used in a previous study.[11] As shown in Table VI, all the relevant lower energy excited states involve excitation from the 9b MO. As discussed above, the change in gross orbital population in going from the ground state to the $^1B(BA)$ or $^1A(BB)$ excited states involves a depletion of 0.46 electrons on the oxygen atom while the singly occupied 9b MO in these excited states is 93% oxygen in orbital character. Thus the orbital character of the open-shell 9b MO is only very roughly close to what it should be in order to fully justify the approximation of using the excited-state orbitals only in calculating intensities. We therefore expect the calculated intensities to be only qualitatively accurate and look to an examination of the agreement between the length and velocity forms to serve as a measure of their reliability.

Table V. Orbital Energies of MO[a]

molec orbital	open-shell $^1A^1$ state
15a	−0.5878
16a	−0.8168
17a	−0.1000
18a	−0.0719
19a	−0.0657
20a	−0.0647
21a	−0.0549
22a	−0.0541
23a	−0.0535

[a] In au; 16a and 17a are the open-shell orbitals.

The MO molecule (Figure 4) has no symmetry elements, and in the ^1A ground-state 16a orbitals are doubly occupied. The open-shell ^1A excited state orbital energies are shown in Table V. The same procedures described above for DMO were used in obtaining the calculated excitation energies, oscillation strengths, and rotational strengths shown in Table VII. All the circumstances that prevent variational collapse in DMO are also present in MO, and therefore, both *a priori* an from the results there is no reason to suspect that the absence of a twofold rotation axis is critical.

Discussion

The assignment of the experimental optical absorption and circular dichroism (CD) spectrum of DMO based on these calculations is also shown in Table VI. The experimental spectra, which are reproduced in Figure 1,[6] show four main regions of absorption in the 1500–1850-Å region, with alternating CD signs. The first peak is clearly the expected $n(O) \rightarrow 3s$ Rydberg transition and the calculated rotational strength in Table VI is of the right sign (positive). Here, the length (**r**) and velocity (∇) forms agree very well with each other, probably better than is to be generally expected. The calculated oscillator strengths (*f*) in the **r** and ∇ forms for this transition, however, differ by almost a whole order of magnitude. This latter discrepancy can be attributed to the errors introduced by using only the upper state single-configuration wave functions to calculate the intensities. The calculated excitation energy (6.36 eV) for this transition is much below the experimental value (7.06 eV) for the reasons cited above.

The next excited state in Table VI, $^1A(BB)$, is calculated at 6.64 eV and is assigned to the negative CD peak centered at 7.45 eV in the observed spectra. The calculated RS is of the right sign but a higher RS is predicted for the second band than for the first band whereas experimentally the opposite trend is observed. For this transition, which is of the $n(O) \rightarrow 3p$ type, the length and velocity forms are in reasonably good agreement both for *f* and RS.

Next in calculated energy come two more $n(O) \rightarrow 3p$ type Rydberg states at 7.08 and 7.18 eV, probably too close to be resolved spectrally. Experimentally, the next band in the spectra

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(15) W. J. Hunt and W. A. Goddard, III, *Chem. Phys. Lett.*, **4**, 146 (1969).

Table VI. Summary of Calculated and Experimental Quantities for DMO

	calcd					exptl			
state	ΔE^a	$f(r)$	$f(\nabla)$	RS(r)^b	RS(∇)^b	ΔE^a	RS^b	f	
^{1}B(BA)-1	6.36	0.0005	0.0042	+3.04	+3.44	7.06	+20	0.02	1755 Å
^{1}A(BB)-1	6.64	0.0013	0.0042	−4.10	−7.34	7.45	−0.4		1665 Å
^{1}B(BA)-2	7.08	0.0005	0.0024	+0.74	+1.52				1602 Å
						7.74	+14	0.05	
^{1}A(BB)-2	7.18	0.0004	0.0002	+0.42	+0.46				1510 Å

^{a} Excitation energy from ground state; in eV. ^{b} In 10^{-40} cgs.

Table VII. Summary of Calculated and Experimental Quantities for MO

	calcd					exptl		
state	ΔE^a	f(r)	$f(\nabla)$	RS(r)^b	RS(∇)^b	ΔE^a	RS^b	f
^{1}A(1)	6.40	0.0004	0.0026	+2.66	+4.92	7.12	11.8	0.025
^{1}A(2)	7.16	0.0005	0.0010	−0.76	−1.30	7.75	−10.8	0.062
^{1}A(3)	7.34	0.0005	0.0026	−1.54	+0.42			
^{1}A(4)	7.36	0.0002	0.0006	+0.06	−0.02			

^{a} Excitation energy from ground state; in eV. ^{b} In 10^{-40} cgs.

is centered at 7.74 eV, has a larger RS than the previous band, and is of positive sign. The experimental transition moment is difficult to estimate because the band seems to lie on a generally increasing intensity slope with increasing energy, but a reasonable estimate puts its intensity higher than the previous band. The calculated *f* and RS intensities for this band both show the wrong trends relative to the previous band, although the signs of the calculated RS values both agree with that observed for the 7.74-eV band.

A dense series of calculated bands are found next starting at 7.49 eV, of the n(O) → 3d type, with bunched alternating signs of the RS. However, in the region of the fourth band, observed at ~8.21 eV, other type transitions not included in the calculations are expected to become important, as will be discussed subsequently. Therefore, Table VI deals only with the assignment of the first three observed bands in the spectra.

A different assignment of the DMO spectra than that proposed above and in Table VI has been suggested by Levi et al.[6] in contrast to the assignment here which correlates both the observed second and third bands at 7.45 and 7.74 eV with a symmetry split n(O) → 3p Rydberg transition, Levi et al.[6] identify the 7.45-eV band with a valence n(O) → σ^* transition. The 7.74-eV band alone is then assigned to the Rydberg transition terminating in the 3p orbital, consistent with the assignment[2] of the parent ethylene oxide spectrum.

Unfortunately, the true location of the lowest energy n(O) → σ^* valence-type transition cannot be found in these calculations. As explained above, the calculated Rydberg state energies are uniformly shifted to lower energy by 0.7–1.2 eV relative to their experimental values. Further, experience has shown[13] that in the absence of extensive CI valence $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ type of transitions, due to their ionic natures,[16] have calculated single configuration SCF energies that are typically much higher than their experimental values. The molecular orbital that has been referred to here constantly as "n(O)" is arbitrary and, in fact, the transition n(O) → Rydberg involves only a net ~50% change in oxygen atom character, as discussed above. The valence-type n(O) → σ^* transition then probably will have significant ionic $\sigma \rightarrow \sigma^*$ character which will tend to push it to a higher calculated energy. In addition, the SCF approximation seems to be incapable of projecting out the pure valence transitions when they lie among a series of Rydberg states, apparently for orthogonality reasons.[2,17] Thus, in the calculations here on DMO, the n(O) → σ^* transition to give a valence excited state is just not found, and even if it were found, the significance of its calculated state energy relative to the Rydberg state energies would not be clear.

On the other hand, the calculated Rydberg excitation energies and RS signs shown in Table VI, neglecting valence-type transitions, give a reasonable account of the observed absorption and CD spectra, at least for the first three bands. If the accuracy of the calculated signs of the RS for the observed bands is accepted, then the 7.45-eV absorption cannot be due to a non-Rydberg transition since that would postpone the assignment of the second calculated band {6.64 eV, n(O) → 3p} to the third observed band (7.65), for which the rotational strength has the wrong calculated sign.

In the absence of any knowledge of the sign of the RS for the valence transition, a reasonable correlation of the observed spectra with these calculations places the n(O) → σ^* excitation energy in the region of the third observed band (7.65 eV), with a positive RS. This choice would also explain the very large discrepancy between the calculated absorption and CD intensities calculated for the third band relative to the first two transitions by adding to this region the intensity of the missing valence-type transition.

As an alternative explanation, it is possible that a positive CD valence $\sigma \rightarrow \sigma^*$ transition is found as low as 7.50 eV and partially cancels the calculated n(O) → Rydberg negative CD, while reinforcing the 7.65-eV positive CD band. This latter assignment, of course, requires that there be two bands in the 7.50-eV region of the spectrum where hardly any prominent features are observed at all. However, it is supported by the results obtained for the absorption spectrum of solid ethylene oxide[2] in which a valence transition is observed at 63000 cm^{-1}.

The assignment of the experimental optical absorption and CD spectra of MO is shown in Table VII. The calculated results account for the signs of the first two bands. The first CD band is positive and is assigned according to Table VII as n(O) → 3s transition. The second band is assigned as the n(O) → 3p transition. The three calculated states ^{1}A(2), ^{1}A(3), and ^{1}A(4) are the three components of the n(O) → 3p transition and are underlying the observed CD band at ~1600 Å. Their splitting in MO is calculated to be smaller than in DMO. The second and third components of the n(O) → 3p transition are seen to have oppositely signed rotational strengths, depending on whether the length or velocity dipole matrix elements are used in their calculation. These discrepancies certainly reflect a deterioration in the accuracy of the higher excited states. However, the calculation clearly predicts a negative RS for the second excited state, as is observed experimentally, and the sign also dominates the ^{1}A(3) transition. A very much weaker RS is predicted for ^{1}A(4).

An interesting question relates to the oppositely signed RS results obtained by Rauk,[3] for the first two transitions in MO. Rauk attributes this disagreement with experiment to the neglect of reorganization of the "unexcited" electrons in his CI method. The theoretical methods used here do allow for such reorganization, assuming it to be the same for all the Rydberg states, and therefore the right signs of the CD are obtained.

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[16] T. H. Dunning, W. J. Hunt, and W. A. Goddard, III, *Chem. Phys. Lett.*, **4**, 146 (1969).

[17] M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5027 (1968).