charge separations which occur in comparison to the parent molecules **11** and **12** (Figure 1) seem to facilitate the formation of an intermediate. This finding makes the experimental distinction between a one-step or a multistep reaction difficult. Only a rather small rate change is expected if the solvent polarity is altered and this even if the reaction takes place by way of an intermediate. The observation of a rate factor of 36 for cyclohexane and acetonitrile as solvents in the concerted reaction and one of 560 for the multistep addition of dimethylketene to pyrrolidinoisobutene confirms the assumption.[16] The superposition of the two rate factors yields a total solvent dependence of 79. This is smaller than the value of 160 for the cycloaddition of diphenylketene and butyl vinyl ether which presumably add exclusively in a concerted fashion.

SCF perturbation theory and the variation perturbation treatment seem to be suited to interpret problems in chemical reactivity. The semiempirical schemes show distinct differences. The CNDO/2 approximation underestimates the repulsive forces between molecules and therefore is unable to account for steric effects. The MINDO/11 and the MINDO/2 proce-

dures compensate this disadvantage by their treatment of nuclear repulsions. MINDO integrals are smaller (about 20%) than the same CNDO/2 integrals over Slater orbitals.[19,20] An analysis of term 2 in eq 1 shows that the difference between electron repulsion and exact point charge repulsion is greater for MINDO/11 and MINDO/2 than for CNDO/2. Even though this difference is multiplied by an exponential, the magnitude of the MINDO α parameters ensures higher repulsive interactions. As far as the second-order energy is concerned, all procedures lead to the same qualitative interpretation. The variation perturbation treatment is attractive because it enables an interpretation of the results analogous to Hückel perturbation theory. The different programs written for an IBM 360/50 computer will be available from QCPE.[31]

Excited-State Geometries of the Singly Substituted Methylpropenals. III.[1a] Geometry, Substituent Interaction, Fermi Correlation, and Spin–Orbit Coupling in $T_1(n,\pi^*)$

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Abstract: The nature of the first excited n,π* triplet states of acrolein, crotonaldehyde, methacrolein, and methyl vinyl ketone was investigated using low and medium resolution vibrational electronic spectroscopy, and molecular orbital and spin–orbit coupling calculations. The spectroscopic analysis and singlet–triplet splitting calculations indicate that the n,π* triplet is planar and is hence of n,π*(π) character. This observation is discussed with reference to recent *an initio* calculations which indicate that acrolein's n,π* triplet relaxes to a nonplanar geometry of y,π* orbital nature. The prominent Fermi correlative mechanism in the n,π* triplet state involves delocalization of the spin-unpaired electrons rather than charge separation, indicating that the n,π* triplet should be less photoreductive than the corresponding n,π* singlet. Oscillator strengths for the $S_0 \rightarrow T_1$ transition in the three aldehydes were experimentally observed and compared to values calculated using spin–orbit coupling theory. These calculations, based on the McClure central field approach utilizing a one-electron Hamiltonian, successfully predict the relative ordering of the oscillator strengths. The principal perturbing singlet is found to be $S_2(\pi,\pi^*)$, but mixing of the ground-state singlet into $T_1(n,\pi^*)$ is also found to be significant because of the relatively large ground-state dipole moments observed for acrolein and its singly substituted methyl derivatives.

$\mathbf{I}$n the first two parts of this three-part investigation,[2,3] the vibrational electronic spectrum of $S_1(n,\pi^*(\pi))$ was analyzed and used in a discussion of substituent interaction in the first excited singet state. The methyl group was found to perturb the energy of the ground-state nonbonding electrons on oxygen and the excited state π^* orbital *via* similar mechanisms involving

"hyperconjugative" charge redistribution. The amount of methyl group electron donation was found to be of lesser importance than the position of the localized electron density within the molecular orbital.[3] The present report investigates substituent interaction in the first excited n,π* triplet manifold to find what effect methyl group position has on the energy and geometry of T_1 and the intensity of the spin-forbidden $S_0 \rightarrow T_1(n,\pi^*)$ transition.

A summary of important experimental and calculated parameters for the triplet states of acrolein and its singly substituted methyl derivatives is given in Table I. The observed singlet–triplet splittings (~ 1600

(1) (a) The Nature of the n → π* Transition. III. (Abstracted from a portion of the Ph.D. Thesis of R. R. B., Wesleyan University, 1972.) For parts I and II, see ref 2 and 3, respectively. (b) Deceased Aug 16, 1971.
(2) R. R. Birge, W. C. Pringle, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **93**, 6715 (1971).
(3) R. R. Birge and P. A. Leermakers, *ibid.*, **93**, 6726 (1971).

Table I. Selected Experimental and Calculated Parameters for the $S_0 \rightarrow T_1(n,\pi^*)$ Transition in Acrolein and the Singly Substituted Methylpropenals

Assignment	Acrolein[a]	Crotonaldehyde	Methacrolein	Methyl vinyl ketone
$0,0(S_0 \rightarrow S_1{}^{n,\pi*})$	25859 cm⁻¹	26497 cm⁻¹	26492 cm⁻¹	26123 cm⁻¹
	73.93 kcal	75.76 kcal	75.74 kcal	74.69 kcal
$0,0(S_0 \rightarrow T_1{}^{n,\pi*})$	24245 cm⁻¹	24925 cm⁻¹	24820 cm⁻¹	?
	69.32 kcal	71.26 kcal	70.96 kcal	?
S_1-T_1	1614 cm⁻¹	1572 cm⁻¹	1672 cm⁻¹	?
S_1-T_1 (calcd)	1623	1537	1663	1522 cm⁻¹
$f(S_0 \rightarrow S_1)$	3.8×10^{-4}	4.2×10^{-4}	4.2×10^{-4}	3.4×10^{-4}
$f(S_0 \rightarrow T_1)$	6.3×10^{-6}	10.0×10^{-6}	2.7×10^{-6}	?
$f(S_0 \rightarrow T_1)$ (calcd)	4.2×10^{-7}	6.1×10^{-7}	3.0×10^{-7}	4.2×10^{-7}

[a] The value shown for the $S_0 \rightarrow S_1(n,\pi^*)$ 0,0 band energy differs slightly from that quoted in part I (26,861 cm⁻¹) which was taken from J. C. D. Brand and D. G. Williamson, *Discuss. Faraday Soc.*, **35**, 183 (1963).

cm⁻¹) and $S_0 \rightarrow T_1$ oscillator strengths ($\sim 10^{-6}$–10^{-5}) are characteristic of n,π^* systems.

Experimental and Calculation Section

Acrolein (propenal), crotonaldehyde (*trans*-2-butenal), methacrolein (2-methylpropenal), and methyl vinyl ketone (3-buten-2-one) were purified as in part I.[2]

Vibrational electronic spectra were recorded under low resolution (spectral band width = 0.3–1.0 Å) using an electronically optimized Cary 14[2] and photographed under medium resolution (spectral band width = 0.11–0.13 Å) in the first order of a Bausch & Lomb Model 10, 1.5-m Stigmatic Grating spectrograph fitted with a precision concave grating providing dispersion of 16 Å/mm in the first order. The photographs were translated using a Joyce-Loebl double-beam recording microdensitometer.

SCF-molecular orbital calculations were based on the CNDO and INDO approximations. The SCF-MO-CNDO calculations utilized Pople-Santry-Segal (PSS) CNDO/II procedures,[4-6] but differed in parametrization in that the valence state ionization potentials and electron affinities used in calculating the $F_{\mu\mu}$ ($= -\frac{1}{2}\cdot(I_\mu + A_\mu) + \ldots$) matrix elements were derived from weighted-average values of the valence-state ionization potential and electron affinity data of Hinze and Jaffe.[7] The modified matrix elements are given in Table II. These parameters improved the calculated

Table II. Matrix Elements Used in SCF-MO-CNDO Calculations

	H	C	O
$\frac{1}{2}(I_s + A_s)$, eV	7.175	14.960	27.255
$\frac{1}{2}(I_p + A_p)$, eV		5.805	10.965

charge distributions and dipole moments for the molecules investigated in this report. As one example, our SCF-MO-CNDO calculation on the ground state of acrolein is compared in Table III with one based on PSS CNDO/II parameters[6] and two more accurate literature calculations.

Comparisons of SCF-MO-CNDO charge distributions, bond orders (multiplied by overlap), and dipole moments for S_0, $S_1(n,\pi^*)$, and $T_1(n,\pi^*)$ of the molecules investigated in this article are collected in Figure 1 since these values will be referenced on numerous occasions throughout this article. Ground states were generated using CNDO/II procedures,[4-6] first excited singlet states were generated using a modified version of Kroto and Santry's CNDO/II approximate open shell theory,[8,9] and first excited triplet states were generated using CNDO/II (unrestricted) open shell theory.[6,10]

(4) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

(5) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965).

(6) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1965).

(7) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

(8) H. W. Kroto and D. P. Santry, *J. Chem. Phys.*, **47**, 2736 (1967).

(9) A discussion and listing of the CNDO-AFAOS (averaged field approximate open shell) program used in the present investigation may be found in the Ph.D. Thesis of R. R. B., Wesleyan University, 1972. A discussion of AFAOS theory will be submitted for publication in the near future.

(10) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

Table III. Calculated Atomic Charges and Dipole Moments for Acrolein Ground State

Atom[a]	PSS[b]	TII[c]	CNDO-CI[d]	PPP[e]
O_1	−0.22	−0.31	−0.35	−0.49
C_2	+0.24	+0.30	+0.31	+0.45
C_3	−0.04	−0.06	−0.03	−0.10
C_4	0.00	−0.01	−0.04	−0.01
H_5	−0.04	−0.03	0.00	−0.01
H_6	+0.03	+0.05	+0.04	+0.07
H_7	+0.02	+0.04	+0.03	+0.02
H_8	+0.02	+0.03	+0.04	+0.06
Dipole moment[f] =	2.63 D	3.38 D	3.46 D	3.60 D

[a] The numbering system is shown in Figure 1. [b] SCF-MO-CNDO/II using Pople-Santry-Segal parametrization. [c] SCF-MO-CNDO/II using the matrix elements of Table II. [d] SCF-MO-CNDO-CI using the parametrization of Del Bene and Jaffe and variable resonance integrals: B. Tinland, *Mol. Phys.*, **16**, 413 (1969). [e] SCF-MO-PPP-CI, extended Pariser-Parr-Pople with configuration interaction; M. Jungen and H. Labhart, *Theor. Chim. Acta*, **9**, 345 (1968). [f] Observed dipole moment = 3.11 D: R. Wagner, *et al.*, *J. Chem. Phys.*, **26**, 634 (1957).

All of these calculations utilized the revised matrix elements listed in Table II. The wave functions for all three states were optimized for the r_s ground-state nuclear configuration as determined by microwave spectroscopy.[11] Therefore, the differences in S_0, S_1, and T_1 electron densities and bond orders are a function solely of the change in the wave function due to electronic excitation and the multiplicity of the resulting excited state.

Results and Discussion

(A) Vibrational Electronic Analysis of $T_1(n,\pi^*)$. Because of the characteristically small singlet–triplet splitting associated with n,π^* systems coupled with the presence of hot bands to the red of the $S_0 \rightarrow S_1$ system origin, the vibrational structure of the $S_0 \rightarrow T_1$ transition could be observed only for a 600–900-cm⁻¹ region. To further complicate vibrational analysis, many of the stronger bands in the $S_0 \rightarrow T_1$ region of acrolein and crotonaldehyde are associated with the $S_0{}^r \rightarrow S_1{}^r$ transition (a superscript "r" indicates rotamer) of the s-cis rotamer masking many triplet state vibronics. Methacrolein was the only compound which had an insignificant s-cis population at room temperature, and consequently a more detailed analysis was possible for this compound. Methyl vinyl ketone's $S_0 \rightarrow T_1$ vibrational spectrum lacked observable vibrational structure at the resolution used in the present investigation.

(11) Acrolein, E. A. Cherniak and C. C. Costain, *ibid.*, **45**, 104 (1966); crotonaldehyde, M. Suzuki and K. Kozima, *Bull. Chem. Soc. Jap.*, **42**, 2183 (1969); methacrolein, M. Suzuki and K. Kozima, *J. Mol. Spectrosc.*, **38**, 314 (1971); methyl vinyl ketone, see Table XIII.

Table IV. Principal Assignments in the 4125-Å System of Acrolein[a]

ν_{vac} (cm⁻¹)	ΔT_1 s-trans	ΔS_1 s-cis	ΔS_1 s-trans	Int[b]	Tentative assignment[c]
23,680	**−565**				**−565** (∠CCO in-plane bend)
23,921	**−324**				**−324** (∠CCC in-plane bend)
24,087	**−158**				**−158** (skeletal torsion)
24,209	**−36**				**2(−158) + 280 = −36**
24,245	**0**		(−1614)	10	**Origin (S₀ → T₁(n,π*))**
24,313		−310		4	−310 (∠CCC in-plane bend)
24,623		0	(−1236)	39	Origin (S₀ʳ → S₁ʳ(n,π*))
24,686	**441**			4	**2(495) − 565 = 425**
24,740	**495**			8	**495** (∠CCO in-plane bend)
24,838		215		18	215 (∠CCC in-plane bend)
24,963	**718**			4	**718** (fundamental?)
24,987		364		6	?
25,037		414		5	414 (∠CCO in-plane bend)
25,137	**892**			1	**4(495) − 2(565) = 870**
25,227			−632	4	4(−158) = −632
25,294			−565	9	−565 (∠CCO in-plane bend)
25,400			−459	8	3(−158) = −474
25,542			−317	43	2(−158) = −316
25,640			−219	33	3(−158) + 250 = −224
25,701			−158	29	−158 (skeletal torsion)
25,726			−133	59	4(−158) + 2(250) = −132
25,744			−115	64	7 (−158) + 4(250) = −106
25,859			0	588	Origin (S₀ → S₁(n,π*))

[a] Bands associated with the S₀ → T₁(n,π*) transition are designated by boldface type. [b] Intensity of discrete bands above continuum; vapor at 23°. [c] A superscript "r" indicates s-cis rotamer.
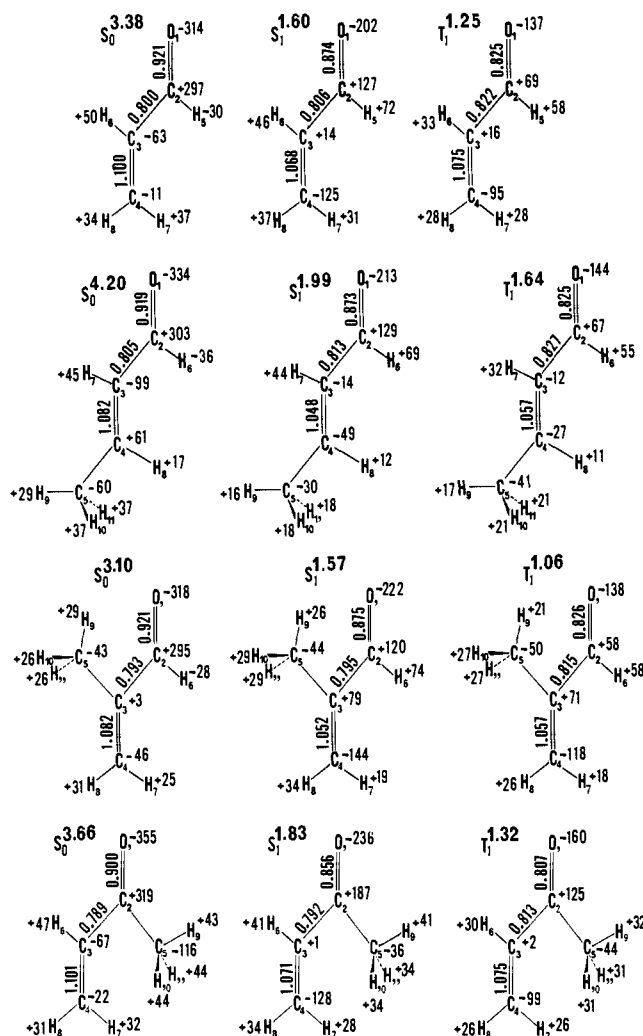

Figure 1. Charge distributions (electron units × 10³), dipole moments (shown in Debye units as superscripts to the state symbols), and bond populations (defined as the product of the bond orders and the overlap) for the S₀, S₁(n, π*), and T₁(n,π*) states of acrolein and the singly substituted methylpropenals.
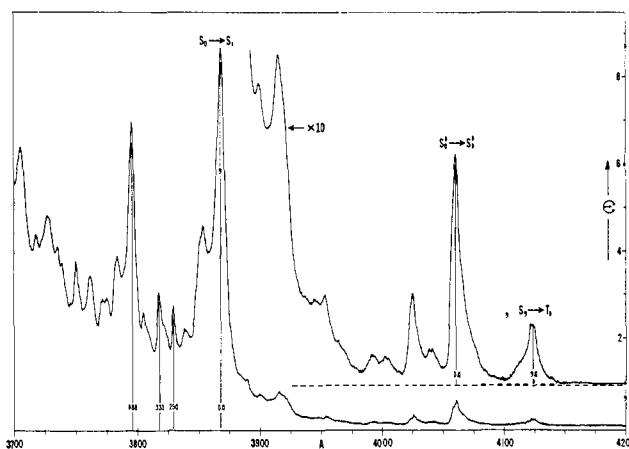

Figure 2. Low resolution S₀ → T₁(n,π*) vibrational electronic spectrum of acrolein vapor.

(A-1) Acrolein. The S₀ → T₁ absorption spectrum of acrolein (shown in Figure 2) has been briefly investigated by Hollas,[12a] Brand and Williamson,[12b] and Alves and coworkers,[13] but these authors differed greatly on assignments. Alves and coworkers have provided convincing evidence based on thermal population effects and band contour analysis that many of the bands in the 3950–4200-Å region are actually associated with the S₀ʳ → S₁ʳ transition of the s-cis (or possibly gauche) rotamer.[13] Our vibrational analysis of acrolein, shown in Table IV, agrees with the assignments of Alves, *et al.*, although we have identified a few additional bands believed to be associated with the S₀ → T₁ transition.

While the excited triplet state skeletal torsion fundamental is apparently obscured by the rotational structure of the S₀ʳ → S₁ʳ(n, π*) system origin, this vibra-

(12) (a) J. M. Hollas, *Spectrochim. Acta*, 17, 1425 (1963); (b) J. C. Brand and D. G. Williamson, *Discuss. Faraday Soc.*, 35, 184 (1963).

(13) A. C. P. Alves, J. Christoffersen, and J. M. Hollas, *Mol. Phys.*, 20, 625 (1970); 21, 384 (1971).

Table V. Principal Assignments in the 4012-Å System of Crotonaldehyde[a]

ν_{vac} (cm⁻¹)	ΔT_1 s-trans	ΔS_1 s-cis	ΔS_1 s-trans	Int[b]	Tentative assignment[c]
24,521	**−404**				**2(−206) = −412**
24,573	**−352**				**3(−206) + 270 = 348**
24,719	**−206**				**−206 (skeletal torsion)**
24,820	**−105**				**−206 + 2(−140) + 2(185) = −116**
24,875	**−50**				**3(−140) + 2(185) = −50**
24,925	**0**		(−1572)	**10**	**Origin (S₀ → T₁(n,π*))**
24,993	**68**			**8**	**270 − 206 = 64**
25,075		−50		40	2(−25) = −50
25,100		−25		57	−25
25,125		0	(−1372)	84	Origin (S₀ʳ → S₁ʳ(n,π*))
25,150		25		77	+25
25,252	**327**			**8**	**2(270) − 206 = 334**
25,290		165		20	185 − 25 = 160
25,310		185		33	185 (methyl torsion?)
25,329		204		23	185 + 25 = 210
25,387		262		13	285 − 25 = 260
25,410		285		33	285 (skeletal torsion?)
25,455		330		10	285 + 185 − 140 = 330?
25,519		394		10	2(185) + 25 = 395
25,595		470		23	285 + 185 = 470
25,859			−638	25	3(−206) = −618
25,980			−517	25	6(−206) + 3(243) = −507
26,082			−415	29	2(−206) = −412
26,202			−295	32	5(−206) + 3(243) = −301
26,291			−206	84	−206 (skeletal torsion)
26,406			−91	100	4(−206) + 3(243) = −95, 2(−140) + 187 = −93
26,497			0	420	Origin (S₀ → S₁(n,π*))

[a] Bands associated with the S₀ → T₁(n,π*) transition are designated by boldface type. [b] Intensity of discrete bands above continuum; vapor at ∼75°. [c] A superscript "r" indicates s-cis rotamer. Combination bands associated with the S₀ʳ → S₁ʳ(n,π*) transition are designated by italics.

tion does appear to interact with the ground-state skeletal torsion at 158 cm⁻¹ to form a weak combination hot band at −36 cm⁻¹ (see Table IV). Assuming this band to be associated with the (2 → 1) transition, and ignoring anharmonic effects, the value for the excited state skeletal torsion can be set at approximately 280 cm⁻¹. Thus, the skeletal torsion increases 30 cm⁻¹ in T₁ over that observed for S₁ (250 cm⁻¹). The analyses of crotonaldehyde and methacrolein support this assignment (see sections A-2 and A-3).

The fundamental at 495 cm⁻¹ can be assigned to the ∠CCO in-plane bending on the basis of intensity (the ∠CCO in-plane bending fundamental for the S₀ → S₁ transition exhibits an intensity of 7.6 relative to the system origin intensity of 10.0), and its combination with the ground-state vibration to form the combination band at 441 cm⁻¹. The high similarity between the ∠CCO in-plane bending vibrations in S₁ and T₁ indicates that the ∠CCO angles and force constants are similar for both states and suggests that the n,π* singlet and triplet have similar, planar geometries. The absence of out-of-plane bending modes supports triplet planarity.

(A-2) Crotonaldehyde. The vibrational analysis of the triplet manifold of crotonaldehyde was complicated by two problems. The presence of relatively strong S₀ʳ → S₁ʳ(n,π*) absorption bands obscured most of the S₀ → T₁ region, and the poorly defined vibrational band structure often limited band center assignment accuracy to ±10 cm⁻¹.

The origin of the S₀ʳ → S₁ʳ(n,π*) transition is found at 25,125 cm⁻¹ indicating a similar shift in S₀ → S₁ transition energy between s-trans and s-cis rotamers (1372 cm⁻¹, see Table V) as was observed for the two

acrolein rotamers (1236 cm⁻¹, see Table IV). Two possible fundamentals associated with S₁ʳ(n,π*) are found at 185 and 285 cm⁻¹. These bands are tentatively assigned to the excited state methyl and skeletal torsions, respectively. While the skeletal torsion assignment appears reasonable, the observation that the methyl torsion has not shifted in relation to the s-trans rotamer must be viewed with suspicion since the inertial axes are considerably different for the two rotamers. We therefore emphasize the tentative nature of these assignments.

The system origin of the S₀ → T₁ transition is assigned to the medium intensity band at 24,925 cm⁻¹ on the basis of hot band analysis, in particular, the presence of the (1 → 0) and (2 → 0) transitions in the skeletal torsion. Consequently, the singlet–triplet splitting is similar for both acrolein (1614 cm⁻¹) and crotonaldehyde (1572 cm⁻¹).

The hot bands at −50 and −105 cm⁻¹ are assigned to methyl torsion combinations assuming an excited state value of 185 cm⁻¹. This assignment is within experimental error of the methyl torsion in S₁(n,π*) of 187 cm⁻¹. Consequently, the methyl torsion is virtually unaffected by the change in multiplicity of the n,π* system.

The bands at −352, +68, and +327 cm⁻¹ cannot be related to methyl torsion combinations and presumably are associated with skeletal torsion interactions. The intensity of the 68-cm⁻¹ band suggests a (1 → 1) or (2 → 2) combination, and given the ground-state torsional value of 206 cm⁻¹, the triplet state fundamental can be tentatively set at either ∼270 cm⁻¹ (assuming 1 → 1) or ∼240 cm⁻¹ (assuming 2 → 2). The latter assignment would at first appear the

Table VI. Principal Assignments in the 4030-Å System of Methacrolein

ν_{vac} (cm^{-1})	ΔT_1 s-trans	ΔS_1 s-trans	Int^a	Tentative assignment
24,591	−229		5	$3(-134) + 173 = -229$
(24,624)	(−196)		Var	Impurity?^{b}
24,644	−176		6	$4(-163) + 2(241) = -170$
24,682	−138		2	-134 (methyl torsion)^c
24,764	−56		6	$3(-134) + 2(173) = -56$
24,820	0	(−1672)	10	Origin ($S_0 \rightarrow T_1(n,\pi^*)$)
24,842	22		9	$241 - 163 + 2(173) + 3(134) = 22$
24,900	80		4	$241 - 163 = 78$
24,937	117		3	$3(173) + 3(-134) = 117$
24,993	173		3	173 (methyl torsion)
25,061	241		3	241 (skeletal torsion)
25,125	305		3	$2(241) - 163 = 319$
25,211	391		3	$3(241) + 2(-163) = 397$
25,264	444		5	$491 + 3(-134) + 2(173) = 435$
25,295	475		6	$2(241) = 482$
25,311	491		7	491 ($\angle$CCO in-plane bending?)
25,390	570		3	$3(241) - 163 = 560$
25,542	722		4	$3(241) = 723$
25,859		−633	150	-633 ($\angle$CCO in-plane bending)
25,966		−526	50	$4(-134) = -536$
26,047		−445	50	$7(-163) + 3(233) = -442$
26,119		−373	50	$8(-163) + 4(233) = -372$
26,224		−268	100	$2(-134) = -268$
26,287		−205	150	$7(-134) + 4(183) = -206$ $7(-163) + 4(233) = -209$
26,372		−120	500	$5(-134) + 3(183) = -121,$ $5(-163) + 3(233) = -116$
26,405		−87	500	$2(-134) + 183 = -85$
26,443		−49	900	$6(-163) + 4(233) = -46$
26,492		0	1500	Origin ($S_0 \rightarrow S_1(n,\pi^*)$)

^{a} Intensity of discrete bands above continuum; vapor at ~75°. ^{b} The 24,624-cm^{-1} band exhibited a small variation in relative intensity depending upon the method of purification. ^{c} The value of -134 cm^{-1} has been chosen as more precise based on analysis of combination bands.

more reasonable since the skeletal torsion in S_1 is found at 243 cm^{-1}.[2] This assignment, however, cannot be reconciled with the other combination bands, whereas the choice of the 270-cm^{-1} assignment provides a means of accounting for all three combination bands (see Table V). Since the latter assignment also correlates with our previous analysis of acrolein, which indicated an increase of 30 cm^{-1} in skeletal torsion in T_1 over S_1, the choice of 270 cm^{-1} for the triplet state skeletal torsion appears to be strongly supported by the available evidence.

(A-3) Methacrolein. The $S_0 \rightarrow T_1(n,\pi^*)$ transition in methacrolein is analyzed in Table VI. Unlike acrolein and crotonaldehyde, vibronics associated with an $S_0^r \rightarrow S_1^r$ (n,π^*) transition were not found, probably because the energy difference between the two ground-state rotamers of methacrolein is sufficient to preclude significant population of the higher energy s-cis rotamer. The origin of the $S_0 \rightarrow T_1(n,\pi^*)$ transition is found at 24,820 cm^{-1} yielding a large singlet–triplet splitting of 1672 cm^{-1}.

Three triplet state fundamentals were observed at 173, 241, and 491 cm^{-1}. The 173 cm^{-1} fundamental is assigned to the methyl torsion because of its similarity in wave number and intensity to the 183-cm^{-1} methyl torsion fundamental in $S_1(n,\pi^*)$. In part I,[2] we were unable to assign a value to the ground-state methyl torsion, but analysis of the band system of the singlet–triplet transition indicates that the ground-state methyl torsion is at 134 cm^{-1}. A slight decrease in methyl torsion is registered for T_1 vs. S_1, but the change is small, indicating a similar geoelectronic environment in both excited states.

The 241-cm^{-1} band is assigned to the skeletal torsion. This fundamental interacts strongly with the ground-state skeletal torsion at 163 cm^{-1} to produce numerous combination bands (see Table VI) and is observed in its first and second overtones, the ($0 \rightarrow 2$) band exhibiting the highest intensity. This observation suggests that the C_s symmetry of the molecule is conserved in the excited state, thereby giving the ($0 \rightarrow 2$) band a totally symmetrical character. Hence, the triplet state of methacrolein is planar, or very nearly so. The similarity in the wave numbers for the methyl and skeletal torsion supports this observation. (The n,π^* singlet has previously been shown to be planar.)[2]

The 491-cm^{-1} fundamental is tentatively assigned to the $\angle$CCO in-plane bending, primarily because its intensity suggests a totally symmetrical vibration.

(A-4) Summary of Vibrational Electronic Analysis. A comparison of fundamentals for the S_0, $S_1(n,\pi^*)$, and $T_1(n,\pi^*)$ states of acrolein, crotonaldehyde, and methacrolein is presented in Table VII. In each molecule, the skeletal torsion is found to increase slightly from S_1 to T_1, suggesting that a higher proportion of the π^* electron density is concentrated in the central lobe of the π^* orbital in the triplet manifold than in the singlet manifold. This observation has important implications with respect to the mode of Fermi correlative electron redistribution, a subject to be discussed in detail in the following section. With respect to excited state geometry, this increased central torsion indicates that bond order reversal in $T_1(n,\pi^*)$ will prohibit any rotation about the central C–C bond. Hence, if the n,π^* triplet is nonplanar, the nonplanarity must involve a rotation about the C_3–C_4 "vinylic" bond. The lack
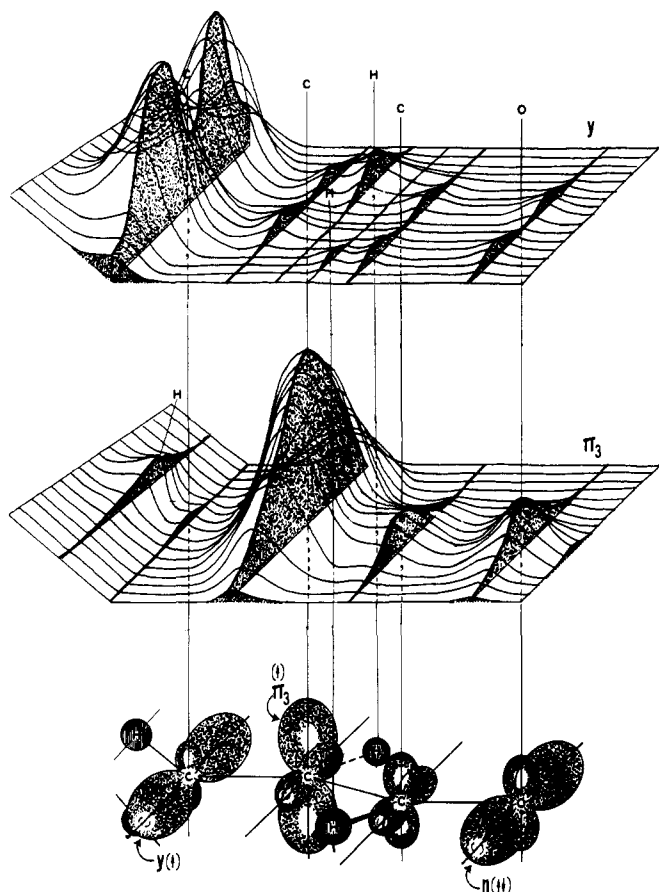
Figure 3. SCF-MO-INDO electron density map for the y,π* "relaxed" triplet of acrolein.[15]

Table VII. Comparison of Some S_0, S_1, and $T_1(n,\pi^*)$ Fundamentals of the Singly Substituted Methylpropenals[a]

Fundamental (s-trans rotamer)	Acrolein, cm^{-1}	Croton-aldehyde, cm^{-1}	Meth-acrolein, cm^{-1}
Skeletal torsion in			
S_0	158	206	163
S_1	250	243	233
T_1	~280	~270	241
Methyl torsion in			
S_0		140	134
S_1		187	183
T_1		185	173
∠CCO in-plane bending in			
S_0	564	537	630
S_1	488	457	535
T_1	495	?	(491)

[a] Values in parentheses are tentative. Values preceded by an approximation symbol (~) were derived from combination band analysis.

of activity in the vinyl C=C torsion, the similarity in methyl torsions for T_1 and S_1, and the similarity in the relative intensities of the totally symmetrical vibrations in T_1 and S_1 vibronics rule out significant rotation about the C_3-C_4 bond. Hence, the n,π* triplet states of the propenals are planar, or very nearly so, and probably have very similar geometries to their corresponding n,π* singlet states.[2,3]

A planar n,π* triplet does not rule out the possibility, as suggested by the ab initio calculations of Devaquet

and Salem,[14,15] that the n,π* triplet relaxes to a non-planar molecular geometry of y,π* orbital nature in which the "vinyl" CH_2 ($CHCH_3$ in crotonaldehyde) moiety is rotated 90° out of the molecular plane (see Figure 3). (Vinylic rotation was the only nonplanar distortion predicted by the ab initio calculations.) Our results do indicate, however, that a barrier must exist between the Franck–Condon n,π* state and the relaxed y,π* state; otherwise, the existence of a relaxed triplet would be evident in the nontotally symmetrical fundamentals of the vibrational electronic spectrum of the ancestral n,π* state. The calculations of Devaquet and Salem, however, do not predict any barrier. The increased torsion in the central C–C bond in the n,π* triplet state might be a manifestation of a π* electron redistribution in which significant antibonding is present in the C_3-C_4 "vinylic" system, permitting the out-of-plane rotation.

The observation that the propenals phosphoresce with a quantum yield less than 10^{-4} [16] provides some support for the existence of a relaxed y,π* triplet, since the resulting geometry (see Figure 3) would have a high probability of intercepting the ground-state potential energy curve and rapidly deactivating through radiationless processes. The extremely weak propenal emission is in marked contrast to the emitting characteristics of the propynal series I, II, and III. All

HC≡C—CHO   CH₃—C≡C—CHO   HC≡C—COCH₃
   I   II   III
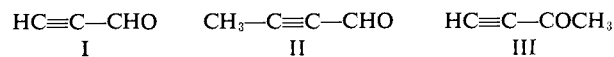
three of these molecules phosphoresce from an n,π* triplet under identical solvent conditions as used to investigate propenal emission (77°K, polar and nonpolar glasses).[16] The propynals exhibit a phosphorescence quantum yield of approximately 0.1 and $S_0 \rightarrow T_1$ oscillator strengths similar to those observed for the propenals.[16] Consequently, the weak propenal emission must be a function of either (1) the presence of the y,π* relaxed geometry or (2) lower molecular rigidity and an increased number of high frequency CH vibrations improving vibrational deactivation.

(B) Singlet–Triplet Splitting and Fermi Correlation in the Triplet State. The difference in energy between

$$S^{n,\pi^*} - T_1^{n,\pi^*} =$$

$$2\sum_i (H_{ii} - H_{ii}') + (H_{\pi^*\pi^*} - H_{\pi^*\pi^*}') +$$

$$(H_{nn} - H_{nn}') + \sum_i\sum_j (2J_{ij} - 2J_{ij}' + K_{ij}' - K_{ij}) +$$

$$\sum_i (2J_{i\pi^*} - 2J_{i\pi^*}') + \sum_i (2J_{in} - 2J_{in}') -$$

$$\sum_i (K_{i\pi^*} - K_{i\pi^*}') - \sum_i (K_{in} - K_{in}') +$$

$$\sum_{A>B}\sum (Z_A Z_B/R_{AB} - Z_A'Z_B'/R_{AB}') +$$

$$K_{n,\pi^*} + K_{n,\pi^*}' \quad (1)$$

(14) A. Devaquet and L. Salem, Can. J. Chem., 49, 977 (1971).

(15) INDO open shell calculations on the triplet state of acrolein do not parallel the ab initio calculations of Devaquet and Salem in that the nonplanar y,π* triplet is observed to have a higher energy than the planar n,π* triplet by roughly 0.5 eV. This observation might be associated with the restriction of the INDO basis set to Slater orbitals of principal quantum number two and "ground state" Slater exponents, thereby neglecting any possible expansion of the radial distribution of the excited electron accompanying excitation.

(16) An analysis of the excited singlet and triplet state geometries of I–III is currently in progress: R. R. Birge, D. Mullis, R. Rusakowicz, and P. A. Leermakers results to be published.

the first excited singlet and triplet n,π^* states (S_1-T_1 splitting) can be expressed by eq 1, where the prime indicates terms associated with the triplet manifold.[17] If the bond lengths and charge distributions are very similar for the singlet and triplet states (in the present calculations we shall assume identical geometries for S_1 and T_1), then all of the relationships in parentheses approach zero. Under these conditions, eq 1 reduces to the evaluation of only the exchange integrals associated with the n and π^* electron distributions in the singlet ($k_{n,\pi^*}{}^{S_1}$) and triplet ($k_{n,\pi^*}{}^{T_1}$) manifolds (eq 2).

$$S_1{}^{n,\pi^*} - T_1{}^{n,\pi^*} \cong K_{n,\pi^*}{}^{S_1} + K_{n,\pi^*}{}^{T_1} \qquad (2)$$

The main purpose in using this approximation is to facilitate the discussion of singlet–triplet splitting and the associated triplet state electron redistribution based on observation of exchange integral functions alone. Clearly, this approximation would break down if a significant change in geometry were realized between the n,π^* singlet and triplet states. We will observe, however, a high degree of correlation between the calculated and observed splittings. This observation provides further evidence in support of our vibrational electronic analysis that the n,π^* triplet is planar and possesses a geometry very similar to the corresponding n,π^* singlet.

(B-1) Exchange Integral Calculations. The electrostatic exchange integral, K_{ij}, is given by eq 3, where X_1

$$K_{ij} = \int\int \varphi_j{}^*(X_1)\varphi_i(X_1)\left\{\frac{e^2}{|X_1 - X_2|}\right\} \times$$
$$\varphi_i{}^*(X_2)\varphi_j(X_2)dX_1dX_2 \qquad (3)$$

and X_2 are position coordinates of electrons 1 and 2, respectively, $\varphi_i(X)$ and $\varphi_j(X)$, the ith and jth wave functions describing the probability distributions for the two electrons, and $\{e^2/|X_1 - X_2|\}$, the coulombic repulsion associated with the interaction of electrons 1 and 2. *The exchange integral, therefore, is the quantitative measure of the extent to which Fermi correlation reduces the coulomb repulsion in the triplet state.*

In the case of n,π^* systems, the spatial orthogonality of the n and π^* molecular orbitals leads to very small overlap, and hence n,π^* singlet–triplet splittings are on the order of only 1500–3000 cm^{-1} [as compared to π,π^* states which exhibit splittings usually in the range from 10,000 (highly conjugated systems) to 28,700 cm^{-1} (ethylene)]. Consequently, n,π^* states are usually very "biradical" in nature, and the approximations inherent in eq 2 are fairly justified.

The spatial orthogonality of the n and π^* orbitals means that the dominant contribution to the exchange integral for planar molecules will be associated with one-center atomic orbital overlap. Figure 4 schematically shows the type and magnitude of one-center exchange integral terms associated with carbonyl n,π^* systems using the formaldehyde molecule as an example. The values for the one-center integrals were taken from Hinze and Jaffe.[18]

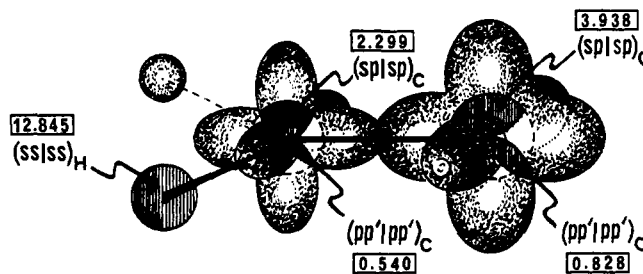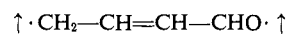The calculation of singlet–triplet splitting based on one-center terms is shown in Table VIII.[19a] Analysis

Figure 4. One-center exchange integrals as displayed for formaldehyde. Magnitudes are given in electron volts and were taken from J. Hinze and H. H. Jaffe, *J. Chem. Phys.*, **38**, 1834 (1963).

of the composite one-center terms given in Table VIII provides a means of differentiating between the various modes of Fermi correlation in the triplet manifold.

(B-2) Fermi Correlation in $T_1(n,\pi^*)$. Correlative considerations suggest that electrons of like spin within a set of two interacting, open shell molecular orbitals will, on the average, be closer together than those of opposite spin due to an exchange correction to the coulombic repulsion. However, electrons of like spin can never occupy the same localized region (atomic orbitals on the same atom), because of the Pauli principal. Consequently, two paths can be active in correlating the $n(\uparrow)$ and $\pi^*(\uparrow)$ electrons, (1) *delocalization* and (2) *charge separation.*[20] If delocalization is the dominant mechanism then the larger one-center exchange integral terms in Table VIII associated with the triplet manifold will tend to decrease in magnitude with respect to the singlet manifold at the expense of an increase in the magnitude of many of the smaller one-center terms. If charge separation is the dominant correlative mechanism, the $n(\uparrow)$ and $\pi^*(\uparrow)$ electrons will be strongly localized at different atomic centers so that the spin-unpaired electrons can avoid each other almost entirely. Charge separation will therefore result in a decrease in all of

S_1 and T_1 states were assumed to have identical nuclear configurations as the ground state (see ref 11). (b) Despite the neglect of differential overlap inherent in the CNDO treatment, the wave functions do obey the Pauli principal and are expected to adequately account for electron redistributions associated with fermi correlation. Improved wave functions using the INDO approximation, which include one-center exchange integrals, were calculated for the S_1 and T_1 states of acrolein to test the quality of the CNDO wave functions used in Table VIII. The INDO calculations registered only small changes in the magnitude of the electron redistribution relative to the CNDO calculations; in particular, less localization of the n orbital on oxygen in both the S_1 and T_1 states. This observation is in contrast to ground state calculations which indicate a greater localization of the n orbital on oxygen with INDO *vs.* CNDO wave functions.

(20) The term "charge separation" will be defined as the spatial separation and partial localization of the two spin unpaired electrons at different regions within the molecule. For example, a charge separation structure like the following

$$\uparrow \cdot CH_2 - CH = CH - CHO \cdot \uparrow$$

is best visualized in terms of the following charge cloud diagram.

(17) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(18) J. Hinze and H. H. Jaffe, *J. Chem. Phys.*, **38**, 1834 (1963).

(19) (a) The eigenvectors for the n and π^* molecular orbitals were derived from CNDO-AFAOS (S_1) (ref 9) and CNDO-OS (T_1) calculations and then used in one-center exchange integral calculations. The
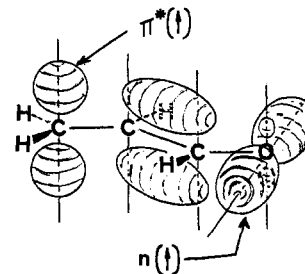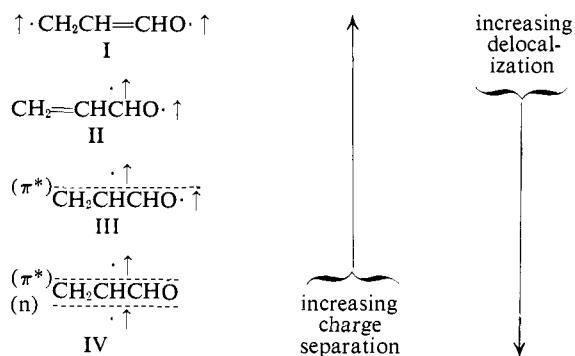
Table VIII. Orbital Contributions to the Singlet and Triplet Manifold One-Center Exchange Integrals

One-center terms[a]		Acrolein, eV	Crotonaldehyde, eV	Methacrolein, eV	Methyl vinyl ketone, eV
$S_1(n,\pi^*)$					
$\langle 1s|1s\rangle_H$	=	0.0000	0.0005	0.0002	0.0016
$\langle 2s|2p_z\rangle$	=	0.0024	0.0023	0.0027	0.0021
$\langle 2p_z|2p_z\rangle$	=	0.0014	0.0016	0.0016	0.0021
$\langle 2p_y|2p_x\rangle_C$	=	0.0132	0.0165	0.0210	0.0142
$\langle 2p_y|2p_x\rangle_O$	=	0.0889	0.0800	0.0869	0.0814
$K_{n,\pi^*}^{S_1}$	=	0.1059	0.1009	0.1124	0.1014
$T_1(n,\pi^*)$					
$\langle 1s|1s\rangle_H$	=	0.0000	0.0013	0.0000	0.0011
$\langle 2s|2p_z\rangle$	=	0.0105	0.0114	0.0130	0.0050
$\langle 2p_z|2p_z\rangle$	=	0.0027	0.0031	0.0034	0.0029
$\langle 2p_y|2p_x\rangle_C$	=	0.0498	0.0470	0.0489	0.0515
$\langle 2p_y|2p_x\rangle_O$	=	0.0323	0.0268	0.0285	0.0268
$K_{n,\pi^*}^{T_1}$	=	0.0953	0.0896	0.0938	0.0873
$K_{n,\pi^*}^{S_1} + K_{n,\pi^*}^{T_1}$	=	0.2012 eV	0.1905 eV	0.2062 eV	0.1887 eV
		1623 cm^{-1}	1537 cm^{-1}	1663 cm^{-1}	1522 cm^{-1}
$S_1 - T_1$, (exptl)		1614 cm^{-1}	1572 cm^{-1}	1672 cm^{-1}	?

[a] The z axis is parallel to the carbonyl bond; the x axis is perpendicular to the molecular plane. Consequently, the π^* system is associated with the $2p_x$ orbitals. All of the terms are composite one-center terms over all appropriate atomic centers unless specified by subscripts. C indicates that the term includes only the carbon atoms; O indicates that the term includes only the oxygen atom; H indicates that the term includes only the hydrogen atoms.

the one-center terms, and consequently, $K_{n,\pi^*}^{T_1}$ will be considerably smaller then $K_{n,\pi^*}^{S_1}$. In schematic terms, correlation via delocalization will favor resonant structure IV, while correlation via charge separation will favor resonant structure I. Since structure I would be

↑·CH₂CH=CHO· ↑
      I

   ·↑
CH₂=CHCHO· ↑
      II

(π*)   ·↑
    CH₂CHCHO· ↑
      III

(π*)   ·↑
(n) CH₂CHCHO
    ·↑
   IV

increasing delocalization

increasing charge separation

far more photoreductive than structure IV (the oxygen atom of structure I would have greater oxy radical character than the oxygen atom of structure IV), the determination of which correlative mechanism is the more important is of photochemical interest.

As the reader has probably anticipated, analysis of Table VIII indicates that delocalization is the prominent mode of Fermi correlation of the triplet electrons in the propenals. Specifically, both the CNDO[19a] and INDO[19b] calculations indicate that in $S_1(n,\pi^*)$ the electron in the singly occupied n orbital has partially reorganized back onto the oxygen atom to compensate for the excitation of one of the n electrons into the π^* orbital. In the $T_1(n,\pi^*)$ state, however, the n electron has delocalized off of oxygen onto the carbon atoms to "avoid" concentrating too much electron density on one atom, hence lowering the probability of the spin unpaired n(↑) and π^*(↑) electrons from ever occupying two interacting orbitals on the same atom. Hence, the one-center exchange integral associated with oxygen ($\langle 2p_y|2p_x\rangle_O$ in Table VIII) is considerably smaller in the triplet state than in the singlet state. Delocalization of the n electron off of oxygen is the principal reason for a decreased dipole moment in the triplet state (see Figure 1). In contrast, the π^* orbital is

only weakly affected by the change in multiplicity. The π^* electron is found to delocalize slightly off of oxygen in the triplet state.

In summary, therefore, the triplet state of the propenals is best described by structure IV, and delocalization of both the n and, to a lesser extent, the π^* electron densities off of oxygen represents the prominent Fermi correlative mechanism in the n,π^* triplet state. Consequently, the n,π^* triplet should be less photoreductive than the n,π^* singlet.

The ability of the SCF-MO-CNDO[19] calculations to correctly predict the effect that methyl group position has on the singlet-triplet splitting is most encouraging and provides considerable support for the use of these wave functions in analyzing Fermi correlative electron redistribution. Furthermore, the observed increase in the skeletal torsion in the triplet state of the propenals (see section A) provides experimental support for the calculated delocalization of the π^* electron density off of oxygen and indicates that much of this electron density is placed in the central lobe of the π^* orbital.

INDO[19b] n and π^* electron densities in the S_0, $S_1(n,\pi^*)$, and $T_1(n\pi^*)$ states of acrolein are shown in Figure 5.

(C) Spin–Orbit Coupling in $T_1(n,\pi^*)$. Singlet–triplet transitions can be observed because the rigorous separation of the electronic wave function into a product including space-dependent and spin-dependent parts is broken down by coupling between the electron's spin magnetic moment and the magnetic field produced by orbital motion of the electron. Within a homologous series of molecules, differences in the oscillator strengths of the $S_0 \rightarrow T_1$ transition can provide a means of studying electron distributions in certain perturbing excited states and provide insight into the relative importance of certain coupling mechanisms. We shall observe that one of the frequently neglected spin–orbit coupling paths, involving interaction of the ground state with the n,π^* triplet state, is very important in the methylpropenals and contributes about 35% to the net oscillator strength calculated.

(C-1) Observed Oscillator Strengths. The experi-

Table IX. Oscillator Strengths for $S_0 \rightarrow T_1(n,\pi^*)^a$

Molecule	$\epsilon_{max}^{S_0 \rightarrow S_1}$	$\epsilon_{00}^{S_0 \rightarrow S_1}$	$\epsilon_{00}^{S_0 \rightarrow T_1}$	$f^{S_0 \rightarrow S_1}$	$f^{S_0 \rightarrow T_1}$
Acrolein	17	7.9	0.13	3.8×10^{-4}	6.3×10^{-8}
Crotonaldehyde	16	4.2	0.10	4.2×10^{-4}	10.0×10^{-6}
Methacrolein	16	6.2	0.04	4.2×10^{-4}	2.7×10^{-8}
Methyl vinyl ketone	13	1.6	?	3.4×10^{-4}	?

^{a} Observed in the vapor phase on a Cary-14 recording spectrophotometer.

mentally observed oscillator strength for the $S_0 \rightarrow T_1$ transition can be calculated using the approximate relationship given in eq 4. The experimental results

$$f^{S_0 \rightarrow T_1} \cong \left[\frac{\epsilon_{00}^{S_0 \rightarrow T_1}}{\epsilon_{00}^{S_0 \rightarrow S_1}} \right] f^{S_0 \rightarrow S_1} \qquad (4)$$

are given in Table IX. Since methyl vinyl ketone did not yield to vibronic analysis, $f^{S_0 \rightarrow T_1}$ could not be calculated for this molecule.

(C-2) Spin–Orbit Coupling Calculations. The spin-dependent Hamiltonian for a many electron system is given by eq 5, where V_{iK} is the potential at electron i as a

$$\mathcal{H}' = \frac{1}{2m^2c^2} \sum_{K=1}^{N} \sum_{i=1}^{n} (\nabla V_{iK} \times \mathbf{p}_i) \cdot \mathbf{s}_i \qquad (5)$$

function of nucleus K, $\mathbf{p}_i$ is the linear momentum, and $\mathbf{s}_i$ the spin–angular momentum of electron i. The summation is carried out over all N electrons (i) and all N nuclei (K). In the present calculation, spin–orbit perturbation will be approximated by considering the electrons to be in a spherically symmetrical potential field and spin–other orbit interactions will be neglected. Accordingly, the McClure central field approach yields the following equation $(6),^{21}$ where the N nuclei are

$$\mathcal{H}' = \frac{1}{2m^2c^2} \sum_{K=1}^{N} \sum_{i=1}^{n} \frac{1}{r_{iK}} \frac{\partial V r_{iK}}{\partial r_{iK}} (l_{x_i}s_{x_i} + l_{y_i}s_{y_i} + l_{z_i}s_{z_i}) \qquad (6)$$

treated as spatially coincident, and the operators for the x components of the orbital and spin–angular momenta of the ith electron are denoted by l_{x_i} and s_{x_i}, respectively. A detailed study by McGlynn has shown that eq 6 yields results that compare favorably with more comphehensive theoretical treatments.^{22a}

The matrix elements of the spin-dependent part of the Hamiltonian $\langle \Phi_{T_j} | \mathcal{H}_{\Sigma}' | \Phi | s_i \rangle$ will determine the amount of mixing between the specific singlet i and triplet j wave functions (states). The transition moment of the singlet–triplet transition, therefore, obtains intensity from the following terms (eq 7), where E_{S_i} and tensity from the following terms (eq 7), where E_{S_i} and

$$M(S_0 \rightarrow T_1) = \sum_{j \neq 0} \frac{\langle \Phi_{T_1} | \mathcal{H}_{\Sigma}' | \Phi_{S_j} \rangle}{E_{T_1} - E_{S_j}} M(S_0 \rightarrow S_j) +$$

$$\sum_{k \neq 1} \frac{\langle \Phi_{T_k} | \mathcal{H}_{\Sigma}' | \Phi_{S_0} \rangle}{E_{T_k} - E_{S_0}} M(T_1 \rightarrow T_k) + \frac{\langle \Phi_{T_1} | \mathcal{H}_{\Sigma}' | \Phi_{S_0} \rangle}{E_{T_1} - E_{S_0}} M(S_0, S_0) +$$

$$\frac{\langle \Phi_{T_1} | \mathcal{H}_{\Sigma}' | \Phi_{S_0} \rangle}{E_{T_1} - E_{S_0}} M(T_1, T_1) \qquad (7)$$

E_{T_i} are the energies of the singlet and triplet states in electron volts. Equation 7 can be rearranged to a more workable form by substituting the relationship between

(21) D. S. McClure, *J. Chem. Phys.*, **17**, 665 (1949).
(22) (a) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969; (b) we have adopted the axes system used in the above ref (p 242); the z axis is parallel to the carbonyl bond; the x axis is perpendicular to the molecular plane.
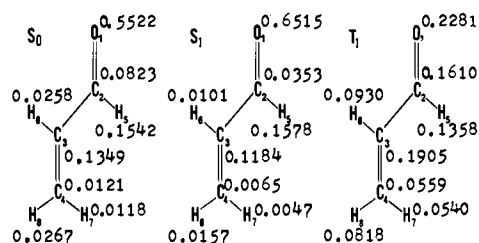
n Electron Densities
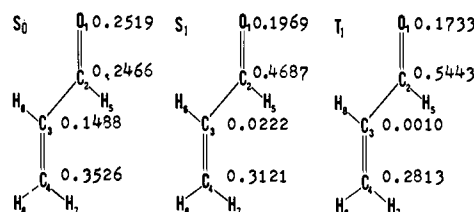
π^* Electron Densities

Figure 5. SCF-MO-INDO n and π^* electron densities in the S_0, $S_1(n,\pi^*)$, and $T_1(n,\pi^*)$ states of acrolein.

oscillator strength and transition moment in the above to yield the following (eq 8) where $\hat{S}_{jk}^x$ is the x symmetry

$$f^{S_0 \rightarrow T_1} = \sum_{j \neq 0} f^{S_0 \rightarrow S_j} \left(\frac{E_{T_1} - E_{S_0}}{E_{S_1} - E_{S_0}} \right) \left| \frac{\langle \Phi_{T_1} | \mathcal{H}_{\Sigma}' | \Phi_{S_j} \rangle}{E_{T_1} - E_{S_j}} \right|^2 +$$

$$\sum_{k \neq 1} f^{T_1 \rightarrow T_k} \left(\frac{E_{T_1} - E_{S_0}}{E_{T_k} - E_{T_1}} \right) \left| \frac{\langle \Phi_{T_k} | \mathcal{H}_{\Sigma}' | \Phi_{S_0} \rangle}{E_{T_k} - E_{S_0}} \right|^2 +$$

$$(3.793 \times 10^{-3})(E_{T_1} - E_{S_0})(\mu_{S_0}{}^D)^2 \left| \frac{\langle \Phi_{T_1} | \mathcal{H}_{\Sigma}' | \Phi_{S_0} \rangle}{E_{T_1} - E_{S_0}} \right|^2 +$$

$$(3.793 \times 10^{-3})(E_{T_1} - E_{S_0})(\mu_{T_1}{}^D)^2 \left| \frac{\langle \Phi_{T_1} | \mathcal{H}_{\Sigma}' | \Phi_{S_0} \rangle}{E_{T_1} - E_{S_0}} \right|^2 \qquad (8)$$

where

$$|\langle \Phi_{T_k} | \mathcal{H}_{\Sigma}' | \Phi_{S_j} \rangle|^2 = |\langle \Phi_{T_k} | \mathcal{H}_x' | \Phi_{S_j} \rangle \cdot \hat{S}_{jk}^x|^2 + |\langle \Phi_{T_k} | \mathcal{H}_y' | \Phi_{S_j} \rangle \cdot \hat{S}_{jk}^y|^2 + |\langle \Phi_{T_k} | \mathcal{H}_z' | \Phi_{S_j} \rangle \cdot \hat{S}_{jk}^z|^2 \qquad (9)$$

unit vector defined as unity for symmetry-allowed mixing (between S_j and T_k) and zero for symmetry-unallowed mixing. For the n $\rightarrow \pi^*$ triplet transition in C_s symmetry, $\hat{S}_{jk}^x = 1$ for perturbing singlets (S_j) having A'' transition symmetry, and $\hat{S}_{jk}^y = \hat{S}_{jk}^z = 1$ for perturbing singlets having A' transition symmetry.^{22b} $\mu_{S_0}{}^D$ and $\mu_{T_1}{}^D$ are the molecular dipole moments for the ground and first excited triplet states in Debyes.

The first term in eq 8 calculates the contribution to the $S_0 \rightarrow T_1$ oscillator strength of the mixing of all possible excited state singlets into T_1. In the case of formaldehyde this term is responsible for roughly 66%

Table X. SCF–MO–INDO Orbital Coefficients for *trans*-Acrolein[a]

Orbital	Atom	π_1	σ	π_2	n	$\pi_3{}^*$	σ^*	$\pi_4{}^*$
2s	O_1	0.0	−0.2288	0.0	0.0060	0.0	0.0416	0.0
	C_2	0.0	−0.0538	0.0	0.0442	0.0	−0.3582	0.0
	C_3	0.0	0.0305	0.0	0.1153	0.0	0.4505	0.0
	C_4	0.0	0.0638	0.0	−0.0111	0.0	−0.3937	0.0
$2p_z$	O_1	0.0	−0.6093	0.0	0.0318	0.0	−0.1081	0.0
	C_2	0.0	0.4071	0.0	−0.0425	0.0	0.1234	0.0
	C_3	0.0	−0.2253	0.0	0.1602	0.0	0.0856	0.0
	C_4	0.0	0.2422	0.0	−0.0721	0.0	0.0440	0.0
$2p_y$	O_1	0.0	−0.1724	0.0	−0.7424	0.0	−0.0312	0.0
	C_2	0.0	−0.0278	0.0	0.2802	0.0	0.0751	0.0
	C_3	0.0	0.1256	0.0	−0.3098	0.0	0.0910	0.0
	C_4	0.0	−0.2413	0.0	0.0821	0.0	0.0691	0.0
$2p_x$	O_1	0.5271	0.0	0.5791	0.0	0.5019	0.0	0.3674
	C_2	0.5760	0.0	0.2783	0.0	−0.4966	0.0	−0.5867
	C_3	0.5068	0.0	−0.4995	0.0	−0.3858	0.0	0.5872
	C_4	0.3655	0.0	−0.5812	0.0	0.5938	0.0	−0.4195
1s	H_5	0.0	−0.2541	0.0	−0.3927	0.0	0.3337	0.0
	H_6	0.0	0.0094	0.0	−0.1605	0.0	−0.4249	0.0
	H_7	0.0	0.1572	0.0	−0.1086	0.0	0.3416	0.0
	H_8	0.0	−0.3154	0.0	0.1635	0.0	0.2182	0.0
Energy, eV		−20.3628	−16.7058	−14.2511	−12.6402	2.8064	6.3155	7.4234

[a] The z axis is parallel to the carbonyl bond; the x axis is perpendicular to the molecular plane. Calculation was performed on the r_s structure of *trans*-acrolein (E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, **45**, 104 (1966)) using a basis set of 20 orbitals. The numbering system used to designate the atoms is shown in Figure 1.

Table XI. SCF–MO–INDO Orbital Coefficients for *trans*-Crotonaldehyde[a]

Orbital	Atom	π_2	σ	π_3	n	$\pi_4{}^*$	σ^*	$\pi_3{}^*$
2s	O_1	0.0	0.0604	0.0	−0.0063	0.0	0.0241	0.0
	C_2	0.0	−0.0583	0.0	−0.0496	0.0	−0.2382	0.0
	C_2	0.0	−0.0271	0.0	−0.1115	0.0	0.3960	0.0
	C_4	0.0	−0.0376	0.0	0.0052	0.0	−0.4222	0.0
	C_5	0.0	−0.0214	0.0	−0.0521	0.0	0.2304	0.0
$2p_z$	O_1	0.0	0.2307	0.0	−0.0390	0.0	−0.0650	0.0
	C_2	0.0	−0.0901	0.0	0.0489	0.0	0.0900	0.0
	C_3	0.0	0.3366	0.0	−0.1689	0.0	0.0613	0.0
	C_4	0.0	−0.2985	0.0	0.0894	0.0	0.0615	0.0
	C_5	0.0	0.1751	0.0	−0.1166	0.0	0.1076	0.0
$2p_y$	O_1	0.0	−0.1886	0.0	0.7402	0.0	−0.0244	0.0
	C_2	0.0	−0.0768	0.0	−0.2783	0.0	0.0622	0.0
	C_3	0.0	0.1806	0.0	0.3098	0.0	0.1273	0.0
	C_4	0.0	−0.3059	0.0	−0.0884	0.0	0.1727	0.0
	C_5	0.0	0.2466	0.0	0.0950	0.0	−0.0073	0.0
$2p_x$	O_1	−0.5671	0.0	−0.5164	0.0	−0.4709	0.0	−0.3906
	C_2	−0.5565	0.0	−0.2017	0.0	0.4557	0.0	0.5994
	C_3	−0.3266	0.0	0.5377	0.0	0.3963	0.0	−0.4972
	C_4	−0.0835	0.0	0.5113	0.0	−0.5823	0.0	0.2670
	C_5	0.3407	0.0	−0.1962	0.0	−0.0857	0.0	0.2639
1s	H_6	0.0	0.0969	0.0	0.3875	0.0	0.2374	0.0
	H_7	0.0	0.3474	0.0	0.1585	0.0	−0.4187	0.0
	H_8	0.0	0.4277	0.0	0.1061	0.0	0.4418	0.0
	H_9	0.0	0.3348	0.0	−0.0086	0.0	−0.1964	0.0
	H_{10}	0.2636	−0.1457	−0.2275	0.0425	0.1832	−0.0601	−0.2236
	H_{11}	−0.2636	−0.1457	0.2275	0.0425	−0.1832	−0.0601	0.2236
Energy, eV		−19.0575	−16.0384	−13.1664	−12.3581	2.7555	6.4120	7.1953

[a] Coordinate system defined as for acrolein. Calculation was performed on the r_s structure of *trans*-crotonaldehyde (M. Suzuki and K. Kozima, *Bull. Chem. Soc. Jap.*, **42**, 2183 (1969)) using a basis set of 26 orbitals. The numbering system is shown in Figure 1.

of the net oscillator strength calculated.[23a] Consequently, this first term is quite important and the present analysis will include the contributions associated with the four lowest singlet states allowed by symmetry and orbital occupation (see following discussion) to mix with $T_1(n,\pi^*)$. The second term in eq 8 calculates the contribution of all possible excited state triplets (above T_1) mixing into the ground state and is found to contribute less than 0.5% to the total oscillator

strength calculated for formaldehyde.[23a] A similar lack of importance is expected for the propenals and consequently, the contribution of the second term will be neglected in the present analysis. The last two terms calculate the effect of mixing of the ground state into T_1 and T_1 into the ground state, respectively, on the $S_0 \rightarrow T_1$ oscillator strength. These two terms are commonly neglected in treatments of this kind despite the fact that they contribute, for example, 23 and 11%, respectively, to the net $S_0 \rightarrow T_1$ oscillator strength calculated for formaldehyde.[23a] Since the dipole moments in terms 3 and 4 are larger in the propenals

(23) (a) L. Goodman and B. J. Laurenzi, *Advan. Quantum Chem.*, **4**, 153 (1968); (b) J. L. Ginsburg and L. Goodman, *Mol. Phys.*, **15**, 441 (1968).

Table XII. SCF–MO–INDO Orbital Coefficients for *trans*-Methacrolein[a]

Orbital	Atom	π_2	σ	π_3	n	π_4^*	σ^*	π_5^*
2s	O_1	0.0	−0.1218	0.0	−0.0084	0.0	−0.0770	0.0
	C_2	0.0	−0.0144	0.0	−0.0520	0.0	0.5551	0.0
	C_3	0.0	−0.0340	0.0	−0.1080	0.0	−0.3688	0.0
	C_4	0.0	0.1068	0.0	0.0147	0.0	0.2117	0.0
	C_5	0.0	−0.0569	0.0	0.0398	0.0	0.2420	0.0
$2p_z$	O_1	0.0	−0.3903	0.0	−0.0323	0.0	0.1929	0.0
	C_2	0.0	0.2288	0.0	0.0494	0.0	−0.1590	0.0
	C_3	0.0	−0.4200	0.0	−0.1587	0.0	−0.1090	0.0
	C_4	0.0	0.3710	0.0	0.0744	0.0	−0.0269	0.0
	C_5	0.0	0.3830	0.0	−0.0309	0.0	−0.1338	0.0
$2p_y$	O_1	0.0	0.0595	0.0	0.7151	0.0	0.0495	0.0
	C_2	0.0	0.0043	0.0	−0.2893	0.0	−0.1090	0.0
	C_3	0.0	−0.1516	0.0	0.3243	0.0	0.1010	0.0
	C_4	0.0	0.1365	0.0	−0.0846	0.0	0.0672	0.0
	C_5	0.0	0.1994	0.0	−0.1740	0.0	0.0602	0.0
$2p_x$	O_1	0.5890	0.0	−0.4547	0.0	−0.4907	0.0	0.3682
	C_2	0.5225	0.0	−0.1742	0.0	0.4828	0.0	−0.5606
	C_3	0.1406	0.0	0.4876	0.0	0.3819	0.0	0.4491
	C_4	0.1145	0.0	0.6189	0.0	−0.5916	0.0	−0.3388
	C_5	−0.3906	0.0	−0.2031	0.0	0.0561	0.0	0.2978
1s	H_6	0.0	−0.1660	0.0	0.3909	0.0	−0.4732	0.0
	H_7	0.0	−0.2500	0.0	0.1130	0.0	−0.0812	0.0
	H_8	0.0	−0.0266	0.0	−0.1666	0.0	−0.2169	0.0
	H_9	0.0	0.3496	0.0	0.0656	0.0	−0.0013	0.0
	H_{10}	−0.3119	−0.0540	−0.2246	−0.0817	−0.1166	−0.1470	−0.2693
	H_{11}	0.3119	−0.0540	0.2246	−0.0817	0.1166	−0.1470	0.2693
Energy, eV		−18.2547	−15.9117	−13.4109	−12.5849	2.7184	6.5319	6.7952

[a] Coordinate system defined as for acrolein. Calculation was performed on the r_s structure of methacrolein (M. Suzuki and K. Kozima, *J. Mol. Spectrosc.*, **38**, 314 (1971)) using a basis set of 26 orbitals. The numbering system is shown in Figure 1.

Table XIII. SCF–MO–INDO Orbital Coefficients for *trans*-Methyl Vinyl Ketone[a]

Orbital	Atom	π_2	σ	π_3	n	π_4^*	σ^*	π_5^*
2s	O_1	0.0	−0.2049	0.0	0.0030	0.0	−0.0178	0.0
	C_2	0.0	−0.0268	0.0	0.0204	0.0	0.1868	0.0
	C_3	0.0	−0.0194	0.0	0.1222	0.0	−0.4277	0.0
	C_4	0.0	0.0437	0.0	−0.0182	0.0	0.4874	0.0
	C_5	0.0	−0.0435	0.0	−0.1124	0.0	−0.1773	0.0
$2p_z$	O_1	0.0	−0.6323	0.0	0.0616	0.0	0.0432	0.0
	C_2	0.0	0.4018	0.0	−0.0402	0.0	−0.0747	0.0
	C_3	0.0	−0.2510	0.0	0.1653	0.0	−0.0284	0.0
	C_4	0.0	0.2406	0.0	−0.0701	0.0	−0.0792	0.0
	C_5	0.0	−0.2954	0.0	−0.1464	0.0	−0.0469	0.0
$2p_y$	O_1	0.0	−0.1426	0.0	−0.7442	0.0	−0.0112	0.0
	C_2	0.0	−0.0028	0.0	0.3014	0.0	0.0282	0.0
	C_3	0.0	0.1107	0.0	−0.3048	0.0	−0.1349	0.0
	C_4	0.0	−0.0787	0.0	0.0814	0.0	−0.1141	0.0
	C_5	0.0	−0.0943	0.0	−0.3049	0.0	−0.0475	0.0
$2p_x$	O_1	−0.3319	0.0	0.6262	0.0	0.5066	0.0	−0.2733
	C_2	−0.2790	0.0	0.3095	0.0	−0.4838	0.0	0.4063
	C_3	−0.4684	0.0	−0.4370	0.0	−0.3725	0.0	−0.5507
	C_4	−0.3913	0.0	−0.5357	0.0	0.5626	0.0	0.4330
	C_5	0.4333	0.0	−0.0906	0.0	−0.0736	0.0	0.3206
1s	H_6	0.0	−0.0618	0.0	−0.1561	0.0	0.4114	0.0
	H_7	0.0	0.0209	0.0	−0.1110	0.0	−0.4537	0.0
	H_8	0.0	−0.1956	0.0	0.1617	0.0	−0.2562	0.0
	H_9	0.0	−0.1915	0.0	0.0874	0.0	0.1039	0.0
	H_{10}	0.3548	0.1686	−0.1139	0.0500	0.1560	0.0715	−0.2886
	H_{11}	−0.3548	0.1686	0.1139	0.0500	−0.1560	0.0715	0.2886
Energy, eV		−17.3773	−15.7774	−13.8909	−12.0694	2.9090	6.5603	6.8830

[a] Coordinate system defined as for acrolein. Calculation was performed on the assumed r_s structure of methyl vinyl ketone using a basis set of 26 orbitals: bond lengths $(r_s),^b$ $C_2=O_1 = 1.219$, $C_3—C_2 = 1.470$, $C_4=C_3 = 1.345$, $C_2—C_5 = 1.501$, $C_5—H_{9,10,11} = 1.090$ Å; bond angles $(r_s),^b$ $C_3C_2O_1 = 120°$, $C_4C_3C_2 = 119° 50'$, $C_5C_2O_1 = 120°$, $C_4C_3H_6 = 122° 50'$, $C_3H_4H_7 = 119° 50'$, $C_3C_4H_8 = 121° 27'$, $C_2H_5H_{9,10,11} = 109° 28'$. [b] The numbering system is shown in Figure 1.

than in formaldehyde, mixing of T_1 and S_0 would be expected to be of even greater significance in the former molecules and will be included in the present calculations.

The various matrix elements of eq 8 can be reduced to the evaluation of matrix elements involving only those molecular orbitals not common to the given singlet and triplet states since these represent the only orbitals remaining after reduction of the state functions. Furthermore, if we choose to neglect mixing of doubly orthogonal configurations, only those states which differ in orbital occupancy by one electron from

Table XIV. Spin-Orbit Coupling in Acrolein and the Singly Substituted Methylpropenals

Perturbing singlet	$E^{S_0 \to S_i}$ eV	$f^{S_0 \to S_i}$	Dipole moment	$\lvert\langle\Phi_{T_1}\lvert\mathfrak{IC}\Sigma'\rvert\Phi_{S_i}\rangle\rvert^2$, eV² × 10⁶	$f_{calcd}^{S_0 \to T_1}$
			Acrolein: $E(S_0 \to T_1) = 3.50$ eV[a]		
π_2,π_3^*	6.11[b,c]	0.23[c]		13.9206	2.69 × 10⁻⁷
σ,π_3^*	6.69[d]	0.001[e]		21.4420	1.10 × 10⁻⁹
n,σ^*	7.71[d]	0.10[e]		0.4369	1.12 × 10⁻⁹
π_1,π_3^*	8.59[d]	0.01[e]		13.2044	2.08 × 10⁻⁹
S_0			$\mu_{S_0} = 3.11$ D[h]	11.9745	1.26 × 10⁻⁷
S_0			$\mu_{T_1} = 1.25$ D[i]	11.9745	2.00 × 10⁻⁸
				Total for acrolein =	4.19 × 10⁻⁷
			Crotonaldehyde: $E(S_0 \to T_1) = 3.58$ eV[a]		
π_3,π_4^*	5.79[b,c]	0.30[c]		11.0792	4.21 × 10⁻⁷
σ,π_4^*	6.44[f]	0.001[e]		3.3141	2.25 × 10⁻¹⁰
n,σ^*	7.63[f]	0.10[e]		0.1097	3.14 × 10⁻⁹
π_2,π_4^*	8.09[f]	0.01[e]		13.3811	2.91 × 10⁻⁹
S_0			$\mu_{S_0} = 3.72$ D[j]	10.3448	1.52 × 10⁻⁷
S_0			$\mu_{T_1} = 1.64$ D[i]	10.3448	2.91 × 10⁻⁸
				Total for crotonaldehyde =	6.08 × 10⁻⁷
			Methacrolein: $E(S_0 \to T_1) = 3.55$ eV[a]		
π_3,π_4^*	5.79[b,c]	0.21[c]		7.4679	1.92 × 10⁻⁷
σ,π_4^*	6.39[f]	0.001[e]		9.7347	7.16 × 10⁻¹⁰
n,σ^*	7.68[f]	0.10[e]		2.1315	5.78 × 10⁻⁹
π_2,π_4^*	7.88[f]	0.01[e]		15.1245	3.63 × 10⁻⁹
S_0			$\mu_{S_0} = 2.80$ D[k]	10.6526	8.93 × 10⁻⁸
S_0			$\mu_{T_1} = 1.06$ D[i]	10.6526	1.26 × 10⁻⁸
				Total for methacrolein =	3.04 × 10⁻⁷
			Methyl Vinyl Ketone: $E(S_0 \to T_1) = 3.55$ eV[g]		
π_3,π_4^*	6.05[b,c]	0.17[c]		16.3018	2.60 × 10⁻⁷
σ,π_4^*	6.41[f]	0.001[e]		24.4957	1.66 × 10⁻⁹
n,σ^*	7.47[f]	0.10[e]		0.0556	1.71 × 10⁻⁹
π_2,π_4^*	7.55[f]	0.01[e]		4.7370	1.39 × 10⁻⁹
S_0			$\mu_{S_0} = 3.16$ S[l]	12.2112	1.30 × 10⁻⁷
S_0			$\mu_{T_1} = 1.32$ D[i]	12.2112	2.27 × 10⁻⁸
				Total for methyl vinyl ketone =	4.17 × 10⁻⁷

[a] Calculated by subtracting the observed S_1-T_1 splitting (see Table VIII) from the energy of the $S_i(n,\pi^*)$ state measured at the absorption maximum. [b] Experimental data for the observed band maxima (not system origins). [c] Observed in the vapor phase on a Cary 14 recording spectrophotometer. [d] M. Jungen and H. Labhart, *Theor. Chim. Acta*, **9**, 345 (1968). [e] Order of magnitude estimates based on literature calculations. [f] Based on SCF-MO-INDO single configuration transition energies modified by presuming equivalent configurational interaction as calculated for acrolein.[d] [g] Calculated as in footnote a assuming the calculated S_1-T_1 splitting of 1522 cm⁻¹ (see Table VIII). [h] R. Wagner, *et al.*, *J. Chem. Phys.*, **26**, 634 (1957). [i] See Figure 1. [j] M. Suzuki and K. Kozima, *Bull. Chem. Soc. Jap.*, **42**, 2183 (1969). [k] M. Suzuki and K. Kozima, *J. Mol. Spectrosc.*, **38**, 314 (1971). [l] P. D. Foster, V. M. Rao, and R. F. Curl, Jr., *J. Chem. Phys.*, **43**, 1064 (1965).

$T_1(n,\pi^*)$ need be considered. Goodman and Laurenzi have demonstrated that two-electron interactions are overwhelmed by the nuclear field term and that mixing of doubly orthogonal configurations is unimportant.[23a] Since nuclear field terms are large in oxygen-containing molecules, a one-electron approximation is justified.[23] The appropriate one-electron operator, $\mathfrak{IC}_x'$, is given by eq 10. Because of the strong inverse dependence of the one-electron mixing on distance (r_K),

$$\mathfrak{IC}_x' = \frac{\hbar e^2}{4m^2c^2}\sum_K^N \frac{z_K{}^\mu l_{zK}}{r_K{}^3} \tag{10}$$

the numerous cross terms arising after the expansion of the molecular orbitals into a linear combination of atomic orbitals can safely be neglected.

In the present calculation, $1/r_K{}^3$ will be related to the spin–orbit coupling constant ζ_K using eq 11, where

$$\frac{1}{r_K{}^3} = \frac{Z_{eff}{}^2}{a_0{}^3 n^3(l+1)(l+\frac{1}{2})l} = \left[\frac{2m^2c^2}{e^2\hbar^2 Z_K}\right]\zeta_K \tag{11}$$

a_0 is the Bohr radius, Z_{eff} is the effective atomic number of the shielded nucleus, and n and l are the quantum numbers of the atomic orbitals (for 2p, $n = 2$, $l = 1$). McClure has determined the values of ζ_K for oxygen and carbon to be 152 and 28 cm⁻¹, respectively.[24]

(24) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

The effect of the angular momentum operator (l_z) on the p atomic orbitals and the coefficients of the matrix elements of the spin Hamiltonian between singlet and triplet states were taken from McGlynn, *et al.*[22a]

As the size of the molecular system increases, the spin–orbit coupling calculations become increasingly sensitive to the quality of the wave functions used in evaluating the matrix elements. Consequently, accurate SCF–LCAO wave functions were generated based on the approximation of intermediate neglect of differential overlap (INDO).[25] Calculations were done in double precision and the eigenvalues and eigenvectors were computed to an accuracy of better than five significant digits. The results are shown in Tables X–XIII. The results of the spin–orbit coupling calculations based on the approximations detailed in the previous discussion are shown in Table XIV.

In comparing the observed oscillator strengths (Table IX) with those calculated using spin–orbit coupling theory (Table XIV), we find that the calculated values are roughly one order of magnitude too small. Given the level of approximation, this discrepancy is not

(25) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967); J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967); J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2965 (1968); J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

surprising. However, the observation that the one-electron approximation correctly predicts the relative $S_0 \rightarrow T_1$ oscillator strengths with respectable accuracy must be considered somewhat of a triumph. The following salient conclusions can be made with reference to Table XIV.

(1) The principal perturbing singlet is the second excited π,π^* state as was found for formaldehyde.[26] The mixing of this singlet into T_1 accounts for roughly 65% of the total oscillator strength calculated.

(2) The oscillator strength of the $S_0 \rightarrow S_2(\pi,\pi^*)$ transition is the most influential variable in determining the oscillator strength for the $S_0 \rightarrow T_1$ transition. The fact that these oscillator strengths could be observed experimentally contributed greatly to the success of these calculations.

(3) Because of the large ground-state dipole moment of the propenals, mixing of S_0 into T_1 is quite important and cannot be neglected. For example, in crotonaldehyde this term alone contributes 1.52×10^{-7} to the oscillator strength, which is equivalent to

the *total oscillator strength* calculated by Sidman for the $S_0 \rightarrow T_1$ transition in formaldehyde.[26]

(4) Mixing of T_1 into S_0 is relatively unimportant and contributes only about 5% to the total $S_0 \rightarrow T_1$ oscillator strength calculated.

(5) Mixing of singlet states higher than $S_2(\pi,\pi^*)$ into T_1 is quantitatively insignificant and could have been safely ignored.

(26) J. W. Sidman, *J. Chem. Phys.*, **29**, 644 (1958).

Stereochemistry of the (2'-Vinylcyclopropyl)cyclobutane Rearrangement. Photochemical 1,3 Addition of Benzene to 3,4-Substituted Cyclobutenes

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Abstract: Thermal isomerization of *cis*-4,5-dimethyl-*endo*-tetracyclo[5.3.0.0^{2,10}.0^{3,6}]decene-8 (IX) at 300° gave rise to *endo,cis*-8,9-dimethyltricyclo[5.2.1.0^{4,10}]deca-2,5-diene (XII) as the major isomeric product. The reaction, which is a typical (2'-vinylcyclopropyl)cyclobutane rearrangement, thus proceeds with retention of the stereochemistry at the migrating σ bond. Arguments are presented to show that this rearrangement is distinct from the homo [1,5] sigmatropic shift which in the tricyclo[3.3.0.0^{2,8}]octene-3 systems involves the migration of hydrogen atoms only. It is also distinct from, although related to, the vinylcyclopropane rearrangement. The use of the (2'-vinylcyclopropyl)cyclobutane rearrangement in synthesis is exemplified by the preparation of *endo*-tetracyclo[8.2.1.0^{2,6}.0^{7,13}]trideca-3,8,11-triene (VII) from benzene and 1,3,5-cycloheptatriene in three steps.

In an earlier publication[1] it had been shown that the endo-photochemical 1,3 adduct of benzene to cyclobutene (I) which incorporates a (2'-vinylcyclopropyl)cyclobutane function, on pyrolysis, is transformed into II in 50% yield. Superficially, this reaction may appear to be a special instance of the homo [1,5] sigmatropic shift[2] that is observed in tricyclo-[3.3.0.0^{2,8}]octene-3.[3] In reality, reaction 2 fails to occur when the 7 position does not have a hydrogen in an endo orientation. Thus, the *cis*-6,7-*endo*-dimethyl derivative of III shows no tendency to isomerize to a 4,6-dimethyl derivative of IV.[4] Polycyclic derivatives
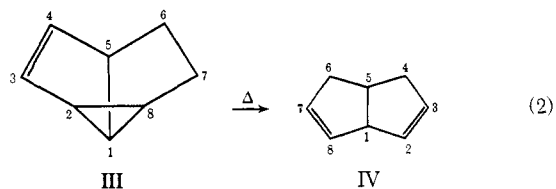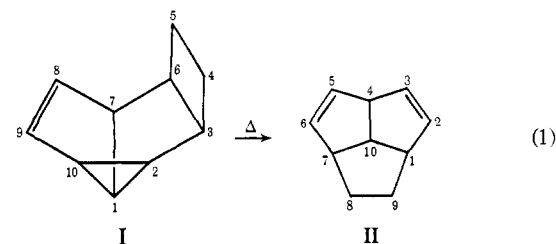
(1) R. Srinivasan, *J. Amer. Chem. Soc.*, **92**, 7542 (1970).
(2) A summary of the literature references to this reaction may be found in R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 132. See, in particular, R. N. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967).
(3) W. R. Roth and B. Peltzer, *Justus Liebigs Ann. Chem.*, **685**, 56 (1965).
(4) R. Srinivasan, *Tetrahedron Lett.*, 4551 (1971).

(1)

I   II

(2)

III   IV

of III which do not contain a (2'-vinylcyclopropyl)-cyclobutane function, on pyrolysis, either give rise to a homo [1,5] sigmatropic shift of *hydrogen*[5] or fragment to