

Electron-impact spectroscopy of acetaldehyde^{a)}

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Acetaldehyde has been studied by the technique of low-energy variable-angle electron energy-loss spectroscopy. With this method the low-lying spin-forbidden transitions have been located via the behavior of the relative differential cross sections, providing the first identification by this technique of such states in acetaldehyde. High-lying states were also investigated and some assignments of dipole symmetry-forbidden/quadrupole symmetry-allowed excitations were made on the basis of characteristic angular behavior, evident for the asymmetric molecule acetaldehyde just as for the symmetric molecules formaldehyde and acetone. Through a comparison of the acetaldehyde results with those for formaldehyde and acetone the trends in the allowed and forbidden transition energies were examined as a function of methyl substitution and found to be relatively linear.

I. INTRODUCTION

Small carbonyl compounds not only play an important role in terrestrial chemical and biological mechanisms, but the prototype molecule formaldehyde has even been detected in interstellar space. Acetone is equally interesting, containing the same symmetry elements as formaldehyde but with each hydrogen replaced by a methyl group. Acetaldehyde acts as a spectroscopically important intermediate case.

By means of optical experiments such compounds are found to possess a weak absorption at approximately 4 eV which is identified as belonging to the lowest $n \rightarrow \pi^*$ transition¹⁻³; the dipole symmetry-forbidden nature of this band explains its weakness. The spectra also possess a congested region above approximately 6.5 eV which is composed almost exclusively of transitions that are Rydberg in nature.⁴⁻⁷ In particular, one sees first a band due to the $3s$ Rydberg series member (plus vibrational components), second a band due to the $3p$ Rydberg series member, next a band due to the $3d$ Rydberg series member, and then higher series members converging to the first ionization potential (IP).

If focus is limited to molecules with either a hydrogen or methyl group adjacent to the CO chromophore, one finds that formaldehyde has been the most extensively studied by electron spectroscopic techniques in the energy-loss region between 2.5 and 7.5 eV⁸⁻¹²; therefore, not a great deal is to be gained from a further detailed analysis of this region. (An area of the formaldehyde spectrum that has not been greatly studied is that above the first IP especially as a function of scattering angle, even though sharp structure has been observed.¹³) Like formaldehyde, the interval of the acetone

spectrum between 2.5 and 7.5 eV has been extensively examined,^{10,12,14-18} but in this case doubt exists as to the identity of some of the transitions.

The low energy-loss portion of the acetaldehyde spectrum has not been thoroughly investigated. Previous electron spectroscopy work has been performed^{10,12,19}; however, the low-lying spin-forbidden states have not been accurately identified through an examination of differential cross section (DCS) behavior. Electron-impact spectroscopy is a powerful technique, both in its ability to elucidate the forbidden or allowed nature of a transition and in its ability to easily examine spectral features in the far ultraviolet. For this reason, such a study was undertaken for acetaldehyde. In addition, similar spectra were taken for formaldehyde and acetone because a comparison of the spectra of small chromophore-bearing molecules often enables one to ascertain the physical and chemical influences of various attached substituents on the chromophore.

II. EXPERIMENTAL

The electron-impact spectrometer and the methods of data accumulation and reduction are described in detail elsewhere.²⁰ In brief, an electron beam is energy selected by a hemispherical electrostatic energy analyzer and scattered from the target vapor in a collision cell. Incident electron beam currents were between 0.5–10 nA and sample pressures in the cell were estimated to be between 1–10 mTorr. The electrons thus scattered at selected angles between -15° and 100° are energy analyzed with a second electrostatic energy analyzer and detected with an electron multiplier.

The typical resolution for these studies was between 50 and 90 meV as measured by the full-width at half-maximum (FWHM) of the elastically scattered peak. Some of the higher resolution spectra were measured with resolutions between 30 and 45 meV FWHM. The best resolution used was thus about 240 cm^{-1} , as compared to about 1 cm^{-1} in typical optical studies. Many vibrational envelopes can be

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resolved; rotational spacings are unresolved.

Acetaldehyde (Baker 99 + %) and acetone (Mallinckrodt 99.5%) were degassed by several freeze-pump-thaw cycles and used without further purification. Formaldehyde was generated by continuous heating of paraformaldehyde (Celanese 91%–93%) at approximately 60 °C. Air and water were removed from the sample by pumping on the paraformaldehyde during heating until the most intense features of the contaminant spectra were less than 1% of the mean intensity of the formaldehyde bands of interest.

The areas under the elastic peak and each of several inelastic features were obtained by numerical integration as described previously.²¹ The relative DCS values for each molecule were also determined by a previously described method.²² These cross sections are normalized by setting the elastic DCS at a given impact energy to 1.0 at the scattering angle $\theta = 40^\circ$. The arbitrary units thus determined are different for each molecule and impact energy.

III. RESULTS AND DISCUSSION

Tables I–III summarize the excitation energies obtained and the assignments made for the transitions discussed in the following sections. Peak locations determined from the electron-impact spectra have an estimated uncertainty of ± 0.04 eV and the Franck–Condon limits for each transition are estimated to be within ± 0.12 eV.

Energy-loss spectra at $E_0 = 25$ eV and $\theta = 10^\circ$ for all three compounds (below the first IP) are shown in Fig. 1. As mentioned previously, some general features are shared. The broad band at approximately 4 eV is due to the lowest spin-allowed $n \rightarrow \pi^*$ transition, the band at 5.5–6 eV is due to the lowest $\pi \rightarrow \pi^*$ spin-forbidden transition, and the sharp bands above 6 eV are due to various Rydberg transitions.

A. Acetaldehyde

Figure 2 shows the low energy-loss region of the acetaldehyde spectrum at $E_0 = 50$ eV, $\theta = 10^\circ$ and $E_0 = 25$ eV, $\theta = 40^\circ$, 70° between 3.0 and 7.0 eV. At $E_0 = 50$ eV and $\theta = 10^\circ$ [Fig. 2(a)] the optical result is reproduced with the lowest band (onset at 3.56 eV, maximum at 4.27 eV) attributed to the $n \rightarrow \pi^*$, singlet–singlet (S–S) transition.³ The low intensity of this band in acetaldehyde, whose symmetry (C_s) that does not make this transition forbidden, indicates that for this molecule the symmetry of the carbonyl local environment (C_{2v}) is more important in determining the selection rules. The coordinate system used is shown in Fig. 3.

TABLE I. Acetaldehyde valence transitions.

Transition	Maximum			End
	Onset	Expt.	Lit.	
$n \rightarrow \pi^*$ (S–T)	3.29	3.97	3.91, ^a 3.75 ^b	4.89
$n \rightarrow \pi^*$ (S–S)	3.56	4.27	4.29 ^c	5.16
$\pi \rightarrow \pi^*$ (S–T)	5.08	5.99	6.31, ^a 6.25 ^b	

^a Reference 10.

^b Reference 12.

^c Reference 3.

TABLE II. Acetaldehyde Rydberg transition, IP = 10.21 eV.

(a) $n_0 \rightarrow ns$:				
E	n^a	δ^a	Calc. ^b	Lit. ^{c,d}
6.81	3	1.00	7.00	6.82, 71.0
6.95	$3(+1\nu)^e$			6.97
7.15	$3(+1\nu')^f$			7.14
7.29	$3(+1\nu'')^g$			
8.82	4	0.87	8.76	8.82
8.95	$4(+1\nu)$			
9.43	5	0.82	9.38	9.43
9.66	6		9.68	9.71
9.86	7		9.84	9.88
9.96	8		9.94	
10.02	9		10.00	
(b) $n_0 \rightarrow np$:				
E	n	δ	Calc. ^h	Lit. ⁱ
7.44	$3p$	0.78	7.52	7.47
7.58	$3p(+1\nu)^j$			7.59
7.74	$3p(+2\nu)$			7.78
7.80	$3p'$	0.62	7.83	
7.91	$3p(+3\nu)$			7.90
7.95	$3p'(+1\nu)$			
8.95	$4p$	0.71	8.92	8.96
9.03	$4p'$	0.60	9.03	9.06
9.50	$5p$		9.46	9.51
9.74	$6p$		9.72	
(c) $n_0 \rightarrow nd$:				
E	n	δ	Calc. ^k	Lit. ^d
8.40	$3d$	0.26	8.36	8.43
8.54	$3d(+1\nu)^d$			8.56
8.69	$3d'$	0.01	8.69	
9.21	$4d$	0.31	9.22	9.24
9.36	$4d'$	0.00	9.36	9.38
9.66	$5d$		9.60	9.64

^a Using formula $E = \text{IP} - R / (n - \delta)^2$.

^b Calculated with $\delta = 0.94$.

^c Reference 10.

^d Reference 19.

^e $\nu_6 = 0.14$ eV.

^f $\nu' = \nu_{10} + 2\nu_6 = 0.34$ eV.

^g $\nu'' = \nu_{10} + 2\nu_6 = 0.48$ eV.

^h Calculated with $\delta = 0.75$ or $\delta = 0.61$.

ⁱ Reference 19.

^j $\nu_6 = 0.16$ eV.

^k Calculated with $\delta = 0.29$ or 0.01 .

As the incident energy is lowered and the scattering angle is increased [Figs. 2(b) and 2(c)], several changes in the spectrum become apparent. The lowest band is observed to shift to a lower energy (onset at 3.29 eV, maximum at 3.97 eV). The cause is the underlying $n \rightarrow \pi^*$, singlet–triplet (S–T) band; the spin-forbidden band being much lower in intensity at high E_0 and low θ but becoming of comparable intensity as E_0 is lowered and θ is increased. With this same angular and energy change two other spectral features become prominent. The first, with an onset at 5.08 eV and a maximum at 5.99 eV, is due to the $\pi \rightarrow \pi^*$ (S–T) band. The second, relatively sharp, is located at 6.65 eV and is assigned as the $n \rightarrow 3s$ (S–T) Rydberg band. The identification of these

TABLE III. Formaldehyde Rydberg transitions, IP = 17.0 eV.

(a) $\pi(1b_2) \rightarrow ns$:			
E	n	δ	Calc. ^a
13.34	3	1.07	13.35
13.50	3(+1 ν) ^b	1.03	
13.66	3(+2 ν)		
13.83	3(+3 ν)		
13.99	3(+4 ν)		
15.41	4	1.07	15.42
16.13	5	1.05	16.12
(b) $\pi(1b_2) \rightarrow np$:			
E	n	δ	Calc. ^c
14.14	3(a_1)	0.82	14.14
14.40	3(b_1)	0.71	14.43
15.66	4(a_1)	0.81	15.65
15.75	4(b_1)	0.70	15.75
16.21	5(a_1)	0.85	16.22
16.27	5(b_1)	0.68	16.26
(c) $\pi(1b_2) \rightarrow nd$:			
E	n	δ	Calc. ^d
14.83	3(a_1)	0.50	14.82
14.86	3(b_1)	0.48	
14.98	3(a_1)(+1 ν) ^e	0.40	
15.01	3(b_1)(+1 ν)	0.39	
15.11	3(a_1)(+2 ν)	0.32	
15.17	3(b_1)(+2 ν)	0.27	
15.25	3(a_2 or a_1)	0.21	15.25
15.89	4($a_1 + b_1$)	0.50	15.89
15.96		0.38	
16.08	4(a_2 or a_1)	0.15	16.05
16.36	5($a_1 + b_1$)	0.39	16.33
16.41	5(a_2 or a_1)	0.20	16.41
16.57	6($a_1 + b_1$)	0.38	16.55

^a Calculated with $\delta = 1.07$.^b $\nu_2 = 0.16$ eV.^c Calculated with $\delta = 0.82$ and $\delta = 0.70$.^d Calculated with $\delta = 0.50$ and $\delta = 0.21$.^e $\nu_2 = 0.15$ eV.

bands as being due to either spin-forbidden or spin-allowed transitions is made on the basis of the behavior of the differential cross section. It is known from previous work^{23,24} that a band that exhibits a nearly constant DCS over the angular range $\theta = 10^\circ$ to 90° and shows a relative intensity enhancement as the incident electron energy approaches threshold is due to a spin-forbidden transition while a band whose DCS falls off by one to two orders of magnitude over the same angular range is due to a fully allowed transition. (A feature having intermediate behavior over that angular range is most likely due to a spin-allowed/symmetry-forbidden transition.) Figure 4 shows the DCS's for the lower lying transitions. One sees that the DCS curve for the $\pi \rightarrow \pi^*$ (${}^3A'$) band is fairly constant with angle, reflecting its spin-forbidden nature. This is contrasted with the $n \rightarrow \pi^*$ (${}^1,3A''$) curve which only exhibits such behavior at high angles, a manifestation of the fact that the spin-allowed and spin-forbidden bands are strongly overlapping. The transitions and assignments are listed in Table I.

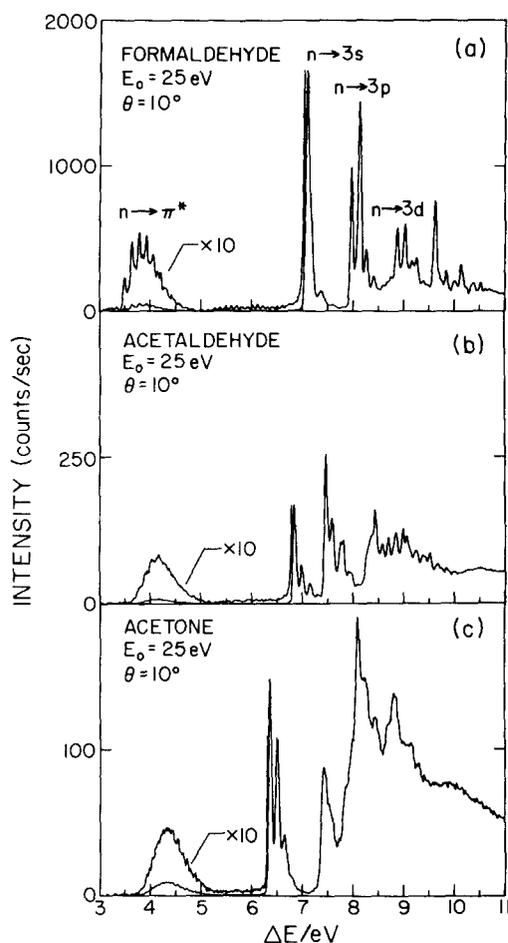


FIG. 1. Energy-loss spectra at 25 eV and 10° for (a) formaldehyde, (b) acetaldehyde, and (c) acetone. Incident electron current = 5 nA, sample pressure = 10 mTorr. Lower energy portion of spectra are multiplied by the indicated expansion factor before plotting.

Beginning with the last strong band in Fig. 2 and continuing up to the first IP (10.21 eV, adiabatic²⁵), the spectrum is dominated by Rydberg features (Fig. 5). A Rydberg transition is one in which the electron is excited into a hydrogen-like orbital surrounding an ionic core. Being hydrogen-like in nature, a simple Rydberg formula,

$$E = \text{IP} - R / (n - \delta)^2,$$

can be used to fit the series.²⁶ E is the transition energy and R is the Rydberg constant 13.605 eV. It is necessary to include a correction term δ called the quantum defect which is a measure of the penetration of the hydrogen-like orbital into the ionic core. For compounds of first row elements $\delta \sim 1.0$ for an s Rydberg series, $\delta \sim 0.6$ for a p Rydberg series, and $\delta \sim 0.1$ for a d Rydberg series.²⁷ Assignments for the transitions discussed in this research were made primarily on the basis of quantum defects. A $n_0 \rightarrow ns$ series is observed out to the $n = 9$ member and fit with $\delta = 0.94$. Series members with one vibrational quantum in either ν_6 (OCH deformation) or ν_{10} (CCO deformation)^{10,19} are also observed (Table II). Two $n_0 \rightarrow np$ series are observed. One is fit with a quantum defect of 0.75, the other with a quantum defect of 0.61. The members of the second of these two series (at 7.80, 7.95, and 9.03 eV) exhibit the angular behavior characteris-

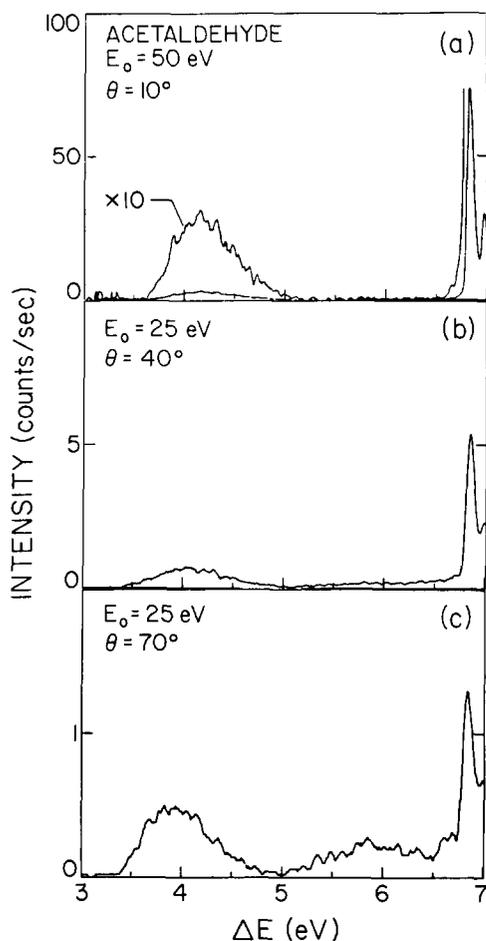


FIG. 2. Acetaldehyde energy-loss spectra at (a) 50 eV and 10° , (b) 25 eV and 40° , and (c) 25 eV and 80° . Conditions same as for Fig. 1.

tic of dipole symmetry-forbidden/quadrupole symmetry-allowed transitions as θ is changed from 0° to 10° , i.e., weak in intensity with respect to the dipole-allowed transitions at $E_0 = 100$ eV and $\theta = 0^\circ$ but of comparable intensity at

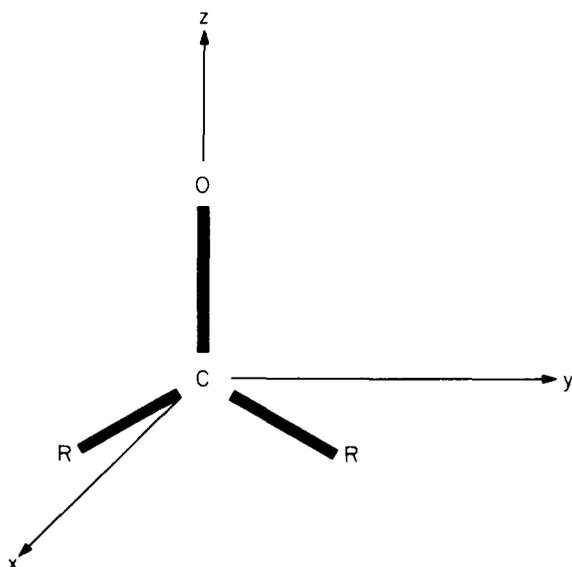


FIG. 3. Coordinate system for the carbonyl molecules, $R = \text{H}$ or CH_3 . The three bond axes represented by the heavy lines are in the yz plane.

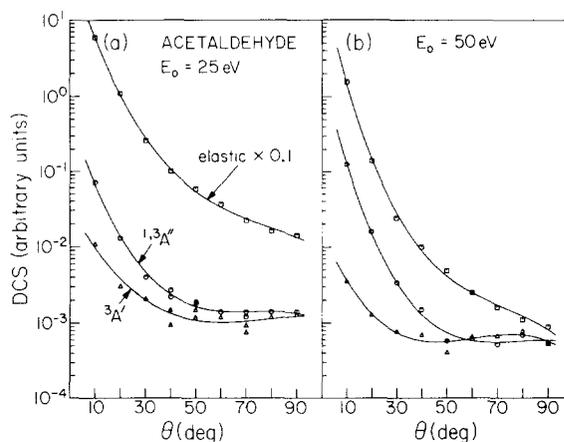


FIG. 4. Acetaldehyde valence band DCS curves: (a) 25 eV, (b) 50 eV. $\square = \text{EP} \times 0.1$, $\circ = n \rightarrow \pi^*$ (3.3 to 5.2 eV), $\Delta = \pi \rightarrow \pi^*$ (S-T) (5.1 to 6.6 eV).

$E_0 = 100$ eV and $\theta = 10^\circ$,²⁸ and are assigned as such. As previously mentioned, the carbonyl group local symmetry makes transitions to some p_π -type Rydberg orbitals dipole symmetry forbidden. Vibrational quanta in either ν_6 or ν_{10} are observed for the $n = 3$ members of both series. Two $n_0 \rightarrow nd$ series are observed and fit with quantum defects of $\delta = 0.29$ and $\delta = 0.01$ out to the $n = 5$ series members. Peaks with a symmetry-forbidden nature are observed at 8.69 and 9.36 eV. Figure 6 shows the DCS curves for the lowest Rydberg excitations illustrating their spin-allowed nature.

The spectrum of acetaldehyde beyond the first IP (Fig. 7) is relatively featureless. Broadbands are observed with maxima at 12.4, 13.5, and 14.7 eV. These correlate roughly with the second through fourth vertical ionization potentials at 13.1,²⁹⁻³¹ 14.1,^{29,30} and 15.3 eV.^{30,31}

B. Formaldehyde and acetone

For completeness, spectra of formaldehyde and acetone were collected under conditions similar to those for acetaldehyde. Almost all the results were in agreement with the work of previous researchers. The results are summarized in the following paragraphs.

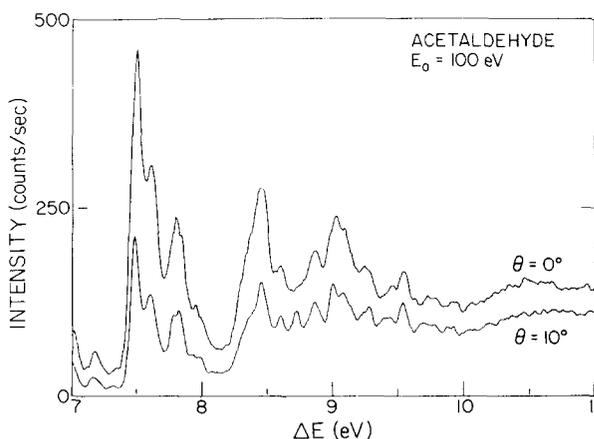


FIG. 5. Acetaldehyde energy-loss spectra between 7 and 11 eV at $E_0 = 100$ eV and $\theta = 0^\circ, 10^\circ$.

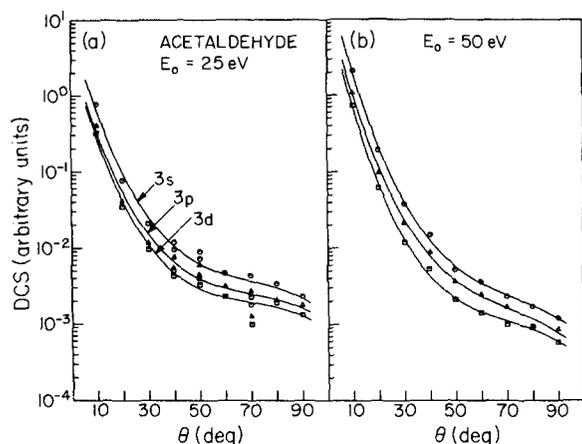


FIG. 6. Acetaldehyde Rydberg band DCS curves: (a) 25 eV, (b) 50 eV. $\circ = 3s$ (6.7 to 7.3 eV), $\Delta = 3p$ (7.3 to 8.0 eV), $\square = 3d$ (8.2 to 8.7 eV).

For formaldehyde the lowest energy band observed is that due to the $n \rightarrow \pi^*$ (1A_2) transition with an onset at 3.35 eV and a maximum at 3.79 eV. Vibrational structure can be seen and is due to various numbers of quanta in both ν_1 (C–H symmetric stretch) and ν_2 (C–O stretch). This agrees to within experimental error with the results of a comparable electron scattering experiment by Taylor *et al.*¹¹ and those of an optical study by Brand.¹ A spin-forbidden band partially overlaps the $n \rightarrow \pi^*$ (1A_2) band, with the onset at 3.00 eV and the maximum at 3.50 eV. The identity of this underlying band is the $n \rightarrow \pi^*$ (3A_2) transition and has been observed previously by Taylor *et al.*¹¹ and Robinson and Digiorgio.³² Vibrational structure is observed and is due to various numbers of quanta in the modes ν_2 and ν_6 (out-of-plane bend). At low incident electron energies and high scattering angles a broadband with an onset at 4.93 eV and a maximum at 5.82 eV is observed, which is attributed to the $\pi \rightarrow \pi^*$ (3A_1) transition.¹¹ Vibrational structure is observed, due to excitation of ν_2 . The corresponding $\pi \rightarrow \pi^*$ (1A_1) band has not been observed even though many workers have calculated the excitation energy, with values spanning the range from 6 to 15 eV.^{13,33–38} The consensus is that the $\pi \rightarrow \pi^*$ (1A_1) transition most likely takes the form of a broad band underlying the somewhat congested Rydberg region between 7 and 12 eV.

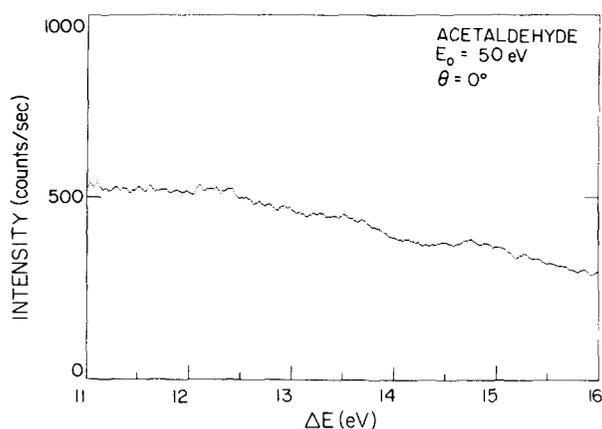


FIG. 7. Acetaldehyde energy-loss spectrum between 11 and 16 eV at $E_0 = 100$ eV and $\theta = 0^\circ$.

Various Rydberg series converging to the first IP (10.88 eV, adiabatic)^{13,39} are also observed.^{4,8,11,40} The $n_0 \rightarrow ns$ (1B_2) transitions are fit to a Rydberg series out to $n = 9$ with $\delta = 1.11$. Also, the $n = 3$ series member possesses vibrational structure by 1 and 2 quanta in ν_1 . Three $n_0 \rightarrow np$ series are observed.⁴⁰ The $n_0 \rightarrow np_y$ (b_2) transitions are dipole symmetry allowed in formaldehyde and are fit with a quantum defect $\delta = 0.83$. The $n_0 \rightarrow np_z$ (a_1) transitions are also symmetry allowed and are fit with a quantum defect $\delta = 0.77$. A new $n_0 \rightarrow np_z$ transition with one quantum of vibrational excitation in ν_2 was also observed. The $n_0 \rightarrow np_x$ (b_1) transitions are dipole symmetry forbidden/quadrupole symmetry allowed. Transitions to the $3p_x$ Rydberg orbital with 1 and 2 vibrational quanta in ν_3 (in-plane bend) are observed; only the one quantum transition has been previously seen.⁴ Two Rydberg series for $n_0 \rightarrow nd$ transitions are found.⁴ The first, with a quantum defect of 0.40, is dipole symmetry allowed and is assigned to transitions to d orbitals of either a_1 or b_2 symmetry. Peaks with both 1 and 2 quanta in ν_2 are observed for transitions to the $3d$ orbital. The second series has a quantum defect of 0.12 and is attributed to a $n_0 \rightarrow nd$ (b_1) series. A peak with 1 quantum also in ν_2 is seen for the transition to the $3d$ (b_1) orbital. A set of spin-forbidden Rydberg transitions at 6.74, 6.83, and 6.93 eV are observed. The peak at 6.74 eV is assigned to the $n \rightarrow 3s$ (3B_2) transition, the peaks at 6.83 and 6.93 eV being excitations of 1 and 2 quanta in ν_2 .

The far-UV spectrum of formaldehyde is very interesting in that it possesses sharp Rydberg structure beyond the lowest ionization potential and up to the fourth ionization potential. There is no difficulty in studying this region (corresponding to about 100–75 nm) by our technique; Fig. 8 shows this region at $E_0 = 100$ eV and angles $\theta = 0^\circ$ and $\theta = 10^\circ$. The spectrum is very complicated due to the proximity of three ionization potentials [IP2($1b_1$) = 14.39 eV (vertical), IP3($3a_1$) = 15.85 eV (adiabatic), IP4($1b_2$) = 17.0 eV (vertical)²⁵] and again assignments are made primarily on the basis of quantum defects. Some aid is gotten by using symmetry arguments to predict that the Rydberg series of p_x (b_1)- and d (b_1)-type converging to the fourth IP

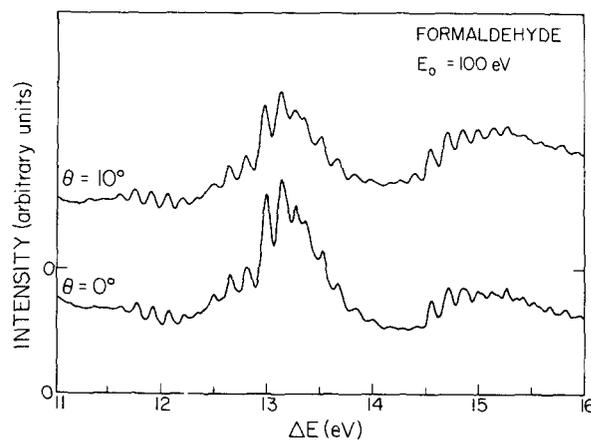


FIG. 8. Formaldehyde energy loss spectra between 11 and 16 eV at $E_0 = 100$ eV and $\theta = 0^\circ, 10^\circ$. The arbitrary units for each of the two spectra differ by a factor of 50 and have different base lines, as indicated.

are dipole symmetry forbidden but quadrupole symmetry allowed; at high incident energy such transitions should be enhanced relative to fully allowed transitions upon an angular change from 0° to 10° .²⁸ Peaks at 14.40, 14.86, 15.01, 15.17, 15.75, and 16.27 eV do indeed exhibit such an enhancement as can be seen in Fig. 8 and summarized in Table III. Weiss *et al.*⁸ examined the spectrum of formaldehyde in this same region at $E_0 = 250$ eV, making assignments on the basis of quantum defects. They also noted that the broad band with a maximum at about 13.1 eV has a strong contribution due to autoionization (based on the work of Praet and Delwiche⁴¹).

As for acetone, the lowest band is due to the $n \rightarrow \pi^*$ (S-S) transition, with an onset at 3.75 eV and a maximum at 4.38 eV. This low intensity band has been observed in previous electron scattering experiments^{14,15} and the agreement is within experimental error. With an increase in scattering angle and a decrease in incident energy the $n \rightarrow \pi^*$ band appears to shift to lower energy, with the onset moving from 3.75 to 3.56 eV and the maximum moving from 4.38 to 4.18 eV.¹⁵ As with the other carbonyls the reason for this apparent band shift is the increasing dominance of the underlying $n \rightarrow \pi^*$ (S-T) transition as E_0 is lowered and θ is increased. Additionally a band with an onset at 5.15 eV and a maximum at 5.88 eV appears that is due to the $\pi \rightarrow \pi^*$ (S-T) band.¹⁵ None of these bands possess discernible vibrational structure.

Rydberg series are found converging to the lowest IP (9.71 eV, adiabatic).⁴² The band visible in the spectrum at 6.36 eV is attributed to the $n \rightarrow 3s$ Rydberg transition. No peaks attributable to a spin-forbidden $3s$ Rydberg transition are found even though Van Veen *et al.*¹⁰ place the position of this spin-forbidden band at 6.26 eV. The $n_0 \rightarrow ns$ series is fit up to $n = 9$ with a quantum defect of 1.03. Transitions having from 0 to 4 quanta in ν_4 (methyl group deformation) are observed for $n = 3$, transitions with 0 to 2 quanta in ν_4 are observed for $n = 4$, and transitions with 0 and 1 quanta in ν_4 are observed for $n = 5$.¹⁶

For Rydberg transitions of the type $n_0 \rightarrow np$, a relatively weak series is fit with a quantum defect of 0.58.^{14,16} The $3p$ member shows structure, with transitions located at 7.42, 7.46, 7.54, and 7.59 eV. Symmetry-forbidden/quadrupole-allowed bands are observed at 7.46, 7.95, and 9.11 eV; a shoulder at 7.59 eV also exhibits behavior characteristic of such an excitation. Rydberg transitions to orbitals of b_1 symmetry are of this type. In this case the transition at 7.46 eV is assigned to the $n = 3$ member of such a series and the transition at 7.59 eV is assigned as the forbidden transition to the $3p(b_1)$ orbital with 1 ν_4 vibrational quantum included. The peak at 7.42 eV is assigned to an allowed $3p$ Rydberg transition, the 7.54 eV transition being the same but with 1 quantum of ν_4 included. Recently there has been some controversy regarding the assignment of the $3p$ Rydberg bands. Doering and McDiarmid¹⁷ studied these $3p$ Rydberg transitions using an electron-impact energy-loss technique and concluded that the band origins that they found at 7.404 and 7.447 eV were due to a forbidden transition to the $3p(b_1)$ orbital and a false origin arising from the same transition enabled by the CO bending mode. In other words, the entire

spectral region between 7.2 and 7.6 eV arises from a single forbidden transition, explaining the observed low intensity; the other two possible Rydberg transitions appeared to be inactive. They also found no evidence for forbidden transitions in the nonsymmetric molecule methyl ethyl ketone. Gedanken¹⁸ performed a magnetic circular dichroism study of this same band in acetone and found evidence for two excited states, the assignment being to the two allowed $3p$ Rydbergs 1A_1 and 1B_2 . The results of the present study suggest that a combination of the interpretations of Doering and McDiarmid and Gedanken is appropriate. All three molecules in this study show similar behaviors and, as in the well-studied case of formaldehyde, the presence of both allowed and forbidden transitions is indicated.

Two $n_0 \rightarrow nd$ Rydberg series are observed.^{14,16} The first is fit out to the $n = 5$ member with a quantum defect of $\delta = 0.37$. The second, which includes the bands at 7.95 and 9.11 eV, is fit with $\delta = 0.24$ and is assigned to a symmetry-forbidden series. The $4d'$ member is not definitively observed; however, there is a slight intensity increase with angle in the shoulder at 8.75 eV which is suggestive of this transition.

The region of the acetone spectrum above the first IP also possesses structure, albeit slight. Broad features are observed at 10.32, 11.65, 12.32, 13.94, 14.51, and 15.27 eV. The bands at 13.94, 14.51, and 15.27 eV correlate fairly well with the ionization potentials at 14.06 (vertical), 14.4 (vertical), and 15.65 eV (vertical).²⁵ In addition, the bands at 10.32, 11.65, and 12.32 eV roughly fit a Rydberg series converging to the second IP (12.78 eV, vertical)²⁵ with $\delta = 0.59$. The values calculated with this quantum defect are 10.44, 11.61, and 12.08 eV. Based on the size of the defect this series could either be assigned to a p series or a strongly perturbed s series.

C. Discussion

The spectra of the three carbonyls examined here are remarkably similar. All exhibit angular behavior that is characteristic of molecules possessing C_{2v} symmetry. This is contrasted with the results for methyl ethyl ketone in which Rydberg features do not behave in this manner, consistent with a compound of C_s symmetry.¹⁷ A size threshold seems to be passed in going from methyl to ethyl as a substituent; symmetry-forbidden Rydberg transitions in propionaldehyde most likely will not be found.

Only formaldehyde shows sharp structure above the first ionization potential. This observation is mirrored in the photoelectron spectra for these three molecules. The lower bands (excluding the lowest) of formaldehyde are composed of sharp vibrational peaks while those of acetaldehyde and acetone are broad and relatively structureless,²⁵ possibly due to the greater number of vibrational modes accessible in the larger compounds.

In Fig. 9 are plotted the two lowest ionization potentials for the three molecules in this study with the "term values" (term value = ionization potential of originating orbital-transition energy) for the three lowest valence transitions. The trends in ionization potentials demonstrate that the π molecular orbital is destabilized more per methyl group than

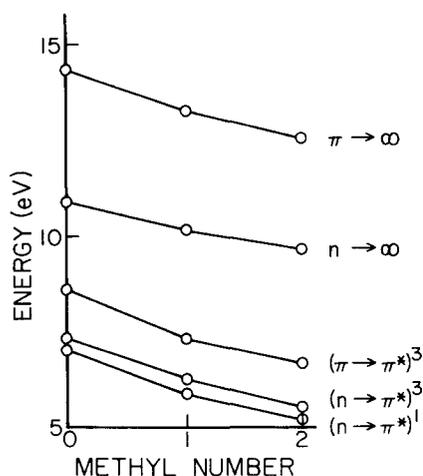


FIG. 9. Transition energies plotted vs the number of methyls for the carbonyl compounds studied, 0 = formaldehyde, 1 = acetaldehyde, 2 = acetone. $n \rightarrow \infty$ and $\pi \rightarrow \infty$ represent the two lowest ionization energies ($n \rightarrow \pi^*$) (Refs. 1 and 3) and $(\pi \rightarrow \pi^*)$ (Ref. 3) represent the "term value" for that transition (term value = IP of the originating orbital-transition energy).

the nonbonding molecular orbital (about 0.9 eV/methyl vs 0.6 eV/methyl, least-squares fit). This has been explained as being caused by a delocalization effect, methylation increasing the delocalization of positive charge created by ionization thus stabilizing the ion,⁴³ and also an inductive effect, the methyl groups donating electron density and destabilizing the neutral.⁴⁴ The decrease in the term values for the three lowest valence transitions demonstrate that the π^* orbital is also destabilized by increasing methylation by nearly the same degree as the π orbital (0.9 eV/methyl). Indeed, all the lower molecular orbitals studied are destabilized with methylation, including the Rydberg orbitals by about 0.2 eV/methyl for the s type and about 0.02 eV/methyl for the d type. The larger affect on the π and π^* orbitals suggests that a delocalization effect is probably dominant to the inductive effect. In fact, calculations by Harding and Goddard⁴⁵ find slightly more delocalization for triplet states than singlet states, which seems to be supported by the slightly larger influence on the 3A_2 and 3A_1 states (0.93 eV/methyl) vs the 1A_2 state and 1A_1 ground state (0.89 eV/methyl).

Since the energy changes are nearly linear with methylation the search for the spin-allowed $\pi \rightarrow \pi^*$ excitations in these compounds is simplified. If this transition is identified in one of the compounds its location can be accurately predicted for the other two compounds. In fact, it can be seen that since both the π and π^* orbitals are affected almost identically by methylation, the transition energy should be equal for all three molecules. Robin⁴⁶ argues for a location of about 9.0 eV but his value has not been definitively assigned.

IV. SUMMARY

Through the application of the technique of variable-angle electron energy-loss spectroscopy both low lying singlet-triplet transitions and high-lying dipole symmetry-forbidden/quadrupole symmetry-allowed transitions have been observed for the small carbonyl compound acetaldehyde. The spin-forbidden bands have been accurately locat-

ed and identified via the behavior of the relative differential cross sections; for acetaldehyde this is the first location of these bands by this method. Apparent symmetry-forbidden Rydberg transitions in acetaldehyde have been detected even though the molecular symmetry is only C_s . (Additionally, symmetry-forbidden autoionizing transitions in formaldehyde converging to the fourth IP have been characterized in a similar manner.) It is observed that the energy of the small methyl-substituted carbonyls depend linearly on the number of methyls and is strongest for the π and π^* orbitals and weakest for the Rydberg orbitals. The effect seems to be primarily due to increased delocalization with increasing methyl substitution. An examination of the trends in the valence transition energies of these molecules indicates that the as yet unidentified spin-allowed $\pi \rightarrow \pi^*$ transition should be at the same spectral location for all three.

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