Table I. Iron Carbonyl Properties

species	EA, eV	Fe–C bond strength, eV
FeCO	1.26 ± 0.02	1.0 ± 0.3
$Fe(CO)_2$	1.22 ± 0.02	1.0 ± 0.3
$Fe(CO)_3$	1.8 ± 0.2	1.4 ± 0.3
$Fe(CO)_4$	2.4 ± 0.3	0.2 ± 0.4
$Fe(CO)_5$	?	2.4 ± 0.5

brations are excited by nuclear geometry changes occurring upon electron detachment.

These data can be used to determine the Fe–C bond strengths in the neutral carbonyls. These determinations are made by combining our EA values with the measurements of Compton and Stockdale[1] of the appearance potentials of various $Fe(CO)_n^-$ species. These bond strengths, shown in Table I, have direct applicability to an understanding of the chemistry of these iron carbonyls.

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Electric Dichroism Spectroscopy in the Vacuum Ultraviolet. 2. Formaldehyde, Acetaldehyde, and Acetone

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Abstract: Electric field studies, including electric linear dichroism and electrochromism spectroscopy, have been completed for the second excited singlet of formaldehyde, acetaldehyde, and acetone in the gas phase. Transition-moment directions, excited-state dipole moments, and excited-state mean polarizabilities are determined. The data support the 3s ← n assignment for these bands. The excited-state dipole moment and mean polarizability determined for acetone are 0.19 D, electron density away from the oxygen, and 450 Å^3, respectively. These values for formaldehyde are 0.33 D and 70 Å^3, respectively. Excited-state parameters of this magnitude give additional support for the extravalent assignment. Acetaldehyde excited state properties cannot be determined quantitatively, but analysis of the spectrum gives some evidence that the transition moment of the absorption in question is in the molecular plane as would be expected for the 3s ← n Rydberg transition. Finally, strong perturbation of the transition-moment lengths suggests the presence of an underlying transition of the same symmetry as the second excited singlet.

Introduction

The second singlet excitation in the electronic absorption spectra of aldehydes and ketones has received a variety of assignments. Recently, a study of this absorption in formaldehyde gave tentative support to the $B_2 \leftarrow A_1$, $3sa_1 \leftarrow nb_2$ assignment for this transition.[1] In this earlier work, the unpolarized light electrochromism spectrum of the 174.9-nm band was reported. A large positive dipole moment change ($a = \mu_g - \mu_{ex}$) of 2.66 D suggested that the dipole moment of this excited state in formaldehyde is very nearly zero, since the ground-state dipole moment is reported to be 2.33 D.[2] This change in dipole moment and the corresponding change in the mean polarizability (b = 60 Å^3), together with other evidence,[3,4] favor an extravalent assignment for this absorption.

The original electric field spectrometer[6] has been modified permitting the acquisition of both electrochromism and electric linear dichroism spectral data. Electrochromism is a differential absorption resulting from molecular orientation in a modulated electric field, where the incident radiation may be either unpolarized or at a fixed polarization angle with respect to the orienting field. Electric linear dichroism results when the polarization angle of photons incident to a oriented molecule in a static dc electric field is modulated between 0 and 90° to that field. The origin of all three types of spectra and the theoretical expressions and dependencies have been given in the literature.[6-10] Only certain aspects of the experiment are discussed here.

The theoretical description of the electric field effect gives rise to this general expression for the intensity of transmitted

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Table I. Compilation of Data for Formaldehyde, Acetaldehyde, and Acetone[a]

	H_2CO	$(CH_3)HCO$	$(CH_3)_2CO$
first ionization potential, cm^{-1}	87 790	82 500	78 420
transition energy, cm^{-1}	57 170	55 000	51 230
term value, cm^{-1}	30 620	27 500	27 190
total oscillator strength (f)	4.0×10^{-2}	3.7×10^{-2}	3.5×10^{-2}
ground state dipole moment, D	2.33 (on C-O axis)	2.69 (14° off C-O axis)	2.89 (on C-O axis)
ground state mean polarizability, $Å^3$	2.45	4.59	6.39

[a] From ref 2, 3, 15, and 33.

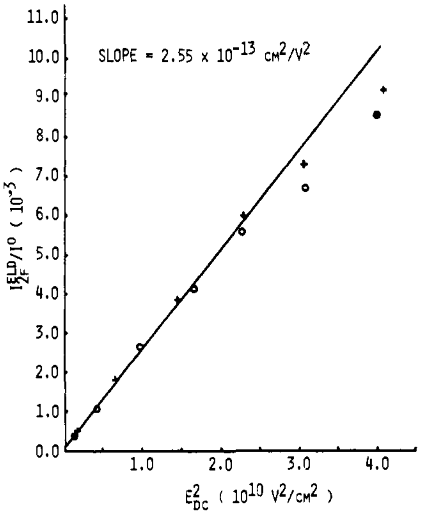

Figure 1. Plot of electric linear dichroism signal (I_{2f}^{ELD}/I^0) against the static electric field strength squared (E_{dc}^2) for acetaldehyde at 181.85 nm. The solid line is the linear least-squares fit to the data up to a field strength of 1.5×10^5 V/cm.

radiation:

$$\frac{I^E}{I^0} = 1 - \log E^2(C_1 + C_1'[3\cos^2\beta - 1])A^0(\bar{\nu}) + (C_2 + C_2'[3\cos^2\beta - 1])\frac{dA^0(\bar{\nu})}{d\bar{\nu}} + (C_3 + C_3'[3\cos^2\beta - 1])\frac{d^2A^0(\bar{\nu})}{d\bar{\nu}^2} \quad (1)$$

where I^E = field-on intensity, I^0 = dc component of intensity, E = electric field strength, β = polarization angle of the photons with respect to the electric field, and A^0 = absorbance as function of wavenumber ($\bar{\nu}$). The measured intensity of the three types of spectroscopy of the present work involves variations of the ($3\cos^2\beta - 1$) term by different experimental conditions. For unpolarized light electrochromism, integration over the possible values of β yields

$$3\frac{\int_0^{\pi}\cos^2\beta\,d\beta}{\int_0^{\pi}d\beta} - 1 = \frac{1}{2} \quad (2)$$

For 0° polarized light electrochromism, $\beta = 0$ and

$$3\cos^2\beta - 1 = 2 \quad (3)$$

For electric linear dichroism only the $3\cos^2\beta$ term is evaluated, where $\beta = \pi/2 \sin 2\pi ft$ and

$$3\cos^2(\pi/2 \sin 2\pi ft) = 1.42 \cos 4\pi ft \quad (4)$$

By obtaining two of the three different types of spectral data that can be observed with the spectrometer in its current configuration and then fitting the electric field data to absorbance data, values of the coefficients C_i and C_i' (i = 1-3) can be determined by solving systems of simultaneous equations. From these coefficients, excited-state parameters are calculated. The parameters which can be determined for molecules that *possess a principal rotation axis* are the polarization of transition moment with respect to the ground-state dipole moment, the dipole moment and mean polarizability change that occur upon excitation, and the extent of field-dependent perturbation of the transition moment ($R^{(1)}$). The latter two properties are determined with less certainty. These excited-state parameters, strictly speaking, cannot be determined for molecules that do not possess axial symmetry using electric field spectroscopy. In molecules of lower symmetry, various moments are not restricted to symmetry axes, and it is possible that the net dipole moment may have an angular shift away from its ground-state position. This will be particularly important in the electric field studies of acetaldehyde, which does not have a principal rotational axis of symmetry.

In this study, the initial work on the second singlet excitation of formaldehyde is expanded to include studies of this absorption in acetaldehyde and acetone. Experimental data for this series of compounds, excluding the electric field results, are compiled in Table I. The results presented here substantiate earlier findings and give additional evidence in favor of the $B_2 \leftarrow A_1$, 3s ← n assignment in formaldehyde and acetone, and give qualitative support to the $A' \leftarrow A'$, 3s ← n assignment in acetaldehyde for the second singlet excitation.

Experimental Section

The spectrometer and those methods employed in sample purification have been described previously.[1,6,11-13] All spectra reported were obtained with 3.0 atm of arc suppressor gas, sulfur hexafluoride, present in the cell. All samples were obtained commercially at the highest purity available. Sample gas pressures varied between 0.1 and 1.0 mmHg. The electric field strength (E_{dc}) for electrochromism spectra was maintained at 10^5 V/cm. Higher field strengths were used to obtain electric linear dichroism spectra, because this dichroism is inherently weaker than electrochromism. In order to use higher field strength, the linearity of the electric linear dichroism effect with respect to E^2 had to be tested. A plot of I_{2f}/I^0, for an intense peak in the electric linear dichroism spectrum of acetaldehyde, against static electric field strength squared is given in Figure 1. In this plot a noticeable nonlinearity begins above a field strength of 1.5×10^5 V/cm. A linear correlation of 0.999 was obtained up to 1.5×10^5 V/cm. As a result of this test, no electric linear dichroism spectra were taken above 1.5×10^5 V/cm. In all cases, spectral coefficients (C_i^{exp}) were normalized to 10^5 V/cm for facile comparison to electrochromism data and use in the final solutions for the C_i and C_i' coefficients. The dc voltages were measured with a Fluke 80k high-voltage probe and ac voltages are continuously monitored using an ITT capacitance high-voltage drop. Both devices are accurate to ±1%.

Results and Discussion

Formaldehyde. In the initial study of the second singlet absorption of formaldehyde, it was found that the unpolarized light electrochromism signal was relatively weak.[1] This inherently weak effect together with a decrease in signal-to-noise has made the acquisition of reliable polarized light electrochromism or electric linear dichroism quite difficult. The de-

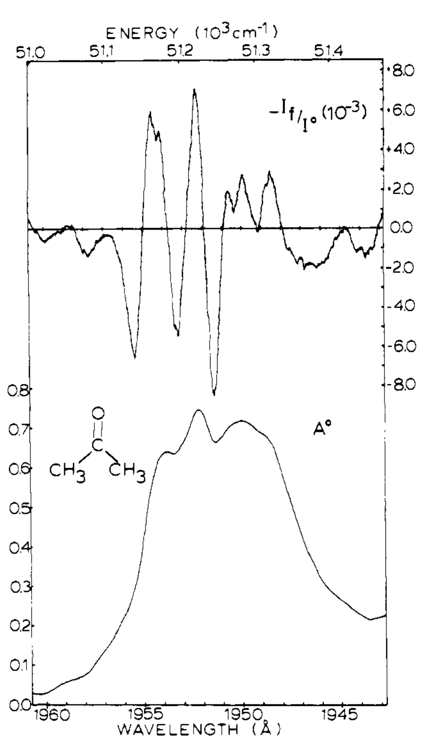

Figure 2. The absorption (A^0) and unpolarized light electrochromism ($-I_f/I^0$) spectra of the second singlet of acetone.

creased signal-to-noise ratio is due in part to the loss in incident intensity by the addition of a prism polarizer to the optical train. The net result is that electric linear dichroism was not observed and the 0° polarized light electrochromism experimental coefficients were difficult to reproduce. However, these coefficients were generally *smaller* than those of the unpolarized light electrochromism study.[1] This is in agreement with the assignment of the transition moment as perpendicular to the ground-state dipole moment (see ref 8 and 10) and adds credence to the previously reported dipole moment change of 2.66 D. Unfortunately, without additional experimental data, the unprimed theoretical coefficients (C_1 and C_2) cannot be separated from the primed terms of eq 1. The primed terms are quite complex and contain a number of parameters which cannot be evaluated. Their values are necessary for an unambiguous calculation of the mean polarizability change and the sign of the dipole moment change. Within the framework of several assumptions discussed in the earlier work,[1] these excited-state parameters were determined and are tentatively reported as a mean polarizability change (b) of 60 Å^3 with a change in dipole moment such that the electron density is away from the oxygen end of the molecule (i.e., positive).

Acetone. The electric field studies of acetone will be considered next as this compound, like formaldehyde, is C_{2v}. Unlike formaldehyde, however, the electric field effect in acetone is relatively intense and all three types of spectra have been obtained. Examples of these are given in Figures 2–4. Two features that are immediately evident are the *reduction* in signal for the 0° polarized light electrochromism spectrum (Figure 3) compared to the unpolarized spectrum (Figure 2) and the *reversal* of sign of the electric linear dichroism spectrum (Figure 4). Note that the electrochromism spectra are recorded as the negative of I_f/I^0 due to experimental conditions. This is not found in the electric linear dichroism spectra. Thus, if a reversal in sign of the electric linear dichroism spectrum is observed, as is the case for acetone, it is the result of a reversal of the sign of the coefficients (C_i^{exp}) when the spectra are recorded as shown in Figures 2–4. These observations support the assignment of a perpendicular orientation of these transition moments with respect to the ground-state dipole moment.[8,10] Table II lists the coefficients that have been obtained from linear least-squares fitting of integrated electric

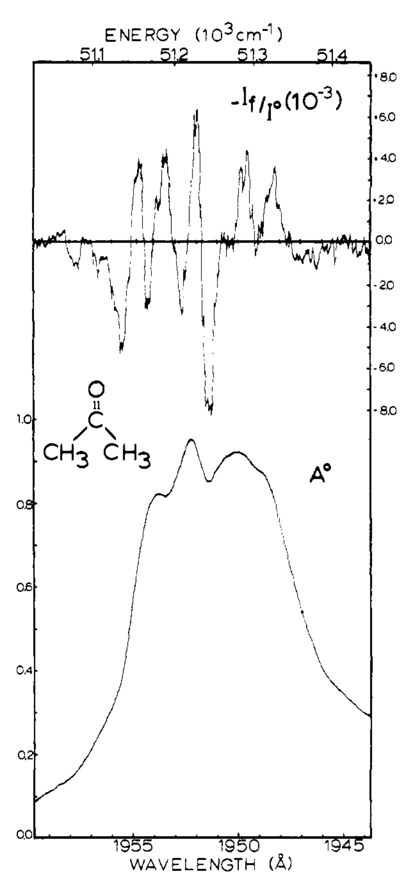

Figure 3. The absorption (A^0) and 0° polarized electrochromism ($-I_f/I^0$) spectra of the second singlet of acetone.

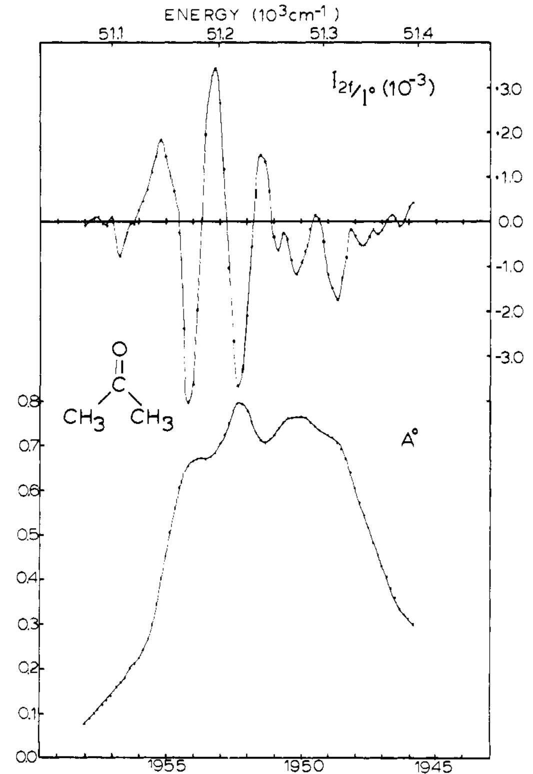

Figure 4. The absorption (A^0) and electric linear dichroism (I_{2f}/I^0) spectra of the second singlet of acetone.

Table II. Experimental Coefficients for Acetone

	C_1^{exp}	C_2^{exp}, cm^{-1}	C_3^{exp}, cm^{-2}
UPE[a]	$-(9.1 \pm 2.0)10^{-4}$	$-(4.8 \pm 3.3)10^{-2}$	$-(13.47 \pm 1.98)$
ZPE[b]	$-(4.3 \pm 3.0)10^{-4}$	$-(8.9 \pm 4.5)10^{-2}$	$-(7.82 \pm 1.55)$
ELD[c]	$+(1.4 \pm 1.3)10^{-4}$	$+(4.7 \pm 6.0)10^{-3}$	$+(1.92 \pm 0.02)$

[a] Unpolarized light electrochromism. [b] Zero degree polarized light electrochromism. [c] Electric linear dichroism.

Table III. Solution Sets for Acetone and Acetaldehyde[a]

	$(CH_3)HCO$	$(CH_3)_2CO$
C_1	$+(0.4 \pm 2.2)10^{-3}$	$+(4.9 \pm 0.6)10^{-4}$
C_1'	$+(1.8 \pm 1.2)10^{-3}$	$-(1.2 \pm 0.4)10^{-4}$
C_2	$-(8.1 \pm 4.3)10^{-2}$	$+(3.1 \pm 1.8)10^{-2}$
C_2'	$+(2.8 \pm 0.5)10^{-2}$	$+(2.3 \pm 9.8)10^{-3}$
C_3	$+(14.03 \pm 1.97)$	$+(7.23 \pm 0.55)$
C_3'	$+(5.40 \pm 1.09)$	$-(1.53 \pm 0.31)$

[a] C_2 and C_2' in cm^{-1}, and C_3 and C_3' in cm^{-2}.

field spectra and field off absorbances. With these coefficients, a set of simultaneous equations can be written.

$$-2.0C_i - 1.0C_i' = C_i^{exp} \text{ (unpolarized light)}$$

$$-2.0C_i - 4.0C_i' = C_i^{exp} \text{ (0° polarized light)}$$

$$-1.42C_i' = C_i^{exp} \text{ (electric linear dichroism)}$$

Solving the three possible combinations of these equations and averaging gives the six types of coefficients (C_i and C_i' for i = 1-3). The solution set for the acetone spectra is given in Table III with the experimental uncertainties. With these values, excited-state parameters may be determined. First, the angle between transition moment and dipole moment change is calculated. This should be 90° for a perpendicular transition, assuming that the molecule does not drastically change its shape upon excitation to the excited state. Using C_3 and C_3' from Table III, the value of the square of the dipole moment change, a^2, and the square of the scalar product, $(\bar{m}\bar{a})^2$, can be determined. These values are 9.48 ± 1.24^2 and -0.19 ± 0.23 D.^{2} Thus, the dipole moment change is $|3.08 \pm 0.20|$ D. The small negative value of $(\bar{m}\bar{a})^2$ results from the fact that its value is very nearly zero (calculated as negative owing to experimental error). For this product to be near zero, the value of the angle between the dipole moment change and transition moment must be near 90°. Since the dipole moment lies on the C-O axis and changes in dipole moment will be along this axis, a transition moment perpendicular to the C-O axis is strongly supported by these data. Whether the transition is in-plane perpendicular ($B_2 \leftarrow A_1$) or out-of-plane perpendicular ($B_1 \leftarrow A_1$) cannot be determined here. However, there is evidence from the acetaldehyde data in favor of the $B_2 \leftarrow A_1$ transition. With the above-stated results for acetone, the perpendicular expression for $C_1(\perp)$ and $C_2(\perp)$ (ref 10, Table 1) may be used in conjunction with their respective experimental values (Table III) to solve for $R^{(1)}$, b, and the sign of a. It must be assumed at this point that the second-order perturbation term, $S^{(1)}$, may be neglected. Within this constraint $R^{(1)}$ is calculated from $C_1(\perp)$ to be $(1.2 + 0.3) \times 10^{-4}$ esu cm/erg. The $R^{(1)}$ field-dependent perturbation term results from configurational mixing of nearby states with the proper symmetry to interact.[6,14] Substitution of $R^{(1)}$ into the equation for the theoretical value of $C_2(\perp)$ gives

$$-5.6 \times 10^{-2}a - 4.6 \times 10^{-4}b = 3.1 \times 10^{-2}$$

In solving the expression for mean polarizability change ($b = \alpha_g - \alpha_{ex}$), a positive value of the dipole moment (a) gives a result of 440 ± 140 Å^3, whereas a negative a generates a value for b that indicates negative polarizability in the excited state, which is impossible. Thus, the assertion that the electron density is moved away from the oxygen end of the molecule, resulting in a net dipole moment of $-0.19 + 0.23$ D in the excited state, is supported. This is also thought to be true for formaldehyde. The uncertainty is high for the calculated value of the mean polarizability change, but its magnitude is thought to be indicative of an extravalent excitation. The excited-state parameters calculated here and the comparison between these results and those from the other compounds will be considered again in the Conclusions section.

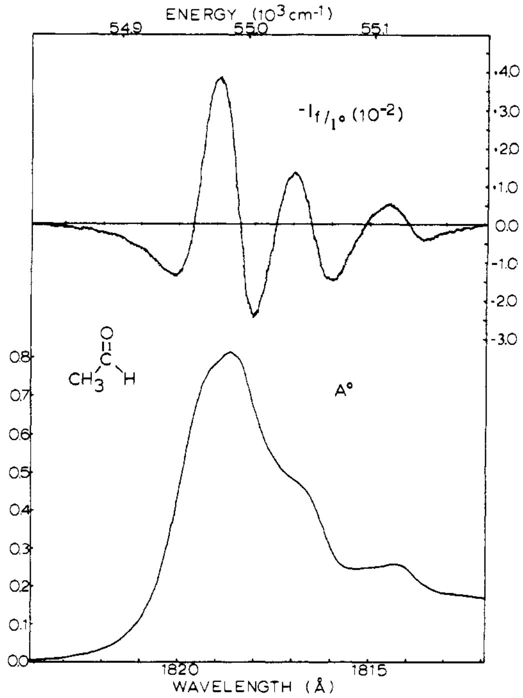

Figure 5. The absorption (A^0) and unpolarized light electrochromism ($-I_f/I^0$) spectra of the second singlet of acetaldehyde.

Acetaldehyde. The electric field spectra of acetaldehyde are quite different, as the electric field effect is very intense for the second singlet absorption for this compound. Another, more unusual, observation involved the apparent polarization of the transition. Seen in Figures 5-7, the unpolarized light spectrum (Figure 5) is *less* intense than the zero polarized light spectrum (Figure 6) and the electric linear dichroism trace (Figure 7) is the *same* sign as both the electrochromism spectra. These observations are manifested in the experimental coefficients for the three spectra, which are compiled in Table IV. Initially, these data suggest that the second singlet of acetaldehyde is not polarized perpendicularly to the ground-state dipole moment as is the case in acetone and formaldehyde. Acetaldehyde is C_s in its ground state and the dipole moment is 2.69 D, 14° off the C-O axis in plane between the H-C-O angle.[15] The major change in molecular symmetry from C_{2v} to C_s upon going from acetone to acetaldehyde has been accompanied by major changes in the experimental results. Before approaching this problem more closely, the six general experimental coefficients (C_i and C_i') must be obtained by solving the simultaneous equations that can be generated from the data. These

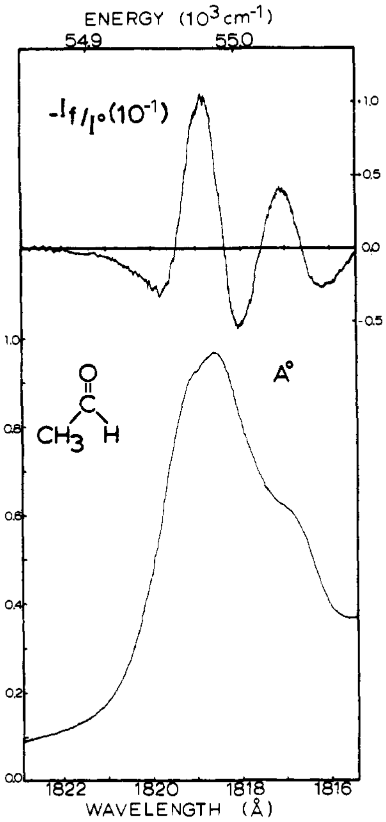

Figure 6. The absorption (A^0) and 0° polarized light electrochromism ($-I_f/I^0$) spectra of the second singlet of acetaldehyde.

Table IV. Experimental Coefficients for Acetaldehyde

	C_1^{exp}	C_2^{exp}, cm^{-1}	C_3^{exp}, cm^{-2}
UPE[a]	$-(1.1 \pm 1.1)10^{-3}$	$+(8.7 \pm 4.6)10^{-2}$	$-(31.57 \pm 1.32)$
ZPE[b]	$(8.7 \pm 5.7)10^{-3}$	$+(6.6 \pm 1.1)10^{-2}$	$-(51.56 \pm 1.44)$
ELD[c]	$(1.7 \pm 0.3)10^{-3}$	$-(6.9 \pm 0.5)10^{-2}$	$-(6.78 \pm 0.26)$

[a] Unpolarized light electrochromism. [b] Zero degree polarized light electrochromism. [c] Electric linear dichroism.

values are shown in Table III. C_3 and C_3' when related to their theoretical counterparts give a value of the dipole moment change $|a|$ of 4.28 ± 0.29 D and a calculated angle between this change and the transition moment of 9 or 171° depending on the sign of $\bar{m}\bar{a}$. The question of the location of these moments with respect to the molecule remains unanswered.

Without additional information there are three possible causes for these results. (1) The ground- and excited-state dipole moments (and also the change in dipole moment) are coaxial and the transition is, in fact, parallel and in plane with respect to this axis. (2) The ground- and excited-state dipole moments are coplanar, but not coaxial, which restricts the transition moment to some orientation in the molecular plane. The out-of-plane transition is ruled out owing to the fact that the value of the angle between the transition moment and the dipole moment change is not 90°, but is either 9 or 171°. (3) The ground- and excited-state dipole moments are neither coaxial nor coplanar (this would be the case if the molecule were badly bent in the excited state) placing no restrictions on the orientation of the transition moment.

The vibronic study of Lucazeau and Sandorfy[16] offers some assistance regarding the question of bending in the excited state. In this work, 18 vibronic components are listed which are found in the energy region of interest. Using deuterated analogues of acetaldehyde, Lucazeau and Sandorfy determined that, in this region of the spectrum, there may be two different transitions: the 3s ← n, which is characterized by the sharp vertical transitions, and a weaker underlying absorption (σ^* ← n). The vibronic components adjoining the 0–0 transition of the 3s ← n manifold have energies of 1188 and 332 cm^{-1} and are assigned to the addition of one quantum of OCH and OCC deformation, respectively. Additional quanta of these vibrations are noted. The relatively harmonic behavior of these transitions coupled with the very vertical structure of these bands suggest that, if the excited state is bent, *it is not to any great extent.* Two features not noted in their study are a prominent shoulder approximately 50 cm^{-1} to the red of the 0–0 band and a weakly resolved component approximately 30 cm^{-1} toward lower energies (see Figures 5–7). These features are thought to result from inversion doubling[17] in both ground and excited states. In the ground state[18] this splitting is observed to be approximately 28 cm^{-1} and is evident in those vibrations that are in plane (a'). The vibronic component to the blue of the 0–0 bond corresponds to the transition from the higher energy level in the ground state to the lower level in the excited state, while the +50-cm^{-1} shoulder can be assigned to the inverse case. It is fairly certain that the molecule is bent in the excited state, but the small value of the observed doubling suggests that this bending is not much more than in the ground state. The near-planar character of the molecule in both ground and excited states forces the dipole moments of these states (and the change in dipole moment) to be coplanar. The value of $\bar{m}\bar{a}$, as noted above, would then suggest a transition in plane (A′ ← A′). These data in no way rule out the Rydberg (3s ← n) assignment of the band in question. Additionally, Robin[3] points out other data which support the Rydberg assignment. The term value (27 500 cm^{-1}) is indicative of the n,3s excited state.[19] Under high pressure or in condensed phase the vibronic structure is drastically changed, an effect observed in extravalent transitions.[20] Finally, the vibrationally excited ion state energy spacings and band shapes are quite similar to those found for the vibronic components of the transition studied here.

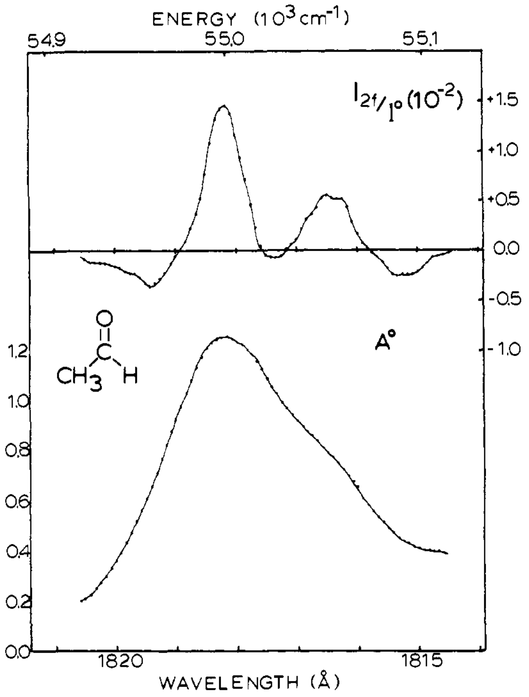

Figure 7. The absorption (A^0) and electric linear dichroism (I_{2f}/I^0) spectra of the second singlet of acetaldehyde.

The character of the second singlet appears to be more clearly defined, but, since the orientation of the various moments in the molecular plane cannot be determined, the cal-

Table V. Calculated Excited State Parameters for Formaldehyde, Acetaldehyde, and Acetone[a,b]

	H_2CO	$(CH_3)HCO$	$(CH_3)_2CO$
a	2.66 ± 0.14	4.29 ± 0.29	3.08 ± 0.20
μ_{ex}	-0.33 ± 0.16		-0.19 ± 0.23
$\angle \vec{m}\vec{a}$	$\pm 90 \pm 10°$	$(9 \text{ or } 171) \pm 5°$	$\pm 90 \pm 10°$
$R^{(1)}$	$-(5.3 \pm 2.2)10^{-5}$		$(1.2 \pm 0.3)10^{-4}$
b	$-(0.6 \pm 0.3)$		$-(4.4 \pm 1.4)$
α_{ex}	(0.7 ± 0.3)		(4.5 ± 1.4)

[a] Where $a = \mu_g - \mu_{ex}$ = dipole moment (D), μ_{ex} = excited state dipole moment (D), $\angle \vec{m}\vec{a}$ = angle between transition moment and dipole moment change, $R^{(1)}$ = perturbation term (esu·cm/erg), $b = \mu_g - \mu_{ex}$ = mean polarizability change (10^2 Å^3), and μ_{ex} = excited state polarizability (10^2 Å^3). [b] Uncertainties shown are the maximum error bars.

culation of the perturbation term $R^{(1)}$ and the mean polarizability (b) change is not possible. Since the size of $R^{(1)}$ or contributions by nearby states are not known, the coefficients C_1 and C_2 do not permit determination of other parameters.

Conclusions

A compilation of the results of electric field spectra for the second singlet in formaldehyde, acetaldehyde, and acetone is given in Table V. This transition is characterized by large changes in dipole moment accompanied also by large changes in polarizability. These observations, together with the apparent in-plane perpendicular moment of this transition with respect to the ground-state dipole moment, are thought to support the assignment of the excitation from nonbonding in-plane p on oxygen to 3s molecular Rydberg.

Recently, theoreticians have turned their attention to higher energy excited-states studies, employing sophisticated ab initio calculations, to determine energies and wave functions for these states in small polyatomic molecules. Experimental values of excited-state properties are needed for the comparison and the evaluation of both theory and experiment. The agreement between the most recent theoretical results and the experimental results herein is qualitatively good. In studies of formaldehyde,[4,22-24] acetaldehyde,[25] and acetone,[26] the assignments of the transitions in question are in agreement with the results given here (i.e., 3s ← n). In only two studies are excited-state dipole moments reported. The study of formaldehyde by Harding and Goddard[4] reports this excited state to be extravalent with a dipole moment change upon excitation of 5.43 D with electron density moving away from the oxygen end of the molecule. Similarly, Hess et al.[26] calculate a dipole moment change of 5.72 D with electron density moving away from oxygen for acetone. The fact that the results of this work and calculated results of Hess et al. agree in order and direction for the dipole moment changes lends additional support to extravalent assignments. For acetaldehyde, which is not an axially symmetric molecule, the experiments yield less information, because angular relationships of some of the excited-state properties are not known. However, it is felt that the in-plane character of the transition of interest has been demonstrated. It has also been observed that upon excitation there is a large change in dipole moment but the electron density of the excited state cannot be determined here.

Finally, both the changes in mean polarizability (b) and direct-field-dependent perturbation terms ($R^{(1)}$) are quite large for excitation to the second singlet of the compounds studied here. A large change in mean polarizability supports the conclusion that the excited state is extravalent. The large values of $R^{(1)}$ suggest a strong mixing of states with the same symmetry in the presence of a perturbing electric field. The perturbation terms have appeared several times in the literature.[7,14,27] The $R^{(1)}$ term is a first-order perturbation term which results from mixing of various excited-state transition moments divided by their respective energy separations, hence the units of esu·cm/erg. The values reported for acetone and formaldehyde are 1.2×10^{-4} and -5.3×10^{-5} esu·cm/erg; or, in more convenient units, 2.4×10^{-2} and -1.1×10^{-2} D/cm^{-1}, respectively. Little can be said about the sign difference in these values owing to the complexity of their origin, but their magnitudes support the assertions, which have appeared in the literature,[28-30] that there are additional excited states in the same general energy regions of the spectra and with the same symmetry as the second excited singlets. This is noted by an underlying diffuse continuum observed in condensed phases or high-pressure gas environments, wherein Rydberg excitations are suppressed. The work of Simpson et al.[31,32] involving crystals of relatively high molecular weight ketones resulted in an assignment of bands similar to those above as σ* ← n (C–O), in-plane perpendicular to the C–O axis. This assignment supports the assertion that the underlying transitions and the sharper Rydberg 3s ← n of acetone and formaldehyde are of the same symmetry.

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