

Low-Lying Excited States of Mono-olefins*

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Semiempirical calculations of energies, oscillator strengths, and rotational strengths for a number of singlet-singlet transitions of ethylene and of the twisted olefin *trans*-cyclo-octene are compared with experiments. The analysis shows that a minimum of three low-lying singlet states are required to explain the data considered: a ${}^1B_{2u}(\pi_x \rightarrow \pi_x^*)$ responsible for the strong, broad olefinic absorption, a ${}^1B_{2u}(\pi_x \rightarrow \sigma^*)$ 3s Rydberg state responsible for the olefin band with $\epsilon \cong 1000$, and a ${}^1B_{2g}(\pi_x \rightarrow \pi_y^*)$ 3p_y Rydberg like state accounting for the low-lying electric quadrupole-allowed transition of ethylene and dominating the optical rotatory properties of the twisted double bond.

I. INTRODUCTION

Elucidation of the low-lying excited states of mono-olefins has long seemed a tractable problem. Nevertheless, the continuous revision of the assignments of these states bears testimony to the complexity of the problem and to the elusiveness of its solution. Recent contributions to this subject¹⁻³ such as the experiments and analyses of Robin, Hart, and Kuebler⁴ have been fruitful and provocative while at the same time emphasizing the complexity of the problem. The only single transition for whose assignment there is general agreement is the first strong optical transition in these molecules—although as late as 1954, Walsh² felt that there was some room for equivocation on even this point.

We here re-examine the problem, paying special attention to the implications of the optical activity of the twisted mono-olefin *trans*-cyclooctene.⁵ This approach allows us to bring to bear more effectively than was previously possible the consequences of the symmetries of the states in question. Such an approach is particularly helpful in light of the paucity of polarization studies on mono-olefins.

From the discussion that follows, we shall infer that at least three singlet-singlet transitions are required for a consistent interpretation of the optical properties associated with low-lying (~ 5 –7.5 eV) excited states of mono-olefins. To anticipate the conclusions, we list these here as (a) the conventional $V \leftarrow N(\pi_x \rightarrow \pi_x^*)$ transition responsible for the best-known optical absorption, (b) an allowed $\pi_x \rightarrow 3s\sigma$ Rydberg-like

transition described first by Price⁶ and Mulliken,⁷ and (c) an electric-dipole-forbidden, electric-quadrupole- and magnetic-dipole-allowed $\pi_x \rightarrow 3p\pi_y$ transition, which is likely to be rather Rydberg-like, due to the non-penetrating nature of the excited orbital. We shall generally use the united-atom notation (e.g., 3s σ) to designate the normally empty orbitals which are non-penetrating, because of the likelihood of their Rydberg nature.⁸

II. SUMMARY OF EXPERIMENTAL DATA

The overlapping bands in the fluid-state spectra presently available have made it impossible to ascertain even the number of optical transitions in the spectra of olefins. Every mono-olefin exhibits a single strong optical transition whose absorption maximum falls between about 7.6 and 6.2 eV, with ϵ_{\max} of about 10⁴. Substituted olefins exhibit a lower-energy transition just to the long-wave side of the strong transition, with ϵ_{\max} of about 1000. This has been called the "mystery band" by Robin and co-workers.⁴

A still weaker shoulder with ϵ_{\max} of order 1 has been reported in the spectra of several olefins⁹; it is not at all clear whether this is an electronic transition distinct from the " $\epsilon \sim 1000$ " transition, a part of it, or an artifact due to trace impurities. Under the assumption that this shoulder is indeed a separate electronic transition, Mulliken has suggested that it is due to the triplet corresponding to the aforementioned Rydberg singlet.¹⁰ With long optical paths¹¹ or with oxygen perturbations¹² it has proved possible to observe a very weak singlet-triplet transition in ethylene at 4.5 eV.

* Based in large part on the doctoral dissertation of M. Yaris, Department of Chemistry, University of Minnesota, July 1967.

¹ An extensive array of references has been given by U. Kaldor and I. Shavitt, *J. Chem. Phys.* (to be published).

² A guide to the literature prior to 1954 was given in the review of A. D. Walsh, *Ann. Rev. Phys. Chem.* **5**, 163 (1954).

³ P. A. Clark and J. L. Ragle, *J. Chem. Phys.* **46**, 4235 (1967).

⁴ M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Chem. Phys.* **44**, 1803 (1966).

⁵ A. C. Cope and A. S. Mehta, *J. Am. Chem. Soc.* **86**, 5626 (1964).

⁶ W. C. Price, *Phys. Rev.* **47**, 444 (1935).

⁷ R. S. Mulliken, *J. Chem. Phys.* **3**, 517 (1935).

⁸ R. S. Mulliken, *J. Am. Chem. Soc.* **86**, 3183 (1964).

⁹ W. J. Potts, *J. Chem. Phys.* **23**, 65 (1955); E. P. Carr and M. K. Walker, *ibid.* **4**, 751 (1936); E. P. Carr and G. F. Walter *ibid.* **4**, 756 (1936); E. P. Carr and H. Stücklen, *ibid.* **4**, 760 (1936).

¹⁰ R. S. Mulliken, *J. Chem. Phys.* **33**, 1596 (1960).

¹¹ C. Reid, *J. Chem. Phys.* **18**, 1229 (1950).

¹² D. F. Evans, *J. Chem. Soc.* **1960**, 1735.

The presumption is that this is due to the $\pi_z \rightarrow \pi_z^*$ triplet. Since we are concerned here with singlet-singlet transitions only, we shall discuss these triplets no further.

There is no definite information on the polarization of any of these transitions. Robin and co-workers⁴ have examined the vibrational structure of the " $\epsilon \sim 1000$ " band of substituted olefins and on this basis assigned it as the first $\pi_z \rightarrow \sigma^*$, i.e., the $\pi_z \rightarrow 3s\sigma$ Rydberg transition. The oscillator strength for the transition lies between about 0.005 and 0.0325.

Data on the positions of the normally occupied orbitals are available from the photoionization efficiency curves.^{13,14} These curves (the relative number of electrons per incident photon as a function of photon energy) show a sharp first ionization threshold at approximately 10.5 eV in ethylene and at lower energies in the substituted species, a second and much broader threshold about 1.5 eV above the first, and still higher-energy thresholds 2 eV and more beyond the second. Complementary to the direct photoionization measurements are the measurements of the kinetic energy of photoelectrons ejected by light of essentially a single frequency. The results of Al-Joboury and Turner¹⁵ show some five ionization thresholds for ethylene, at 10.48, 12.50, 14.39, 15.63, and possibly 19.13 eV.

Electron impact excitation is capable in principle of providing considerable information about excited states. The work of Kupperman and Raff¹⁶ and of Doering¹⁷ unequivocally shows two maxima in the excitation cross section, at 4.5 and 7.6 eV. These are due (at least) to the $T \leftarrow N$ and $V \leftarrow N$, $\pi_z \rightarrow \pi_z^*$ excitations.¹⁸ The spectrum of solid ethylene exhibits the $V \leftarrow N$ transition and two unexplained bands at 2044 and 2079 Å.¹⁹

The energy-loss spectrum²⁰ of ethylene for moderately high-energy electrons indicates that there is an electric quadrupole-allowed transition (which could also be magnetic-dipole-allowed) overlapping the electric-dipole-allowed $V \leftarrow N$ transition in the 7.45-eV region.

Finally, spectral and optical rotatory properties are

¹³ R. I. Schoen, J. Chem. Phys. **37**, 2032 (1962).

¹⁴ B. Steiner, C. F. Geise, and M. G. Inghram, J. Chem. Phys. **34**, 189 (1961).

¹⁵ M. I. Al-Joboury and D. W. Turner, J. Chem. Soc. **B1964**, 4434.

¹⁶ A. Kupperman and L. M. Raff, J. Chem. Phys. **38**, 1607 (1963); **37**, 2497 (1962); Discussions Faraday Soc. **35**, 30 (1963).

¹⁷ J. P. Doering, J. Chem. Phys. **46**, 1194 (1967).

¹⁸ The initial report in Ref. 14 also noted a maximum at 6.5 eV. It now appears that there are difficulties in reproducing this result, and hence this particular datum should be considered with caution. In this connection, the elastic scattering cross section for electrons by ethylene shows no change in slope or curvature as it passes through the 6.5-eV region. [J. A. Simpson and S. R. Mielczarek, J. Chem. Phys. **39**, 1606 (1963) and Ref. 15, just cited.]

¹⁹ See also the crystal spectra reported by A. Lubezky and R. Kopelman, J. Chem. Phys. **45**, 2526 (1966).

²⁰ K. J. Ross and E. N. Lassette, J. Chem. Phys. **44**, 4633 (1966). See also E. N. Lassette and S. A. Francis, *ibid.* **40**, 1208 (1964) for data taken with faster electrons.

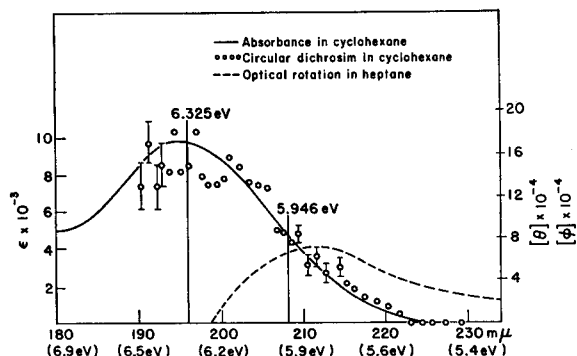


Fig. 1. Ultraviolet spectrum, circular dichroism, and optical rotatory dispersion of (+)-*trans*-cyclo-octene (see Ref. 21).

known for the twisted olefin *trans*-cyclo-octene. This molecule is exceptionally well suited for investigation of optical activity, because its single olefinic chromophore is inherently dissymmetric as a result of the molecule's twisted geometry. The ultraviolet spectrum, circular dichroism, and optical rotatory dispersion of (+)-*trans*-cyclo-octene are shown in Fig. 1.²¹ The absolute configuration shown in Fig. 2 is that of the (–) enantiomer, corresponding to a positive twist angle δ as defined below. The wavelength-weighted area under the circular dichroism (cd) curve in Fig. 1 corresponds to a rotational strength of 1.7×10^{-38} cgs units. If a Lorentz-Lorenz correction for medium polarization is used, this corresponds to a vacuum value of 1.3×10^{-38} cgs. The vapor spectra of *trans*-cyclo-octene and *trans*-cyclo-nonene are shown in Fig. 3; the sample²² was photographed with a McPherson Model 240 spectrograph. The absorption by *trans*-cyclo-octene in the 2000–2200-Å region, best shown in the -45°C spectrum, is likely to be due to the " $\epsilon \sim 1000$ " transition.

In summary, the data show one intense singlet-singlet transition for all mono-olefins and at least one other weaker singlet-singlet excitation in the substituted olefins which may largely underlie the strong transition. The most recent history of the problem has focused on the assignment of the state or states that are responsible for the weak absorption.

III. COMPUTATIONS

A. Orbitals and Energies

Our goal in carrying out the computations reported in this section is to obtain theoretical estimates for the excited-state energies in simple olefins, and for the optical properties of the transitions to these states. The general scheme and immediate conclusions of the calculations are given in this section; details are presented in the appendixes.²³ In Sec. IV we examine

²¹ As determined by G. Holzwarth and H. J. S. Winkler (private communication).

²² Provided by H. J. S. Winkler.

²³ The calculations and results are presented in extensive detail in the doctoral dissertation of M. Yaris (footnote to the title).

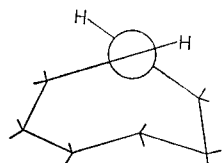


FIG. 2. The absolute configuration of $(-)$ -*trans*-cyclo-octene as determined by Cope and Mehta (Ref. 5). This figure is drawn to correspond to the positive twist angle as defined and illustrated in the text, rather than to the $(+)$ enantiomer used to obtain the data of Fig. 1 and the actual absolute configuration.

the calculated results in light of the experimental data and draw our inferences.

To discuss the possible excited states, their ordering, and their roles in real olefins, we refer to the coordinates as defined in Fig. 4. We shall speak in terms of the prototype, ethylene. The axis of the olefinic carbon-carbon bond is the x axis; the z axis of a planar olefin is taken perpendicular to the molecular plane, and the local coordinate systems at the olefinic carbon atoms are right-handed.

The energies of the orbitals of ethylene (based on atomic $1s$, $2s$, and $2p$ orbitals) have been calculated by several authors and by several procedures. The results of these calculations are all in essential agreement with regard to the order and grouping of the normally filled orbitals and, with the exception of the calculations by Robin, Hart, and Kuebler,^{4,24,25} with regard to the ordering of excited orbitals as well. The results have been summarized in detail by Kaldor and Shavitt¹ in connection with their optimized LCAO-SCF (minimal Slater basis) calculations. Table I contains the results of Kaldor and Shavitt and those of Shulman, Moskowitz, and Hollister,²⁶ the two most extensive *a priori* ethylene calculations at the present time, as well as the results of our own semiempirical calculations described below.

The notation for orbitals is based on that for axially symmetric molecules. Thus any orbital with a single nodal plane containing the C-C axis is called a π orbital,

²⁴ These authors used a set of Gaussian basis functions which included a highly expanded s -like function centered about each carbon. The lowest virtual molecular orbitals containing these functions, the $3s\delta$, $(4ag)$, and $3b_{2u}$ orbitals are composed almost entirely of the expanded s -like functions; moreover, the energies of both these orbitals are positive, only about $\frac{1}{2}$ eV above zero. To rely on virtual orbitals is a perilous process under any circumstances. It becomes particularly dangerous when one's basis set admits the opportunity for the virtual functions to take on the character of continuum states of very low positive energy, because in this circumstance an SCF calculation will tend to converge to the continuum function with $E=0$. This phenomenon can be diagnosed by trying to optimize the exponential constant of the suspected basis function; in such cases, the constant tends toward zero as the orbital energy decreases. Examples arise when one tries to compute Hartree-Fock functions for negative ions of atoms having negative electron affinities; such examples were pointed out to us by Dr. Paul Cade. No such diagnostic procedure was reported in the work of Robin, Hart, and Kuebler, but the energies and the composition of the virtual MO's strongly suggest that the lowest of these suffer from a surfeit of low-energy continuum functions. This difficulty has since been noted also by Robin, Hart, and Kuebler (private communication).

²⁵ H. P. Kelly, Phys. Rev. **131**, 684 (1963); H. P. Kelly and H. S. Taylor, J. Chem. Phys. **30**, 1478 (1964).

²⁶ J. M. Schulman, J. W. Moskowitz, and C. Hollister, J. Chem. Phys. **46**, 2759 (1967).

and the subscript denotes the axis perpendicular to this plane. Hence the highest normally-filled π orbital is the π_z .²⁷ Superscript stars are used to denote normally empty orbitals. There are two normally filled π_y 's and two normally empty π_y 's: for brevity we denote the lowest as π_{yy} and the highest as π_{yy}^* . The molecular orbitals discussed below are composed in LCAO approximation, of carbon $2s$ and $2p$ functions and of hydrogenic $1s$ functions.

We define the molecular orbitals in terms of the AO basis functions as follows (Symmetries for the planar molecule are indicated in parentheses. See Ref. 25 for an explanation of symbols b_{zu} , etc.):

$$\pi_z = N_z^{-1}(z_a^t + z_b), \quad (b_{zu}), \quad (1)$$

$$\pi_z^* = (N_z^*)^{-1}(z_a^t - z_b), \quad (b_{y\sigma}), \quad (2)$$

$$\pi_{yy} = (N_{yy})^{-1}(\omega_a^t + \omega_b), \quad (b_{yu}), \quad (3)$$

$$\pi_y = (N_y)^{-1}(\chi_a^t - \chi_b), \quad (b_{z\sigma}), \quad (4)$$

$$\pi_y^* = (N_y^*)^{-1}(\chi_a^{*t} + \chi_b^*), \quad (b_{yu}), \quad (5)$$

$$\pi_{yy}^* = (N_{yy}^*)^{-1}(\omega_a^* - \omega_b^*), \quad (b_{z\sigma}), \quad (6)$$

and

$$\sigma^* = (N_\sigma)^{-1}(\sigma_a^t + \sigma_b), \quad (a_\sigma). \quad (7)$$

The N 's are normalizing factors; z_a is a $2p\pi_z$ carbon AO on atom a ; the χ 's, ω 's, and σ 's are group orbitals defined in terms of the atomic S_a , $S_b(2s)$, x_a , $x_b(2p_x)$, y_a , y_b , composite hydrogen orbitals H_a , H_b , and single hydrogen

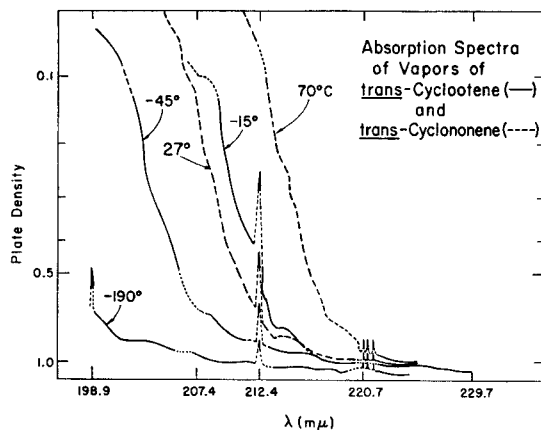


FIG. 3. The gas-phase ultraviolet spectra of *trans*-cyclo-octene and *trans*-cyclononene at various temperatures (cell length = 20.8 cm) (samples furnished by H. J. S. Winkler). The sharp spikes are due to lines in the light source, which served as internal wavelength standards.

²⁷ We are aware that the choice of x and z axes does not follow the convention suggested by Mulliken. The calculations were carried out with the notation presented here, and we have chosen to leave the results in the original notation and avoid the possibility of errors of transcription, rather than to convert the results into the other notation with which we are in sympathy. We have followed one suggestion of Professor Mulliken, namely to write b_x , b_y , and b_z instead of b_1 , b_2 , and b_3 , respectively, so as to indicate explicitly the twofold rotation axis with respect to which the orbital or state is invariant.

1s orbitals h_{1a} , etc.:

$$\chi_a = \alpha y_a + \beta H_a^y, \quad (8)$$

$$H_a^z = h_{1a} + h_{2a}, \quad (9)$$

$$H_a^y = h_{1a} - h_{2a}, \quad (10)$$

$$\chi_a^* = \alpha^* y_a - \beta^* H_a^y, \quad (11)$$

$$\omega_a = \epsilon y_a + \kappa H_a^y, \quad (12)$$

$$\omega_a^* = \epsilon^* y_a - \kappa^* H_a^y, \quad (13)$$

$$\sigma_a = \gamma_s S_a - \gamma_h H_a^{z^t} + \gamma_x \chi_a^t, \quad (14a)$$

and

$$\sigma_b = \gamma_s S_b - \gamma_h H_b^{z^t} - \gamma_x \chi_b^t. \quad (14b)$$

The superscript "t" denotes that in the twisted-olefin calculations described below one is to consider the orbitals carrying this superscript as twisted through the angle δ about the C-C axis, with respect to their "original" positions in the planar configuration (see

TABLE I. Molecular orbital eigenvalues (values in electron volts).

Orbital	Ethylene			<i>trans</i> -cyclo-octene This work
	Kaldor and Shavitt	Shulman, Moskowitz, and Hollister	This work	
π_{yy}, b_{yu}	-17.4987	-17.8198	-20.85	-15.91
π_y, b_{zu}	-13.7519	-13.9995	-17.87	-13.55
π_z, b_{zu}	-10.0432	-10.1657	-13.25	-9.91
π_s^*, b_{y0}	6.6719	3.9074	0.427	2.32
π_y^*, b_{yu}	16.1029	...	2.430	4.00
π_{yy}^*, b_{su}			6.26	6.99
σ_g^*, a_g	17.0471	6.4896		
σ_u^*, b_{zu}	17.5804	6.9358		

Fig. 4). The constants α , β , α^* , β^* , γ_s , γ_h , and γ_x are taken to be real and positive.

Figure 5 is a correlation diagram for the ethylene orbitals as the molecule is twisted about its C-C bond from the planar form with D_{2h} symmetry through the D_2 -symmetric intermediate shape to the form for which the dihedral or twist angle δ is 90° . All orbitals that can be constructed from our basis are included. The orbitals of particular concern to us are the normally filled $1b_{zu}(\pi_z)$ and $1b_{yg}(\pi_y)$, the normally empty $1b_{yu}(\pi_z^*)$, $2b_{yu}(\pi_y^*)$, and $4a_g(3s\sigma_g)$ orbitals. The lower normally filled orbitals play essentially no part in the spectral region we are examining; similarly, the higher normally empty orbitals, the $3b_{zu}(\sigma_u)$, $2b_{zg}$, and $4b_{zu}$ orbitals affect only slightly the quantitative details of the picture, and not the general qualitative conclusions we seek.

We have performed the following calculations for energies, orbitals and state functions:

- (1) A semiempirical self-consistent-field (SCF) cal-

Coordinates for the Mono-olefin

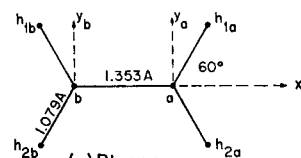
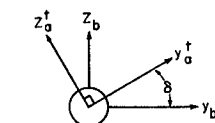


FIG. 4. The coordinates for ethylene and *trans*-cyclo-octene calculations.



(b) Twisted
(x axis toward reader)

ulation of orbitals and orbital energies was carried out in the spirit of the Pariser-Parr-Pople approximation.²⁸ The basis set consisted of hydrogen 1s and carbon $2p_y$ and $2p_z$ orbitals. Molecular orbitals involving the carbon 2s and $2p_x$ orbitals (molecular σ orbitals) were considered only at a later stage. The parameters entering into the calculation and their evaluation are

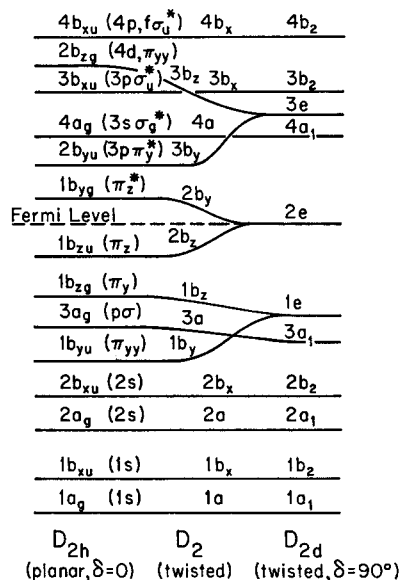


FIG. 5. The orbital correlation diagram for planar and twisted ethylene. For the lowest four normally filled orbitals, the parenthetic symbols denote the general character in terms of separated-atom AO composition. The parenthetic symbols for the next five orbitals, through the first normally-empty orbital, refer to the MO's of the axially-symmetric O_2 molecule. The higher normally empty orbitals have their Rydberg united-atom designations in parentheses. All these designations are intended to be guides only and at best can only describe the dominant nature of the orbitals. For example, the $2b_z(2s)$ orbital is surely very much like the oxygen $2\delta_u$ MO, but both retain considerable 2s separated-atom character, also. The $3b_y(3p\pi_y^*)$ likewise may have considerable valence-orbital character; this is not inconsistent with Rydberg character because any approximate representations of $3b_y$ based on valence and Rydberg models would be very nonorthogonal.

²⁸ See, for example, R. G. Parr, *The Quantum Theory of Molecular Electron Structure* (W. A. Benjamin, Inc., New York, 1963).

TABLE II. Lower singlet excitation energies in ethylene and *trans*-cyclo-octene (electron volts).

Upper state	Orbital excitation	Ethylene					<i>trans</i> -Cyclo-octene		
		KS ^a	SMH ^b	R ^c	This Work ^d	Exptl	This work ^d 0°	This work ^d 15°	Exptl
¹ B _{2u}	$\pi_x(1b_{2u}) \rightarrow \pi_x^*(1b_{2g})$	13.20 (12.33 with 15° twist)	9.30	9.40	(7.81)	7.6	(6.37) 6.31	(6.21) 5.84	6.32
¹ B _{2g}	$\pi_x \rightarrow \pi_y^*(1b_{2u})$			8.04	(8.31)	~7.5?°	(6.54) 6.51	(6.47) 6.65	5.95?†
¹ B _{2g}	$\pi_y(1b_{2g}) \rightarrow \pi_x^*$		9.79	9.60	(10.91)		(8.49) 8.52	(8.40) 8.39	
¹ B _{2u}	$\pi_x \rightarrow \sigma^*(4a_g)$		9.82	7.55		7.1–7.6			5.95?†

^a Reference 1.^b Reference 19.^c M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, "Assignments in the Ultraviolet Spectra of Olefins" (unpublished).^d Numbers in parentheses are from SCF calculations; numbers without parentheses are based on CI calculations.^e Reference 16.^f Possible assignments of shoulder in Fig. 3.

described in Appendix A. These were determined both for ethylene and for *trans*-cyclo-octene.

(2) The SCF transition energies were computed for the nine transitions to excited configurations involving π_y and π_z orbitals. This was done for planar ethylene and for (hypothetical) planar *trans*-cyclo-octene. For the five most important of these transitions, i.e., the $\pi_x \rightarrow \pi_x^*$ and the other four that can develop significant rotatory power by mixing with this transition, similar calculations were carried out for $0 \leq \delta \leq 90^\circ$, at intervals of 5° , with the same orbital coefficients used for 0° except for adjustments due to overlap. (See Appendix A.) The calculated energies are given in Table II for planar ethylene and the hypothetical planar *trans*-cyclo-octene.

(3) Configuration interaction (CI) was carried out for the five interacting states for δ from 0° – 90° . No CI was attempted for the ground state since its effects are negligible within the context of the present discussions. The evaluation of the relevant matrix elements was carried out with the same semiempirical procedures used to obtain the SCF matrix elements. The energies for ethylene, planar *trans*-cyclo-octene, and twisted ($\delta = 15^\circ$) cyclo-octene are included in Table II. Figure 6 shows the behavior of all $5B_x$ states as δ is varied.

B. Optical Properties of the Transitions

Our interpretation of the low-lying excited states of olefins depends on comparing theoretical and experimental energies, intensities, and especially optical activity. Having obtained energies, orbitals, and state functions, we now evaluate the necessary matrix elements of the electric dipole and magnetic dipole operators and, from them, the oscillator strengths, and the rotational strengths for each of the transitions

that might be of any importance. The dipole velocity form was used for these calculations; the reasons are discussed elsewhere.^{29–31}

The oscillator strength for the transition between the ground state and state ξ is

$$f_{0\xi} = (\hbar/3\pi m_e) \nu_{0\xi}^{-1} \left| \langle 0 | \sum_{j=1}^n \nabla_j | \xi \rangle \right|^2, \quad (15)$$

where m_e is the electron mass, $\nu_{0\xi}$ is the frequency [(second)⁻¹] of the transition, and ∇_j is the gradient operator with respect to the coordinates of electron j . The sum is over all electrons. For real wavefunctions,

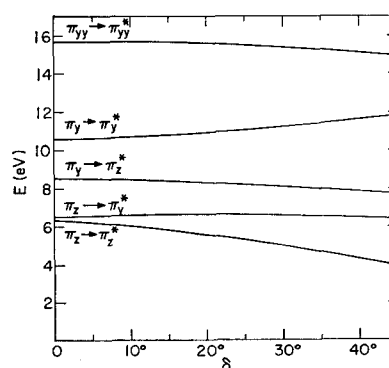


FIG. 6. Calculated energies of the B_x transitions as functions of the twist angle δ (computed energies of the $1A \mp 1B_x$ transitions after CI). The designations in this and the following curves refer to the character of the transitions for $\delta = 0^\circ$. As δ grows, there is, of course, increasing mixing among the configurations. However, even for $\delta = 65^\circ$, the principal configuration in each state is responsible for over 50% of its composition.

²⁹ H. Shull, J. Chem. Phys. **20**, 18, 1095 (1952).³⁰ M. Wolfsberg, J. Chem. Phys. **23**, 793 (1955).³¹ A. Moscowitz, in *Modern Quantum Chemistry*, O. Sinanoglu, Ed. (Academic Press Inc., New York, 1966), Vol. 3.

TABLE III. MO electric and magnetic dipole transition moments.

Orbital excitation	$\langle \nabla \rangle$	$\langle \mathbf{r} \times \nabla \rangle$
$\pi_x \rightarrow \pi_z^*$	$\cos\delta \nabla_{ba} \hat{\mathbf{x}}$	$\sin\delta S_{ba} \hat{\mathbf{x}}$
$\pi_x \rightarrow \pi_y^*$	$\alpha^* \sin\delta \nabla_{ba} \hat{\mathbf{x}}$	$-\left[\alpha^*(1+\cos\delta S_{ba}) - \beta^* \langle y_a H_d^y \rangle\right] \hat{\mathbf{x}}$
$\pi_y \rightarrow \pi_z^*$	$\alpha \sin\delta \nabla_{ba} \hat{\mathbf{x}}$	$\left[\alpha(1-\cos\delta S_{ba}) + \beta \langle y_b H_d^y \rangle\right] \hat{\mathbf{x}} - \alpha\alpha^* \sin\delta S_{ba} \hat{\mathbf{x}}$
$\pi_y \rightarrow \pi_y^*$	$-\left[(\alpha\beta^* + \beta\alpha^*) \langle y_a \nabla_x H_a^y \rangle + \alpha\alpha^* \cos\delta \nabla_{ba}\right] \hat{\mathbf{x}}$	
$\pi_{yy} \rightarrow \pi_{yy}^*$	$-\left[(\epsilon\kappa^* + \kappa\epsilon^*) \langle y_a \nabla_x H_a^y \rangle - \epsilon\epsilon^* \cos\delta \nabla_{ba}\right] \hat{\mathbf{x}}$	$\epsilon\epsilon^* \sin\delta S_{ba} \hat{\mathbf{x}}$
$\pi_x \rightarrow \sigma^*$	$\cos(\frac{1}{2}\delta) (\gamma_x \langle z_a \nabla_z s_a + s_b \rangle + \gamma_x \nabla_{ba} - \gamma_h \langle z_a \nabla_z H_a^z + H_b^z \rangle) \hat{\mathbf{z}}$	$-\sin(\frac{1}{2}\delta) \left\{ \left[\frac{1}{2} R_{ab} \langle z_a \nabla_z s_a + s_b \rangle + \langle s_a x_b \rangle \right] \gamma_x - \left[1 + \frac{1}{2} R_{ab} \nabla_{ba} - S_{ba} \right] \gamma_x + \left[\frac{1}{2} R_{ab} \langle z_a \nabla_z H_a^z + H_b^z \rangle - \langle H_a^z x_a - x_b \rangle \right] \gamma_h \right\} \hat{\mathbf{z}}$

$\nabla_{ba} = \langle z_b | \nabla_x | z_a \rangle > 0, \quad \langle y_a | \nabla_x | H_a^y \rangle > 0, \quad R_{ab} = \text{C-C distance} \quad S_{ba} = \langle y_a | y_b \rangle > 0, \quad \langle y_a | H_a^y \rangle > 0.$

the rotational strength is given as

$$R_{0\xi} = (e^2 \hbar^2 / 4\pi m_e^2 c) \nu_{0\xi}^{-1} \sum_{j=1}^n \langle 0 | \nabla_j | \xi \rangle \cdot \langle 0 | \mathbf{r}_j \times \nabla_j | \xi \rangle, \tag{16}$$

where \mathbf{r}_j is the position vector of electron j . The molar rotation $[\phi]$ at frequency ν , exclusive of corrections for polarization of the medium, is given by

$$[\phi] = (96\pi N/hc) \sum_{\xi} \sum_{\zeta} R_{\xi\zeta} [\nu^2 / (\nu_{\xi}^2 - \nu^2)]; \tag{17}$$

N is Avogadro's number.

The matrix elements connecting one configuration with another can be reduced in the usual way to integrals involving only the orbitals associated with the transition in question. These are in turn readily reduced to the forms shown in Table III. Note that the entries omit the factor $2(N_i N_j)^{-1}$, where N_i and N_j are the normalizing factors as defined by Eqs. (1)-(12).

The oscillator strengths and rotational strengths of the B_x states as functions of δ are displayed in Figs. 7 and 8.

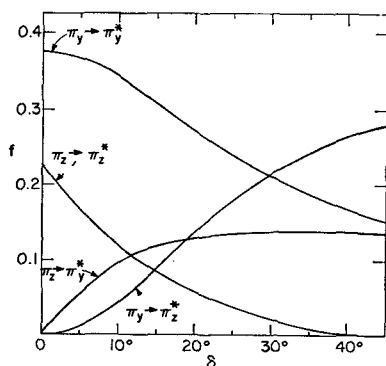


FIG. 7. Calculated oscillator strengths of the B_x transitions as functions of the twist angle δ .

The five transitions to states of B_x symmetry (B_{xy} or B_{xz} in the planar molecule) give rise to the matrix elements, oscillator strengths, and rotational strengths shown in Table IV. The table includes values for $\delta=0^\circ$ and $\delta=10^\circ$ for wavefunctions with configuration interaction.

The transition to the 3s Rydberg state, $\pi_x \rightarrow \sigma^*$, must also be considered, but its optical properties cannot be evaluated from the results of our SCF calculations as were those for the $A_g \rightarrow B_x$ transitions. We have estimated probable ranges for the magnitudes of oscillator and rotational strengths of this transition by evaluating these quantities with different sets of AO coefficients, as elaborated in Appendix B. These results are also included in Table IV.

The results of the calculation show that the only state with a large negative rotational strength ($\sim 10^{-38}$ cgs) and a low excitation energy is the 1B_x , $\pi_x \rightarrow \pi_y^*$. We recall that the area under the cd curve of Fig. 1 corresponds to a vacuum value of $+1.3 \times 10^{-38}$ cgs for

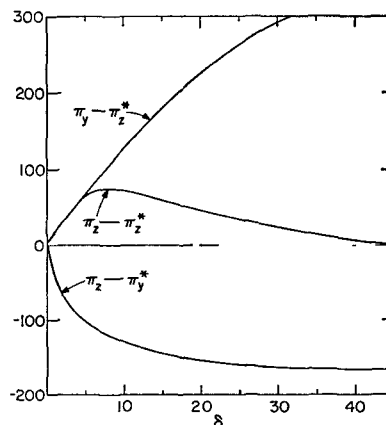


FIG. 8. Calculated rotational strengths of the B_x transitions as functions of the twist angle δ . Units are 10^{-40} cgs.

TABLE IV. Optical properties of the twisted double bond in *trans*-cyclo-octene after CI, for $\delta = +10^\circ$.

Transition (principal component)	Energy (eV)	Transition moments			
		Electric (10^8 cm^{-1})	Magnetic (Bohr magneton)	Oscillator strength f_i	Rotational strength (10^{-40} cgs)
$\pi_x \rightarrow \pi_x^*$	6.06	+0.3760 \hat{x}	+0.3390 \hat{x}	0.1186	+71.39
$\pi_x \rightarrow \pi_y^*$	6.62	+0.3545 \hat{x}	-0.7230 \hat{x}	0.0965	-131.39
$\pi_y \rightarrow \pi_x^*$	8.46	+0.0273 \hat{x}	+1.176 \hat{x}	0.0447	+128.81
$\pi_y \rightarrow \pi_y^*$	10.68	-0.8473 \hat{x}	+0.1186 \hat{x}	0.3412	-31.90
$\pi_x \rightarrow \sigma^*$ ^a	(5.95)	+0.1084 \hat{z}	+0.0048 \hat{z}	0.0100	+0.297
		+0.3577 \hat{z}	+0.0212 \hat{z}	0.109	+4.33
		Exptl			
$\pi_x \rightarrow \sigma^*$	5.95 ^b			0.005-0.032 ^c	
$\pi_x \rightarrow \pi_x^*$	~ 6 . ^b				

^a Upper line is based on the coefficients $\gamma_s = 0.721$, $\gamma_x = 0.421$, $\gamma_{Hx} = 0.550$; lower line is based on the coefficients $\gamma_s = \gamma_x = \gamma_{Hx} = (3)^{-1/2}$.

^b From Fig. 3.

^c See Ref. 4.

the rotational strength in the 6.5-eV region for the enantiomer with δ negative. The calculations with CI yield +0.3, +0.6, +0.9, +1.08, and $+1.26 \times 10^{-38}$ cgs for $\delta = -5^\circ, -10^\circ, -15^\circ, -20^\circ$, and -25° , respectively, as the sum of the rotational strengths of the two 1B_x transitions, the $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$, which contribute to the cd in the 6.5-eV region. It would be possible to find a value of δ for which the theoretical rotational strength would be equal to the observed value, but to attempt to infer quantitative geometric information from such a parameter-fitting procedure would be out of keeping with the approximate nature of the methods we have used.

IV. CONCLUSIONS

Comparison of the experimental results with the calculated energies, intensities, and rotational strengths compels us to draw the following conclusions:

(1) The only strong absorption in the region of interest is indeed due to the $\pi_x \rightarrow \pi_x^*$ excitation, as everyone more or less knows.

(2) The only transition which could conceivably account for the absolute sign and magnitude of the observed rotational strength of *trans*-cyclo-octene is the $\pi_x \rightarrow \pi_y^*$, ${}^1A_g \rightarrow {}^1B_{xg}$ transition. The rotational strength of the $\pi_y \rightarrow \pi_x^*$ process has a reasonable magnitude but the wrong sign; the same is true of the $\pi_x \rightarrow \pi_x^*$ transition. However, from conclusion (1) we know that the $\pi_x \rightarrow \pi_x^*$ transition is in the 5-7-eV region. Hence another state must be present, one which more than matches the rotational strength of the $\pi_x \rightarrow \pi_x^*$ transition. The only state in the energy region of interest which has this property is the ${}^1B_{xg}$ arising from the

$\pi_x \rightarrow \pi_y^*$ excitation. Therefore, two singlet-singlet transitions must be available in the 5-7-eV range, the $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$. With this conclusion, a new question arises. Could the $\pi_x \rightarrow \pi_y^*$ transition, a transition to a $3p\pi_y$ near-Rydberg orbital, be responsible for the " $\epsilon \sim 1000$ " absorption?

(3) The olefinic transition with $\epsilon \sim 1000$ cannot be due to the ${}^1A_g \rightarrow {}^1B_{xg}$, $\pi_x \rightarrow \pi_y^*$ process. Such an assignment would be incompatible with the observed intensities in flat alkylated olefins with centers of inversion, where such $g \rightarrow g$ processes are formally forbidden.

(4) The olefinic transition with $\epsilon \sim 1000$ cannot be due to the ${}^1A_g \rightarrow {}^1B_{xg}$, $\pi_y \rightarrow \pi_x^*$ process. The calculated energy value is too high, but much more compelling, in *trans*-cyclo-octene the signed magnitude of the rotational strength is such that, combined with the contribution from the $\pi_x \rightarrow \pi_x^*$ transition, it would yield a circular dichroism curve of the wrong sign.

(5) The only transition we have considered to which the " $\epsilon \sim 1000$ " absorption can be assigned is the ${}^1A_g \rightarrow {}^1B_{zu}$, $\pi_x \rightarrow 4a_g(3s\sigma^*)$ transition. This is the only transition with a calculated energy of reasonable value, an oscillator strength of the right magnitude and a rotational strength compatible with the observed cd curve. As can be seen from Table IV, the $\pi_x \rightarrow \sigma^*$ transition is weakly rotating. Therefore the assignment of the " $\epsilon \sim 1000$ " band as this transition cannot disturb the theoretical accounting of the observed cd curve already given in terms of the $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ transitions.

(6) Finally, as noted in Sec. II, the energy-loss spectra of Ross and Lassette²⁰ have indicated the presence of an electric quadrupole-allowed transition in ethylene at approximately the same energy at the

$\pi_z \rightarrow \pi_z^*$ transition. The ${}^1A_g \rightarrow {}^1B_{2g}$ transition cited in (2) above, to account for the rotational properties of *trans*-cyclo-octene correlates with just such an electric-quadrupole-allowed (and also magnetic-dipole-allowed) transition in planar ethylene.

We therefore conclude that at least three excited singlet states lie in the 5–7-eV region in simple olefins:

(a) The ${}^1B_{2u}$, $\pi_x \rightarrow \pi_z^*$, which is responsible for the strong absorption;

(b) The ${}^1B_{2g}$, $\pi_x \rightarrow \pi_y^*$, which accounts for the electric-quadrupole- and magnetic-dipole-allowed transition of planar systems, and which becomes that 1B_x state which dominates the optical activity of twisted double bonds; and

(c) The ${}^1B_{2u}$, $\pi_x \rightarrow \sigma_g^*$, which is responsible for the “ $\epsilon \sim 1000$ ” transition of substituted olefins. The Rydberg character of this ${}^1B_{2u}$ state has long been recognized. The ${}^1B_{2g}$ state is also Rydberg-like; indeed, in the united-atom limit, they are the s and p_y orbitals corresponding to the principal quantum number $n=3$.

We cannot rule out the possibility that other singlet states lie in the 5–7-eV region. The available experimental evidence does not require any states other than the three cited. Nevertheless, the same body of evidence could accommodate further states, provided they are optically and rotationally weak. One candidate would be the ${}^1B_{2g}$ state arising from the $\pi_x \rightarrow 3p\sigma_u^*$ transition, whose upper orbital becomes the $3p_x$ of the united atom. However, within the limited manifold of states for which we have performed energy calculations, there are no further low-lying states with these requisite optical properties.

It has come to our attention that Robin *et al.* have recently carried out a computation of the rotational strengths of various transitions in twisted ethylene. Their signs for the rotational strengths agree with ours in all cases except for the $\pi_x \rightarrow \pi_z^*$ transition. Insofar as we can tell, the discrepancy in the two calculations seems to lie with the sign of the contribution of the

$$h_{pq} = -\frac{1}{2}(W_p + W_q) S_{pq} - \sum_{\substack{\text{atoms } \alpha \text{ excluding} \\ \text{that of orbital } q}} \sum_{\text{orbitals } t \text{ on } \alpha} \langle \chi_p(1) \chi_t(2) | e^2/r_{12} | \chi_q(1) \chi_t(2) \rangle, \quad (\text{A1})$$

where W_p , W_q are valence-state ionization energies on atoms p and q , χ_p , χ_q , χ_t are atomic orbitals, and S_{pq} is the overlap of χ_p and χ_q . We have taken interaction

TABLE V. AO Coulomb integrals (in electron volts).

	z_a	y_a	H_a^y	z_b	y_b	H_b^y
z_a	10.53	9.29	8.58	7.42	7.00	6.25
y_a	9.29	10.53	8.82	7.00	7.42	6.32
H_a^y	8.58	8.82	10.27	6.25	6.32	5.30
z_b	7.42	7.00	6.25	10.53	9.29	8.58
y_b	7.00	7.42	6.32	9.29	10.53	8.82
H_b^y	6.25	6.32	5.30	8.58	8.82	10.27

hydrogen AO's, relative to that of the carbon orbitals, in the magnetic dipole transition moment. To check our results and to put them in a form most suitable for easy comparison with those of Robin *et al.*, we have now carried out an independent calculation based on SCF wavefunctions for the twisted geometry.

The $\pi_x \rightarrow \pi_z^*$ matrix element of the magnetic dipole is closer to zero in the SCF approximation than in either our starting basis or the final CI set; possibly, in some other intermediate approximation, its sign does change. However the supplementary SCF results in no way affect our conclusions and assignments.

ACKNOWLEDGMENTS

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APPENDIX A: THE SCF AND CI CALCULATIONS

The self-consistent-field calculations were carried out in an extended π -electron approximation, in which the π_y and π_z carbon orbitals y_a , y_b , z_a , and z_b and the hydrogenic π_y -like orbitals H_a^y and H_b^y were all included. The carbon orbitals were Slater functions with $z=3.18$; the C–C distance was taken as 1.353 Å. We let E_s^i represent the energy of the electrons occupying these orbitals in the i th excited singlet state, and E_T^i for the corresponding triplet. Hence, for ethylene, $E_s^1 - E_s^0 = 7.6$ eV, $E_s^1 - E_T^1 = 7.6 - 4.5 = 3.1$ eV. For *trans*-cyclo-octene, $E_s^1 - E_s^0 = 6.325$ eV, based on the wavelength of the absorption maximum.

The well-known semiempirical approximate expression for the elements of the SCF orbital matrix elements in the atomic-orbital representation is

elements h_{pq} between nonnearest-neighbor atoms as zero.

The carbon-carbon element h_{ab} between corresponding p orbitals on C_a and C_b may be evaluated semiempirically or empirically, by either of two pathways: from the relations

$$-2h_{ab} + K_{zz^*} = E_s^1 - E_s^0 \quad (\text{A2a})$$

and

$$-2h_{ab} - K_{zz^*} = E_T^1 - E_s^0 \quad (\text{A2b})$$

(where K_{zz^*} is the molecular-orbital exchange integral between π_z and π_z^*), which give $h_{ab} = 3.025$ eV for

TABLE VI. Core Hamiltonian matrix for ethylene (in electron volts).

	z_a	y_a	H_{a^2}	z_b	y_b	H_{b^2}
z_a	-49.760	0	0	-3.11	0	0
y_a	0	-50.070	-7.250	0	-3.11	0
H_{a^2}	0	-7.250	-48.865	0	0	0
z_b	-3.11	0	0	-49.760	0	0
y_b	0	-3.11	0	0	-50.070	-7.250
H_{b^2}	0	0	0	0	-7.250	-48.865

ethylene, or from the relation

$$\begin{aligned} h_{ab} &= -W_c S_{ab} \\ &= -3.11 \text{ eV.} \end{aligned} \quad (\text{A3})$$

[The Coulomb contributions to (A3) cancel in our approximation.] The values from (A2), which we used, and (A3) are essentially the same for our purposes.

TABLE VII. Core Hamiltonian matrix for hypothetical planar *trans*-cyclo-octene (electron volts).

z_a	y_a	H_{a^2}	z_b	y_b	H_{b^2}
-47.153	0	0	-2.387	0	0
0	-47.463	-5.566	0	-2.387	0
0	-5.566	-45.710	0	0	0
-2.387	0	0	-47.153	0	0
0	-2.387	0	0	-47.463	-5.566
0	0	0	0	-5.566	-45.710

We have obtained an effective W_c and h_{ab} for *trans*-cyclo-octene by requiring that the two relations again be consistent, and by assuming that K_{zz^*} is unchanged from ethylene. We obtain, from (A2a),

$$h_{ab}(\text{trans-cyclo-octene}) = -2.387 \text{ eV} \quad (\text{A4})$$

and, from (A3),

$$W_c(\text{trans-cyclo-octene}) = 8.613 \text{ eV.} \quad (\text{A5})$$

For ethylene, we take

$$W_H = 13.595 \text{ eV} \quad (\text{A6})$$

TABLE VIII. Eigenvalues and eigenvectors of the SCF matrix for planar ethylene.

	π_{yy}	π_y	π_z	π_z^*	π_y^*	π_{yy}^*
	Eigenvalues					
	-20.85	-17.87	-13.25	+0.427	+2.430	+6.26
	Eigenvectors					
z_a	0	0	0.707107	0.707107	0	0
y_a	0.51337	0.41528	0	0	0.48626	0.57231
H_{a^2}	0.48626	0.57231	0	0	-0.51337	-0.41528
z_b	0	0	0.707107	-0.707107	0	0
y_b	0.51337	-0.41528	0	0	0.48626	-0.57231
H_{b^2}	0.48626	-0.57231	0	0	-0.51337	0.41528

and

$$\begin{aligned} h_{CH} &= -\frac{1}{2}(W_C + W_H) S_{CH} \\ &= -7.249 \text{ eV.} \end{aligned} \quad (\text{A7})$$

To obtain the corresponding W_H and h_{CH} for *trans*-cyclo-octene, we have assumed that the ratio W_c/W_H is the same for *trans*-cyclo-octene as it is for ethylene, which gives a value $W_H(\text{trans-cyclo-octene}) = 10.44$, and, with the same overlap integrals as for ethylene, a value $h_{CH}(\text{trans-cyclo-octene}) = -5.57$ eV. Note that these h_{CH} elements refer to the $2p_y$ carbon orbitals, not to hybrid orbitals.

The Coulomb one-center integral

$$j_{pp} = \langle z_p(1) z_p(2) | e^2/r_{12} | z_p(1) z_p(2) \rangle$$

was taken as 10.53 eV, and the corresponding two-center Coulomb integrals

$$j_{pq} = \frac{1}{2}(j_{pp} + j_{qq}) + C_1 d + C_2 d^2, \quad (\text{A8})$$

where d is the distance between centers p and q , and C_1 and C_2 are taken to be the same as the coefficients of the linear and quadratic terms in the power series expansion in d for j_{pq} in the uniformly charged sphere approximation.²³ Numerically, $C_1 = 1.3596$, $C_2 = +0.05657$, with d in angstroms.

The remaining two-electron integrals were calculated as follows: The two-center integral

$$\begin{aligned} &\langle z_a(1) y_b(2) | e^2/r_{12} | y_a(1) z_b(2) \rangle \\ &= \frac{1}{2}(j_{z_a, z_b} - j_{z_a, y_b}) \\ &= \frac{1}{2}(7.42 - 7.00) = 0.21 \text{ eV.} \end{aligned} \quad (\text{A9})$$

TABLE IX. Eigenvalues and eigenvectors of the SCF matrix for hypothetical planar *trans*-cyclo-octene.

	π_{yy}	π_y	π_z	π_z^*	π_y^*	π_{yy}^*
	Eigenvalues					
	-15.91	-13.55	-9.91	+2.32	+4.00	+6.99
	Eigenvectors					
z_a	0	0	0.707107	0.707107	0	0
y_a	0.51360	0.41870	0	0	0.48602	0.56981
H_a^y	0.48602	0.56981	0	0	-0.51360	-0.41870
z_b	0	0	0.707107	-0.707107	0	0
y_b	0.51360	-0.41870	0	0	0.48602	-0.56981
H_b^y	0.48602	-0.56981	0	0	-0.51360	0.41870

The corresponding two-center integral can be evaluated in terms of the Slater-Condon parameter G_2 for carbon:

$$\langle z_a(1)y_a(2) | e^2/r_{12} | y_a(1)z_a(2) \rangle = 3b_2 = 0.619 \text{ eV.} \quad (A10)$$

The one-center Coulomb integral

$$j_{z_a, y_a} = \langle z_a(1)y_a(2) | e^2/r_{12} | z_a(1)y_a(2) \rangle = j_{z_a, z_a} - 2(0.619) = 9.29 \text{ eV.} \quad (A11)$$

Table V contains the Coulomb integrals in the AO basis. The core matrices for ethylene and planar *trans*-cyclo-octene are given in Tables VI and VII, and the corresponding eigenvalues and eigenvectors are given in Tables VIII and IX. The SCF excitation energies were given earlier in Table II.

The matrices of the core Hamiltonian and of e^2/r_{12} are changed when the double bond is twisted. The overlap matrix \mathbf{S} that transforms the core Hamiltonians of (A2) and (A3) is given as Table X. The Coulomb integrals in twisted species are given by

$$j_{z_a, z_b}^t = j_{z_a, z_b} \cos^2\delta + j_{z_a, y_b} \sin^2\delta$$

TABLE X. Overlap matrix for the core Hamiltonian of the twisted olefin.

z_a^t	y_a^t	$H_a^y^t$	z_b	y_b	H_b^y
1.0	0	0	$\cos\delta S_{ab}$	$-\sin\delta S_{ab}$	0
0	1.0	S_{CH}	$\sin\delta S_{ab}$	$\cos\delta S_{ab}$	0
0	S_{CH}	1.0	0	0	0
$\cos\delta S_{ab}$	$\sin\delta S_{ab}$	0	1.0	0	0
$-\sin\delta S_{ab}$	$\cos\delta S_{ab}$	0	0	1.0	S_{CH}
0	0	0	0	S_{CH}	1.0

Note: $S_{ab} = \langle z_a | z_b \rangle$ and $S_{CH} = \langle y_a | H_a^y \rangle$.

and the nonclassical integral

$$\langle z_a^t(1)y_b(2) | e^2/r_{12} | y_a^t(1)z_b(2) \rangle = (\cos^2\delta - \sin^2\delta) \langle z_a(1)y_b(2) | e^2/r_{12} | y_a(1)z_b(2) \rangle. \quad (A12)$$

The introduction of a twist lowers the local approximate symmetry of the double bond from D_{2h} to D_2 . Without the center of inversion, the irreducible representations B_{2g} and B_{2u} become B_z . Thus all these excited states of the $\pi \rightarrow \pi^*$ type may mix together via configuration interaction in a twisted olefin: $\pi_z \rightarrow \pi_z^*$, $\pi_x \rightarrow \pi_y^*$, $\pi_y \rightarrow \pi_x^*$, $\pi_y \rightarrow \pi_y^*$, and $\pi_{yy} \rightarrow \pi_{yy}^*$. The second and third of these are B_{2g} states in the planar chromophore, while the rest are B_{2u} and are accessible by electric dipole-allowed transitions. The off-diagonal matrix elements of the molecular Hamiltonian are all reducible to the same integrals that enter into the SCF calculation. Reference 17 contains full tables of eigenvectors, eigenvalues, transition moments of ∇ and $\mathbf{r} \times \nabla$, oscillator strengths, and rotational strengths for the B_z states before and after CI, for 5° intervals from 0° through 90° .

APPENDIX B: OSCILLATOR AND ROTATIONAL STRENGTH OF THE ${}^1A_g \rightarrow {}^1B_z(\pi_s \rightarrow \sigma^*)$ TRANSITION

The final line of entries in Table III, the oscillator and rotational strengths for the $3s$ Rydberg transition, suggest that these quantities depend on more parameters than do the $\pi \rightarrow \pi^*$ transitions. Specifically, we have

$$\langle \pi_z | \nabla | \sigma^* \rangle = \hat{z} \cos(\frac{1}{2}\delta) \times [-0.629\gamma_s + 0.625\gamma_h + 0.443\gamma_x] 10^8 \text{ cm}^{-1} \quad (A13)$$

and

$$\langle \pi_z | \mathbf{r} \times \nabla | \sigma^* \rangle = -\hat{z} \sin(\frac{1}{2}\delta) \times [-0.036\gamma_s + 0.760\gamma_h - 1.023\gamma_x] \text{ Bohr magnetons.} \quad (A14)$$

The value of the $\langle z_a | \nabla | S_a \rangle$ contribution to the matrix element of ∇ is based on the experimental value of 0.09 for the carbon $2s \rightarrow 2p$ oscillator strength.

Fortunately we do not need to find accurate values for (A13) or (A14), provided one or both are small. We have evaluated these with two sets of coefficients γ_s , γ_{Hx} and γ_x ; one set simply takes

$$\gamma_s = \gamma_x = \gamma_{Hx} = (3)^{-1/2}.$$

The second set was that of the SCF calculation of

Palke and Lipscomb,³² namely

$$\gamma_s = 0.721, \quad \gamma_x = 0.421, \quad \gamma_{Hx} = 0.550.$$

A calculation was also performed for the unrealistic assumption that $\langle z_a | \nabla | S_a \rangle = 0$, but this led to far too large oscillator strengths for the $\pi_z \rightarrow \sigma^*$ transition (> 0.1). Even with this assumption, the rotational strength of the $\pi_z \rightarrow \sigma^*$ remained of order $1-4 \times 10^{-40}$ cgs, far too small to contribute noticeably to the cd curve.

³² W. E. Palke and W. Lipscomb, *J. Am. Chem. Soc.* **88**, 2384 (1966).

Some Aspects of Electron Correlation in Open-Shell States. 2^1P and 2^3P Helium*

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Accurate wavefunctions for the 2^3P and 2^1P states of helium have been analyzed into pair, polarization, and semi-internal correlation effects. The dynamical, transferable pair-correlation energies account for approximately 90% of the total correlation energies. The special open-shell effects, symmetry polarizations, and semi-internal correlation, account for half the remaining correlation energy. It is shown computationally that the polarization and semi-internal correlation energies can be computed separately from the pair energies to about 96% accuracy.

I. INTRODUCTION

In closed-shell states of atoms and molecules the main electron correlation effect is pair correlation.¹⁻⁶ Open-shell states are characterized by three additional physically important correlation effects⁷⁻⁹: internal correlation, in which no electrons leave the Hartree-Fock sea; semi-internal correlation, in which one electron leaves the Hartree-Fock sea and a second moves from an occupied to a vacant spin orbital in the sea; and polarizations, which are one-electron excitations out of the sea which tend to make the spatial parts of doubly occupied orbitals different or which tend to break the spatial symmetry of an orbital. Pair correlations, to a high degree of accuracy, can be computed independently

of one another,^{1-6, 10-15} and dynamical pair-correlation energies are relatively invariant from atom to atom.¹⁻⁶ It has been suggested^{7-9, 16} that the specifically open-shell correlation effects can be computed independently from the pair-correlation effects, but there are not yet extensive numerical results which gauge the accuracy lost by calculating the open-shell effects separately. Moreover, the open-shell correlation effects are strongly subject to "exclusion effects" which change from atom to atom.

Our purpose here is to analyze an accurate wavefunction for two simple atomic states, 2^1P and 2^3P , which comprise the $1s2p$ configuration of helium, into the various physically meaningful correlation effects as formulated in Refs. 7-9. The relative magnitudes of the various effects are compared, and the loss of accuracy of computing some of the effects "separately" is assessed. This study is the first analysis of an accurate

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¹⁰ References 11-15 are given as examples and are not meant to exhaust the many recent accurate calculations which have grown out of the theory developed in Refs. 1 and 2.

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