lit.[3] rotation $[\alpha]^{25}_{D}$ +54° (c = 1, MeOH).

In a similar fashion, 100 mg (0.2 mmol) of **16b** was converted to 38 mg (54%) of (*S*)-6-chloro-2,3-dihydrospiro[4*H*-1-benzopyran-4,4′-imidazolidine]-2′,5′-dione (**17b**) as the monohydrate: mp 244–246 °C; $[\alpha]^{25}_{D}$ +46.6° (c = 1, MeOH); ^{1}H NMR (XL-100, CD_3OD–Me_4Si) δ 2.05–2.5 (m, 2 H), 3.3 (m, CD_2HOD), 4.1–4.35 (m, 1 H), 4.22–4.8 (m, 1 H), 4.85 (s, CD_3OH), 6.85 (d, 1 H), 7.1–7.3 (m, 2 H). Anal. Calcd for $C_{11}H_9ClN_2O_3{\cdot}H_2O$: C, 48.80; H, 4.09; N, 10.35. Found: C, 49.14; H, 3.69; N, 10.13.

(*R*)-6-Fluoro-2,3-dihydro-5′-imino-3′-[(*R*)-1-phenylethyl]spiro[4*H*-1-benzopyran-4,4′-imidazolidin]-2′-one (11). To a solution of 50 mg (0.17 mmol) of **3** in 2 mL of CH_2Cl_2 was added 24 mg (0.17 mmol) of chlorosulfonyl isocyanate. After the mixture was stirred at room temperature for 20 min, 1 mL of water was added and the mixture agitated at room temperature for 1 h. After extraction with CH_2Cl_2 the organic layers were dried over $MgSO_4$ and evaporated, and the residue (52 mg) was crystallized from EtOAc–hexane to give hygroscopic crystals. A slow recrystallization from EtOAc–hexane gave 12 mg of **11** as the hemisulfate hydrate: mp 224–226 °C dec; IR 1810, 1725 cm^{-1}; MS, *m/e* 339. Anal. Calcd for $C_{19}H_{18}FN_3O_2{\cdot}H_2O{\cdot}0.5H_2SO_4$: C, 56.15; H, 5.21; N, 10.34. Found: C, 56.08; H, 4.90; N, 10.07.

Hydrolysis of 10 mg of **11** with 2 mL of 1 N HCl for 20 min at 100 °C gave after cooling and filtering a white solid: mp 224–226 °C; MS, *m/e* 340; identical by TLC (CH_2Cl_2) with **12**.

(*S*)-1′-Chloro-6-fluoro-2,3-dihydro-5′-imino-3′-[(*S*)-1-phenylethyl]spiro[4*H*-1-benzopyran-4,4′-imidazolidin]-2′-one (23). In one experiment a solution of 1.5 g (0.005 mol) of **15a** and 0.44 mL (0.005 mol) of chlorosulfonyl isocyanate in 25 mL of CH_2Cl_2 was stirred at room temperature for 20 min, and the solvent removed in vacuo to give a pale yellow foam. To this material was added 45 mL of 1 N HCl, and the suspension was heated immediately for 1.5 h on a steam bath, cooled to room temperature, and filtered to give 1.67 g of a pale yellow solid. This inhomogeneous material was chromatographed on 60 g of 230–400-mesh silica gel, eluting with CH_2Cl_2, to give 0.4 g of **16a** (mp 226–229 °C), 0.04 g of **17a** (mp 238–239.5 °C), and 0.965 g of **23** as a white solid: mp 73–75 °C dec; IR 1725, 1650 cm^{-1}; MS, *m/e* 373/375; NMR (T-60A, CD_3OD–Me_4Si) δ 1.75 (d, 3 H), 2.0–2.9 (m, 2 H), 3.3 (m, CD_2HOD), 4.1–4.5 (m, 2 H), 4.6–4.9 (m, 3 H), 6.25 (m, 1 H), 6.9 (m, 2 H), 7.2 (s, 5 H); starch–KI test positive. The ^{13}C NMR was also consistent with this structure assignment. Anal. Calcd for $C_{19}H_{17}ClFN_3O{\cdot}HCl$: C, 55.62; H, 4.42; N, 10.24. Found: C, 55.65; H, 4.50; N, 9.91.

Treatment of **23** with 1 N HCl at 100 °C for 2 h gave a white solid: mp 224–226 °C dec; MS, *m/e* 340; identical by TLC with **16a**.

These experiments suggest that it is important, after the reaction of the amino nitriles **3** or **15** with chlorosulfonyl isocyanate, to stir the mixture with aqueous HCl at room temperature for 10 min prior to heating in order to obtain good yields of the hydantoins **12** or **16**.

Imidazolidine-2,4-dione (19). Treatment of 2 g (0.021 mol) of aminoacetonitrile hydrochloride in 25 mL of CH_2Cl_2 with 3 mL (0.021 mol) of triethylamine, followed by 1.88 mL (0.021 mol) of chlorosulfonyl isocyanate, stirring at room temperature for 30 min, evaporation, treatment of the residue with 30 mL of 1 N HCl at room temperature for 30 min and on a steam bath for another 30 min, gave, after evaporation and fractional crystallization of the residue, 10 mg of **19**, mp 222–224 °C dec (lit.[21] mp 221–223 °C).

5-Phenylimidazolidine-2,4-dione (22). A solution of 3.45 g (26.1 mmol) of 2-phenylglycinonitrile in 50 mL of CH_2Cl_2 was stirred with 2.27 mL (26.1 mmol) of chlorosulfonyl isocyanate for 45 min at room temperature. After evaporation, the residue (*m/e* 271.9842; $C_9H_7ClN_3S^+$) was stirred with 1 N HCl at room temperature for 30 min and on a steam bath for 1 h. After the mixture cooled, the solids were filtered to give 2.15 g (50%) of **22**: mp 171–173 °C dec; after recrystallization from aqueous EtOH, mp 177.5–179 °C (lit.[22] mp 179 °C). The aqueous filtrate gave after evaporation and crystallization from acetone 2.08 g (41%) of the ureido acid **21**; mp 191–194 °C (lit.[23] mp 197 °C); MS, *m/e* 194.

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Registry No. **1**, 66892-34-0; **2**, 82808-07-9; **3**, 82799-08-4; **6**, 69881-27-2; **11** hemisulfate, 82799-11-9; **12**, 82799-09-5; **13b**, 37674-72-9; **14a**, 79791-44-9; **14b**, 79791-45-0; **15a**, 79791-46-1; **15b**, 79791-47-2; **16a**, 79791-48-3; **16b**, 79791-49-4; **17a**, 68367-52-2; **17b**, 79791-50-7; **18**·HCl, 6011-14-9; **19**, 461-72-3; **20**, 16750-42-8; **21**, 5616-20-6; **22**, 89-24-7; **23**·HCl, 82799-12-0; HCN, 74-90-8; (*R*)-(+)-α-methylbenzylamine, 3886-69-9; (*S*)-(−)-α-methylbenzylamine, 2627-86-3; chlorosulfonyl isocyanate, 1189-71-5.

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(21) Catalog/Handbook of Fine Chemicals, Aldrich Chemical Co., 1981–1982, p 525.

(22) H. J. Fisher, J. B. Ekeley, and A. R. Ronzio, *J. Am. Chem. Soc.*, 64, 1434 (1942).

(23) L. Crombie and K. Hooper, *J. Chem. Soc.*, 3010 (1955).

Semiempirical Investigation of n-π-σ Excitations in Carbonyl Species

Donald W. Boerth

Department of Chemistry, Southeastern Massachusetts University, North Dartmouth, Massachusetts 02747

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Application of a modified INDO procedure (INDOUV) developed by Van-Catledge has been extended to carbonyl systems. Transition energies and oscillator strengths have been calculated for transitions to low-lying excited states of formaldehyde, acetaldehyde, acetone, acrolein, *trans*-crotonaldehyde (*trans*-2-butenal), methyl vinyl ketone (3-buten-2-one), 3-penten-2-one, and methyl cyclopropyl ketone (acetylcyclopropane) by using limited configuration interaction involving single excitations. The ordering of excitations to observed non-Rydberg states was reproduced. Whereas both n → π^* and nσ → π^* states are predicted to be too low in energy, π → π^* states are within 0.5 eV of their experimental locations insofar as these are obtainable. The n → σ^* transition was calculated to occur at greater energies than the π → π^* transition in agreement with ab initio results. In cyclopropyl ketones, the existence of two intense bands designated as $\Delta_p(a) \rightarrow \pi^*$ and $\Delta_p(s) \rightarrow \pi^*$ was reproduced, as well as the effects of conformation on the location and intensity of the $\Delta_p(a) \rightarrow \pi^*$ band. The theory of cyclopropyl interaction with the carbonyl π system was explored.

The ground and low-lying excited states of molecules containing the carbonyl group, C=O, play a significant role in organic and biological chemistry. Its strongly dipolar character and the presence of two sets of high-energy nonbonding electrons create some important differences in electronic structure between systems containing the C=O double bond and those containing the C=C double bond. Previous work[1-3] has considered excited σ → π states

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of hydrocarbons arising in part from orbitals associated with the C=C double bond. In this paper, we turn attention to similar low-lying states found in carbonyl species. Molecular orbital studies of excited states of carbonyl systems are not new. However, we were prompted to expand our earlier investigation of $\sigma \rightarrow \pi$ excitations to carbonyl systems using a previously developed modification of the INDO formalism to provide an important means of further calibration. For this purpose we have investigated several pertinent carbonyl systems, involving perturbations by CC π systems and by alkyl and cyclopropyl substituents, and have compared our results with previous reports.

Computational Methods

The INDO formalism as modified by Van-Catledge[1,2] has been preserved. Throughout this paper we refer to this method as INDOUV. The revised scheme was originally built upon the INDO SCF method as developed by Pople et al.[4] The rationale and details of the modifications are given elsewhere.[1] The salient features are briefly reviewed below.

To produce the correct order of molecular orbitals, we altered the original INDO equations for the off-diagonal core-matrix elements, $H_{\mu\nu}{}^{\mathrm{core}}$, where μ and ν are orbitals on different atoms. A set of orbital β's, related to Mulliken-type electronegatives,[5] were employed:

$$H_{\mu\nu}{}^{\mathrm{core}} = S_{\mu\nu}\beta_{\mu\nu}{}^{0} \tag{1}$$

where

$$\beta_{\mu\nu}{}^{0} = -0.5[(I_\mu + A_\mu) + (I_\nu + A_\nu)] \tag{2}$$

The quantities I_μ and A_μ are the ionization potential and electron affinity, respectively, for the orbital μ.

To produce state orderings in keeping with accepted spectral assignments we scaled repulsion integrals γ_{AB}:

$$\gamma_{\mathrm{AB}}{}^{\mathrm{emp}} = \gamma_{\mathrm{AB}}{}^{\mathrm{theo}} - 0.5S_{\mathrm{AB}}[(\gamma_{\mathrm{AA}}{}^{\mathrm{theo}} - \gamma_{\mathrm{AA}}{}^{\mathrm{emp}}) + (\gamma_{\mathrm{BB}}{}^{\mathrm{theo}} - \gamma_{\mathrm{BB}}{}^{\mathrm{emp}})] \tag{3}$$

where S_{AB}, $\gamma_{\mathrm{AA}}{}^{\mathrm{theo}}$, $\gamma_{\mathrm{BB}}{}^{\mathrm{theo}}$, and $\gamma_{\mathrm{AB}}{}^{\mathrm{theo}}$ are calculated from the STO valence s orbitals of atoms A and B. The repulsion integral $\gamma_{\mathrm{AA}}{}^{\mathrm{emp}}$ is derived empirically from ionization potentials and electron affinities of s orbitals on atom A:

$$\gamma_{\mathrm{AA}}{}^{\mathrm{emp}} = I_{\mathrm{s}} - A_{\mathrm{s}} \tag{4}$$

In addition to alteration of two-electron terms, scaling affects the one-center core integrals $U_{\mu\nu}$ since now

$$F^0 = \gamma_{\mathrm{AA}} = I_{\mathrm{s}} - A_{\mathrm{s}} \tag{5}$$

In our procedure the ground state Ψ^0 is described by a single Slater determinant of n doubly occupied molecular orbitals ψ_i (MO):

$$\Psi^0 = (1/(2n!)^{1/2})|\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2 \ldots \psi_n\bar{\psi}_n| \tag{6}$$

Each molecular orbital ψ_i is constructed as a linear combination of atomic orbitals ϕ_μ (LCAO) which form an undefined, symmetrically orthogonalized basis set, *nominally* based upon Slater-type functions:[6]

$$\psi_i = \sum_\mu c_{\mu i}\phi_\mu \tag{7}$$

The LCAO coefficients are determined for the ground state by solution of the Hartree–Fock–Roothaan equations.[7] The unoccupied or virtual orbitals arising from the Roothaan self-consistent-field procedure are used to construct singlet and triplet excited states, ${}^1\Psi_k$ and ${}^3\Psi_k$, by promotion of an electron from occupied orbital i to virtual orbital j. The corresponding determinantal spin-projected wave functions are the following:

$${}^1\Psi_{k(\equiv i\rightarrow j)} = 2^{-1/2}\{|\psi_1\bar{\psi}_1 \ldots \psi_i\bar{\psi}_j \ldots \psi_n\bar{\psi}_n| - |\psi_1\bar{\psi}_1 \ldots \bar{\psi}_i\psi_j \ldots \psi_n\bar{\psi}_n|\} \tag{8}$$

$${}^3\Psi_{k(\equiv i\rightarrow j)} = |\psi_1\bar{\psi}_1 \ldots \psi_i\psi_j \ldots \psi_n\bar{\psi}_n| \tag{9}$$

Descriptions of all excited states are improved by performing configuration interaction calculations with up to 100 configurations nearest the Fermi level. The excited-state wave functions ${}^1\Phi_l$ (and ${}^3\Phi_l$) are written as linear combinations of singly excited configurations ${}^1\Psi_k$ (or ${}^3\Psi_k$)

$$\Phi_l = \sum_k^{\mathrm{config}} C_{kl}\Psi_{k(\equiv i\rightarrow j)} \tag{10}$$

where C_{kl} are the expansion coefficients derived from application of the variational principle.

The intensities of transitions from ground to singlet excited states were calculated by methods summarized by Mulliken and Rieke[8] and modified for NDO wave functions by Pariser and Parr[9a] and by Pople et al.[9b] The oscillator strength for transitions between states described by wave functions Ψ^0 and ${}^1\Phi_l$ is

$$f_l = 1.085 \times 10^{-5}\omega \sum_{\vec{r}}^{x,y,z} Q_l(\vec{r})^2 \tag{11}$$

where ω is the transition frequency in reciprocal centimeters and Q_l is the transition moment integral between the ground state and state l:

$$Q_l(\vec{r}) = \int \Psi^0\vec{q}\Phi_l d\vec{r} \tag{12}$$

In terms of the configurations k, $Q_l(\vec{r})$ becomes

$$Q_l(\vec{r}) = 2^{1/2}\sum_k C_{kl}q(\vec{r})_k \tag{13}$$

where

$$q(\vec{r})_{k(\equiv i\rightarrow j)} = \sum_\mu^{\mathrm{AO's}} \sum_\nu^{\mathrm{AO's}} c_{\mu i}c_{\nu j}\mu(\vec{r})_{\mu\nu} \tag{14}$$

The atomic dipole moment matrix elements $\mu(\vec{r})_{\mu\nu}$ are calculated with the dipole length approximation. At the NDO level of approximation, $\mu(\vec{r})$ can be compartmentalized into a charge separation term and a hybridization term, accounting for coupling of s and p orbitals on the same center:

$$\mu(\vec{r})_{\mu\nu} = \mu_{\mathrm{chg}}(\vec{r})_{\mu\nu} + \mu_{\mathrm{hyb}}(\vec{r})_{\mu\nu} \tag{15}$$

The charge separation term reduces to

$$\mu_{\mathrm{chg}}(\vec{r})_{\mu\nu} = R_\mu \text{ if } \mu = \nu \\ = 0 \text{ if } \mu \neq \nu \tag{16}$$

where R_μ is the coordinate location of orbital μ. The hybridization term reduces to

$$\mu_{\mathrm{hyb}}(\vec{r})_{\mu\nu} = 0 \tag{17}$$

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(1) Van-Catledge, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 4365.

(2) Van-Catledge, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1173.

(3) Boerth, D. W. Ph.D. Dissertation, University of Minnesota, 1975.

(4) (a) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970. (b) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026.

(5) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782.

(6) Slater, J. C. *Phys. Rev.* **1930**, *36*, 57.

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

(8) Mulliken, R. S.; Rieke, C. A. *Rep. Prog. Phys.* **1941**, *8*, 231.

(9) (a) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 767. (b) Pople, J. A.; Segal, G. A. *Ibid.* **1965**, *43*, S136.

except when μ and ν are s and p orbitals on the same center. In this case

$$\mu_{\text{hyb}}(\vec{r})_{\mu\nu} = 0.763\,79\zeta^{-1} \tag{18}$$

where ζ is the orbital exponent for μ and ν.

The molecular geometries, used in the calculations reported here, were based upon standard values. A summary of the internal coordinates is as follows: formaldehyde, $r(\text{C=O}) = 1.23$ Å, $r(\text{C—H}) = 1.06$ Å; acetaldehyde, acetone, *trans*-acrolein, *trans*-crotonaldehyde, methyl vinyl ketone, 3-penten-2-one, $r(\text{C=O}) = 1.22$ Å, $r(\text{C}_{\text{tri}}\text{—C}_{\text{tet}}) = 1.52$ Å, $r(\text{C=C}) = 1.34$ Å, $r(\text{C}_{\text{tri}}\text{—C}_{\text{tri}}) = 1.46$ Å, $r(\text{C}_{\text{tri}}\text{—H}) = 1.08$ Å, $r(\text{C}_{\text{tet}}\text{—H}) = 1.09$ Å. All bond angles adhere to strict tetrahedral or trigonal values. The adopted dihedral angles are as follows: *trans*-crotonaldehyde, $\theta(\text{C=C—C}_{\text{tet}}\text{—H}) = 0°$; methyl vinyl ketone, $\theta(\text{O=C—C}_{\text{tet}}\text{—H}) = 0°$; 3-penten-2-one, $\theta(\text{C=C—C}_{\text{tet}}\text{—H}) = 0°$, $\theta(\text{O=C—C}_{\text{tet}}\text{—H}) = 0°$. For cyclopropyl methyl ketone bond lengths and angles were taken from the values (above) for carbonyl systems and from the previous study of vinylcyclopropane:[2] $r(\text{C=O}) = 1.22$ Å, $r(\text{C}_{\text{tri}}\text{—C}_{\Delta}) = 1.501$ Å, $r(\text{C}_{\Delta}\text{—C}_{\Delta}) = 1.54$ Å, $r(\text{C}_{\text{tri}}\text{—C}_{\text{tet}}) = 1.52$ Å, $r(\text{C}_{\text{tet}}\text{—H}) = 1.09$ Å, $r(\text{C}_{\Delta}\text{—H}) = 1.10$ Å, $\theta(\text{H—C}_{\Delta}\text{—H}) = 114°$.

Results and Discussion

Some preliminary comments are in order regarding INDOUV calculations performed on carbonyl systems. First, to facilitate consistent orbital descriptions, we have followed the usual convention regarding orientation of carbonyl molecules in a Cartesian coordinate system. The CO bond with appended atoms has been placed in the yz plane with the C–O bond axis colinear with the z axis. The orbital characterization employed throughout is essentially that previously adopted[1] with appropriate modifications for the carbonyl group. The conventions are as follows: (1) Any orbital whose composition is >50% of the pπ (2p$_x$) atomic orbitals will be classified as "π". (2) An orbital which consists chiefly (>50%) of the 2p$_y$ orbital of oxygen will be called "n". (3) An orbital composed primarily of the 2p$_z$ and 2s oxygen orbitals and secondarily of the 2p$_z$ and 2s orbitals of carbon is essentially the second nonbonding oxygen orbital with considerable CO single bonding. This orbital will be classified as "nσ". (4) An orbital involving predominantly C–C bonding will be called "σ_{CC}". (5) An orbital which is primarily C–H bonding in character will be called "σ_{CH}". (6) Orbitals arising from CC bonding within the cyclopropane ring will be classified as "Δ". Further distinctions among Δ orbitals will be described later.

It must be emphasized that INDOUV is only a valence-shell method. Transitions to Rydberg states cannot be reproduced. Valence states with considerable diffuse or Rydberg character will be poorly described. Furthermore, no attempt has been made to optimize excited-state geometries. Therefore, the excitation energies correspond to Franck–Condon or vertical transition energies among valence shell levels.

Formaldehyde. Formaldehyde is the parent species containing the C=O chromophore. As such, it is a logical starting point for studies involving more complex carbonyls. A recent review of experimental and theoretical results is provided by Moule and Walsh.[10] Due to the abundance of experimental data and theoretical computations, formaldehyde permits an important means of calibration for the INDOUV formalism (see Table I and Figure 1).

Table I. Vertical Transition Energies (eV) for Formaldehyde from Representative Calculations[a]

method	state symmetry/excitation type						
	A_2 (n → π^*)	B_1 (nσ → π^*)	A_1 (π → π^*)	A_1 (n → σ^*)	A_2 (σ_{CH} → π^*)	B_2 (nσ → σ^*)	B_2 (n → σ^*)
INDOUV[b]	2.84 [f = 0.000] (2.28)	4.69 [f = 0.005] (3.87)	8.09 [f = 0.287] (4.16)	10.70 [f = 0.347] (9.68)	11.40 [f = 0.000] (11.00)	11.92 [f = 0.005] (11.80)	12.30 [f = 0.174] (11.25)
DRS[c] INDO-CI	4.54	9.56		6.03		10.68	9.38
GPP[d] INDO-CI	4.69 (4.14)	9.22	11.76 (7.24)	10.29			
ALM[e]	4.10 (3.69)		8.17 (4.80)	8.16 (6.68)		7.28 (6.44)	
HST[f] INDO-RPA	4.55 (3.98)	8.93 (7.82)	11.59 (5.66)			10.32 (8.02)	
BP[g] GTF-CI[h]	3.43 (3.01)	8.61 (7.62)	11.72 (4.99)			10.44 (9.95)	
PBKH[i] GTF-CI[h,j]	3.81 (3.41)	9.03 (8.44)	11.41 (5.56)				
WH[k] GTF-CI[h,j]	3.80 (3.38)	9.35	11.31 [9.9][l] (5.66)				
YM[m] GTF-EOM[n]	4.04 (3.46)	9.19	10.10 (5.29)				
DS[o] GTF-SCF[p]	2.74 (2.37)	7.87 (6.97)	(4.24)			9.70 (9.21)	
LD[q] GTF-CI[r]	3.47 (3.13)	8.69 (7.78)	11.49 (5.39)				
GP[s] GTF-CI[t]	3.67 (3.29)	8.85 (7.66)	9.67, 10.43[u] (6.16)			7.15 (6.76)	8.15 (7.51)

[a] Energies and oscillator strengths transitions from ground state to excited singlet states. Transition energies to excited triplet states are given in parentheses. [b] This work. All (24) singly excited configurations. [c] Modified INDO with CI including all single excitations (see ref 18a). [d] Original INDO with CI including all single excitations (see ref 18d). [e] An all-valence-electron semiempirical method (see ref 13). [f] Random-phase approximation applied to INDO wave functions (see ref 18c). [g] Reference 15a. [h] Ab initio calculation using Gaussian functions and configuration interaction involving selected single and double configurations constructed from SCF MO's of the parent configuration of a given spin and spatial symmetry type. [i] Reference 15b. [j] Basis set includes diffuse Gaussian functions. [k] Reference 16a. [l] Reference 16b. [m] Reference 17d. [n] Equations of motion method with Gaussian basis including diffuse functions. [o] Reference 14a. [p] Single-configuration SCF using a Gaussian basis set including diffuse functions. [q] Reference 17b. [r] Ab initio calculation using a Gaussian basis set with diffuse functions and configuration interaction including singly excited configurations and an extrapolation procedure. [s] Reference 17a. [t] Ab initio calculation using a 4-31G basis set augmented with diffuse orbitals and a perturbative configuration interaction method. [u] The $\pi \rightarrow \pi^*$ state and n → 4p(b$_2$) Rydberg state are heavily mixed.

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[10] Moule, D. C.; Walsh, A. D. *Chem. Rev.* **1975**, *75*, 67.

Table II. Calculated Vertical Transition Energies (eV) for Acetaldehyde[a]

state symmetry/ excitation type	INDOUV[b]		DRS[c] INDO-CI		DRS[d] RCNDO-CI	
	ΔE	f	ΔE	f	ΔE	f
A″ ($n \rightarrow \pi^*$)	2.92 (2.41)	5.0×10^{-5}	4.51	0.00	3.53	0.00
A″ ($n\sigma \rightarrow \pi^*$)	4.78 (4.05)	0.005			6.71	0.00
A′ ($\pi \rightarrow \pi^*$)	7.76 (4.23)	0.287			7.28	0.02
A″ ($\sigma_{CH} \rightarrow \pi^*$)	9.29 (8.97)	0.001				
A′ ($n \rightarrow \sigma^*$)	9.97 (8.68)	0.419	6.16	0.20	5.39	0.12
			7.29[e]	0.06		
			8.93[e]	0.02		

[a] Energies and oscillator strengths are for transitions from the ground state to excited singlet states. Transition energies to excited triplet states are given in parentheses. [b] This work; all (63) singly excited configurations. [c] Modified INDO with CI *including all single excitations* (see ref 18a). [d] Modified CNDO with diffuse (Rydberg) orbitals and CI including all single excitations (see ref 18a). [e] Additional $n \rightarrow \sigma^*$ transitions.

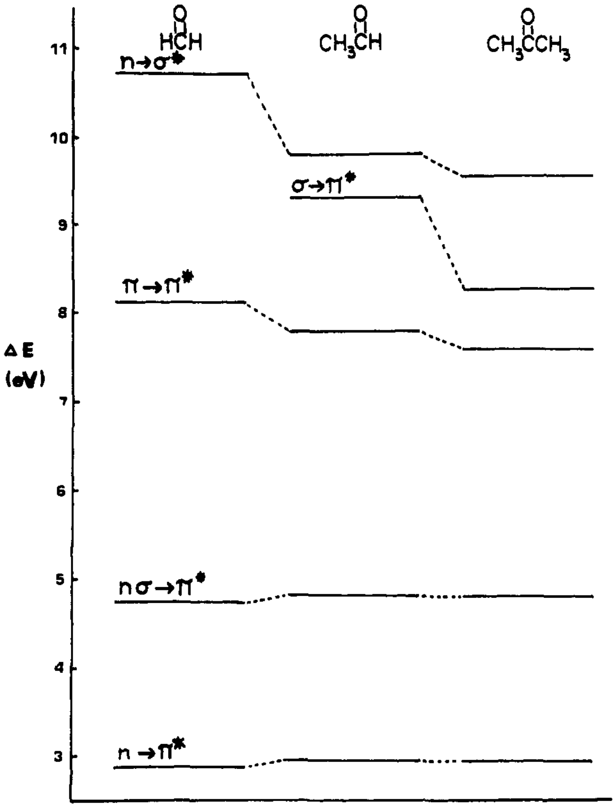

Figure 1. Low-lying excited states of formaldehyde, acetaldehyde, and acetone.

The $^1A_2$ ($n \rightarrow \pi^*$) transition has been studied most extensively since Henri and Schou[11a,b] first recorded the band in the 3530–2300-Å (3.5–5.4 eV) region. (Other experimental work on this system is found in ref 11 and 12; theoretical studies appear in ref 13–19). Although this $n \rightarrow \pi^*$ transition is formally symmetry forbidden, it becomes weakly allowed by vibronic interaction from b_1 out-of-plane motion of C=O. However, a recent study[11i] suggests that intensification of the band is promoted more strongly by the asymmetric CH stretch. An $^3A_2$ ($n \rightarrow \pi^*$) band is also visible at $\Delta\epsilon_{max}$ = 3.6 eV on the leading edge of the singlet absorption in both ultraviolet[11d–f] and electron-impact[12] studies. INDOUV values (2.84 and 2.28 eV, respectively) are too low although the singlet–triplet separation (0.56 eV) is within 0.1 eV of the experimental splitting. Low predictions for the $n \rightarrow \pi^*$ state relative to the ground state are not uncommon problems in both semiempirical[13] and ab initio[14–16] treatments. Buenker and Peyerimhoff[15] and Whitten and Hackmeyer[16a] have found that this difficulty can be partially overcome by addition of Rydberg-like orbitals.

A third low-lying state assigned as $^3A_1$ ($\pi \rightarrow \pi^*$) has been identified at 5.6–6.2 eV in the electron-impact spectrum of Chutjian.[12] INDOUV places the $^3A_1$ state in this vicinity. A perusal of Table I shows that a representative sampling of ab initio[14–17] and semiempirical[13,18] predictions for this state are generally 4.0–6.1 eV.

The 7–9-eV region was originally thought to contain the $^1B_2$ ($n \rightarrow \sigma^*$) transition primarily at the impetus of semiempirical computations.[13,18a,b,g,h] It is now generally accepted that this portion of the spectrum is the origin of several Rydberg series: $^1B_2$ ($n \rightarrow 3s$) at 7.09 eV (with quantum defect δ = 1.11), $^1A_1$ ($n \rightarrow 3p_z$) at 7.97 eV (δ = 0.83), $^1B_2$ ($n \rightarrow 3p_y$) at 8.14 eV (δ = 0.74), $^1B_2$ ($n \rightarrow 3d\sigma$) at 8.88 eV (δ = 0.39), and $^1B_2$ ($n \rightarrow 3d\delta$) at 9.03 eV (δ = 0.29). Assignment from vacuum ultraviolet absorption spectra[10,20] and electron-impact spectra[12,21] are confirmed by ab initio calculations including Rydberg orbitals.[15b,16a,17a,b,d] As to the whereabouts of the symmetry-allowed $^1B_2$ ($n \rightarrow \sigma^*$) band, there remains no convincing evidence. INDOUV places $n \rightarrow \sigma^*$ states in the region 10.7–14.4 eV above the ground state. This is in accord with

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(11) (a) Henri, V.; Schou, S. A. *Z. Phys.* **1928**, *49*, 774. (b) Schou, S. A. *J. Chim. Phys.* **1929**, *26*, 665. (c) Dieke, G. H.; Kistiakowsky, G. B. *Phys. Rev.* **1934**, *45*, 4. (d) Brand, J. C. D. *J. Chem. Soc.* **1956**, 858. (e) Cohen, A. D.; Reid, C. *J. Chem. Phys.* **1956**, *24*, 85; *J. Chem. Soc.* **1957**, 2386. (f) Robinson, G. W. *Can. J. Phys.* **1956**, *34*, 699. (g) Yeung, E. S.; Moore, C. B. *J. Am. Chem. Soc.* **1971**, *93*, 2059. (h) Sidman, J. W. *J. Chem. Phys.* **1958**, *29*, 644. (i) Miller, R. G.; Lee, E. K. C. *Chem. Phys. Lett.* **1975**, *33*, 104.

(12) Chutjian, A. *J. Chem. Phys.* **1974**, *61*, 4279.

(13) Absar, I.; Lin, C. S.; McEwen, K. L. *Can. J. Chem.* **1972**, *50*, 646.

(14) (a) Dykstra, C. E.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1976**, *98*, 401. (b) Dykstra, C. E. *Ibid.* **1976**, *98*, 7182.

(15) (a) Buenker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1970**, *53*, 1368. (b) Peyerimhoff, S. D.; Buenker, R. J.; Kammer, W. E.; Hsu, H. *Chem. Phys. Lett.* **1971**, *8*, 129.

(16) (a) Whitten, J. L.; Hackmeyer, M. *J. Chem. Phys.* 1969, *51*, 5584. (b) Whitten, J. L. *Ibid.* **1972**, *56*, 5458.

(17) (a) Gouyet, J. F.; Prat, M. T. *J. Chem. Phys.* **1976**, *64*, 946. (b) Langhoff, S. R.; Davidson, E. R. *Ibid.* **1976**, *64*, 4699. (c) Dunning, T. H., Jr.; McKoy, V. *Ibid.* **1968** *48*, 5263. (d) Yeager, D. L.; McKoy, V. *Ibid.* **1974**, *60*, 2714. (e) Ditchfield, R.; Del Bene, J. E.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 703. (f) Langhoff, S. R.; Elbert, S. T.; Jackels, C. F.; Davidson, E. R. *Chem. Phys. Lett.* **1974**, *29*, 247.

(18) (a) Salahub, D. R. *Theor. Chim. Acta* **1971**, *22*, 330. (b) Ellis, R. L; Squire, R.; Jaffé, H. H. *J. Chem. Phys.* **1971**, *55*, 3500. (c) Ho, J. C.; Segal, G. A.; Taylor, H. S. *J. Chem. Phys.* **1972**, *56*, 1520. (d) Giessner-Prettre, C.; Pullman, A. *Theor. Chim. Acta* **1969**, *13*, 265. (e) Del Bene, J.; Jaffé, H. H. *J. Chem. Phys.* **1969**, *50*, 1126. (f) Davies, D. W.; Elvin, R. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 727. (g) Sidman, J. W. *Chem. Rev.* **1958**, *58*, 689. (h) Pople, J. A.; Sidman, J. W. *J. Chem. Phys.* **1957**, *27*, 1270. (i) Allinger, N. L.; Stuart, T. W.; Tai, J. C. *J. Am. Chem. Soc.* **1968**, *90*, 2809.

(19) The effects of solvation upon $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions has been studied by: Cremaschi, P.; Gamba, A.; Simonetta, M. *Theor. Chim. Acta* **1973**, *31*, 155.

(20) (a) Mentall, J. E.; Gentieu, E. P.; Krauss, M.; Neumann, D. *J. Chem. Phys.* **1971**, *55*, 5471. (b) Fleming, G.; Anderson, M. M.; Harrison, A. J.; Pickett, L. W. *Ibid.* **1959**, *30*, 351. (c) Allison, K.; Walsh, A. D. Chemical Institute of Canada Symposium, Ottawa, 1957.

(21) Weiss, M. J.; Kuyatt, C. E.; Mielczarek, S. *J. Chem. Phys.* **1971**, *54*, 4147.

ab initio calculations[14-16,17b-d] and semiempirical calculations of Ho, Segal, and Taylor[18c] and Giessner-Prettre and Pullman,[18d] which place this state consistently higher in energy (10.4–11.0 eV).[22]

The absence of the ${}^1A_1$ ($\pi \rightarrow \pi^*$) excitation remains a mystery. One explanation is that the dissociative nature of the ${}^1A_1$ ($\pi \rightarrow \pi^*$) state precludes its being observed.[15a] Whitten[16b] has suggested absorption takes place to a continuum, thus explaining the intense absorptions in the 8–11-eV region. Mentall et al.[20a] and Langhoff and Davidson[17b] offer the explanation that the ${}^1A_1$ state is autoionized into a limiting continuum of the Rydberg series. In addition, Whitten,[16b] Yeager and McKoy,[17d] and Mentall et al.[20a] propose extensive Rydberg–valence mixing of the ${}^1A_1$ ($\pi \rightarrow \pi^*$) state with the n $\rightarrow$ 3p and n $\rightarrow$ 3d Rydberg series. The evidence of perturbations in the Rydberg series in the inelastic electron-scattering spectrum of Weiss et al.[21] would tend to confirm this hypothesis. Our value of 8.09 eV is a reasonable valence-shell estimate of the excitation energy to the ${}^1A_1$ ($\pi \rightarrow \pi^*$) state although the exact location cannot be properly determined without inclusion of diffuse orbitals. Ab initio calculations uniformly place this state too high in energy (10–13 eV) due to the difficulty in deriving a starting basis set for this second ${}^1A_1$ state.[14-17] Careful treatment of the configuration interaction with inclusion of $\sigma \rightarrow \sigma^*$ configurations produces a transition energy of 9.9 eV.[16b,23] Semiempirical treatments,[13,18,19] like INDOUV, place the ${}^1A_1$ ($\pi \rightarrow \pi^*$) state uniformly lower in energy (7.7–9.3 eV) than the ab initio calculations.

Acetaldehyde. In acetaldehyde the basic carbonyl chromophore is augmented with an alkyl substituent. Unfortunately there is a scarcity of experimental and theoretical studies available for comparison. INDOUV results appear in Table II and Figure 1.

The ${}^1A''$ (n $\rightarrow$ π^*) band was first recorded by Henri and Schou.[11a] More recent studies[24,25a] place the 0–0 transition at 3.87 eV (and 3.56 eV[24c]) with maximum intensity at 4.28 eV. The later value is to be compared with our vertical excitation energy of 2.92 eV. In addition, a phosphorescence band was discovered with a maximum at 2.38 eV.[24c] In contrast to the ${}^1A_2$ (n $\rightarrow$ π^*) excitation of formaldehyde, the ${}^1A''$ transition has an allowed component which must be polarized out of the skeletal plane. However, polarization studies by Chandler and Goodman[24c] led to the conclusion that the transition is in-plane polarized and hence is largely forbidden. The proposed mechanism for intensification of this band was via configuration mixing from the n $\rightarrow$ σ^* configurations. These configurations have substantial in-plane transition moment components both parallel and perpendicular to the C=O axis. Examination of our CI coefficient matrix corroborates the importance of n $\rightarrow$ σ^* configurations in the total ${}^1A''$ (n $\rightarrow$ π^*) state function. Although INDOUV places this band 1.4 eV below its experimental appearance, the observed hypsochromic shift from formaldehyde to acetaldehyde upon methyl substitution is reproduced by our calculations.

Table III. Calculated Vertical Transition Energies (eV) for Acetone[a]

state symmetry/ excitation type	INDOUV[b]		HBBP[c] GTF-CI[d]	
	ΔE	f	ΔE	f
A_2 (n $\rightarrow$ π^*)	2.92 (2.45)	0.000	4.41 (4.04)	0.000
B_1 (nσ $\rightarrow$ π^*)	4.78 (4.11)	0.001		
A_1 ($\pi \rightarrow \pi^*$)	7.58 (4.24)	0.255	11.30 (5.73)	0.41
A_2 ($\sigma_{CH} \rightarrow \pi^*$)	8.27 (7.99)	0.000		
A_1 (n $\rightarrow$ σ^*)	9.53 (8.11)	0.450		
B_2 (n $\rightarrow$ σ^*)	10.09 (9.58)	0.057		
B_1 ($\sigma_{CH_3} \rightarrow \pi^*$)			9.91 (9.90)	

[a] Energies and oscillator strengths are for transitions from the ground state to excited singlet states. Transition energies to excited triplet states are given in parentheses. [b] This work; 100 singly excited configurations. [c] Reference 26. [d] Ab initio computation using Gaussian functions (with diffuse orbitals) and configuration interaction involving selected single and double configurations constructed from the SCF MO's of the parent configuration of a given spin and spatial symmetry type.

The band system at 6.82 eV has been identified as the beginning of the n $\rightarrow$ ns Rydberg series.[25] However, strong evidence persists for an underlying transition. The assignment of this band to the n $\rightarrow$ σ^* transition by Walsh[25b] is supported by the experimental evidence of Lucazeau and Sandorfy[25a] and the semiempirical calculations of Salahub.[18a] However, this underlying band is about 100 times weaker than would be expected for an allowed n $\rightarrow$ σ^* transition.[25a] In addition, semiempirical calculations of spectral properties based upon the original INDO or CNDO specifications must be used with extreme caution. As the calculations of Salahub[18a] point out, INDO-CI and CNDO-CI calculations have a tendency to place several $\sigma \rightarrow \pi$ and n $\rightarrow$ σ^* states below the $\pi \rightarrow \pi^*$ states of ethylene, formaldehyde, and acetaldehyde. Hence, the prediction of a low-energy n $\rightarrow$ σ^* state is probably not reliable. Unlike other semiempirical calculations, INDOUV places the first n $\rightarrow$ σ^* excitation at 9.97 eV, mimicing ab initio calculations on formaldehyde[14-17] and acetone.[26] Like Barnes and Simpson[25d] and Ogata et al.,[25c] we would assign the underlying band in the vicinity of 6.8 eV to the nσ $\rightarrow$ π^* transition on the basis of the INDOUV state ordering. It should be noted that the nσ $\rightarrow$ π^* state arises from promotion from an orbital which is as much σ_{CO} as it is n(p_z) in character. This means that arguments of Lucazeau and Sandorfy[25a] regarding sensitivity to fluorine substitution may also be used to support an nσ $\rightarrow$ π^* assignment for this underlying band. It should be also noted that nσ $\rightarrow$ π^* meets the requirement of polarization perpendicular to the C=O axis.[25e]

There seems to be little controversy regarding assignment of the spectral ranges 7.38–8.06 and 8.06–8.80 eV to the n $\rightarrow$ np and n $\rightarrow$ nd Rydberg series. However, the effects of fluorine and alkyl substitution lead to the conclusion that other valence bands underlie these Rydberg series. We would assign the low-frequency band as $\pi \rightarrow \pi^*$ and the other as n $\rightarrow$ σ^* on the basis of state orderings and relative oscillatory strengths. However, Lucazeau and Sandorfy[25a] present persuasive experimental evidence that the reverse is true. Above 8.8 eV, higher members of Rydberg series are found, in addition to higher intervalence transitions.

Acetone. Like other carbonyls, the lowest energy band of acetone is unambigously assigned as A_2 (n $\rightarrow$ π^*). Both singlet (4.42, 4.50 eV) and triplet (4.16 eV) transitions have

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(22) For an exception, see ref 17a.

(23) Yeager and McKoy[17d] obtained an excitation energy of 9.9 eV when diffuse s and p orbitals were used. An energy of 9.66 eV was obtained when diffuse d orbitals were included.

(24) (a) Rao, V. R.; Rao, I. A. *Indian J. Phys.* **1954**, *28*, 491. (b) Worden, E. F. *Spectrochim. Acta* **1966**, *22*, 21. (c) Chandler, W. D.; Goodman, L. *J. Mol. Spectrosc.* **1971**, *37*, 33. (d) Hanson, D. A.; Lee, E. K. C. *J. Chem. Phys.* **1975**, *63*, 3272.

(25) (a) Lucazeau, G.; Sandorfy, C. *J. Mol. Spectrosc.* **1970**, *35*, 214. (b) Walsh, A. D. *Proc. R. Soc. London, Ser. A* **1945**, *185*, 176. (c) Ogata, H.; Kitayama, J.; Koto, M.; Kojima, M.; Nihei, Y.; Kamada, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 958. (d) Barnes, E. E.; Simpson, W. T. *J. Chem. Phys.* **1963**, *39*, 670. (e) Johnson, W. C., Jr.; Simpson, W. T. *Ibid.* **1968**, *48*, 2168.

(26) Hess, B.; Bruna, P. J.; Buenker, R. J.; Peyerimhoff, S. D. *Chem. Phys.* **1976**, *18*, 267.

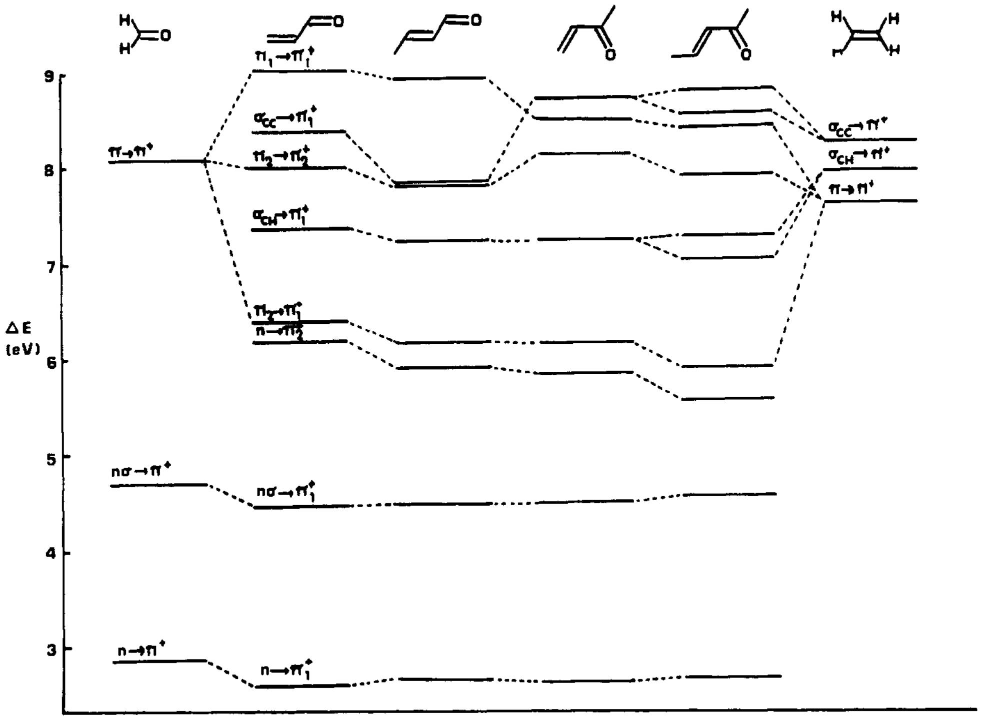

Figure 2. Low-lying excited states of α,β-unsaturated carbonyl systems.

been investigated in detail by ultraviolet absorption[24b,27] and electron-impact spectroscopy.[28] Both states, like those in formaldehyde, have a pyramidal C(CO)C skeleton (C_s symmetry). This has been confirmed for the singlet by comparison of vibrational progressions in acetone and acetone-d_6.[27c] Phosphorescent emission from the triplet is negatively polarized, requiring that the transition remain forbidden or that it becomes allowed in C_s symmetry.[27b] Chandler and Goodman[27b] propose a 25° distortion of C=O from the CCC plane. The b_2 out-of-plane vibration is responsible for intensification of the emission. Although we again show the singlet and triplet at lower energies than those in the experiment, INDOUV correctly predicts these states as the lowest energy excited states (Table III and Figure 1). The ab initio calculations of Hess et al.,[26] using Gaussian lobe functions augmented with diffuse orbitals and CI over selected single and double excitations, predict these states at 4.04 and 4.14 eV, respectively.

A second low-lying triplet appears at 5.88 eV in the low-energy electron-impact spectrum of St. John et al.[28b] A $^3A_1$ ($\pi \rightarrow \pi^*$) assignment is consistent with the ab initio work of Hess et al.,[26] who find a second triplet at 5.73 eV, and with INDOUV results (4.24 eV).

The first allowed singlet absorption at 6.35 eV was originally thought to be the n → σ^* transition.[28a,29] The current assignment of this band to the origin of the $^1B_2$ (n → 3s) Rydberg series is widely accepted.[25c,28c,30] This characterization is in complete accord with the ab initio computations of Hess et al.[26] Nevertheless, studies of the effects of pressure on this band by Robin and Kuebler[30b] show significant valence character, suggesting an underlying band. Scott and Russell[30a] and Johnson and Simpson[25e] believe this to be an n → σ^* transition. Johnson and Simpson[25e] performed randomization studies on the spectrum of crystalline and liquid 9-heptadecanone and found that this band must be polarized perpendicular to the C=O axis. According to an assumed crystal structure, y polarization was assigned. In view of the unknown crystal structure, x polarization cannot be excluded. If the underlying band is x polarized, the $^1B_1$ ($n\sigma \rightarrow \pi^*$) transition becomes a likely candidate. Both INDOUV and ab initio[26] results show the $^1B_1$ ($n\sigma \rightarrow \pi^*$) state as the only intervalence state between the $^1A_2$, $^3A_2$, and $^3A_1$ states and the $^1A_1$ ($\pi \rightarrow \pi^*$) state.

The weak system beginning at 7.4 eV in optical[25c,29c] and electron-impact[28b,c] spectra has also been attributed to the n → σ^* transition.[25c] Huebner et al.,[28c] however, identify this as an n → 3p Rydberg system with a quantum defect δ of 0.81. The ab initio results of Hess et al.[26] indicated two n → 3p Rydberg series beginning at 7.17 and 7.32 eV. Another Rydberg series (n → 3dσ) with a quantum defect of 0.315 begins at 7.84 eV.[28c] Hess et al.[26] found this state at 7.91 eV.

No definitive assignment has been made for the $^1A_1$ ($\pi \rightarrow \pi^*$) state. However, the Rydberg bands from 7.1 to 8.5 eV appear to be superimposed upon a very intense absorption. Hess et al.[26] and Huebner et al.[28c] suggested that the $^1A_1$ ($\pi \rightarrow \pi^*$) state is dissociative and that its continuum contributes to the underlying intensity in this region. It is conceivable that this state is stabilized in heptane solution and, hence, is nondissociative. The result may be the significantly red-shifted band at 6.66 eV.[31] Our calculations predict the appearance of this transition at 7.58 eV precisely in the midst of the enhanced background intensity attributed to the $^1A_1$ ($\pi \rightarrow \pi^*$) transition in the vapor-phase spectrum.

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(27) (a) Noyes, W. A., Jr.; Duncan, A. B. F.; Manning, W. M. *J. Chem. Phys.* **1934**, *2*, 717. (b) Chandler, W. D.; Goodman, L. *J. Mol. Spectrosc.* **1970**, *36*, 141. (c) Rao, C. N. R.; Chatuvedi, G. C.; Randhawa, H. S. *Chem. Phys. Lett.* **1970**, *7*, 563.

(28) (a) Silverman, S. M.; Lassettre, E. N. *J. Chem. Phys.* **1965**, *43*, 194. (b) St. John, W. M., III; Estler, R. C.; Doering, J. P. *Ibid.* **1974**, *61*, 763. (c) Huebner, R. H.; Celotta, R. J.; Mielczarek, S. R. Kuyatt, C. E. *Ibid.* **1973**, *59*, 5434.

(29) (a) Holdsworth, R. S.; Duncan, A. B. F. *Chem. Rev.* **1941**, *41*, 331. (b) McMurray, H. L. *J. Chem. Phys.* **1941**, *9*, 231, 241. (c) Ito, H.; Nogata, Y.; Matsuzaki, S.; Kuboyama, A. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2453.

(30) (a) Scott, J. D.; Russell, B. R. *J. Chem. Phys.* **1975**, *63*, 3243. (b) Robin, M. B.; Kuebler, N. A. *J. Mol. Spectrosc.* **1970**, *33*, 274. (c) Brundle, C. R.; Robin, M. B.; Kuebler, N. A.; Basch, H. *J. Am. Chem. Soc.* **1972**, *94*, 1451.

(31) Yates, K.; Klemenko, S. L.; Csizmadia, I. G. *Spectrochim. Acta, Part A* **1969**, *25A*, 765.

Table IV. Vertical Excitation Energies (eV) for Acrolein from Representative Calculations[a,b]

state symmetry/ excitation type	INDOUV[c]		BT[d] CNDO/ S-CI[e]	JL[f] PPP- $(\pi + \sigma)$- CI[g]	KI[h]/IB[i] PPP,[j]	CED,[k] GTF,[l]	IM[n] GTF-EHP,[o]
	ΔE	f	ΔE	ΔE	ΔE	ΔE	ΔE
$\mathrm{A}'' (n \rightarrow \pi_1^*)$	2.59 (2.10)	6.0×10^{-5}	3.21	3.71	3.85 (2.85),[h] 3.29 (2.77)[i]	2.77 (2.45)	4.53 (3.77)
$\mathrm{A}'' (n\sigma \rightarrow \pi_1^*)$	4.46 (3.75)	0.002					
$\mathrm{A}'' (n \rightarrow \pi_2^*)$	6.19 (5.95)	0.002	8.20	6.69	6.53 (6.00)[h]		
$\mathrm{A}' (\pi_2 \rightarrow \pi_1^*)$	6.39 (3.19)	0.763	6.49	6.18	6.08 (4.17),[h] 5.96 (2.94)[i]	3.52[m] (3.40)	7.86 (3.40)
$\mathrm{A}'' (\sigma_{\mathrm{CH}} \rightarrow \pi_1^*)$	7.36 (7.04)	5.0×10^{-4}	8.36				
$\mathrm{A}' (\pi_2 \rightarrow \pi_2^*)$	7.98 (4.75)	0.011	8.02	8.59	7.76 (5.85)[h]		

[a] Energies and oscillator strengths are for transitions from the ground state to excited singlet states. Transition energies to excited triplet states are given in parentheses. [b] Additional semiempirical results can be found in ref 36b. [c] This work; 100 singly excited configurations. [d] Reference 36b. [e] Modified CNDO/S method with CI including the 30 lowest singly excited states. [f] Reference 36f. [g] Extended Pariser–Parr–Pople method including π and σ oribtals and configuration interaction. [h] References 32a and 36a. [i] Reference 36j. [j] Modified Pariser–Parr–Pople method. [k] Reference 14b. [l] Ab initio calculation with a double ζ basis set of Gaussian functions. [m] Not a true excited $\pi \rightarrow \pi^*$ state. Davidson and Nitzsche[39] place this state at 7.52 eV. [n] Reference 37d. [o] Ab initio calculation with corrections using the electron-hole-potential method (EHP) with an STO-3G basis set augmented with diffuse p functions.

Acrolein. Acrolein is the prototype for conjugated carbonyl molecules, which explains, in part, the extensive attention given to this species. Although most studies have focused on *trans*-acrolein, the spectral features of *cis*-acrolein have been identified by a number of workers.[32] For simplicity, we have directed attention only to the trans conformation. Computational results are tabulated in Table IV and are displayed in Figure 2.

Like simple carbonyl species, the experimental spectrum displays an $\mathrm{A}'' (n \rightarrow \pi^*)$ system at 3.0–3.9 eV, which has been well studied at high resolution.[32-35] In addition to the singlet A″ transition with the 0–0 band at 3.21 eV, Brand and Williamson[33] identified a triplet with the 0–0 band at 3.01 eV. (The 0–0 bands for both singlet and triplet are the most intense bands of the system and, hence, correspond to the vertical transitions.) Analysis of band contours from the rotational fine structure by Alves et al.[32d] and Bair et al.[32b] provided confirmation of the identity of the 3.01-eV band. Since the $n \rightarrow \pi^*$ transition is polarized perpendicular to the molecular plane, the relative absence of out-of-plane bends strongly implicates planar or near-planar singlet and triplet excited states.[35]

All theoretical calculations,[14b,32a,35c,36,37] including INDOUV, indisputably find the $\mathrm{A}'' (n \rightarrow \pi^*)$ states (singlet and triplet) as the lowest excited states of acrolein. The low calculated transition energies for singlet and triplet $n \rightarrow \pi^*$ excitations is again apparent.

In addition to the $^3\mathrm{A}'' (n \rightarrow \pi^*)$ state, optical absorption measurements show another low-lying triplet at 3.05 eV which has been assigned as the $^3\mathrm{A}' (\pi \rightarrow \pi^*)$ state.[38] INDOUV calculations place this state at 3.19 eV near to the experimental value. Other calculations point to the close proximity of the $^3\mathrm{A}'' (n \rightarrow \pi^*)$ and $^3\mathrm{A}' (\pi \rightarrow \pi^*)$ states.[14b,36e,37] Devaquet and Salem[37b,c] have performed extensive CI calculations on potential energy surfaces pointing to the extensive mixing and indistinguishability of these two states at many points on the energy surface. Dykstra[14b] and Lucchese et al.[37a] suggested that the mixing leads to many avoided crossings of the two states. Interestingly, Iwata and Morokuma[37d] found the $^3\mathrm{A}' (\pi \rightarrow \pi^*)$ state at lower energy than the $^3\mathrm{A}'' (n \rightarrow \pi^*)$ state.

The band system centered at 5.96 eV is attributed firmly to the $^1\mathrm{A}' (\pi \rightarrow \pi^*)$ transition. The INDOUV transition energy is within 0.4 eV of the measured value. Several other semiempirical calculations place this transition in this vicinity.[32a,36b,f,g,i] Dykstra[14b] calculated the $^1\mathrm{A}' (\pi \rightarrow \pi^*)$ state at 3.52 eV which, like the triplet, he claimed to be extensively biradical in character. However, more recently, Davidson and Nitzsche[39] have criticized this result and have recalculated this state at 7.52 eV using a nonorthogonal SCF procedure including configuration interaction. Iwata and Morokuma,[37d] using an STO-3G basis set plus diffuse p orbitals in a two-configuration MCSCF procedure, calculated this state at 7.86 eV. These calculations also correctly predicted the red shift for the $^1\mathrm{A}' (\pi \rightarrow \pi^*)$ transition and the blue shift for the $^1\mathrm{A}'' (n \rightarrow \pi^*)$ transition for acrolein in water.

In addition to the Rydberg bands between 7.1 and 7.9 eV, Walsh[40] has identified a second $n \rightarrow \pi^*$ transition at 8.38 eV. This probably corresponds to the $^1\mathrm{A}'' (n \rightarrow \pi_2^*)$ excitation which we find at 6.19 eV from INDOUV results. In fact, a third, unverified $n \rightarrow \pi^*$ state, classified specifically as $^1\mathrm{A}'' (n\sigma \rightarrow \pi_2^*)$, is predicted at 4.46 eV. An unassigned band at 8.49 eV is possibly another $\pi \rightarrow \pi^*$ excitation. This is consistent with our calculations which place $^1\mathrm{A}' (\pi_2 \rightarrow \pi_2^*)$ at 7.98 eV. Other semiempirical computations also produce this state in the 6.8–8.8-eV region.[36b–d,f–h]

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(32) (a) Inuzuka, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2649. (b) Bair, E. J.; Goetz, W.; Ramsay, D. A. *Can. J. Phys.* **1971**, *49*, 2710. (c) Osborne, G. A.; Ramsay, D. A. *Ibid.* **1973**, *51*, 1170. (d) Alves, A. C. P.; Christoffersen, J.; Hollas, J. M. *Mol. Phys.* **1971**, *20*, 625; **1971**, *21*, 384. (e) Becker, R. S.; Inuzuka, K.; King, J. *J. Chem. Phys.* **1970**, *52*, 5164.

(33) Brand, J. C. D.; Williamson, D. G. *Discuss. Faraday Soc.* **1963**, *35*, 184.

(34) Inozuka, K. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 678; **1961**, *34*, 729.

(35) (a) Birge, R. R.; Pringle, W. C.; Leermakers, P. A. *J. Am. Chem. Soc.* **1971**, *93*, 6715. (b) Birge, R. R.; Leermakers, P. A. *Ibid.* **1971**, *93*, 6726. (c) Birge, R. R.; Leermakers, P. A. *Ibid.* **1972**, *94*, 8105.

(36) (a) Inuzuka, K. *Bull Chem. Soc. Jpn.* **1961**, *34*, 6. (b) Tinland, B. *Mol. Phys.* **1969**, *16*, 413. (c) Edwards, T. G.; Grinter, R. *Theor. Chim. Acta* **1968**, *12*, 387. (d) Edwards, T. G.; Grinter, R. *Mol. Phys.* **1968**, *15*, 357. (e) Kato, H.; Konishi, H.; Yamabe, H.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2761. (f) Jungen, M.; Labhart, H. *Theor. Chim. Acta* **1968**, *9*, 345. (g) Nagakura, S. *Mol. Phys.* **1960**, *3*, 105. (h) Ainbinder, B. Y.; Krivnov, I. Y., *Teor. Eksp. Khim.* **1965**, *1*, 707. (i) Hammond, H. A. *Theor. Chim. Acta* **1970**, *18*, 239. (j) Inuzuka, K.; Becker, R. S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1557.

(37) (a) Lucchese, R. R.; Schaefer, H. F., III; Dykstra, C. E. *Chem. Phys. Lett.* **1977**, *51*, 600. (b) Devaquet, A.; Salem, L. *Can. J. Chem.* **1971**, *49*, 977. (c) Devaquet, A. *J. Am. Chem. Soc.* **1972**, *94*, 5160. (d) Iwata, S.; Morokuma, K. *Ibid.* **1975**, *97*, 966.

(38) Hollas, J. M. *Spectrochim. Acta* **1963**, *19*, 1425.

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

(40) Walsh, A. D. *Trans. Faraday Soc.* **1945**, *41*, 498.

Table V. INDOUV Vertical Excitation Energies (eV) for Alkyl-Substituted α,β-Unsaturated Carbonyls[a]

state symmetry/ excitation type	*trans*-crotonaldehyde (*trans*-2-butenal)		methyl vinyl ketone (3-buten-2-one)		3-penten-2-one	
	ΔE	f	ΔE	f	ΔE	f
A″ ($n \rightarrow \pi_1^*$)	2.63 (2.14)	2.0×10^{-5}	2.61 (2.17)	4.0×10^{-7}	2.66 (2.23)	3.0×10^{-6}
A″ ($n\sigma \rightarrow \pi_1^*$)	4.48 (3.79)	0.003	4.48 (3.84)	0.001	4.53 (3.92)	0.001
A″ ($n \rightarrow \pi_2^*$)	5.90 (5.63)	4.0×10^{-4}	5.83 (5.61)	0.002	5.64 (5.40)	7.0×10^{-5}
A′ ($\pi_2 \rightarrow \pi_1^*$)	6.16 (3.09)	0.862	6.15 (3.27)	0.337	5.90 (3.29)	0.444
A″ ($\sigma_{CC,CH} \rightarrow \pi_1^*$)	7.24 (6.95)	9.0×10^{-6}	7.25 (6.98)	1.0×10^{-4}	7.04 (6.85)	0.002
A′ ($\pi_2 \rightarrow \pi_2^*$)	7.81 (4.66)	0.008	8.15 (4.71)	0.260	7.91 (4.88)	0.220

[a] Energies and oscillator strengths are for transitions from the ground state to excited singlet states. Transition energies to excited triplet states are given in parentheses.

***trans*-Crotonaldehyde, Methyl Vinyl Ketone, and 3-Penten-2-one.** The effects of alkyl substituents upon the excited-state manifold is important since it measures the degree to which the method of calculation properly handles states involving σ and σ^* configurations. Placement of these states is significant, but more critical is the proper treatment of interactions with low-lying $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states through configuration mixing. The previous study[1] demonstrated that INDOUV predicts the effect of methyl substitution to the C=C double bond, consistent with the observed experimental trends embodied in Woodward's rules.[41] Namely, alkyl substituents produce lower $\pi \rightarrow \pi^*$ transition energies. However, several unverified $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ states were placed too low in energy.

In carbonyl systems, alkyl substitution produces a well-known blue shift in $n \rightarrow \pi^*$ bands. Sidman[18g] and Birge and Leermakers[35b] attributed this effect to electron donation, resulting in increased electron density at oxygen, which raises the $n \rightarrow \pi^*$ state. Semiempirical[42] and ab initio[43] interpretations have indicated that electron reorganization occurs through the hyperconjugative π system rather than by inductive effects through the σ system. From our carbonyl study (Table V and Figure 2), INDOUV reproduces the hypsochromic shift upon methyl substitution for both singlet and triplet A″ ($n \rightarrow \pi^*$) bands.[34,35a,c] The INDOUV formalism is also sensitive to the location of the methyl substituent. The qualitative relative order of experimental transition energies (acrolein < methyl vinyl ketone < crotonaldehyde < 3-penten-2-one) is predicted exactly.[35a,c]

For the $\pi \rightarrow \pi^*$ transition a red shift is well established (Woodward's rules[44]). Again, INDOUV calculations reproduce this trend, including proper sensitivity to the substitution pattern, i.e., transition energies are predicted in the order acrolein > crotonaldehyde $\gtrsim$ methyl vinyl ketone > 3-penten-2-one.[45,46]

From investigation of alkyl-substituted α,β-unsaturated carbonyls, we conclude that alkyl perturbations are correctly treated in terms of effects upon observed low-lying states. As to the presence of unreasonably low $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ states, this problem does not seem to surface in the case of the carbonyls. Only one $\sigma \rightarrow \pi^*$ state appears below 8 eV in the INDOUV results. In contrast to the close proximity of the important $\sigma_{CH} \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states in substituted ethylenes, the corresponding states in carbonyl species are separated by 0.7–1.5 eV. Nevertheless, the problems in substituted ethylenes are apparently replaced by $n \rightarrow \pi^*$ states situated too low in the state manifold.

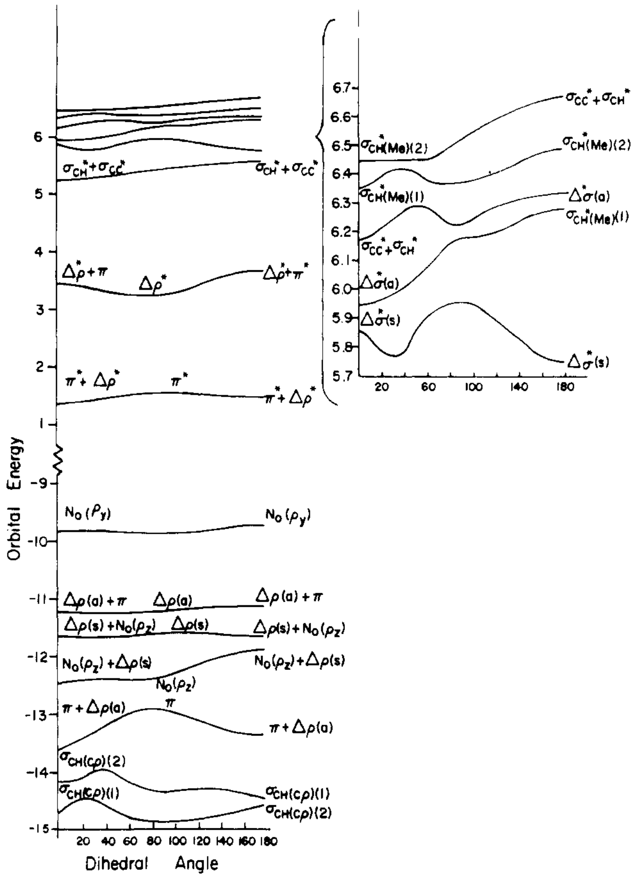

Figure 3. Molecular orbital energies of cyclopropyl methyl ketone as a function of the dihedral angle θ.

Methyl Cyclopropyl Ketone. The effect of the coupling interaction between cyclopropane rings and adjacent π systems is a well-documented phenomenon.[47,48] In this study we focused not only on the most stable conformation but also on the consequences of rotation about the CC bond joining the cyclopropyl ring to the carbonyl group. The predicted effects upon the orbital and state manifolds are presented in Tables VI and VII and in Figures 3 and 4. Several experimental studies allude to conformation dependence of the ultraviolet spectra of cyclopropyl carbonyl species.[49] Here this system is viewed in particular

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(41) (a) Woodward, R. B. *J. Am. Chem. Soc.* **1942**, *64*, 72. (b) Fieser, L. F.; Fieser, M. "Steroids"; Reinhold: New York, 1959; p 15.

(42) (a) Pople, J. A.; Gordon, M. *J. Am. Chem. Soc.* **1967**, *89*, 4253. (b) Hehre, W. J.; Pople, J. A. *Ibid.* **1970**, *92*, 2191.

(43) Newton, M. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1967**, *89*, 4261.

(44) Woodward, R. B. *J. Am. Chem. Soc.* **1941**, *63*, 1123.

(45) Jaffé, H. H.; Orchin, M. "Theory and Applications of Ultraviolet Spectroscopy"; Wiley: New York, 1970.

(46) Haskell, W. W.; Read, I. A. *Appl. Spectrosc.* **1969**, *23*, 532.

(47) See ref 2, 3, and 48 and citations therein.

(48) Van-Catledge, F. A.; Boerth, D. W.; Kao, J. *J. Org. Chem.*, following paper in this issue.

Table VI. Orbital Energies and Ionization Potentials for *s-cis*-Cyclopropyl Methyl Ketone ($\theta = 180°$)

MO	assignment	orbital energy,[a] eV	ionization potential,[b] eV	MO	assignment	orbital energy,[a] eV
8	σ_{CC}	−17.617	17.4	19	$\Delta_p^* + \pi^*$	3.669
9	σ_{CH}(methyl)	−16.922	16.8	20	$\sigma_{CH}^* + \sigma_{CC}^*$	5.553
10	Δ_σ	−15.576	15.9	21	Δ_σ^*(s)	5.746
11	σ_{CH}(cyclopropyl)	−14.575	14.9	22	σ_{CH}^*(methyl)	6.276
12	σ_{CH}(cyclopropyl)	−14.453	14.4	23	Δ_σ^*(a)	6.325
13	$\pi + \Delta_p$(a)	−13.371	13.2	24	σ_{CH}^*(methyl)	6.484
14	$n_0(p_z)$	−11.898	12.60	25	$\sigma_{CC}^* + \sigma_{CH}^*$	6.668
15	Δ_p(s)	−11.646	11.40	26	σ_{CH}^*(cyclopropyl)	7.033
16	$\Delta_p(a) + \pi$	−11.135	10.62	27	σ_{CC}^*	7.498
17	$n_0(p_y)$	−9.755	9.50	28	σ_{CH}^*(cyclopropyl)	9.460
18	$\pi^* + \Delta_p^*$	1.480				

[a] This work. [b] Reference 51.

Table VII. Calculated Vertical Transition Energies to Singlet Excited States of Cyclopropyl Methyl Ketones and First Far UV Maximum

	$\theta = 180°$ [a]	$\theta = 150°$	$\theta = 120°$	$\theta = 90°$	$\theta = 60°$	$\theta = 30°$	$\theta = 0°$ [b]
				Vertical Transition Energies			
trans	$n \to \pi^*$	$n \to \pi^*$	$n \to \pi^*$	$n \to \pi^*$	$n \to \pi^*$	$n \to \pi^*$	$n \to \pi^*$
ΔE, eV	2.90	2.90	2.88	2.85	2.86	2.88	2.89
f	6.0×10^{-5}	4.0×10^{-5}	3.0×10^{-5}	3.0×10^{-5}	5.0×10^{-5}	4.0×10^{-5}	2.0×10^{-5}
trans	$n\sigma \to \pi^*$	$n\sigma \to \pi^*$	$n\sigma \to \pi^*$	$n\sigma \to \pi^*$	$n\sigma \to \pi^*$	$n\sigma \to \pi^*$	$n\sigma \to \pi^*$
ΔE, eV	4.76	4.75	4.72	4.70	4.71	4.75	4.77
f	0.0021	0.0019	0.0012	0.0014	0.0037	0.0026	0.0005
trans	$\Delta_p(a) \to \pi^*$	$\Delta_p(a) \to \pi^*$	$\Delta_p(a) \to \pi^*$	$\Delta_p(a) \to \pi^*$	$\Delta_p(a) \to \pi^*$	$\Delta_p(a) \to \pi^*$	$\Delta_p(a) \to \pi^*$
ΔE, eV	6.72	6.70	6.75	6.88	6.97	6.97	6.97
f	0.2509	0.1693	0.0623	0.0036	0.1591	0.3662	0.4632
trans	$\Delta_p(s) \to \pi^*$	$\Delta_p(s) \to \pi^*$	$\Delta_p(s) \to \pi^*$	$n \to \Delta_p^* + \Delta_p(s) \to \pi^*$	$n \to \Delta_p^* + \Delta_p(s) \to \pi^*$	$n \to \Delta_p^*$	$n \to \Delta_p^*$
ΔE, eV	7.19	7.30	7.42	7.39	7.50	7.54	7.51
f	0.1005	0.1831	0.2032	0.1015	0.0264	0.0985	0.0756
trans	$n \to \Delta_p^*$	$n \to \Delta_p^*$	$n \to \Delta_p^*$	$n \to \Delta_p^* + \Delta_p(s) \to \pi^*$	$n \to \Delta_p^* + \Delta_p(s) \to \pi^*$	$\Delta_p(s) \to \pi^*$	$\Delta_p(s) \to \pi^*$
ΔE, eV	7.74	7.70	7.64	7.69	7.70	7.88	8.02
f	0.0084	0.0187	0.0959	0.1755	0.0927	0.0394	0.1481
trans	$\Delta_p(a) \to \Delta_p^*$	$\Delta_p(a) \to \Delta_p^*$	$\Delta_p(a) \to \Delta_p^* + \pi \to \pi^*$	$\pi \to \pi^* + \Delta_p(a) \to \Delta_p^*$	$\pi \to \pi^* + \Delta_p(a) \to \Delta_p^*$	$\pi \to \pi^* + \Delta_p(a) \to \Delta_p^*$	$\Delta_p(a) \to \Delta_p^*$
ΔE, eV	8.54	8.52	8.36	8.20	8.16	8.40	8.42
f	0.2693	0.2970	0.0882	0.1850	0.1670	0.0578	0.1009
trans	$\Delta_p(s) \to \Delta_p^*$	$\pi \to \pi^*$	$\pi \to \pi^* + \Delta_p(a) \to \Delta_p^*$	$\Delta_p(a) \to \Delta_p^* + \pi \to \pi^*$	$\Delta_p(a) \to \Delta_p^* + \pi \to \pi^*$	$\Delta_p(a) \to \Delta_p^* \to \pi \to \pi^*$	$\sigma_{CH} \to \pi^*$
ΔE, eV	8.75	8.58	8.50	8.55	8.52	8.46	8.55
f	0.1486	0.0448	0.2369	0.2157	0.2529	0.1844	0.0027
trans	$\pi \to \pi^*$	$\Delta_p(s) \to \Delta_p^*$	$\Delta_p(s) \to \Delta_p^*$	$\Delta_p(s) \to \Delta_p^*$	$\Delta_p(s) \to \Delta_p^*$	$\sigma_{CH} \to \pi^*$	$\pi \to \pi^*$
ΔE, eV	8.81	8.83	8.72	8.65	8.86	9.05	9.04
f	0.0144	0.0985	0.1426	0.1284	0.0937	0.0486	0.0359
trans	$n \to \sigma^*$	$n \to \sigma^*$	$\sigma_{CH} \to \pi^*$	$\sigma_{CH} \to \pi^*$	$\sigma_{CH} \to \pi^*$	$\Delta_p(s) \to \pi^*$	$\Delta_p(s) \to \pi^*$
ΔE, eV	9.55	9.53	9.43	9.28	9.19	9.26	9.34
f	0.1305	0.1113	0.0339	0.0341	0.0335	0.0532	0.0560
				Fitted First Far UV Maximum			
λ_{max}, nm	183	182	182	161	177	177	178
$\log \epsilon$	3.92	3.75	3.35	3.89	3.70	4.05	4.15

[a] The most stable geometry is the *s*-cis conformation ($\theta = 180°$). [b] The *s*-trans conformation.

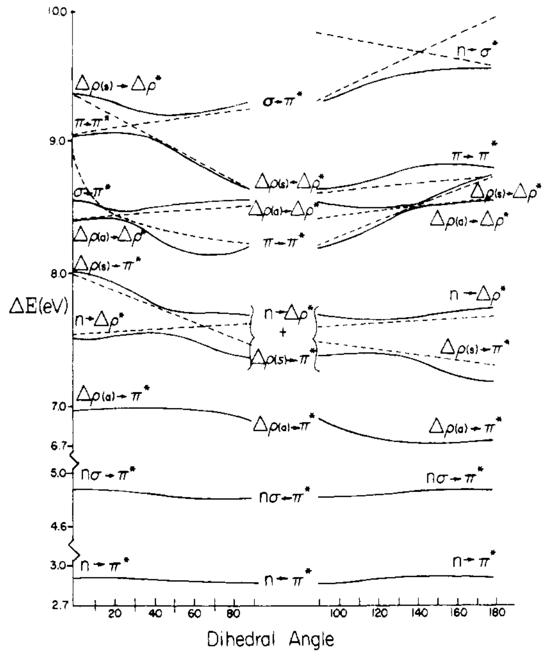
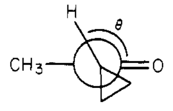


Figure 4. Energies of low-lying excited states of cyclopropyl methyl ketone as a function of the dihedral angle θ.

detail since important comparisons may be made with the results of a systematic experimental investigation of conformational effects reported in the following paper.[48]

The molecular orbitals effectively demonstrate the consequences of interactions between the cyclopropyl orbitals and the n and π orbitals of the carbonyl moiety. Before considering these interactions in detail, it is first profitable to understand the unperturbed chromophores. Earlier in this paper we have already extensively discussed the carbonyl orbitals and states. In the unperturbed cyclopropane, a pair of degenerate (3e′) orbitals arises in the Walsh model[50] from symmetric and antisymmetric overlap of p-type orbitals around the outside of the ring. (See the following paper[48] for details.) In perturbed systems, we have designated these as $\Delta_p(s)$ and $\Delta_p(a)$, respectively, after Meyer et al.[49c] An antibonding orbital ($4a_2'$), which we classify as Δ_p^* in perturbed cyclopropyl species, also results from the Walsh model. In the *s*-cis and *s*-trans conformations of methyl cyclopropyl ketone, mixing takes place between the $\Delta_p(a)$ orbital and the π orbital of the carbonyl group, resulting in considerable stabilization of the π molecular orbital and destabilization of $\Delta_p(a)$. The highest occupied carbonyl MO, $n(p_y)$ remains unmixed while the other nonbonding orbital $n\sigma(p_z)$ interacts with the symmetric component $\Delta_p(s)$. Below these important orbitals there lie a number of σ orbitals, including Δ_σ arising from σ-type cyclopropyl orbitals from the $3a_1'$ Walsh orbitals.[50] Excitations from a number of these σ orbitals figure in the excited configurations found in the manifold of states below 10 eV. Comparison of the INDOUV results with the photoelectron spectrum[51] of methyl *s-cis*-cyclopropyl ketone shows striking agreement. The uncorrected orbital energies coincide quite well with the observed vertical ionization potentials (Table VI), giving added confidence in the INDOUV description of the occupied molecular orbitals. In addition, our assignments of the highest occupied molecular orbitals are in accord with those made by Kelder et al.[51]

In discussions of conformational effects arising from different orientations of the cyclopropyl ring relative to the carbonyl group, we have again employed the dihedral angle θ used in our study of vinylcyclopropane. According



to our earlier convention, the *s*-cis conformation has a dihedral angle of θ = 180°; in the *s*-trans conformation, θ is 0°. It should be noted that electron-diffraction[52] and force-field[48] studies of methyl cyclopropyl ketone indicate that the *s*-cis (θ = 180°) conformation is the most stable. Rotation about the CC bond in the direction of the θ = 90° (gauche) conformation results in "turning off" the perturbation between the two interacting groups. Pronounced energy changes occur in the π and $n\sigma(p_z)$ orbitals. Only minor fluctuations are present in $\Delta_p(s)$, $\Delta_p(a)$, and $n(p_y)$ orbitals.

In the virtual orbitals, extensive mixing takes place between π^* and Δ_p^* orbitals at θ = 0° and 180° with π^* lowered in energy and Δ_p^* raised in energy. Approach to the 90° conformation results in the π^* orbital rising in energy and the Δ_p^* orbital decreasing in energy. From the CI studies described later, these two orbitals appear to be the predominant unoccupied orbitals to which excitations occur.

Above the Δ_p^* orbital is a plethora of closely packed σ^* orbitals, including $\Delta_\sigma(s)$ and $\Delta_\sigma(a)$ from the 4e′ Walsh cyclopropyl orbitals.[50] All of these appear to be significantly affected by conformational variations. In several cases orbital assignments change upon rotation. No orbitals actually cross, however, due to the fact that in the region 0° < θ < 180° all orbitals belong to the same irreducible representation (A) of the point group C_1. Thus, avoided crossings are the rule, resulting in oscillations in orbital energies.

Configuration-interaction calculations have also been performed to identify low-lying excited states (<10 eV; see Table VII and Figure 4). We first review the predicted excitations from the most stable *s*-cis conformation. INDOUV again shows a weak, low-energy $n \rightarrow \pi^*$ transition corresponding to the observed low-intensity band at 4.49 eV.[49c] The second $n\sigma \rightarrow \pi^*$ transition is similar to those predicted from the other carbonyl calculations (vide supra). As before, its location is undoubtedly several electron volts too low in energy.

Above the $n \rightarrow \pi^*$ states are the significant intramolecular charge-transfer states, $\Delta_p(a) \rightarrow \pi^*$ (6.72 eV) and $\Delta_p(s) \rightarrow \pi^*$ (7.19 eV), not present in the unperturbed chromophores. These states were first characterized by Meyer, Muel, and Kasha using semiempirical methods.[49c] Allowed excitations to these states lead to two intense bands observed at 6.48 and 7.04 eV in the experimental vapor-phase ultraviolet spectrum.

Above these states lie several states whose existence has yet to be established by vacuum ultraviolet spectra, namely, $n \rightarrow \Delta_p^*$, $\Delta_p(a) \rightarrow \Delta_p^*$, $\pi \rightarrow \pi^*$, and $\Delta_p(s) \rightarrow \Delta_p^*$. The last three states are predicted to be very close in energy. The extensive mixing of the $\pi \rightarrow \pi^*$ configuration

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[49] (a) Dauben, W. G.; Berezin, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 3449. (b) Kosower, E. M.; Ito, M. *Proc. Chem. Soc.* **1962**, 25. (c) Meyer, A. Y.; Muel, B.; Kasha, M. *J. Mol. Spectrosc.* **1972**, *43*, 262. (d) Al-Khafaji, J. A.; Shanshal, M. *Z. Naturforsch., A* **1975**, *30A*, 1023. (e) Pete, J. P. *Bull Soc. Chim. Fr.* **1967**, 357. (f) Julia, S.; Julia, M.; Tchen, S. Y.; Graffin, P. *Ibid.* **1964**, 3207.

[50] (a) Walsh, A. D. *Nature (London)* **1947**, *159*, 167, 712. (b) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179.

[51] Kelder, J.; Cerfontain, H.; Higginson, B. R.; Lloyd, D. R. *Tetrahedron Lett.* **1974**, 739.

[52] Bartell, L. S.; Guillory, J. P.; Parks, A. T. *J. Phys. Chem.* **1965**, *69*, 3043.

into the $\Delta_p(a) \rightarrow \Delta_p^*$ state and also into the $\Delta_p(s) \rightarrow \Delta_p^*$ state results in the anticipation of very strong $\Delta_p \rightarrow \Delta_p^*$ transitions with intensity stolen from the $\pi \rightarrow \pi^*$ transition.

As expected, considerable conformational dependence is predicted in the ultraviolet spectrum similar to that for butadiene[53] and vinylcyclopropane.[2] Reduction in the dihedral angle θ from the *s*-cis geometry brings about marked alteration in the energies of most of the excited states. The only states relatively unaffected are the two low $n \rightarrow \pi^*$ states. The most intense far-ultraviolet transition is characterized as $\Delta_p(a) \rightarrow \pi^*$. It is fairly insensitive to changes in the range θ = 0–90° and then is bathochromically shifted in the 120–180° region. The principal feature is the decrease in oscillator strength of this transition in the vicinity of θ = 90°. The second far-ultraviolet band, arising ostensibly from the $\Delta_p(s) \rightarrow \pi^*$ excitation, appears to be relatively unaffected in the 0–60° region but is bathochromically shifted and gains intensity near 90–120°. From 120° to 180° the band continues to be red shifted but decreases slightly in intensity.

The three lowest excited states, including $\Delta_p(a) \rightarrow \pi^*$, retain their assignments upon complete rotation, θ = 0° → 180°. The higher states are all extensively coupled in the 60–120° region, making distinctions among excited states difficult. All of the states between 7.3 and 9.5 eV undergo changes in assignment upon rotation about the CC single bond. Again a multitude of avoided crossings occur in the state manifold since all states belong to the totally symmetric representation of the C_1 point group in the region $0° < \theta < 180°$. It is interesting to note that several states experience more than one avoided crossing during correlation from the *s*-cis to the *s*-trans conformation.

Also noteworthy in this portion of the manifold is the absence of an unequivocally "clean" $\pi \rightarrow \pi^*$ state even in the *s*-cis or *s*-trans geometries. Instead, $\pi \rightarrow \pi^*$ character (and also intensity) appears to be diluted into several other important states at various points across the correlation diagram (e.g., $\Delta_p(a) \rightarrow \pi^*$, $\Delta_p(s) \rightarrow \pi^*$, $\Delta_p(a) \rightarrow \Delta_p^*$, $\Delta_p(s) \rightarrow \Delta_p^*$, $n \rightarrow \Delta_p^*$). The orbital mixing of $\Delta_p(a)$ and π at θ = 0° and 180° is doubtless instrumental in enhancing the intensity of the nominally $\Delta_p(a) \rightarrow \pi^*$ transition. In the vicinity of the gauche (θ = 90°) conformation, there is no $\Delta_p(a) \rightarrow \pi$ interaction, and the $\Delta_p(a) \rightarrow \pi^*$ band at 6.88 eV appears to vanish in the 60–120° range of the dihedral angle. The $\pi \rightarrow \pi^*$ intensity is transferred to several higher energy transitions, including $n \rightarrow \Delta_p^*$, $\Delta_p(s) \rightarrow \pi^*$, $\Delta_p(a) \rightarrow \Delta_p^*$, and $\Delta_p(s) \rightarrow \Delta_p^*$.

At this point, it is instructive to compare the excited states of cyclopropyl ketone species with those obtained earlier for vinylcyclopropane. In contrast to the ketones, the vinylcyclopropane manifold consists of low-lying states of quite different assignment. We may ignore the $n \rightarrow \pi^*$ states of the ketones since these are obviously lacking in the hydrocarbon. In vinylcyclopropane, the lowest excited state is $\pi \rightarrow \pi^*$ in character, whereas in the cyclopropyl ketones the $\pi \rightarrow \pi^*$ state is ill-defined due to conformational mixing. Where it can be distinguished, it occurs at much greater energy. Its presence is, nevertheless, apparent in the $\Delta_p(a)$ orbital which is heavily coupled to the π orbital near the *s*-cis and *s*-trans conformations. It is significant to note that in both systems, $\pi \rightarrow \pi^*$ character and intensity are shifted to higher energy transitions in the near-90° conformations. The second and third states in vinylcyclopropane are $\Delta_p(s) \rightarrow \pi^*$ and $\sigma_{CC+CH} \rightarrow \pi^*$, respectively. The state distinction between these becomes blurred in the θ = 90–180° region due to extensive interactions. In cyclopropyl ketones the second far-ultraviolet transition can also be characterized as $\Delta_p(s) \rightarrow \pi^*$ at almost all dihedral angles, but the $\sigma_{CC+CH} \rightarrow \pi^*$ state is at considerably greater energy in cyclopropyl ketones.

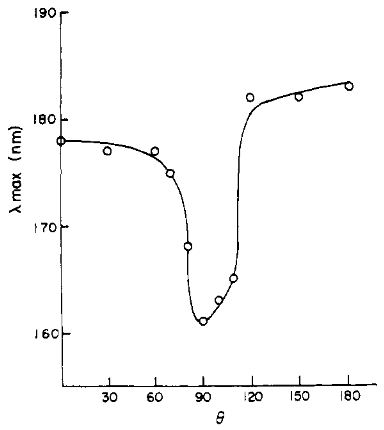

Figure 5. Predicted first far-ultraviolet maximum as a function of the dihedral angle for cyclopropyl methyl ketone.

As in our earlier treatment of the vinylcyclopropane spectrum, we have prepared "synthetic" spectra of methyl cyclopropyl ketone since the experimental spectrum is actually a composite of overlapping bands. Our "synthesis" is accomplished in eq 19 by representing each transition

$$\epsilon(\bar{\nu}) = 30\,000\sum_i f_i \exp[-\alpha(\bar{\nu} - \bar{\nu}_i^{\,0})^2] \qquad (19)$$

by a Gaussian-shaped band with α adjusted to give a half-bandwidth of 2500 cm^{-1}. The extinction coefficient at a given wavenumber is calculated as a sum over all transitions, where f_i are the oscillator strengths and $\bar{\nu}_i^0$ are the frequencies in wavenumbers. The constant (30 000) was obtained by fitting the calculated results for ethylene to the observed molar extinction coefficient for the $\pi \rightarrow \pi^*$ band.[1,2] The resulting "synthesized" spectra of the far-ultraviolet region give the appearance of solution-phase spectra which will be useful for comparison with experimental findings.

The conformational dependence of the first far-ultraviolet maximum is portrayed in Figure 5. The auxochromic effect upon the first transition is pronounced. A variation of 22 nm is predicted, with the $\Delta_p(a) \rightarrow \pi^*$ band disappearing into the $\Delta_p(s) \rightarrow \pi^*$ band near θ = 90°. These predictions regarding conformational dependence are substantiated by earlier reports of cyclopropyl ketone spectra.[49a–d] Our own systematic investigation of conformationally rigid cyclopropyl ketones (see the following paper)[48] also confirms the INDOUV results. Especially significant in our experimental study is the first spectrum of a cyclopropyl ketone with a dihedral angle near 90°. The first far-ultraviolet maximum of this conformer vanishes or appears to be shifted by 22 nm from that of the near-*s*-cis conformation and 12 nm from that of the near-*s*-trans conformation.

Conclusions

In an overall assessment, INDOUV predictions for carbonyl species are in reasonably good agreement with experimental and ab initio ordering of low-lying excited states. Predictions relative to $n \rightarrow \pi^*$ transitions are consistently too low in energy. As pointed out earlier, this is a well-known problem which has plagued other semiempirical and ab initio methods alike. In so far as $\pi \rightarrow$

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(53) Allinger, N. L.; Miller, M. A. *J. Am. Chem. Soc.* **1964**, *86*, 2811.

π^* excitations can be located, INDOUV transition energies are in general agreement with experimental spectra to within ±1.0 eV. Other $\sigma \rightarrow \pi^*$ excitations appear in regions consistent with available experimental and ab initio data. Unlike several other semiempirical methods, $n \rightarrow \sigma^*$ states are calculated to be well above the $\pi \rightarrow \pi^*$ state. This aspect of state ordering cannot be confirmed, but it is in accord with almost all ab initio calculations. Also unique to our results is the determination that the weakly allowed $n\sigma \rightarrow \pi^*$ transition takes place at lower energy than the $n \rightarrow \sigma^*$ transition. This feature is apparent in the experimental spectrum of formaldehyde and is ostensibly present as an underlying band in other carbonyl spectra. To be sure, our calculated state energies are too low to obtain an accurate state ordering of the $n\sigma \rightarrow \pi^*$ state relative to the $\pi \rightarrow \pi^*$ state. Yet the prediction of $n\sigma \rightarrow \pi^*$ as a low-lying state is surprisingly consistent with ab initio calculations.

Thus, our previously stated goal of relative state orderings accurate to ±1.0 eV seems to have been substantially met by the INDOUV formalism. In addition, the qualitative effects of perturbations on the carbonyl chromophore by methyl, vinyl, and cyclopropyl substituents appear to be correctly represented.

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On Conformational Sensitivity in the Ultraviolet Spectra of Cyclopropyl Ketones and Olefins

Frederic A. Van-Catledge,*[1a] Donald W. Boerth,[1b] and James Kao[1c]

Departments of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, Southeastern Massachusetts University, North Dartmouth, Massachusetts 02747, and University of Georgia, Athens, Georgia 30602

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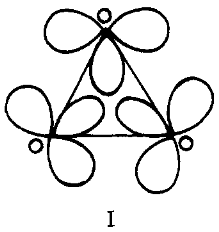
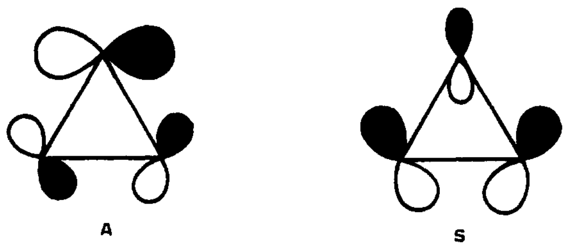
Selected cyclopropyl ketones and olefins have been prepared to approximate the three principal conformers (*s*-trans, *s*-cis, and gauche) of vinylcyclopropane and cyclopropanecarboxaldehyde. The model systems are as follows: for the *s*-cis form, 4-oxo- (VI) and 4-methylene-1(*E*)-methylspiro[2.5]octane (VII); for the *s*-trans form, 2-oxo- (IV) and 2-methylene-1-methylbicyclo[4.1.0]heptane (V); for the gauche form, 2-oxo- (VIII) and 2-methylenetricyclo[5.2.1.$0^{3,5}$]decane (IX). The geometries of IV–IX were taken from empirical force-field calculations. Spectral measurements on the ketones give support to the notion of conformational sensitivity in that the λ_{max} values are in the expected order, VI > IV > VIII. Further, the sensitivity of λ_{max} to solvent polarity supports the earlier assignment of the ketone band as $\Delta \rightarrow \pi^*$ in nature. For the olefins the ultraviolet maxima are in the order IX > V > VII. On the basis of the calculated geometries, IX is felt to be anomalous, and a rationale is given to account for this. It is concluded that the internal coordinate governing the value of λ_{max} is the dihedral angle defining the *s*-cis–*s*-trans relationship.

The conjugative interaction of the cyclopropane ring with neighboring p orbitals is a well-documented phenomenon. Of the several models[2-7] proposed for bonding among the ring carbons, the Walsh model,[5,6] based on the union of three sp^2-hybridized carbons (I), permits the simplest interpretation of the origin of this interaction and its conformational requirements. A simple description of the bonding is as follows. Interaction among the inward-pointing sp^2 hybrids leads (in D_{3h} symmetry) to an a_1' bonding level (Δ_σ) and a doubly degenerate e′ antibonding level (Δ_σ^*). The p orbitals yield an e′ bonding level (Δ_p) and an a_2' antibonding level (Δ_p^*). These symmetry orbitals are depicted in Figure 1. The six electrons corresponding to the carbon–carbon bonds are assigned to the Δ_σ and Δ_p levels. Formation of molecular orbitals for the carbon–carbon bonds should lead to mixing of Δ_p and Δ_σ^*. Indeed, Hoffmann and Davidson[7] have given a better representation of the Δ_p orbitals as in II.



I



II

On the basis of these orbital representations, the symmetric conformation (IIIb) is preferred if a neighboring p orbital is doubly occupied, while single occupancy or vacancy will stabilize the bisected conformation (IIIa). The general features outlined above find ample experimental support for cationic,[8-25] radical, and anionic[26-28] systems.

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(1) (a) Current address: Central Research Department, Experimental Station, E. I. duPont deNemours and Co., Wilmington, DE 19898. (b) Southeastern Massachusetts University. (c) Northeast Solar Energy Center, Boston, Massachusetts 02110.

(2) Coulson, C. A.; Moffit, W. *Philos. Mag.* **1949**, *40*, 1.

(3) Mulliken, R. S. *J. Chem. Phys.* **1935**, *1*, 492.

(4) Sugden, T. M. *Nature (London)* 1947, *160*, 361.

(5) Walsh, A. D. *Nature (London)* **1947**, *159*, 167, 712.

(6) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179.

(7) Hoffmann, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699.