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THE SPECTRA OF SOME ALIPHATIC ALDEHYDES AND THEIR MONODEUTERO DERIVATIVES

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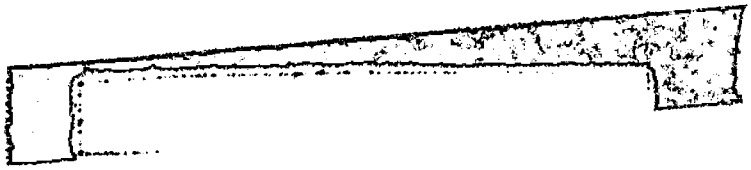

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THE SPECTRA OF SOME ALIPHATIC ALDEHYDES AND THEIR MONODEUTERO DERIVATIVES

Earl Fremont Worden, Jr.

(Part I of Thesis)

October 9, 1958

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PART ONE

THE SPECTRA OF SOME ALIPHATIC ALDEHYDES AND THEIR MONODEUTERO DERIVATIVES*

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October 9, 1958

ABSTRACT

An investigation of the infrared and near-ultraviolet spectra of three aliphatic aldehydes and their monodeutero derivatives is described.

The infrared spectra of the acetaldehydes (CH_3CHO and CH_3CDO) were in agreement with work reported recently. A few new bands are reported and discussed. The infrared spectra of C_2H_5CHO, C_2H_5CDO, C_3H_7CHO, and C_3H_7CDO from 450 to 4000 cm^{-1} have been observed, and an assignment of the observed bands has been made.

The weak absorption of the aliphatic aldehydes which extends from λ3500 A to λ2300 A has been investigated. The strength of the absorption (f-value) is decreased by deuterium substitution at the aldehyde CHO group. The decrease in the f-value can be accounted for by the theory of vibrationally induced electronic transitions.

The effect of isotopic substitution on the intensity of symmetry-allowed as well as symmetry-forbidden (vibrationally allowed) electronic transitions in polyatomic molecules is discussed.

*Part One of thesis submitted for the degree of Doctor of Philosophy in Chemistry. Part Two is "High Intensity Light Sources," UCRL-8509, Oct.,1958.

INTRODUCTION

The infrared and near-ultraviolet spectra of the aliphatic aldehydes CH_3CHO, C_2H_5CHO, and C_3H_7CHO and their monodeutero derivatives CH_3CDO, C_2H_5CDO, and C_3H_7CDO have been investigated. The compounds studied were prepared in connection with a proposed kinetic problem discussed later in this Introduction.

At the time of this infrared investigation, acetaldehyde had been extensively investigated in the infrared as a vapor.[1,2] The vibrational assignment, however, was somewhat in doubt,[3] and an attempt to resolve the difficulties or confirm one of the assignments was in progress when the spectrum of CH_3CDO and an assignment for the two derivatives appeared in the literature.[4] The infrared work on the acetaldehydes confirms the data of Evans and Bernstein[4] and adds new information in the form of some previously unreported bands.

Infrared measurements on the remaining four molecules are scarce, especially for propional and propional-d_1. No complete vibrational assignment has been given in the literature, to date, for any of these molecules. Because the infrared frequencies of the bands of these molecules and the vibrational assignments for acetaldehyde and acetaldehyde-d_1 are available, tentative assignments for these four molecules have been made.

The near-ultraviolet spectra of the normal aliphatic aldehydes have been previously investigated,[5-16] but no investigation of the deutero derivatives studied in this research has been reported.

The investigation has revealed an isotope effect on the oscillator strength of the near-ultraviolet absorption of these aliphatic aldehydes. In each case, the oscillator strength is lowered upon substitution of a deuterium atom for the hydrogen atom of the formyl group. It appears that

this represents the first investigation in which an isotope effect on the f-value or intensity of an electronic transition in a complex organic molecule has been determined.

In general, ultraviolet investigations of complex molecules and their isotopic derivatives have been confined to the determination of frequency shifts of the bands and to the significance of these shifts with regard to the vibrational assignments for the combining states. In a few cases, the relative intensities of the normal and isotopically substituted compounds have been measured over a restricted region of the absorption.

Hydrogen iodide and hydrogen bromide and their deutero derivatives have been investigated by Bates and co-workers,[17] and H_2O and D_2O have been investigated by Frank and Wood.[18] The isotope effects observed in these investigations (usually a shift of the absorption to shorter wave lengths) were readily explained on the basis of zero-point energy changes and the Frank-Condon principle.

The ultraviolet spectra of acetylene and dideutero acetylene have been studied by Ingold and King[19] and the intensities of the bands of the deutero compound are reported to be weaker than the corresponding bands in the normal compound, at least in the long-wave-length region of the absorption. The transition responsible for the absorption has been called "Frank-Condon forbidden" because of a large change in the equilibrium nuclear positions of the combining states. The weaker absorption by C_2D_2 at low quantum numbers is attributed to the lower zero-point amplitude of the CD motions in the ground state. That is, the vibronic wave functions for the CD motions are more compact in space and offer less chance for overlap. The integrated absorption over the complete spectrum was not determined for both compounds; consequently, the ratio of the f-values for the transition is not known.

In a study of the near-ultraviolet absorption of acetone and acetone-d_6 in hexane solutions, Korchagin and Pjonthowskaja found no differences in the spectra of the two derivatives within the limits of experimental accuracy.[20] Photographic tehniques were employed, however, and the sensitivity may not have been great enough for detection of an isotope effect on the intensity of absorption.

The isotope effect on the near-ultraviolet absorption in the aliphatic aldehydes can be explained on the basis of the theoretical treatment of the transition advanced by Pople and Sidman.[16] The experimentally determined isotope effect supports the theoretical arguments concerning the origin of the intensity of the near-ultraviolet absorption in aldehydes.

The goal of the proposed kinetic study was to determine if an isotope effect could be detected in the primary process of the photodecomposition of acetaldehyde.[21-25] It was felt that the results would lend information about the exact nature of the reaction coordinate for the primary process.

The reaction to be studied was the direct split of the acetaldehyde molecule into methane and carbon monoxide, Reaction (I-1). The acetaldehyde molecule also splits into methyl and formyl radicals, Reaction (I-2).

$$CH_3CHO + h\nu \longrightarrow CH_4 + CO \qquad \text{(I-1)}$$

$$CH_3CHO + h\nu \longrightarrow CH_3 + CHO \qquad \text{(I-2)}$$

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO \qquad \text{(I-3)}$$

Reaction (I-2) leads to the formation of methane after hydrogen abstraction from an acetaldehyde molecule by Reaction (I-3).[26] This reaction can be eliminated by the use of iodine as a radical trap.[23-25] In this manner, Reaction (I-1) could be isolated for kinetic studies. By use of acetaldehyde containing a very small amount of CH_3CTO, the isotope

effect, if any, on the rate of Reaction (I-1) was to be determined at various wave lengths of exciting light by using counting techniques.[27] The tritium atom is a source of weak β rays, so that scintillation counting is possible.

To check the effectiveness of locating the tritium atom at the desired position in the acetaldehyde molecule. CH_3CDO was prepared by using heavy water and the reactions used to prepare the tritiated acetaldehyde.

The absorption coefficient of CH_3CDO, throughout the region of absorption, was observed to be lower than that of CH_3CHO by a factor of approximately 0.86. The CH_3CTO molecule would be expected to have a lower absorption coefficient than CH_3CHO, also. Since the absorption coefficient for CH_3CTO remained unknown,* a continuation of the proposed investigation using tritium and counting methods did not appear feasible because the results would contain an unknown isotope effect - the difference in the absorption coefficients for the two molecules - before the primary process could occur.

To demonstrate that the isotope effect on the extinction coefficient was not due to impurities, and that the effect occurred in the other aliphatic aldehydes, propionaldehyde and butyraldehyde were studied.

Since isotope effects on the extinction coefficient of the type found here can be expected in a number of compounds, it is important that such effects be determined before kinetic studies of isotope effects on photochemical reactions are carried out.

---

*To extrapolate to CH_3CTO from the information available for CH_3CHO and CH_3CDO seemed unreliable. No sample of pure CH_3CTO or a sample with sufficient, known concentration was available.

EXPERIMENTAL METHODS

Syntheses

For preparation of the isotopically substituted aldehydes, a reaction scheme suggested by Streitwieser and Schaefer was adopted.[28*] The reactions employed were

$$D_2O + (CH_3CO)_2O \longrightarrow 2CH_3COOD, \qquad (I\text{-}4)$$

$$4CH_3COOD + RCOOR' + 4Na \longrightarrow RCD_2OD + R'OD + 4CH_3COONa \qquad (I\text{-}5)$$

$$3RCD_2OD + 4H_2SO_4 + K_2Cr_2O_7 \longrightarrow 3RCDO + Cr_2SO_4 + 4H_2O + 3D_2O \; . \qquad (I\text{-}6)$$

The reactions were carried out in all-glass apparatus previously treated with hot deuteroacetic acid.

CH_3COOD. Freshly distilled acetic anhydride was added slowly to refluxing D_2O, and the refluxing was continued for 7 hours. The CH_3COOD produced was used directly in Reaction (I-5).

The Acetaldehydes

CH_3CD_2OD. This compound was prepared by the reduction of n-butyl acetate with sodium and acetic acid, Reaction (I-5). The procedure for this reaction given by Hill et al. was followed.[29]

After the reaction was completed, the excess sodium, if any, was removed by filtering, and the reaction mixture was distilled. The CH_3CD_2OD obtained was contained in the fractions of material distilling between 65 and 85°C retained for use in Reaction (I-6). Isooctane was used in place of diethyl ether[29] in order to facilitate the separation of the alcohol by distillation.

*A simple exchange reaction between the aldehyde and heavy water could not be used since the hydrogens exchanged are mainly those attached to the carbon adjacent to the formyl group.

CH_3CDO. The alcohol from Reaction (I-6) was converted to CH_3CDO by Reaction (I-6) and by the procedure given by Blatt.[30] A condenser kept at 23°C and a cold finger trap cooled by dry ice were used in series to separate the aldehyde vapors from the reactants. Several fractions of the aldehyde were collected during the reaction and transferred to a vacuum line for purification.

CH_3CHO. Samples of this compound were also prepared by this procedure.

The Propionaldehydes

$C_2H_5CD_2OD$. This compound was prepared by the reduction of n-amyl propionate by sodium and deuteroacetic acid, Reaction (I-5).[29] Diethyl ether was used as a solvent and the sodium acetate was removed before the alcohol was separated.

After the ether had been removed by distillation, fractions distilling from 80 to 100°C which contained the $C_2H_5CD_2OD$, were collected for use in Reaction (I-6).

C_2H_5CDO. The same method as outlined for CH_3CDO was used. The condenser was maintained at about 30°C; the cold finger was cooled by a salt-ice mixture; an additional trap cooled with dry ice was added, and dry nitrogen was passed through the system to aid the passage of the propionaldehyde to the traps. Fractions of the crude propionaldehyde were collected and transferred to a vacuum line for purification.

C_2H_5CHO. Samples of this compound were prepared by the same procedures.

Butyraldehyde-d_1.

The butyraldehyde-d_1 was generously given to the author by Dr. A. Streitwieser. The aldehyde, as received, was contained in an ether solution.

Reagents

D_2O. Stuart Oxygen Company. 99.5% D_2O was used directly as received.

Acetic anhydride. Technical grade acetic anhydride was distilled under anhydrous conditions and the fraction boiling at 139.6 ± 0.2°C was used.*

n-Butyl acetate. Technical grade n-butyl acetate was distilled and the 126-7°C fraction was collected for use.

Isooctane. The isooctane used as a solvent (2,2,4 trimethylpentane) had a boiling point of 99.2°C, and gave no fractionation when distilled.

n-Amyl propionate. The 163-6°C fraction of a commercial sample of the compound was collected for use.

Diethyl ether. The diethyl ether was dried over sodium, distilled through a small column, and stored over sodium.

Sodium. Commercially available sodium was weighed into mole lots and stored under white oil. The sodium was cut into thin pieces and washed in solvent before it was added to the reaction.

Purification

The Acetaldehydes

A sample of acetaldehyde (Mallinckrodt Co.) taken from a freshly opened bottle was purified by several bulb-to-bulb distillations under vacuum (the first one-fifth and the last one-fifth of the sample were rejected in each distillation). The pure acetaldehyde was stored as a vapor in a large lighttight** flask behind a mercury float valve.‡

---

*A column containing 36 bubble plates was employed for all distillations except the diethyl ether.

**Since all the aldehydes are light-sensitive, they were stored with adequate protection from light.

‡The vacuum line employed for handling the aldehydes was kept grease-free by the use of mercury float valves as stops.

The crude CH_3CHO or CH_3CDO from reaction were dried over anhydrous copper sulfate and subjected to purification by gas chromatography.

The gas chromatography column, designed by John Zinn,[31] consisted of a flash vaporizer, a 1-m column containing celite treated with n-butyl phthalate as a packing, a detection circuit, a receiver network, and a system for the control of the carrier gas, hydrogen. Samples were introduced as liquids into the flash vaporization section of the column by means of a hypodermic syringe.

The flash vaporizer was heated to 50°C and the column to 43°C, and the traps for collecting the acetaldehydes were cooled with dry ice baths. Liquid samples of 0.1 to 0.3 cc allowed a clean separation of the aldehydes from the impurities present. Isooctane and ethyl acetate were believed to be the major impurities, and they passed through the column considerably slower than the acetaldehydes. The collected aldehydes were transferred to a vacuum line, dried over anhydrous copper sulfate, and stored as a vapor.

The Propionaldehydes

Technical grade propionaldehyde* was distilled in nitrogen atmosphere and the fraction distilling at constant temperature (47.5°C, uncorrected) was transferred to a vacuum line where it was dried over anhydrous copper sulfate and further purified by trap-to-trap distillation.

The C_2H_5CHO and C_2H_5CDO prepared as described above were purified by gas chromatography in the same manner as the acetaldehydes.

The Butyraldehydes

Technical grade n-butyraldehyde* was purified in the same manner as the technical grade propionaldehyde.

---

*From Carbide and Carbon Chemical Company

The crude n-butyraldehyde-d_1 was distilled under nitrogen and various fractions were collected. Two fractions, which distilled from 54 to 62°C and 62 to 74°C, were further purified by gas chromatography.

Purity

The infrared and ultraviolet spectra of the compounds served as criteria for the purity of all the aldehydes. The infrared spectrum was used to follow the purification of each aldehyde. The absence of a change in the infrared spectrum when further purification was attempted indicated that the compound was pure. For the undeuterated aldehydes, the prepared compounds were purified until their infrared spectra contained only the bands present in the spectra of the purified commercial compound.

The absorption or extinction coefficients from the ultraviolet spectra of the compounds were used as follows to check the purity. The value of the absorption coefficient for a top fraction was compared with that for a bottom fraction of a purified sample of aldehyde. If the two values were the same within experimental error, the compound was considered pure.

Further checks on the purity of acetaldehyde and acetaldehyde-d_1 were possible. Values of the absorption coefficient for acetaldehyde were available from data reported by Rollefson and Grahame.[22] A comparison is given in Table I. The infrared bands for both CH_3CHO and CH_3CDO were compared with those published by Evans and Bernstein[4] after our observations were completed. As will be seen from Table II, the comparison is very good except for a few very weak bands.

Table I

Extinction coefficients of CH_3CHO at λ3130 and λ2652 A

(ε in liters/mole-cm)

Wave length	Rollefson and Grahame[22]	This Research
3130 A	14.9	15.0 ± 0.3
2652 A	17.9	17.8 ± 0.2

The isotopic purity of the sample of C_3H_7CDO used in obtaining the spectra is somewhat questionable. The infrared spectrum indicates the presence of more highly deuterated derivatives. Because of the presence of an intense band at 1247 cm^{-1}, the sample is suspected of containing considerable amounts of $CH_3CH_2CDHCDO$ and $CH_3CH_2CD_2CDO$.[32-34] These deutero derivatives could have been formed while the crude $CH_3CH_2CH_2CDO$ was stored in an ether solution which contained a considerable amount of D_2O. The storage period was about one year and the exchange would be confined largely to the methylene group adjacent to the formyl group.[35]

From analyses of the CH-stretch band in the infrared spectra of the aldehydes, estimates of the -CHO content of the deuteroaldehyde samples were made. The CH_3CDO sample contained 9 to 10% of -CHO; the C_2H_5CDO sample about 7%, and the C_3H_7CDO sample less than 4%.

The presence of about 5% dideuteroacetaldehyde and smaller amounts of more highly deuterated derivatives was estimated from mass spectra of the acetaldehydes.

Procedures and Results

The Infrared Spectra

Three instruments were used to obtain the infrared spectra. A Perkin-Elmer (PE) Model 21 double-beam infrared spectrometer provided with sodium chloride and calcium fluoride optics served to determine the vibrational bands present in the regions 4000 to 1200 cm^{-1} and 4000 to 625 cm^{-1}, respectively. The calcium fluoride optics give better resolution in the high-frequency region. The second instrument, a Baird Associates double-pass recording spectrometer with sodium chloride optics, was generally used to follow the preparation and purification of the compounds. The spectrometer covers the infrared region from 5000 to 625 cm^{-1}. In order to extend the frequency region to 450 cm^{-1} a PE Model 12C single-beam spectrometer equipped with potassium bromide optics was employed.

Two gas-sample cells supplied with sodium chloride and potassium bromide windows were 11 and 10 cm in path length respectively. These cells were used with the PE Model 21 and 12C instruments. A cell with 8 cm path length and sodium chloride windows was employed to obtain the spectra with the Baird Associates spectrometer.

The cells were evacuated to less than 10^{-5} mm Hg before a sample of degassed aldehyde was introduced. The pressure of the vapor in the cell was measured with a mercury manometer to the nearest mm. The aldehydes were degassed by pumping on the liquid held at -80°C in one U tube, distillation to another U tube, and again pumping on the liquid at -80°C. The U tubes were flamed in order to remove traces of the previous aldehyde or possible polymer before another aldehyde was introduced into the U-tube system.

Reproductions of the spectra observed for the molecules studied are shown in Figs. 1 through 6. The intensity scale is absorbance in arbitrary units; however, the intensities of the bands are comparable and the pressures, optics, and instruments used are identified by small letters on the figures and a key. In general, only the strongest bands are shown, but some weak bands which have been assigned as fundamentals are included. The frequencies in wave numbers of all the bands observed for each molecule under the conditions stated in the respective tables are given in Tables II, III, and IV.

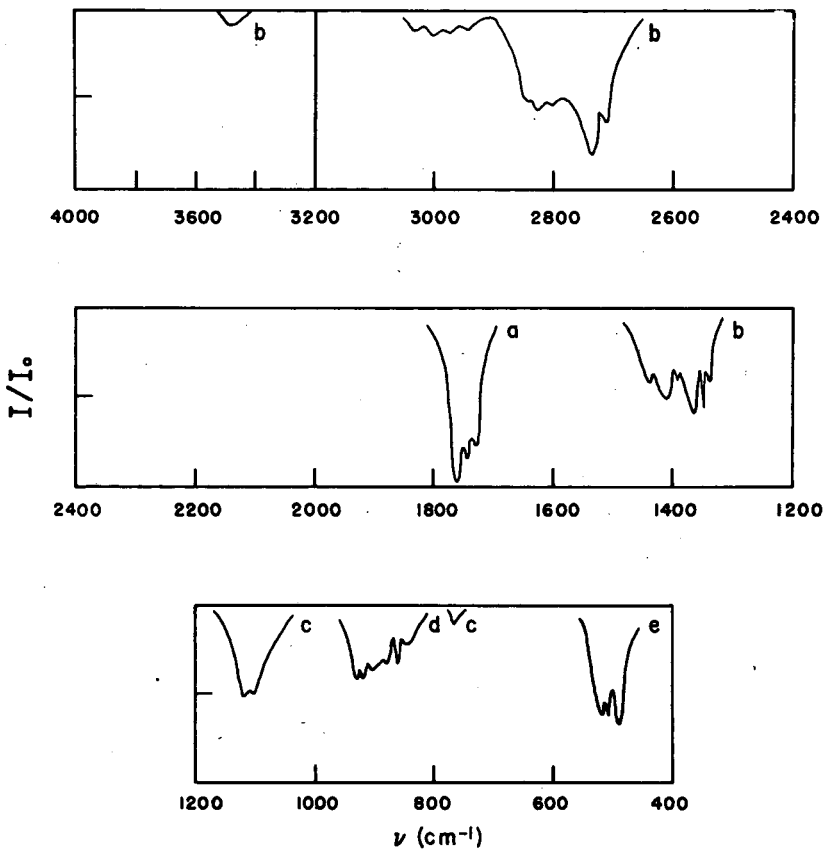
The frequency scale of the Perkin-Elmer 21 instrument was calibrated whenever the optics had been changed; CH_4, NH_3, and atmospheric CO_2 and H_2O were used as calibrating gases. The Perkin-Elmer 12C instrument had been recently calibrated by R. C. Millikan, using CO_2 and H_2O frequencies to make up a plot of drum number versus frequency. The spectra obtained with this instrument were reconstructed into plots of percent transmission versus frequency, and the frequencies of the bands in the region 650 to 450 cm^{-1} were read from these plots. The frequency scales of the Baird-instrument spectra were calibrated by using the polystyrene spectrum.

The Ultraviolet Spectra

The ultraviolet spectra were obtained by using a Cary Recording Spectrophotometer, Model 14M, and a 10-cm quartz absorption cell. All the spectra were taken with the compounds in the vapor phase at pressures at which Beer's law holds. The samples for analysis were prepared by the same method used for the infrared studies, and the observations were carried out at room temperature, 24 + 1°C. The spectrometer is a double-beam instrument and when the spectra were being obtained, one of the beams

passed through the absorption cell and sample while the other beam passed through air. A base line of absorption by the evacuated cell versus air was also determined.

The spectrometer recording is linear in wave length, and the wavelength scale is accurate to better than 4 A, with a reproducibility of 0.5 A, throughout the range. The resolving power of the monochromator is about 1 A in the ultraviolet and visible regions.[36]

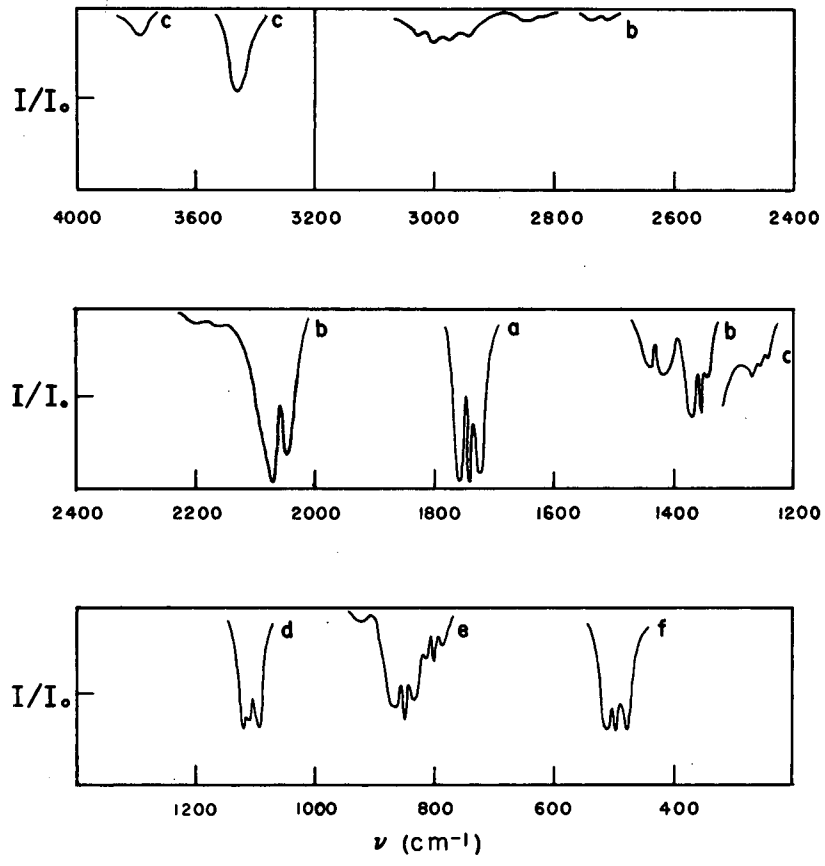


MU-14950

Fig. 1. The infrared spectrum of acetaldehyde, CH_3CHO.

Key:

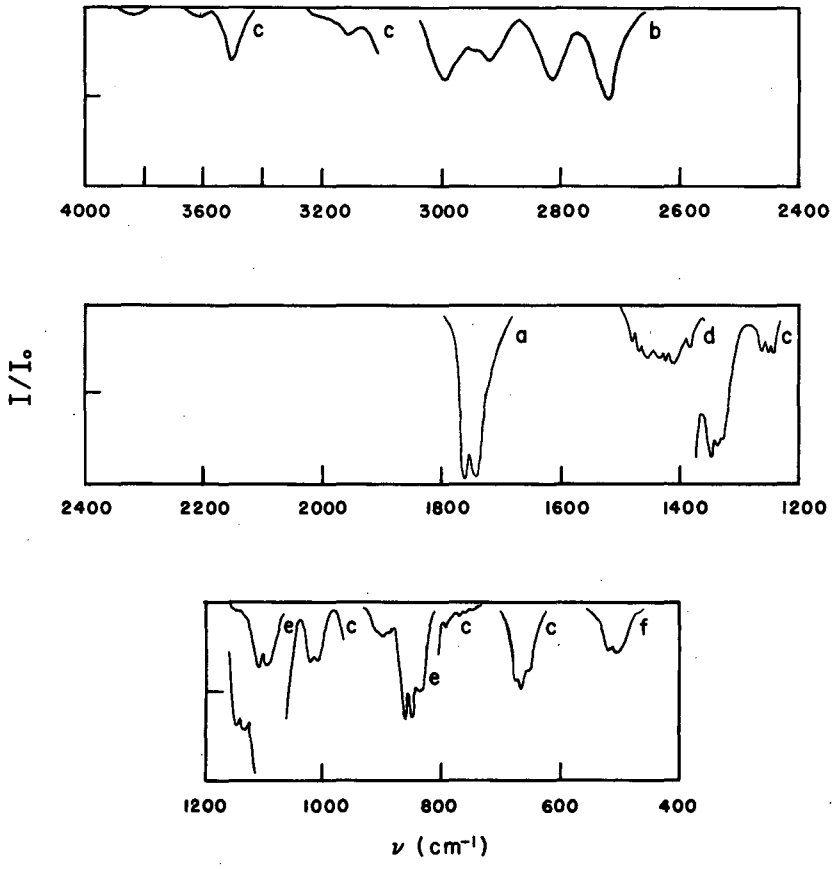
Curve	Instrument	Optics	p (mm Hg)	Path length (cm)
a	PE 21	CaF_2	20	11
b	PE 21	CaF_2	50	11
c	PE 21	NaCl	50	11
d	PE 21	NaCl	100	11
e	PE 12C	KBr	85	10



MU-14951

Fig. 2. The infrared spectrum of acetaldehyde-d_1, CH_3CDO.

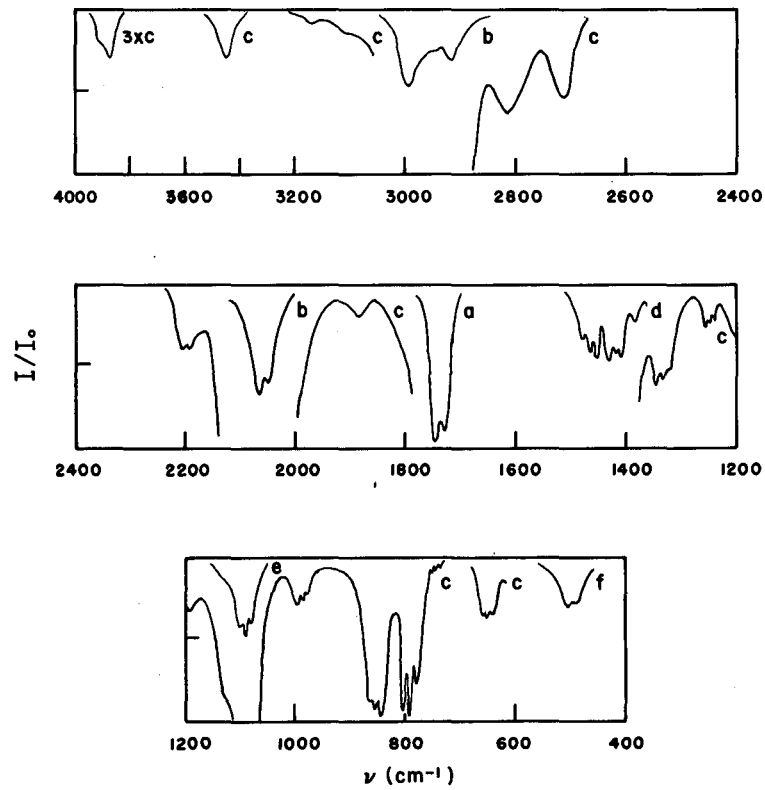
Key: Curve	Instrument	Optics	p (mm Hg)	Path length (cm)
a	PE 21	CaF_2	20	11
b	PE 21	CaF_2	50	11
c	PE 21	NaCl	400	10
d	PE 21	NaCl	50	11
e	Baird	NaCl	325	8
f	PE 12C	KBr	101	10



MU-14952

Fig. 3. The infrared spectrum of propionaldehyde, C_2H_5CHO.

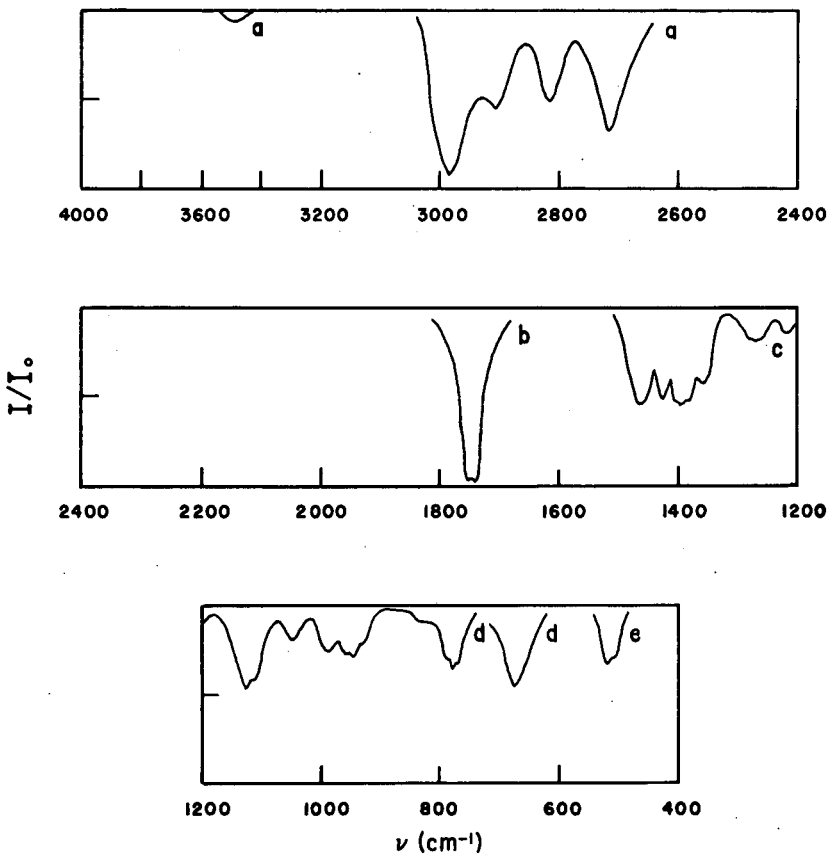
Key: Curve	Instrument	Optics	p (mm Hg)	Path length (cm)
a	PE 21	CaF_2	10	11
b	PE 21	CaF_2	20	11
c	PE 21	NaCl	235	10
d	PE 21	CaF_2	40	11
e	PE 21	NaCl	54	11
f	PE 120	KBr	101	10



MU-14953

Fig. 4. The infrared spectrum of propionaldehyde-d_1, C_2H_5CDO.

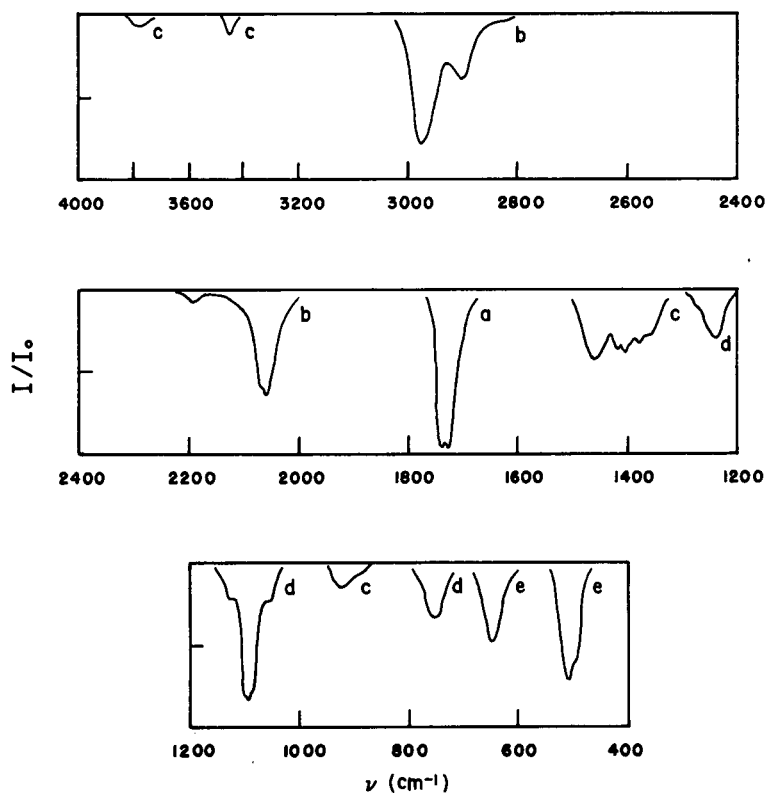
Key: Curve	Instrument	Optics	p (mm Hg)	Path length (cm)
a	PE 21	CaF_2	10	11
b	PE 21	CaF_2	22	11
c	PE 21	NaCl	235	10
d	PE 21	CaF_2	43	11
e	PE 21	NaCl	34	11
f	PE 12C	KBr	101	10



MU-14954

Fig. 5. The infrared spectrum of butyraldehyde C_3H_7CHO.

Key: Curve	Instrument	Optics	p (mm Hg)	Path length (cm)
a	PE 21	NaCl	23	11
b	PE 21	NaCl	10	11
c	PE 21	CaF_2	60	11
d	PE 21	NaCl	70	11
e	PE 12C	KBr	80	10



MU-14955

Fig. 6. The infrared spectrum of butyraldehyde-d_1, C_3H_7CDO.

Key: Curve	Instrument	Optics	p (mm Hg)	Path length (cm)
a	PE 21	CaF_2	10	11
b	PE 21	CaF_2	20	11
c	PE 21	NaCl	70	11
d	PE 21	NaCl	46	11
e	PE 12C	KBr	70	10

Table II

Infrared frequencies (in cm^{-1}) of the acetaldehydes

Evans and Bernstein[4]	This Research	Assignment
	CH_3CHO	
3485	3482	2 x 1743
~3120	~3115	1743 + 1400
3024	3033	ν_{11}
2996	3000	ν_2
2967	2974	
	2946	ν_1
2840	2841	
2822	2824	Fermi band
2804	2803	
2736	2736	ν_3
2704	2710	
2550		1743 + (830)
2464	2460	1352 + 1111
2282	~2284	1352 + 919
2268	~2262	
2236	~2245	
2218	~2210	2 x 1111
2206		
2040	2040	
2000	2000	1111 + 919
1960	1970	
1790	1788	2 x 919
1761	1761	
1743	1746	ν_4
1732	1734	
1441	1440	
~1420		ν_7
~1410	1410	
~1390	1395	ν_8
1369	1367	
1352	1351	ν_6
1341	1342	

Table II (Continued)

Evans and Bernstein	This research	Assignment
1122 1104	1121 1102	ν_5
930 919 909	928 918 902	ν_9
880 867 853	878 865 850	ν_{13}
777		509 + tors?
763	762	ν_{14}
521 509 493	518 509 494	ν_{10}
	CH_3CDO	
	4360	3000 + 1356[a]
	4030	2 x 2048[a]
	3835 3790	1742 + 2069, 2048[a]
3490 3462	3467	2 x 1743
3173	~3185	1743 + 1431
3096	~3090	1743 + 1353
3028 3000	3029 3001	ν_{11}
2970	2968	ν_2
2946	2941	ν_1
2840	2846 2800	2 x 1431
2733 2704	2736 2709	2 x 1353 + Residual CH_3CHO[a]
2600	2606	1743 + (890)
2528	2575 2530	1431 + 1109

[a]Assignment by the author.

Table II (Continued)

Evans and Bernstein	This research	Assignment
2476		
2465	2460	1353 + 1109
2450		
2416	2405	1743 + 668
2400		
2222	2223	1431 + 802
2200	2200	2 x 1109
2175	2173	1346 + 833
2148	2146	(1040) + 1109
2120	2119	Fermi doublet?
2096	2095	ν_3
2071	2069	
2050	2048	
2038		1353 + 668
2018		
1970	1982	
1958	1951	1109 + 849
1945		
	1900	1094 + 802[a]
1757	1757	
1743	1742	ν_4
1730	1728	
1442	1440	ν_7
1420	1420	
1366	1370	
1353	1356	ν_6
~1345	1343	
	1270	
	1256	CH_2DCDO, CHD_2CDO[a]
1244 vvw	1243	2 x 668
1192 vvw	1193	?; CH_2DCDO[a], CD_2HCDO[a]
1118	1119	
1109	1110	ν_3, ν_5 overlapped
1094	1093	
1043	1044	803 + tors (?)
1025	1022	2 x 513

[a]Assignment by the Author

Table II (Continued)

Evans and Bernstein	This research	Assignment
924 vvw 913	930) 916)	668 + tors (?); Residual CH_3CHO[a]
865 849 837	863 850 835	ν_9
816 802 799	816 802 792	ν_{13}
668	766? vvw 666 vw	ν_{14}
513 500 487	512 498 482	ν_{10}

The frequencies reported under the heading "This research" were read from spectra obtained under the following conditions:

CH_3CHO: P E 21, NaCl optics, 11-cm path length, 54 and 16 mm Hg pressure.

P E 21, CaF_2 optics, 11-cm path length, 18 mm Hg pressure.

P E 12C, KBr optics, 10-cm path length, 81 mm Hg pressure.

CH_3CDO: P E 21, NaCl optics, 11-cm path length, 400.54, and 47 mm Hg pressure.

P E 21, CaF_2 optics, 11-cm path length, 17 mm Hg pressure.

P E 12C, KBr optics, 10-cm path length, 85 mm Hg pressure.

Baird, NaCl optics, 8-cm path length, 325 mm Hg pressure.

[a]Assignment by the Author.

Table III

Infrared frequencies (in cm^{-1}) of the propionaldehydes

CH_3CH_2CHO			CH_3CH_2CDO		
ν cm^{-1}	Intensity	Assignment	ν cm^{-1}	Intensity	Assignment
3840	w	2721 + 1105; 2993 + 850	3820	wsh	2993 + 856
			3780	w	2066 + 1730
3612	vw	2721 + 895			
3490	m	2 x 1750	3453	m	2 x 1730
3220	vw	2720 + 507			
3154	w	1750 + 1423	3170	vw	1730 + 1465
			3040	vwsh	2066 + 2 x 507
2993	vs	ν_2; ν_{16}	2993	vs	ν_2; ν_{16}
2943(?)	vw	ν_{17}(?)	2946(?)	vw	ν_{17}(?)
2919	vs	$\nu_{1,3}$	2917	vs	$\nu_{1,3}$
2813	vs	Fermi doublet of 1400 overtones and ν_4	2815	w	1400 overtones
2721	vs	ν_4	2719	w	1350 overtones; Residual CH_3CH_2CHO
2504	vvw	1423 + 1094	2539	vw	1465 + 1092
2402	w	1750 + 664	2427	vw	1334 + 1092
2331	vw	1468 + 848	2356	vw	1251 + 1099
			2316	vw	1465 + 856
2251	vw	1146 + 1105	2195	w	2 x 1092
2181	w	2 x 1094	2180	w	
2101	vw	1465 + 664			
2026	vw	1384 + 664	2066	vs	ν_4
1960	vw	1105 + 858	2050	vs	
1930	vw	1094 + 848			
1850	vw	1340 + 507	1887	w	1092 + 794; 1384 + 496
1763	vvs	ν_5	1746	vvs	ν_5
1744	vvs		1729		
1480			1478		
1468	s	ν_9	1465	s	ν_9
1456			1455		
1434			1430		
1423	s	ν_{10}	1419	s	ν_{10}
1410			1410		
1384	m	ν_8	1383	m	ν_8

Table III (Continued)

CH_3CH_2CHO			CH_3CH_2CDO		
ν cm^{-1}	Intensity	Assignment	ν cm^{-1}	Intensity	Assignment
1349 1340 1332	m	ν_{12}	1344 1334 1324	m	ν_{12}
1261 1254 1247	w	ν_{19}	1257 1251 1241	w	ν_{19}
1146 1129	m	ν_6	1194 1134 1119? 1099	w wsch vwsch	ν_6(?) or combination ν_6
1105 1094	s	ν_7	1092 1080	s	ν_{13};ν_7Overlapped
1020 1003	m	2 x 507	995 984 978	m	2 x 496
907 895 883	s	ν_{11}	863 856 849	s	ν_{11}
858 848 836	s	ν_{20}	804 794 783	s	ν_{20}
791	vvw	ν_{22}			
768 760 745	vvw	ν_{21}	753 747 740	vvw	ν_{21}
672 664 652	s	ν_{14}	660 653 644	s	ν_{14}
519 507	s	ν_{15}	509 496	s	ν_{15}

The frequencies reported in this table were read from spectra obtained under the following conditions:

CH_3CH_2CHO: PE 21, NaCl optics, 11-cm path length, 235 and 18 mm Hg pressure
PE 21, CaF_2 optics, 11-cm path length, 20 mm Hg pressure
PE 12C, KBr optics, 10-cm path length, 101 mm Hg pressure

CH_3CH_2CDO: PE 21, NaCl optics, 11-cm path length, 235 and 18 mm Hg pressure
PE 21, CaF_2 optics, 11-cm path length, 22 and 18 mm Hg pressure
PE 12C, KBr optics, 10-cm path length, 101 mm Hg pressure.

Table IV

Infrared frequencies of the butyraldehydes

$CH_3CH_2CH_2CHO$			$CH_3CH_2CH_2CDO$		
ν cm^{-1}	Intensity	Assignment	ν cm^{-1}	Intensity	Assignment
			3790	w	2071 + 1735
3488	m	2 x 1748	3450	m	2 x 1735
			3178	vw	1735 + 1465
2982	vs	$\nu_{2,21,23}$	2977	vs	$\nu_{2,21,23}$
2906	vs	$\nu_{1,3,4}$	2901	vs	$\nu_{1,3,4}$
2818	vs	Fermi doublet; 1400 overtones and ν_5	2820 2757	vw	1400 overtones and combinations
			2187	w	2 x 1094; in F.R. with ν_5(?)
2717	vs	ν_5	2071 2061	vs	ν_5
1754 1744	vvs	ν_6	1740 1729	vvs	ν_6
1466	s	ν_{11}	1465	s	ν_{11}
1427	m	$\nu_{12,13}$	1425	m	$\nu_{12,13}$
1410 1385	s	ν_{10}	1407 1384	s	ν_{10}
1363	s	$\nu_{14,15}$	1362	s	$\nu_{14,15}$
1272	m	ν_{25}	1280	m	ν_{25}
			1247	s	$CH_3CH_2CD_2CDO$ or other "impurity"
1220	m	ν_{26}	1212	m	ν_{26}
1126) 1116)	m	$\nu_{6,7}$	1127	m	$\nu_{6,7}$
			1099 1093 1086	vs	ν_{17}
1049	m	ν_8	1051	m	ν_8
988	m	ν_{16}			

Table IV (Continued)

$CH_3CH_2CH_2CHO$			$CH_3CH_2CH_2CDO$		
ν cm^{-1}	Intensity	Assignment	ν cm^{-1}	Intensity	Assignment
963 946 931	m	ν_{30}	925	m	ν_{16}
			~900	wsh	ν_{30}
~826	wb	ν_{17}			
788 781 774	s	$\nu_{27,28}$	756	s	$\nu_{27,28}$
676	s	$\nu_{19,20}$	649	s	$\nu_{19,20}$
519 509	s	ν_{18}	509 498	s	ν_{18}

The frequencies reported in this table were taken from spectra obtained under the following conditions:

C_3H_7CHO: PE 21, NaCl optics, 11-cm path length, 23 mm Hg pressure.
PE 21, CaF_2 optics, 11-cm path length, 21 mm Hg pressure.
PE 12C, KBr optics, 10-cm path length, 81 mm Hg pressure.

C_3H_7CDO: PE 21, NaCl optics, 11-cm path length, 23 mm Hg pressure.
PE 21, CaF_2 optics, 11-cm path length, 20 mm Hg pressure.
PE 12C, KBr optics, 10-cm path length, 71 mm Hg pressure.

Positions on the recorder chart were read to 1 A with an accuracy of ± 1 A. The wave lengths read from the chart recordings were corrected by using the position of the mercury 2537 A line, assuming that the wavelength scale was exactly linear. These corrections usually amounted to -1 to -4 A units.

The spectrometer records optical density, $\log_{10}(I_o/I)$, with an accuracy of ± 0.002 absorbance unit in the range from 0 to 1.0 and ± 0.005 unit in the range from 1.0 to 2.0. The chart-recording error may be as much as ± 0.006 unit because of possible slippage or shrinkage of the paper chart. Most of the observations were carried out in the range 0.0 to 1.0 absorbance unit. Chart readings of the optical density were made to the nearest 0.002 absorbance unit.

Tracings of the near-ultraviolet spectra of the molecules investigated are shown in Figs. 7 through 9. The pressures and the compounds are identified by small letters on the curve and in the legend. The closely spaced band structure in the spectra of acetaldehyde and acetaldehyde-d_1 was superimposable when the spectra were obtained at the same pressure at different times. (The frequencies of these closely spaced bands are not given, since they receive no interpretation here and, further, the exact values of the frequencies would be somewhat in doubt because of inadequate calibration.) The wave lengths (in A) and frequencies (in cm^{-1}) of the "band centers" of the broad bands or features present in the spectra of all the molecules studied were determined. The exact centers of the broad bands are difficult to determine, especially in the long-wave-length region of the spectra of the acetaldehydes. The positions determined were uncertain by about ± 5 A units.

The separations between adjacent "band centers" were determined from these frequencies. The average values of the separations in each compound are given in Table V.

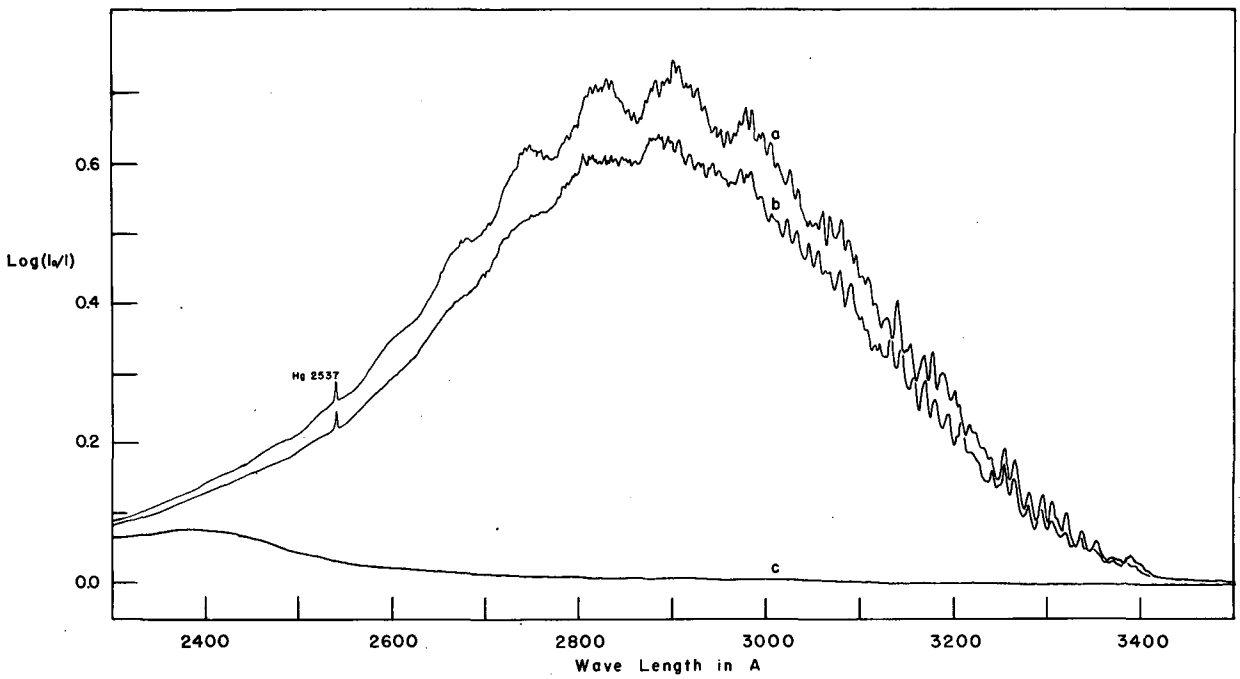


Fig. 7. The near ultraviolet spectra of acetaldehyde and acetaldehyde-d_1.

Key: a, CH_3CHO vapor at 105 mm Hg pressure with 10 cm path length.

b, CH_3CDO vapor at 105 mm Hg pressure with 10 cm path length.

c, Base line, evacuated quartz cell.

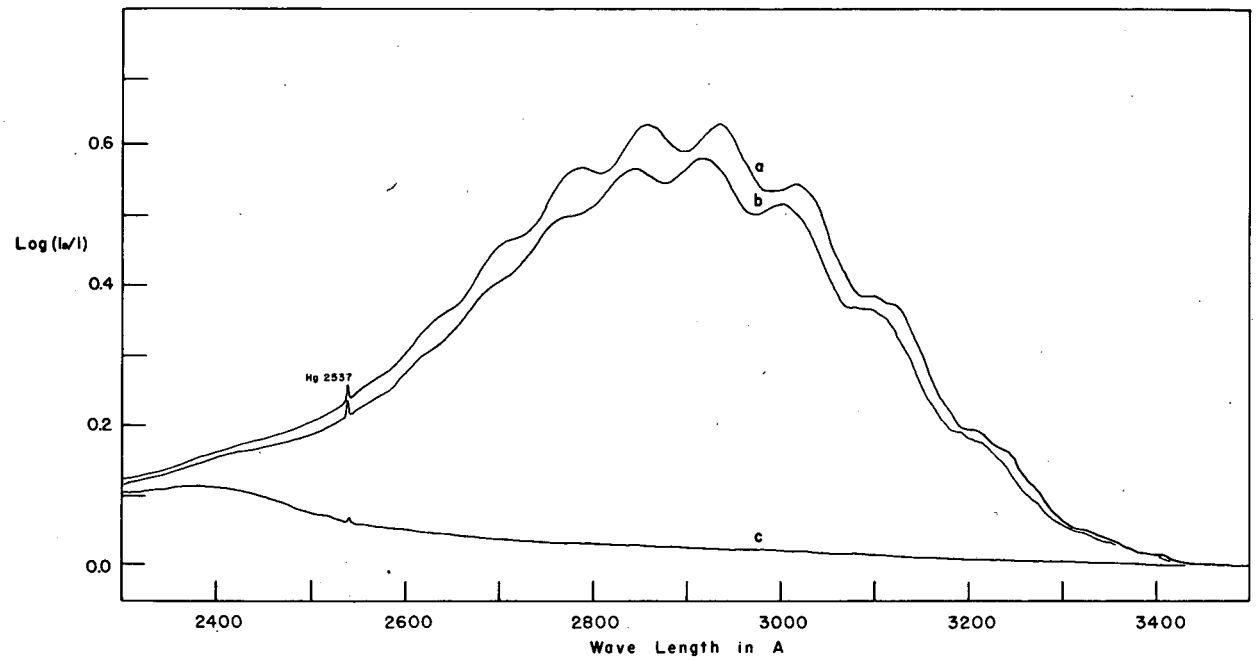


Fig. 8. The near ultraviolet spectra of propionaldehyde and propionaldehyde-d_1.

Key: a, C_2H_5CHO vapor at 72 mm Hg pressure with 10 cm path length.

b, C_2H_5CDO vapor at 72 mm Hg pressure with 10 cm path length.

c, Base line, evacuated quartz cell.

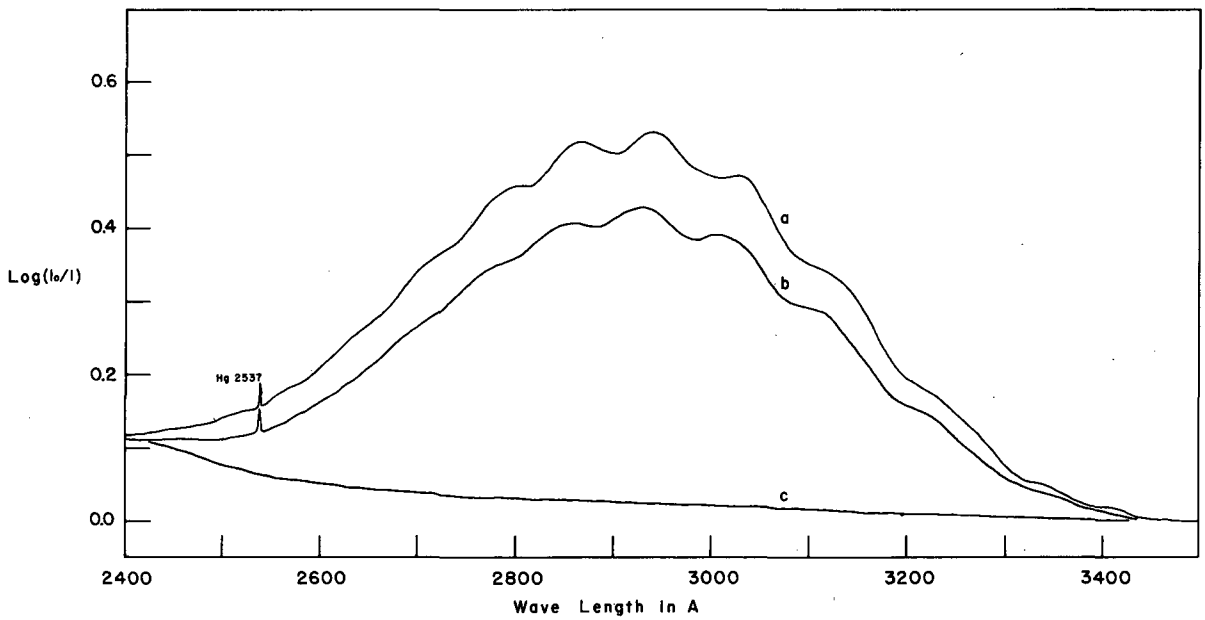


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Fig. 9. The near ultraviolet spectra of butyraldehyde and butyraldehyde-d_1.

Key: a, C_3H_7CHO vapor at 59 mm Hg pressure with 10 cm path length.

b, C_3H_7CDO vapor at 59 mm Hg pressure with 10 cm path length.

c, Base line, evacuated quartz cell.

Table V

Average separation between the centers of the broad bands in the near-ultraviolet spectra of each aldehyde investigated.[a]

	$\Delta\nu_{av}$ (in cm^{-1})	
Compound	This Research	Eastwood and Snow[33]
CH_3CHO	1016	1053
CH_3CDO	1023	
C_2H_5CHO	1032	1023
C_2H_5CDO	1039	
C_3H_7CHO	1015	1027
C_3H_7CDO	1034	

[a]The deviations from the average value by the individual separations was as much as $\pm$ 50 cm^{-1}; see Ref. 6.

The values of the extinction coefficient at various wave lengths are given in Table VI. The frequencies and extinction coefficients at maximum absorption are given in Table VII. The values of the extinction coefficient were calculated by the relation

$$\epsilon = \frac{2.303 \log_{10}(I_o/I)}{cd} \quad \text{liters/mole-cm} \qquad \text{(I-7)}$$

In the equation, ϵ is the extinction coefficient, d is the length of the absorption path (in cm), c is the concentration (in moles per liter), and $\log_{10}(I_o/I)$ is the corrected optical density. The corrected optical density is obtained by subtracting the base-line value of the optical density from the value read from the absorption curve: see Figs. 6 through 9.

The range of vapor pressures used for the ultraviolet studies was 50 to 100 mm Hg, although higher pressures were used to ascertain that Beer's Law as obeyed.

The Determination of f-Values.

The oscillator strength or f-values for the near-ultraviolet absorption have been determined from the integrated absorption coefficient for each compound studied. The f-values determined are given in Table VIII. The values were determined as follows. A plot of optical density, $\log_{10}(I_o/I)$, versus frequency, ν (in cm^{-1}), for the blank cell (base line) and the absorption spectrum of each compound were made and the area A enclosed by the two curves was determined with a planimeter. The value of the integrated absorption coefficient was obtained by using

$$\int k_\nu \, d\nu = 2.303(A)(T/273)(760/p)(1/L), \qquad \text{(I-8)}$$

where T is the temperature in ^oK, p is the pressure in mm Hg of gas with path length L cm, and k_ν is the absorption coefficient defined by

Table VI

Extinction coefficients at various wave lengths for the aldehydes investigated

Wave length (A)	ε CH_3CHO	ε CH_3CDO	ε C_2H_5CHO	ε C_2H_5CDO	ε C_3H_7CHO	ε C_3H_7CDO
3250			7.85	6.44	10.05	
3100	17.5	15.1	21.5	20.4	24.6	
2950	25.3	23.4	34.1	29.6		
2900					34.8	29.7
2700	19.4	17.6	24.7	21.6	23.5	18.6
2550	9.69	8.12	11.2	9.71	10.2	7.95

Table VII

Frequency and extinction coefficient at maximum absorption

Compound	Frequency (cm^{-1})	ϵ_{max} (liters/mole-cm)	Ratio H/D
CH_3CHO	34,496	29.0 ± 0.4	1.15
CH_3CDO	34,612	25.2 ± 0.4	
C_2H_5CHO	34,065	35.6 ± 1.0	1.09
C_2H_5CDO	34,295	32.6 ± 1.0	
C_3H_7CHO	33,969	37.0 ± 0.5	1.20
C_3H_7CDO	34,155	30.8 ± 0.4	

Table VIII

f-values and lifetimes for compounds of the type $R_1R_2 > CO$

R_1	R_2	$f \times 10^4$	$\tau \times 10^6$
H	H	2.4[a]	
CH_3	H	3.48	3.66
CH_3	D	3.04	4.11
C_2H_5	H	4.29	3.02
C_2H_5	D	3.85	3.23
nC_3H_7	H	4.48[b]	2.93
nC_3H_7	D	(3.76)[b]	3.44
CH_3	CH_3	4.54[c]	
C_2H_5	C_2H_5	4.50[c]	
CH_3	C_2H_5	5.82[c]	
CH_3	iC_3H_7	5.14[c]	

[a]Value obtained experimentally by Duncan and reported by Pople and Sidman.[16]

[b]The accuracy of these values is somewhat doubtful because of apparent overlap of the weak absorption (the n-π^* transition) with the strong absorption (the n-σ transition) at shorter wave lengths. The limits of accuracy are contained in the text. The f value for butyraldehyde-d, is quite doubtful since it is lower than the f value for propionaldehyde-d_1. The low value can be explained if more highly deuterated derivatives are present in the sample of butyraldehyde-d_1.

[c]Values from McClure.[37]

$$I_\nu = I_\nu^{\circ} \exp(k_\nu L). \qquad \text{(I-9)}$$

The integrated absorption coefficient is substituted into Eq. (I-8) in order to obtain the f-value,[38]

$$f = (mc)/(\pi e^2 N) \int k_\nu d\nu = 4.20 \times 10^{-8} \int k_\nu \, d\nu. \qquad \text{(I-10)}$$

Here N is the number of absorbers per cubic cm and m is the mass of the electron.

The absolute accuracy of the f-values is within $\pm$ 5 % for the acetaldehydes and propionalidehydes. For the butyraldehydes the accuracy is probably less because the near-uv absorption band appears to overlap the strong absorption band toward the violet, making the frequency region for the integrated absorption somewhat in doubt. The value for butyraldehyde is probably within $\pm$ 10% of the true value. Because of doubtful isotopic purity of the butyraldehyde-d_1, the estimated limits are +5 and -20%.

The lifetime τ of the excited state, if processes other than emission of radiation with return to the ground electronic state are unimportant, can be calculated from the f-value by

$$\tau = (mc)/(8\pi^2 e^2)(g'/g'')(\lambda_o^2/f) = 1.51(g'/g'')(\lambda_o^2/f). \qquad \text{(I-11)}$$

The ratio (g'/g") is the ratio of the statistical weights of the combining electronic states, which has been assumed equal to 1 for the near-ultraviolet absorption of the aldehydes, and λ_o is the wave length of maximum absorption.

The lifetimes determined by Eq. (I-11) are reported in Table VIII.

The lifetimes reported agree with lifetimes found by direct measurement,[39,40] only if there are no mechanisms, other than fluorescence with deexcitation to the initial state that can remove the molecule from the state reached directly by the absorption of light. Since the aldehydes are known to

dissociate when excited by near-ultraviolet light,[21-26] the lifetimes reported are probably too long. The quantum yield for the primary process ranges in value from 0.26 at 3130 A to 0.7 as 2380 A for acetaldehyde, with higher values reported for the other aldehydes.[41] Internal conversion to states of lower energy, as well as other de-excitation processes, could be in effect. All these processes, if operative, produce discrepancies between a directly observed lifetime (fluorescent lifetime)[39,40] and the lifetime from the integrated absorption coefficient.

DISCUSSION OF THE INFRARED SPECTRA

Acetaldehydes, CH_3CHO and CH_3CDO

The infrared and Raman spectra of acetaldehyde have been studied by numerous investigators,[1-4,42-46] but until recently no completely consistent vibrational assignment for both the infrared and Raman bands had been presented. The recent assignment for CH_3CHO and CH_3CDO by Evans and Bernstein[4] appears to be consistent with isotope shifts on deuteration, Raman depolarization ratios, and the thermodynamic functions.

The acetaldehyde molecule has at most C_s symmetry, with the formyl-group hydrogen and one methyl-group hydrogen in the plane of symmetry defined by the oxygen and two carbon atoms. There are ten a' and five a" fundamental modes of vibration, all infrared-active and Raman-active. The first complete infrared investigation of acetaldehyde was carried out by Thompson and Harris,[2] but their assignment was soon revised by Morris,[1] who investigated the infrared spectra of CH_3CHO and CD_3CDO. Pitzer and Weltner,[3] when calculating the thermodynamic properties of acetaldehyde, found it necessary to revise previous assignments[1,2] in order to attain agreement with the heat capacity of gaseous acetaldehyde, the observed spectra, and the product-rule ratios. A band reported at 440 cm^{-1} and assigned as a fundamental,[2] the CCO deformation; that it could not be detected, necessitated reassignment. The absence of this band has been confirmed by Evans and Bernstein[4] and in this investigation. The reassignment by Pitzer and Weltner[3] was confined to the low-frequency modes, where the assignment has greater effect on the thermodynamic functions.

The Raman spectrum of acetaldehyde with a complete assignment consistent with depolarization ratios was reported by Seewan-Albert

and Kahovec[45] at about the same time as the assignment by Pitzer and Weltner.[3] The two assignments are in good agreement except in the high-frequency region, where the Raman assignment[45] is more accurate. These assignments together with the Raman assignments of CH_3CHO and CH_3CDO by Evans and Bernstein[4] are given in Table IX. The reassignment of CD_3CDO[3] with added revisions in the high-frequency region is included in the table.

An assignment of the vibrational bands of CH_3CHO and CH_3CDO on the basis of isotope shifts observed in the infrared spectra was in progress here when the assignment appeared in the literature.[4] In view of the completeness of the assignment, little new information can be added; however, the frequencies of the vibrational bands of CH_3CHO and CH_3CDO observed in this research, presented in Table II with those of Evans and Bernstein,[4] in general independently confirm their values. For CH_3CHO, a band at 1395 cm^{-1} has been observed in this research which apparently remained unresolved in previous work.[4] The band is absent in the spectrum of CH_3CDO and is therefore assigned to the a' CH wagging mode in CH_3CHO, which had been assigned at $\sim$ 1390 cm^{-1} on the basis of a weakening of bands at $\sim$ 1410 cm^{-1} in the spectrum of CH_3CDO and the presence of a band at 1391 cm^{-1} in the Raman spectrum of CH_3CHO not found in CH_3CDO.[4]

The frequencies of the observed infrared bands agree very well with the reported values[4] except for a few very weak bands. The presence of very weak bands at 1270, 1256, and 1243 cm^{-1} in the spectrum of the CH_3CDO used in this research is attributed to the presence of about 5% CH_2DCDO and smaller amounts of more highly deuterated species, which were known to be present from a mass spectrometric analysis.

Table IX

Vibrational assignments for CH_3CHO, CH_3CDO and CD_3CDO by various investigators

		CH_3CHO			CH_3CDO	CD_3CDO
Symmetry	Motion	Infrared[2,3]	Raman[4]	Raman[45]	Raman[4]	Infrared[2,3]
a'	ν_1, CH_3 sym. str.	2710	2917	2917	2917	2235[b]
	ν_2, CH_3 asym. str.	2915	2964	2961	2965	2235[b]
	ν_3, CH str.	3004	2843 2751 2731	2844 2758 2729	2097 2069	2089[b] 2033[b]
	ν_4, CO str.	1740	1714	1718	1702	1730
	ν_5, CC str.	1114	1109	1115	1080	944
	ν_6, CH_3 sym. def.	1370	1342	1350	1343	1036[b]
	ν_7, CH_3 asym. def.	1414	1426	1428	1426	1155
	ν_8, CH wag	1350	1391	1390	1111	1048,[b](1090[b]R[46])
	ν_9, CH_3 rock	918	911	917	858	760
	ν_{10}, CCO def.	525	512	512	505	479
a"	ν_{11}, CH_3 asym. str.	2976	3001	2997	2998	2235[b]
	ν_{12}, CH_3 asym. def.	1440	1426	1428	1426	1155
	ν_{13}, CH_3 rock	883	885	883	~825	730
	ν_{14}, CH wag	767	767	768	674	570 or 650[b]
	ν_{15}, CH_3 torsion					

[b]Revised by the author.

Bands in the frequency region 1200 to 1300 cm^{-1} have been assigned to modes of motion in compounds containing the $-CD_2H$ group.[32,33,34]

The assignments given for the frequencies in Table II are for the most part those of Evans and Bernstein.[4] The assignments marked with "a" were added by the author.

The frequency shifts of the fundamental vibrational bands produced by the replacement of the formyl hydrogen with deuterium are discussed because the reasoning used for CH_3CHO and CH_3CDO in making an assignment is applied to the other aldehydes. From Tables II and IX, one can easily pick out motions whose frequencies are unchanged or only slightly altered in CH_3CHO and CH_3CDO. These motions are internal modes[47] or pure motions, which do not interact with other modes of motion in the molecule. The CH_3 stretching and deformation modes are examples. The CO stretch, the CC stretch, and the CCO deformation frequencies are lowered slightly, ~ 20 cm^{-1}, from their value in CH_3CHO, as would be expected if the reduced mass of the system were increased, therefore the formyl hydrogen must be involved in these three modes. The motions expected to show the largest shift upon isotopic substitution of the formyl hydrogen are the CH a' stretch, a' wag, and a" wag. The ratios of the frequencies in CH_3CHO to those in CH_3CDO for these motions are 1.32, 1.25, and 1.14 respectively. The reduction in size of the ratio as the frequency of the motion decreases (see Table IX) indicates increasing interaction with other motions of the same symmetry in the molecule. These interactions are indeed necessary to explain the observed frequency shifts of the bands assigned to the in-plane (a' CH_3) and out-of-plane (a" CH_3) rocking motions of the methyl group. The shifts are from 918 cm^{-1} in CH_3CHO to 850 cm^{-1} in CH_3CDO and from 846 cm^{-1}

to 802 cm^{-1}, respectively, for the two motions. The bands retain the same contours and order, indicating that they are to be associated with the same two motions in both molecules. The intensities are lower in the spectrum of CH_3CDO, for no apparent reason.

Evans and Bernstein[4] have offered the following explanations for these shifts. A coupling of the a" CH_3 rock and the a" CH wag in CH_3CHO produces bands at 846 cm^{-1} and 763 cm^{-1} respectively. In CH_3CDO the coupling is broken and the a" CH_3 rock falls to its "normal" frequency of 802 cm^{-1}. The corresponding shift of the a' CH_3 rock may be explained if the a' CD wag and a" CH_3 rock in CH_3CDO are coupled to produce bands at 1119 cm^{-1} and 856 cm^{-1}, respectively; if the interaction were absent the a' CD wag might lie at $\sim$ 1050 cm^{-1} and the a' CH_3 rock at $\sim$ 920 cm^{-1}. An equally plausible explanation involves a coupling of the a' CC stretch and the a' CH_3 rock in CH_3CDO to produce bands at 1080 cm^{-1} and 856 cm^{-1}. As before, in the absence of the interaction the CC stretch might have occurred at $\sim$ 1050 cm^{-1}. For further details of the assignment the reader is referred to the papers discussed here.[1-4,42-46]

Propionaldehydes, CH_3CH_2CHO and CH_3CH_2CDO

The infrared and Raman spectra of propionaldehyde have received little attention. Pinchas[48] has reported the infrared bands arising between 3000 and 2400 cm^{-1} for solutions of propionaldehyde in carbon tetrachloride. Bands with frequencies of 2970, 2900, 2710, and 2830 cm^{-1} were reported.[48] The Raman spectrum of propionaldehyde has been investigated by Kohlrausch and Koppl,[49] and the frequencies observed and the assignment are shown in Table X. An assignment by H. Seewan-Albert[50] based on the data by Kohlrausch and Koppl is also included in the table. This Raman investigation appears to be the only reported study of propionaldehyde covering the complete vibrational frequency region.

Table X

The Raman spectrum of propionaldehyde and assignments

Band frequency[49] (cm^{-1})	Kohlrausch and Koppl[49]	Seewan-Albert[50]
265	-	def.
512	CCO def.	CCO def.
846	-	CCC str.
893	-	CH a" wag
996	-	CCO str.
1089	-	1089 to 1454 CH_3 and
1246	-	CH_2 motions
1392	CH a' wag	CH a' wag
1416	-	
1454	-	
1722	CO str.	CO str.
2724	CH str.	CH str.
2823	Fermi band	
2893	CH_3 and CH_2 str. modes	CH_3 and CH_2 str. modes
2939	CH_3 and CH_2 str. modes	CH_3 and CH_2 str. modes
2978	CH_3 and CH_2 str. modes	CH_3 and CH_2 str. modes

The infrared spectra of CH_3CH_2CHO and CH_3CH_2CDO have been observed and the frequencies of the bands observed in the region 4000 to 450 cm^{-1} are reported in Table III. Tracings of the infrared spectra of the two compounds are shown in Figs. 3 and 4. With these data and the complete vibrational assignment for CH_3CHO and CH_3CDO available, an assignment of the bands observed for the propionaldehydes was made.

CH_3CH_2CHO and CH_3CH_2CDO have C_s symmetry, since the molecules contain, at most, one plane of symmetry. This plane contains the three carbon atoms, the oxygen atom, and two hydrogen atoms (one the formyl hydrogen and one methyl group hydrogen). The plane also bisects the angle between the methylene group hydrogens. The molecules each have 15 a' and 9 a" fundamental modes of vibration which are characterized as stretch, deformation, and other types of motion and are listed in Table XI. All the modes are infrared-active and Raman-active. Columns 4 and 6 of Table XI give the frequencies of the bands assigned to the fundamental modes of the two molecules. The assignments of all the observed bands of C_2H_5CHO and C_2H_5CDO to fundamental and overtone or combination tones are given in Table III.

In the discussion of the assignment, the fundamental modes of vibration are divided into groups and the assignment within the group is discussed.

The CH_3 and CH_2 Stretch Motions

The three CH_3 stretch motions, ν_1, ν_2, and ν_{16}, and the two CH_2 stretch motions, ν_3 and ν_{17}, have been assigned with reference to an assignment of the same motions in 3-pentanone by Nolin and Jones.[51] Their assignment was based on the disappearance of bands in the spectra

Table XI

Assignments for the propionaldehydes[a]

Symmetry	Designation	Motion	CH_3CH_2CHO Infrared (cm^{-1})	CH_3CH_2CHO Raman (cm^{-1})	CH_3CH_2CDO Infrared (cm^{-1})
a'	ν_1	CH_3 sym. str.	2919	2939) Fermi 2883) doublet	2919
	ν_2	CH_3 asym. str.	2993	2978	2993
	ν_3	CH_2 sym. str.	2919	2939	2919
	ν_4	CH str.	2813) 2721)	2823) Fermi 2724) doublet	2050
	ν_5	CO str.	1744	1722	1729
	ν_6	CC str.	1129	1089	1134
	ν_7	CC str.	1094	996	1080
	ν_8	CH_3 sym. def.	1384	over-lapped?	1383
	ν_9	CH_3 asym. def.	1468	1454	1465
	ν_{10}	CH_2 sym. def.	1423	1416	1419
	ν_{11}	CH_3 rock	895	893	856
	ν_{12}	CH_2 wag	1340	-	1334
	ν_{13}	CH wag	~ 1395	1392	1094
	ν_{14}	CCC def.	664	666	653
	ν_{15}	CCO def.	509	512	496
a"	ν_{16}	CH_3 asym. str.	2993	2978	2993
	ν_{17}	CH_2 asym. str.	2943	2939	2946
	ν_{18}	CH_3 asym. def.	1468	1454	1465
	ν_{19}	CH_2 twist	1254	1246	1251
	ν_{20}	CH_3 rock	848	846	794
	ν_{21}	CH_2 rock	760	-	747
	ν_{22}	CH wag	791	-	> 660
	ν_{23}	CH_3 torsion	-	-	-
	ν_{24}	CHO torsion	-	-	-

[a]The Raman frequencies used in this assignment are from Kohlrausch.[43]

of various deutero derivatives of 3-pentanone. A summary of some of their results is given in Table XII. A comparison of the frequencies in Table III observed for C_2H_5CHO and C_2H_5CDO with the assigned frequencies in Table XII, gives the assignment immediately. The weak band at 2943 cm^{-1} assigned to ν_{17} is a doubtful band and the ν_{17} motion may well belong at 2993 cm^{-1}.

The CH and CD Stretch Motions

The assignment of the CH stretch, ν_4, and the Fermi resonance band associated with the motion at 2721 and 2813 cm^{-1} follows directly from the observed shift upon deuteration. Further evidence in support of this assignment is the absence of these bands in the Raman spectra of propionyl chloride and propionyl bromide[43] and the assignment for CH_3CHO.[4,43] The Fermi doublet is undoubtedly the result of the a' CH stretch fundamental and the first harmonic of the a' CH wag at $\sim$ 1395 cm^{-1} plus other combination tones in that region. The corresponding motion in C_2H_5CDO, the CD stretch, occurs at 2066 and 2050 cm^{-1}, the R and P branches respectively. The bands nearest in frequency to this strong fundamental occur at 2203, 2195, and 2179 cm^{-1}. These bands are quite weak, indicating little or no Fermi resonance with the fundamental. The bands are undoubtedly overtones of the a' CD wag and a' CC stretch motions which produce bands in the 1100 cm^{-1} region. The absence of a Fermi doublet in C_2H_5CDO may result from an interaction between the a' CD wag and a' CH_3 rock (see below) to produce a CD wag band at 1094 cm^{-1} when its normal positions might have been lower. The overtone is now too high for interaction with the CD stretch fundamental.

The Skeletal Stretch Motions

The CO stretch, ν_5, is assigned at 1744 in CH_3CHO and at 1729 in

Table XII

Assignment for diethyl ketone[a]

Band frequency (cm^{-1})	Related group	Nature
2977	CH_3	Attributed to a pure asymmetric stretch
2936 2883	CH_3	Could arise from the symmetrical stretch vibration and a harmonic of the 1461-cm^{-1} band
2902	CH_2	Symmetrical stretch
2955	CH_2	Present in the spectrum of $(CD_3CH_2)_2CO$ but swamped out in $(CH_3CH_2)_2CO$. May be the CH_2 asymmetric stretch
1461 1454	CH_3	Associated with the asymmetrical bend
1414	CH_2	Bend
1379	CH_3	Symmetrical bend
1355	CH_2	Identified with the CH_2CO group

[a]The information contained in this table was taken from a paper by Nolin and Jones.[51]

CH_3CDO in accordance with the observation of a band in this frequency region for all carbonyl compounds.[43] The two a' CC stretch motions, ν_6 and ν_7, are set at 1146 and 1129, and at 1105 and 1094 cm^{-1} in C_2H_5CHO on the basis of the assignment of the CC stretch at 1122 and 1104 cm^{-1} in CH_3CHO.[3,4] These frequencies are within the limits set by Brown, Sheppard, and Simpson[47] for the paraffins and by Colthup[52] for the aliphatic aldehydes. In C_2H_5CDO, these bands are overlapped strongly by the a' CD wag, but the shoulders at 1134 and ~ 1119 cm^{-1} and some of the intensity at 1094 to 1080 may be assigned as the frequencies of the CC stretch motions in this molecule. A band at 1194 cm^{-1} appears in the spectrum of this molecule and may be one of the a' CC stretch modes displaced from its normal position by interaction with the strong a' CD wag frequency. A band at 1192 cm^{-1} is present very weakly in the spectrum of CH_3CDO and remained unexplained in the assignment.[4] This band could be a combination band of a low-lying fundamental and bands present in the 850-cm^{-1} region. It may also be a band produced by more highly deuterated species present in the sample. The assignment of the CC stretch motions in C_2H_5CDO at 1134 and 1119 cm^{-1} and at 1094 and 1080 cm^{-1} is preferred.

The CH_3 and CH_2 Deformation Motions

These motions ν_8, ν_9, ν_{10}, ν_{12}, ν_{18}, and ν_{19} in Table XI show little interaction with other motions and are therefore classified as internal modes. The assignments of these motions were made with reference to the corresponding assignments in 3-pentanone.[51] The discussion of these motions in the paraffins by Brown, Sheppard, and Simpson[47] was useful in making the assignments, especially for the CH_2 twist motion at

1254 cm^{-1}. It should be noted that the three bands at 1478, 1464, and 1455 cm^{-1} assigned to the a' and a" asymmetric deformation of the CH_3 group, are somewhat in doubt. Because of the presence of strong water bands in this region of the spectrum, the splitting of the band may not be real but only the result of water "emission" bands caused by atmospheric water vapor in the blank beam path.

The a' CH and the a' CD wag motions

The a' CH wag, ν_{13}, although no band is actually observed, is assigned at $\sim$ 1395 cm^{-1} because of an observed weakening of the absorption in this region in the spectrum of C_2H_5CDO and the presence of a band at 1392 cm^{-1} in the Raman spectrum of C_2H_5CHO which is absent in the spectra of propionyl chloride and bromide.[43,49] The assignment in acetaldehyde also supports this assignment. The corresponding CD motion in C_2H_5CDO is assigned at 1094 cm^{-1} in accordance with the assignment in CH_3CDO.[4]

Of the eight remaining normal modes of motion, two are torsional modes, ν_{23} and ν_{24}, which undoubtedly occur outside the frequency region investigated. The six remaining modes are rocking, wagging, and deformation motions, which occur in the low-frequency region with the possibility of considerable interaction with motions of the same symmetry. The descriptions of these motions, therefore, are only approximate, and the shifts observed in the spectra of the isotopic derivatives indicate the degree of mixing of the motions with other modes.

The a" CH_2, the a' and a" CH_3 Rocking, and the CH a" Wag Motions

The a' and a" CH_3 rocking motions in C_2H_5CHO are assigned to bands at 895 and 848 cm^{-1}, respectively, which shift in frequency by approximately 50 cm^{-1} in C_2H_5CDO to 856 and 794 cm^{-1}. The bands in

C_2H_5CDO have the same contours and order as those in C_2H_5CHO. They are weaker in intensity for no apparent reason. These observations are analogous to the occurrences in the spectra of CH_3CHO and CH_3CDO and therefore are believed to arise from interactions of the same nature as those proposed for the latter molecules.[4]

The a' CD wag and a" CH_3 rock interact to produce bands at 1094 and 856 cm^{-1}; the CD motion moving up in frequency from its "normal" position, $\sim$ 1050 cm^{-1}, while the CH_3 motion shifts down in frequency. This interaction is absent in C_2H_5CHO, since the bands are separated considerably more than in C_2H_5CDO. The a" CH_3 rock is assumed to interact with the a" CH wag in C_2H_5CHO to produce bands at 848 and 791 cm^{-1}, respectively, but upon deuteration the coupling is broken and the a" CH_3 rock drops in frequency to its normal position at 794 cm^{-1}. Thus the shift in frequency of the CH_3 rock motions upon deuteration of the formyl group are explained.

The a" CH and a" CD wagging motions are assigned at 791 and $\sim$ 660 cm^{-1}, respectively, following the corresponding assignment in CH_3CHO and CH_3CDO.[4] The 791-cm^{-1} band is a very weak band, but the corresponding band in CH_3CHO at 764 cm^{-1} is also very weak. No band is observed at $\sim$ 660 cm^{-1}, where the a" CD wag is assigned, because an intense band, present in this region, assigned to a motion of a' symmetry, undoubtedly obscures the a" CD band which is expected to be weak. The band observed at 688 cm^{-1} in CH_3CDO is, indeed, a very weak band, barely detectable at 400 mg Hg pressure.

The a" CH_2 rock, ν_{21}, is assigned to a weak band at 760 cm^{-1} in C_2H_5CHO and at 747 cm^{-1} in C_2H_5CDO, in accordance with a similar assignment in propane[53] and the assignment of this motion in this region in

other molecules.[47] The weakness of this band, and its absence in the Raman spectrum,[43] remain unexplained.

The Skeletal Deformation Motions

Of the two skeletal deformation motions, the CCO deformation, ν_{15}, is most confidently assigned. This motion is assigned to the band at 509 cm^{-1} in C_2H_5CHO and at 496 cm^{-1} in C_2H_5CDO with reference to the corresponding assignment in CH_3CHO and CH_3CDO[8] and the presence of a band in this frequency region in the spectrum of a large number of compounds containing the CCO group.[43,49] The CCC deformation motion, ν_{14}, is assigned at 664 cm^{-1} in C_2H_5CHO and at 653 cm^{-1} in C_2H_5CDO on the basis of the presence of a band in this frequency region in a large number of compounds containing the CCC group.[43,49] In propane[53] this motion is assigned at a much lower frequency, 383 cm^{-1}; however, the motions are undoubtedly different in the two molecules. An alternate assignment would be to assign this strong band at $\sim$ 660 cm^{-1} to the a" CH_2 rock. This assignment would leave the band at 760 cm^{-1} unexplained and the frequency, 660 cm^{-1}, is outside the region (700 to 1000 cm^{-1}) where the frequency of the CH_2 rock is expected.[47]

One band in the low-frequency region at 1020 and 1003 cm^{-1} in C_2H_5CHO and at 995, 985, and 978 cm^{-1} in C_2H_5CDO has been assigned as an overtone of the strong CCO deformation band at 519 and 509 cm^{-1} and at 509 and 496 cm^{-1}. The frequency shifts certainly indicate that the assignment is correct, since the combination or overtone frequency shift is nearly twice the shift of the fundamental frequency. The presence of a band at 996 cm^{-1} in the Raman spectrum of C_2H_5CHO cases some doubt upon the band as a combination band.[43] If the a' overtone were in Fermi resonance with strong a' fundamental bands in the 1100 region, the presence of

This band in the Raman spectrum would be explained, since strong Fermi bands are observed in the Raman effect.[43] The band could be assigned to an a' CC stretch motion, but this leaves the band at 1146 and 1129 unexplained except for possible combination of the fundamental bands in the 850 cm^{-1} region with some low-lying fundamental modes. The assignment of the band as an overtone of the CCO deformation fundamental (2 x 509 = 1018 and 2 x 496 = 992) is favored.

Butyraldehydes, C_3H_7CHO and C_3H_7CDO

Butanal (n-butyraldehyde) and butanal-d_1 have C_s symmetry, with the chain and two hydrogens defining the plane of symmetry which bisects the angle between the hydrogens of each methylene group. The molecules in this arrangement have 33 normal modes of vibration each -- 20 of a' symmetry and 13 of a" symmetry -- and all the modes are infrared-active and Raman-active.

The infrared spectrum of n-butanal has been investigated in the 3000-to-2500 cm^{-1} region by Pinchas.[48] Pinchas was interested in the position of the CH stretch band and the Fermi band associated with it, and reported values of 2710 and 2820 cm^{-1}, with weaker bands at 2580 and 2650 cm^{-1} for n-butanal in carbon tetrachloride solution. The infrared spectrum of n-butanal and n-butanal-d_1 in solutions of carbon tetrachloride have been observed by Eggers and Lingren.[54] The reported shifts in frequency upon deuteration of the n-butanal are 2785 to 2180 cm^{-1}, 2690 to 2060 cm^{-1}, and 1385 to 1095 cm^{-1}; these bands were assigned to a Fermi band, the CH stretch, and the a' CH wag, and to the corresponding CD motions.

The Raman spectrum of n-butanal has been reported by Kholrausch and Koppl.[49] These Raman frequencies and the infrared frequencies (observed in this research for n-butanal and n-butanal-d_1) have been assigned (see Table XIII).

The frequencies of the infrared bands for the two molecules in the vapor phase are reported in Table IV. The conditions under which the observations were made are included at the end of the table. The assignment of all the observed bands is given in Table IV. The assignments presented for these two molecules are based on the assignments for the other aldehydes reported here.

The assignments for the n-butanals in the high-frequency region, 4000 to 1200 cm^{-1}, are nearly identical with the assignments for the propionals. The a" CH_2 twisting motions in butanal are assigned to two bands at 1272 and 1220 cm^{-1}, which probably arise from in-phase and out-of-phase twistings of the two CH_2 groups. These bands occur at $\sim$ 1280 and $\sim$ 1212 cm^{-1} in butanal-d_1 and are strongly overlapped by a strong band at 1247 cm^{-1}, which may be a band produced by $CH_3CH_2CHDCDO$, $CH_3CH_2CD_2CDO$, or some impurity.*

In the low-frequency region, the assignments for the butanals are similar to those in the propionals, with the same reasoning applied to explain the frequency shifts of the a' and a" CH_3 rocking modes. The a" CH wag is assigned at 826 cm^{-1} since the broad band at 826 cm^{-1} in butanal is very weak in the spectrum of butanal-d_1. The assignment of the a" CD wag at >660 cm^{-1} was made with reference to the assignment in the other aldehydes. A band at this frequency has not been resolved in the spectrum of butanal-d_1.

*See the section on Purity, p. 15

Table XIII

Assignment for the butyraldehydes

Symmetry	Designation	Motion	C_3H_7CHO Infrared (cm^{-1})	C_3H_7CHO Raman (cm^{-1})	C_3H_7CDO Infrared (cm^{-1})	
a'	ν_1	CH_3 sym. str.	2906	2937)Fermi 2876)doublet	2901	
	ν_2	CH_3 asym. str.	2982	2968	2977	
	$\nu_{3,4}$	CH_2 sym. str.	2906	2907	2901	
	ν_5	CH str.	2818 2717	2817)Fermi 2732)doublet	2187 2061	Weak Fermi band?
	ν_6	CO str.	1744	1718	1729	
	ν_7	CC str.	1126	1112	1127	
	ν_8	CC str.	1126	1112	1127	
	ν_9	CC str.	1049	1040	1051	
	ν_{10}	CH_3 sym. def.	1384	Overlapped	1384	
	ν_{11}	CH_3 asym. str.	1466	1450	1466	
	$\nu_{12,13}$	CH_2 sym. str.	1427	1409	1425	
	$\nu_{14,15}$	CH_2 wag	1363	-	1357	
	ν_{16}	CH_3 rock	988	934	925	
	ν_{17}	CH wag	~ 1390	1389	1093	
	ν_{18}	CCO def.	509	512	498	
	$\nu_{19,20}$	CCC def.	676	666	649	
a"	ν_{21}	CH_3 asym. str.	2982	2968	2977	
	$\nu_{22,23}$	CH_2 asym. str.	2982	2937	2977	
	ν_{24}	CH_3 asym. def.	1466	1450	1466	
	ν_{25}	CH_2 twist	1272	1289	1280	
	ν_{26}	CH_2 twist	1220	1218	1212	

Table XIII (Continued)

Symmetry	Designation	Motion	C_3H_7CHO Infrared (cm^{-1})	C_3H_7CHO Raman (cm^{-1})	C_3H_7CDO Infrared (cm^{-1})
a"	ν_{27}	CH_3 rock	946	890	~ 900
	$\nu_{28,29}$	CH_2 rock	781	780	756
	ν_{30}	CH wag	826	836	> 660
	ν_{31}	CH_3 torsion			
	ν_{32}	CHO torsion			
	ν_{33}	CH_3CH_2 torsion			

The Raman frequencies used in this assignment were obtained from tables contained in Kohlrausch.[43]

The assignment presented for the butanals is only tentative, particularly in the low-frequency region. Some of the bands reported for butanal-d_1 may be doubtful because of possible impurities or, more likely, because of the presence of more highly deuterated species in the sample of butanal-d_1.

CONCLUSIONS -- INFRARED SPECTRA

The infrared investigation of the acetaldehydes (CH_3CHO and CH_3CDO) has confirmed some reported work,[4] and added understanding for the work on the higher aldehydes. The infrared spectra and vibrational assignments for propional, propional-d_1, butyraldehyde, and butyraldehyde-d_1 are believed accurate in the high-frequency region, but modifications of the low-frequency assignment may result from further work on the spectra in this region, from 900 cm^{-1} down. The Raman spectra of these compounds would be helpful and undoubtedly would reveal the frequency of the CD out-of-plane wag motion. The solid-phase infrared spectra would also be of assistance in resolving some of the remaining difficulties.

DISCUSSION OF THE ULTRAVIOLET SPECTRA

The Regions of Absorption and the General Appearance of the Spectra

All the aliphatic aldehydes have characteristic absorptions in the near and vacuum ultraviolet.[5-15] The near-ultraviolet absorption occurs between 3500 and 2300 A, while the second absorption starts at roughly 2000 A and continues into the vacuum ultraviolet.[7,14] The long-wave-length absorption is quite weak, but the absorption at shorter wave lengths has the strength expected for an allowed transition.[12,14] Some very weak bands have been reported for formaldehyde at wave lengths longer than 3500 A, and the absorption has been attributed to a transition between the singlet ground state and a triplet upper state.[10,13] The nature of the near-ultraviolet absorption in the aliphatic aldehydes is discussed later.

The near-ultraviolet absorption is of greater interest here because the investigation has been confined to this wave-length region. The first two members of the series, formaldehyde and acetaldehyde, have a large number of sharp bands on the long-wave-length side of the absorption.[5,6] These bands become diffuse quite rapidly, especially in acetaldehyde and eventually converge to take on the appearance of a continuum. Rotational analyses of several of the bands in formaldehyde have been carried out,[9,15] and several vibrational analyses of the spectrum of formaldehyde have been published.[10] In acetaldehyde, approximately 70 bands occur between 3500 and 2600 A, but no satisfactory analysis of these bands has been presented and no analysis is attempted here. The sharp bands in acetaldehyde are underlain by a broad band structure which is present throughout the region of absorption (see Curve a, Fig. 7). In propionaldehyde and the higher aldehydes, the sharp band structure is absent but the broad bands remain.

The loss of sharp bands as the molecular weight increases probably results from the increase in the number of vibrational modes in the molecule - - 6, 15, 23, 33, etc. -- and an increase in the moments of inertia. The increase in the number of vibrational levels produces a large amount of overlap of bands, while the increase in the moments of inertia causes the rotational lines to lie closer together. As a result, the spectrum has the appearance of a continuous absorption. Another process complicating the appearance and leading to continuous or pseudocontinuous absorption is predissociation, which probably occurs more readily and at lower frequencies as the first few members of the series are ascended.

Isotope Effects on the Near-Ultraviolet Spectra

Reproductions of the near-ultraviolet spectra observed for the aldehydes investigated are shown in Figs. 7 through 9. All the spectra have the same general appearance, with the broad bands the predominant feature. The positions of these bands in the normal compounds were compared with the values determined by Eastwood and Snow.[6] The agreement was as good as could be expected considering the nature of the bands (see Figs. 7 through 9). The separation between adjacent band centers is nearly constant for each aldehyde, and about the same for all the aldehydes.

These broad bands have been attributed to the CO valence stretch in the upper state.[6,10,11] The average values of the band-center separations are given in Table V for the aldehydes investigated. The separation is unaffected by the isotopic substitution.

The centers of the broad bands in the spectrum of each deutero-aldehyde lie at higher frequencies (shorter wave length) than the centers of the corresponding bands in the normal aldehyde (see Figs. 7 through 9). The explanation lies in a consideration of zero point energies.

The electronic energies of the combining states and the shapes of their n-dimensional hypersurfaces are expected to remain unchanged on isotopic substitution.[18,55] The zero-point energy in each electronic state is determined by the frequencies of the fundamental modes of vibration in that state. In the aldehydes, the fundamental vibrations are undoubtedly lower in frequency in the upper than in the ground electronic state.[10] As a result, the lowering of the zero-point energy upon substitution of a deuterium atom for a hydrogen atom is larger in the ground state than in the upper state of the combining electronic levels. The electronic energy or frequency of the radiation for excitation from the zero vibration level of the ground state to the zero vibration level of the upper state is greater for the deutero derivative. Since the CO valence stretch in the upper state is not appreciably changed by the isotopic substitution (see Table V), excitation from the zero vibronic level of the ground electronic state to vibronic levels in the upper state in which the CO valence stretch is excited by one or more quanta requires more energy with the deutero derivative; thus, the shift of the broad bands to shorter wave lengths upon isotopic substitution can be accounted for.

If the zero-zero transition is forbidden, and these broad bands result from a progression of the CO vibration which originates with the vibronic transition, zero + (v'(CH) or v'(CD)) <— zero,* the same

*This would be the case for a vibrationally allowed transition,[16,56] with v' representing one quantum of the mode responsible. See Appendices AII and AIII.

shift may be expected provided the difference v'(CH)- v'(CD) is less than the difference $\nu_{oo}(D) - \nu_{oo}(H)$. Here v'(CH) and v'(CD) are the frequencies of the CH and CD out-of-plane wag vibrations in the upper state, and $\nu_{oo}(H)$ and $\nu_{oo}(D)$ are the frequencies of the "zero-zero" transitions in the normal and deutero derivatives, respectively.

There is a marked effect on the specific absorbance of each aldehyde upon deuteration. In each case, the deuteroaldehyde has a lower extinction coefficient than the normal aldehyde at the same wave length throughout the entire region of absorption (see Figs. 7 through 9). (Also see extinction coefficients in Tables VI and VII). Because of this, the f-value (calculated from the integrated absorption coefficient), which is a measure of the strength of the absorption, is lower for the deuteroaldehyde.

It was realized that impurities could be responsible, and precautions were taken to remove this possibility. (The normal and deuteroderivatives of the acetaldehydes and propionaldehydes were synthesized and purified by the same procedures. The normal compounds prepared by these procedures had extinction coefficients which were in exact agreement with those for purified commercial compounds.)

An examination of the nature of the transition and the mechanism responsible for the intensity of the absorption has led to an explanation as given below.

The transition involved is a forbidden transition, but there is intensity (that is, an observable absorption) because of interactions dependent on the zero-point nuclear displacements of the formyl hydrogen or deuterium atom in a specific vibration. The intensity of the transition increases

directly with the magnitude of the displacement, and, since the magnitude of the displacement is inversely proportional to the nuclear mass, the intensity of the transition (absorption) is greater for the normal than for the deutero compound. Thus, the theory and experiment are in agreement.

The Nature of the Transition

Analyses of the absorption in various aldehydes have contributed considerable information about the transition.* The weakness of the absorption, f-value $\sim 3 \times 10^{-4}$, requires that the transition describing the absorption must be a forbidden type. The f-value is much larger than that expected for a multiplicity forbidden transition in a molecule of this type (f about 10^{-6}).[37] The analyses also indicate a weaker CO bond in the upper state of the combining levels.[‡]

The nature of the transition is discussed with formaldehyde used as a model molecule, since the arguments are exact for this molecule.

1. Formaldehyde. The description of the transition presented is essentially the same as the description given by Pople and Sidman.[16] The transition is confined to the CO group of the molecule. The molecular orbitals for this group are given in Fig. 10, Column 1.

Electronic states that are possible with these orbitals, are given in Column 1 of Table XIV in order of increasing energy from top to bottom. In the column, the first symbol in the parentheses designates the orbital, the second designates the symmetry species of the orbital (see Fig. 10, Column 2), and the exponent designates the number of electrons in the orbital. The second column in the table gives the symmetry species

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*The transition responsible for the near uv absorption in aldehydes and ketones has been considered in numerous papers.[6-16] Those by Mulliken,[11] McMurry,[12] and Pople and Siman[16] are the most complete.

‡ From rotational analyses for formaldehyde,[9,15] the CO bond length is known to increase in the upper state. In addition, the CO stretch frequency in the upper state is about 2/3 the ground-state value (see Tables V and IX).

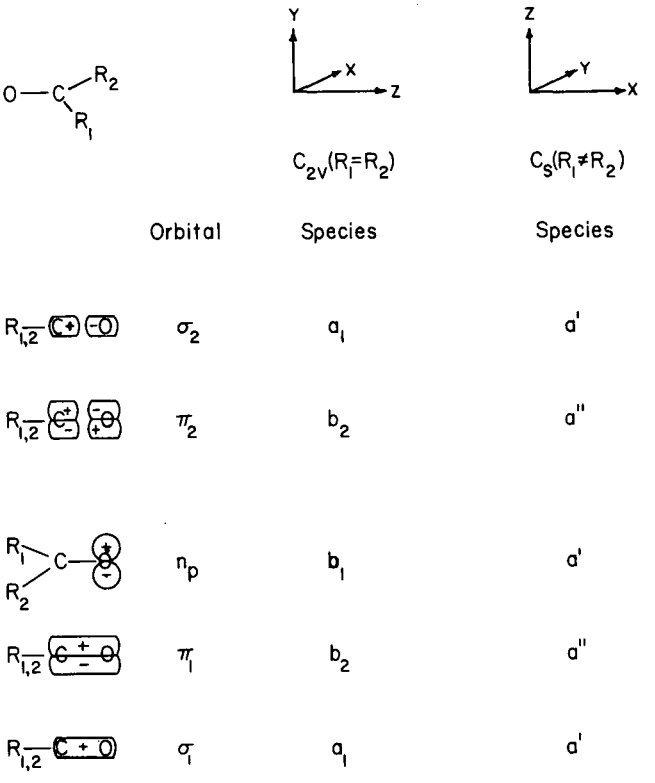

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Fig. 10. Molecular orbitals for R_2CO molecules and species of the orbitals from C_s and C_{2v} point groups.

Table XIV

Electronic states of the carbonyl group in $R_1R_2>CO$ and their symmetry species[a]

State	Species ($R_1=R_2$)	Species ($R_1\neq R_2$)
$(\sigma_1,a_1)^2(\pi_1,b_2)^4(n_p,b_1)^2$	A_1	A'
" " $(n_p,b_1)^1(\pi_2,b_2)^1$	A_2	A"
" " $(n_p,b_1)^1(\sigma_2,a_1)^1$	B_1	A'
" $(\pi_1,b_2)^3(n_p,b_1)^2(\pi_2,b_2)^1$	A_1	A'

[a]Residual bonding and core electrons remaining essentially unchanged.

Table XV

Transitions and electronic selection rules for the carbonyl group

Transition	Electronic selection rules	
	C_{2v}	C_s
n-π	$^1A_2 \leftarrow\!\!- {}^1A_1$, forbidden	$^1A" \leftarrow\!\!- {}^1A'$, allowed
n-σ	$^1B_1 \leftarrow\!\!- {}^1A_1$, allowed	$^1A' \leftarrow\!\!- {}^1A'$, allowed
π-π	$^1A_1 \leftarrow\!\!- {}^1A_1$, allowed	$^1A' \leftarrow\!\!- {}^1A'$, allowed

of each state in formaldehyde.* These state-symmetry species are used to determine the symmetry-selection rule for combining states.[56] Possible transitions and their symmetry selection rules are given in Table XV, Columns 1 and 2, for formaldehyde.

As stated earlier, the transition describing the absorption must have forbidden characteristics. The n-π^* transition, $^1A_2 \leftarrow {}^1A_1$, symmetry-forbidden, fulfills this requirement and is the generally accepted description of the near-ultraviolet absorption.

The transition involves the excitation of a nonbonding electron of the n_p oxygen orbital to the π_2 antibonding orbital of the CO group (see Fig. 10). The excitation from the nonbonding orbital to the antibonding π orbital is in agreement with the reduced strength of the CO bond in the upper state.

a. The intensity of the transition.

The intensity of symmetry-forbidden electronic transitions generally arises because of vibrationally induced mixing of electronic states by vibrations of proper symmetry,[56,57] (see Appendix A-II, also).

Certain requirements must be fulfilled in order for intensity to result. First, the transition from the ground state to the perturbing state (i.e., the state mixing with the upper state of the forbidden transition) must be allowed by the symmetry-selection rules. Second, the mode of vibration responsible for the mixing must be of a symmetry species which makes the total symmetry of the upper state the same as that of the perturbing state (see Sponer and Teller[56]).

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*The state symmetry species are derived from the orbital species and the direct product tables; see Sponer and Teller, Ref. 56.

Pople and Sidman have employed this theory to calculate quantitatively the intensity of the n-π^* transition in formaldehyde.[16] They conclude that the perturbing state is the state of B_1 species (see Table XIV, Row 3). The transition from the ground state to this state is allowed. The vibration responsible for the mixing is concluded to be the out-of-plane bend of the two hydrogen atoms, ν_6, of b_2 symmetry.

The f-value calculated by Pople and Sidman, $f = 3 \times 10^{-4}$, is in good agreement with Duncan's experimental value, $f = 2.4 \times 10^{-4}$.[16] The agreement supports the description of the transition and the mechanism responsible for the intensity of the transition.

b. Isotope effect from the calculated intensity.

In a review of the method for calculation of the intensity,[16] it was noted that the intensity was dependent on the zero-point nuclear displacements of the hydrogen atoms of formaldehyde in the motion ν_6. An expression was derived from the equations given by Pople and Sidman[16] which relates the effect of isotopic substitution on the intensity of the transition. In effect, the ratio of the f-values is given by the ratio of the frequencies of the vibration ν_6 in the respective derivatives,

$$f_H/f_D = (\nu_a)_H/(\nu_a)_D \ , \qquad \text{(AII-6')}$$

where H and D indicate normal and deuteroaldehyde values, and ν_a is ν_6.* The details of the derivation are given in Appendix A-II. It should be noted, however, that equations from Murrel and Pople[58] were employed in the derivation (of course, the result is the same when using the equations in Pople and Sidman[16]). It is important that an omission in one of the

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*The frequency ν_a is the ground-state frequency of the vibration a (see Appendix A-II).

equations in Pople and Sidman be corrected. Their Eq. 13 should read:

$$\overline{Q_a^2} = h/8\pi\nu_a\mu.$$

In order to apply Eq. (AII-6!) to the higher aldehydes where the experimental data are available, it is necessary to propose that the intensity arises in the same manner as described for formaldehyde. Let us discuss briefly some justification for this proposal.

2. The higher aldehydes

Since the absorption appears at approximately the same wave length for all the aldehydes, the transition must involve the same orbitals of the CO group. Thus, the transition is n-π in all the aldehydes (see Fig. 10).

The higher aldehydes have at most C_s symmetry ($R_1 \neq R_2$), and, by strict application of symmetry considerations, the n-π transition is $A'' \leftarrow A'$, allowed. (On this basis, the transition becomes allowed in HDCO, also; see Tables XIV and XV, Columns 3). The experimentally observed f-values are in contradiction to this result. The values show some increase (see Table XII), but they are still far below the value expected for a fully allowed transition.

The increase in the f-value from formaldehyde to acetaldehyde, 2.4×10^{-4} to 3.5×10^{-4}, is small, which indicates that the transition retains its forbidden characteristics even though the symmetry of the molecule is reduced and the transition becomes formally allowed. Thus, all the aldehydes retain the C_{2v} symmetry characteristics of the formaldehyde molecule. (This was originally proposed by Mulliken[11] and McMurry,[12] and arguments are presented in their papers in support of the proposal. Appendix A-II of this thesis contains a discussion of the exactness of symmetry selection rules, and further consideration of the transition is given there.)

For an R_1R_2CO molecule, R_1 and (or) R_2 are instrumental in changing the characteristics of the transition only to the extent that they interact with the orbitals of the CO group. (See the work of Sklar[60] on the effect of group substitution on the analogous forbidden transition in benzene.) In the aliphatic aldehydes, the R-CO bonds are localized bonds, σ bonds, therefore they offer little interaction with the CO orbitals involved in the transition. The alkyl groups show only a slight increase in interaction relative to a hydrogen atom.[60] In essence, the C_{2v} symmetry of the >CO group remains essentially unchanged, and the description of the transition for formaldehyde applies to all the aliphatic aldehydes.

The greater part of the intensity in the higher aldehydes, therefore, is derived by the same mechanism as given for formaldehyde. That is, the intensity results from the vibrationally induced mixing of excited states, and the vibration responsible for the interaction must give the same relative motion in all the aldehydes.

This vibration, in formaldehyde, is the out-of-plane bend of the hydrogen atoms.[16] The corresponding vibration in the higher aldehydes is the out-of-plane bend of the hydrogen (deuterium) atom of the CHO group, the a"CH wag.

Comparison of experiment with theory

From Eq. (A-II-6') and the frequencies of the vibration a in the deutero and normal aldehydes, the ratio of the f-values can be calculated and compared with the ratios from experiment.

Accurate values for the a"CH wag frequencies in both the normal and deuteroaldehyde are available for acetaldehyde only.* The values

*No band which could be assigned to the a"CD vibration in propional-d_1 was observed; see Discussion, Infrared, p. 55.

of these frequencies, the calculated ratio, and the observed ratio are given in Table XVI. The agreement between the values is very good, and can be accepted as support for the description of the transition and the theoretical methods of calculating the intensity of such forbidden transitions.

Table XVI

f-Value ratios from theory and experiment for acetaldehyde and propionaldehyde[a]

Compound	ν_a cm^{-1}	f_H/f_D (theory)	f_H/f_D (experimental)
CH_3CHO	763	1.14	1.14 ± 0.02
CH_3CDO	668		
C_2H_5CHO	791	-	1.11 ± 0.02
C_2H_5CDO	~ 690		

[a]The frequencies of the vibration a are taken from Tables II and XI.

The experimental ratio for propionaldehyde is included in the table, also.[†] Although no reliable calculated value can be given,* the experimental value is in agreement with theory, that is, it is greater than unity. The agreement between this value and the value for acetaldehyde is support for the experimentally determined ratio in acetaldehyde.

*No band which could be assigned to the a"CD vibration in propional-d_1 was observed; see Discussion, Infrared, p. 55.

[†]The value for the ratio for butyraldehyde, 1.2, is doubtful because of the questionable purity of the sample of butyraldehyde-d_1. The f-value obtained from the spectrum of this sample was lower than the f-value for propional-d_1, in contradiction to the observations in the normal compounds.

CONCLUSIONS -- ULTRAVIOLET INVESTIGATION

The absorption envelopes of the n-π^* transitions in higher aliphatic aldehydes show little change upon isotopic substitution of the formyl hydrogen.

The broad bands present in all the spectra, assigned as the CO upper-state stretch progression, are shifted to the violet in the spectra of the deuteroaldehydes. The shift is explained by zero-point energy considerations.

The reduction in the intensity of the n-π^* absorption in each aldehyde when the formyl hydrogen is replaced by deuterium is a result of the mechanism responsible for the intensity of this symmetry-forbidden transition.

By the method outlined in Appendix A-II, the effect of isotopic substitution on the intensity of symmetry-forbidden electronic transitions can be calculated.

The effect of isotopic substitution on the intensity of allowed electronic transitions has been considered (see Appendix I). It was concluded that small but possibly detectable effects on the f-value may occur.

The exactness of the electronic selection rules derived from the nuclear symmetry of a molecule has been discussed (see Appendix A-III). It is suggested that better qualitative insight into the nature of a transition may be gained by deriving the selection rules from the effective potential field of the nuclear array of a molecule.

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APPENDIX A-I

INTENSITIES OF ELECTRONIC TRANSITIONS IN POLYATOMIC MOLECULES: EFFECT OF ISOTOPIC SUBSTITUTION

Here, the intensity of electronic transitions in polyatomic molecules will be considered with regard to possible changes in intensity resulting from isotopic substitution. The theory of the intensity of electronic transitions in molecules has been the subject of numerous publications,* and considered in a number of texts.

The theory will be given briefly and then each term in the expressions will be considered with regard to possible isotope effects.

The probability of an electronic transition between any two electronic states k and k' is proportional to the square of the transition moment,

$$R = \int \Psi_{kl}(X,Q) M(X,Q) \Psi_{k'l'}(X,Q) dQ, \qquad \text{(A-I-1)}$$

where the Ψ_{kl}'s are the complete wave functions of the combining states, k and l are quantum numbers describing the electronic and vibration states, and Q and X are collective symbols for the electronic and nuclear coordinates, respectively. Through the usual assumptions,* the transition moment becomes

$$R = \int \Phi_{kl} R_{kk'}(Q) \Phi_{k'l'} dQ, \qquad \text{(A-I-2)}$$

where the Φ_{kl}'s are vibrational wave functions of the klth vibronic level and

$$R_{kk}(Q) = \int \Theta_{k}(X,Q) M(X) \Theta_{k'}(X,Q) dX \qquad \text{(A-I-3)}$$

*See Reference 61, p. 200 , and references given therein. Also see Refs. 38, 56, 57, 58, and 62.

is a variable electronic-transition moment dependent on the nuclear configuration (Q). The electronic selection rules[56] are determined from the symmetries or symmetry species of the electronic wave functions Θ_k given by the nuclear configuration $(Q)_o$ of the initial of the combining states.

When the transition is allowed, the integral will have value and the oscillator strength of the vibronic transition k'l' $\leftarrow$ kl is given by

$$f_{k'l' \leftarrow kl} = \frac{8\pi^2 m c}{3h^2 e^2} E_{k'l' \leftarrow kl} |R|^2 \quad \text{(A-I-4)}$$

where $E_{k'l' \leftarrow kl}$ is the excitation energy for the transition, m is the mass of the electron, c is the velocity of light, h is Planck's constant, and e is the electron charge. The oscillator strength of the total electronic band for absorption from the initial vibronic level kl is

$$f_{kk'} = \sum_{l'} f_{k'l' \leftarrow kl}, \quad \text{(A-I-5)}$$

where $f_{k'l' \leftarrow kl}$ is given by Expression (A-I-4). In general, the assumption is made that $R_{k'k}(Q)$ varies slowly with (Q) and may be replaced by an average value $\overline{R_{k'k}}$ and removed from the integral over Q. Then from the quantum-mechanical sum rule,[61] expression (A-I-5) is given by

$$f_{k'k} = CE_{k'k} \left|\overline{R_{k'k}}\right|^2, \quad \text{(A-I-6)}$$

where C contains the constants of (A-I-4) and $E_{k'k}$ is an average energy for the transition. The validity of the assumption that the variation of $R_{k'k}(Q)$ with change in Q is slow has been questioned recently.[62]

The following discussion is in general confined to absorption from the ground vibrational level of the initial electronic state.

The Excitation Energy

Changes in the total oscillator strength resulting from differences in the excitation energy will be of the order of magnitude of

$$(E_{k'k})_I/(E_{k'k})_{II} \cong (E_{k'k})_I/[(E_{k'k})_I + (\Delta e_k - \Delta e_{k'})], \qquad \text{(A-I-7)}$$

where I and II are different isotopic species of a given molecule and Δe is the zero-point energy change in the respective electronic states as a result of the changes in nuclear masses. When both k and k' are bound states, the value of $(\Delta e_k - \Delta e_{k'})$ will be small with respect to $E_{k'k}$, and negligible isotope effects (usually less than 1%) can be expected.

In comparing the oscillator strengths of particular vibronic transitions $k'l' \leftarrow kl$, the energy $E_{k'l \leftarrow kl}$ may change by a significant amount of the total energy, that is, the value of the expression

$$\frac{(E_{k'l' \leftarrow kl})_I}{(E_{k'l' \leftarrow kl})_{II}} \qquad \text{(A-I-8)}$$

may be greater or less than unity by an observable amount. Here, however, the overlap integral may play a more important role in intensity determinations. Changes of the excitation energy because of vibrational energy complications are more important as the energy for electronic excitation becomes smaller. The electronic energies of the combining states, which are functions of the nuclear configurations, are expected to remain unchanged with isotopic substitution. (See Ref. 63, especially Part XII.)

The Electronic Transition Moment

The value of $R_{k'k}(Q)$ is dependent on the nuclear configuration (Q) which includes, of course, internuclear distances.* The expression

*See Fraser[62] or Sponer and Teller.[56]

(A-I-3) is usually evaluated for the equilibrium configuration of the initial vibronic state for use in (A-I-6). If the initial vibronic state is the vibrational ground state of the electronic state, the value of $\overline{R_{k'k}}$ should remain unchanged by isotopic substitution, as the equilibrium configuration remains unaltered unless the potential surface of the molecule is considerably anharmonic in the coordinates of the substituted nuclei.

When the electronic state contains anharmonic potential surfaces, changes in $R_{k'k}(Q)$ upon isotopic substitution can be expected, especially when the initial state is one highly excited in vibrations that are anharmonic. Thus, for absorption at high temperatures or in emission, the electronic-transition moment for corresponding vibronic levels kl in different isotopic derivatives of a molecule may well differ by a significant amount.

When $R_{k'k}$ is not assumed constant and not evaluated at the equilibrium configuration, but rigorously considered a function of Q and retained in the integral as in Expressions (A-I-2) and (A-I-3), isotope effects may arise because of changes in the magnitude of the nuclear displacements in the normal modes. The dependence on nuclear configuration may be realized by expanding $R_{k'k}(Q)$ in a power series in nuclear displacements*

$$R_{k'k}(Q) = R_{k'k}(Q)_0 + \Sigma_i R_{k'k}(Q)_i q_i + \cdots , \qquad \text{(A-I-9)}$$

where $R_{k'k}(Q)_0$, $R_{k'k}(Q)_i$, ... are coefficients in the expansion and the q_i represent the magnitude of the displacements in the ith normal vibration. The terms in the summation add contributions to the transition moment R, in Eq. (A-I-2), given by

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*See Sponer and Teller,[56] p. 97.

$$R_{k'k}(Q)_i \, \Phi_{ki} \, q_i \, \Phi_{k'i} \, dQ \qquad \text{(A-I-10)}$$

plus higher terms. The values of these terms are dependent on the mass of the vibrating system, as can be demonstrated by using simple harmonic-oscillator wave functions.

Let

$$q_i = x,$$

$$\Phi_{ki} = \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha x^2/2}$$

and

$$\Phi_{k'i} = \left(\frac{4(\alpha')^3}{\pi} \right) x \, e^{-\alpha' x^2/2},$$

where $\alpha = 4\pi^2 m\nu/h$ and $\alpha \neq \alpha'$; that is, the restoring-force constants are different in the two electronic states. Now, the value of the integral in Eq. (A-I-10) becomes

$$\left[\frac{4\alpha(\alpha')^3}{\pi^2} \right]^{1/4} \int_{-\infty}^{\infty} \exp\left(-\alpha x^2/2\right) x^2 \exp\left(-\alpha' x^2/2\right) dx, \qquad \text{(A-I-11)}$$

which upon evaluation gives

$$\frac{(\alpha)^{1/4} (\alpha')^{3/4}}{2^{1/2}(\alpha - \alpha')^{3/2}} , \qquad \text{(A-I-12)}$$

and since α and α' are mass-dependent, the contributions are different for various isotopic species. Thus, possible isotope effects on the total intensity of an electronic band may result from the electronic transition moment's being a variable in nuclear displacement.

The Overlap Integral

When $R_{k'k}(Q)$ is assumed constant and removed from the integral in Eq. (A-I-2) we are left with the Frank-Condon overlap integral,

$$\int \Phi_{k'l'}(Q)\ \Phi_{kl}(Q)\, dQ, \qquad \text{(A-I-13)}$$

which differs in value in many cases for a specific transition $k'l' \longleftarrow kl$ because the vibrational states l and l' in the electronic states k and k' lie at different energies for different isotopic derivatives. Since the equilibrium configurations for k and k', in general, differ, the region and the magnitude of the range in Q where Φ_{kl} and $\Phi_{k'l'}$ both have value may be markedly different for two isotopic derivatives. Therefore, the integral in (A-I-13) may also be different. Evaluation of the overlap integrals for polyatomic molecules would require accurate knowledge of the combining wave functions, and considerable difficulty would undoubtedly be encountered with very complicated molecules. However, a few generalizations can be made.

The frequency range of absorption is expected to be smaller for the heavier isotopic derivative because the vibrational wave functions are more restricted in coordinate space. Since the bonding in the upper electronic state is usually weaker, the absorption, in general, is shifted to the violet. These simple effects are self-explanatory when suitable diagrams are constructed.

If the sum rule is invoked here, the total electronic band intensity is expected to be independent of the overlap integral. That is, for

$$\left(\sum_{l'} \left| \int \Phi_{k'l'}(Q)\ \Phi_{kl}(Q)\, dQ \right| \right) = 1,$$

for I and II, the f-values of I and II are dependent only on the quantities in Expression (A-I-6).

Summary

The magnitude of the effects discussed here is, of course, larger the greater the relative change in the mass of the nuclei of the molecule of concern. In general, small but possible significant (i.e., possibly observable) isotope effects on the total oscillator strength of allowed transitions in polyatomic molecules are expected. To the author's knowledge, no reports of experimental observation of isotope effects of this type have been published (a few anomalies have been reported for diatomic molecules, but total intensities were not obtained[64]). The experimental observation of isotope effects on the total intensity of allowed transitions in polyatomic molecules, which may have been too small for detection by photographic techniques, may now be possible with sensitive photoelectric instruments.

APPENDIX A-II

FORBIDDEN ELECTRONIC TRANSITIONS: EFFECT OF ISOTOPIC SUBSTITUTION

The general theory for the original of the intensity in symmetry forbidden electronic transitions was developed by Herzberg and Teller[57] in 1933 and the selection rules for these transitions in polyatomic molecules have been discussed in detail by Sponer and Teller.[56] Since the general theory was developed, considerable advances in the determination of electronic wave functions have been made and as a result, quantitative applications of the theory have been possible.[16,58,65]

The results of the investigations discussed in the main body of the thesis indicate that the application of isotopic substitution to the study of symmetry-forbidden electronic transitions may well prove to be a useful tool. The general theory of these transitions is discussed here with regard to what effects may be expected upon isotopic substitution.

As stated in Appendix A-I, the intensity of an electronic transition is, to a first approximation, proportional to the square of the electric dipole transition moment (Eqs. (A-I-1), (A-I-2), and (A-I-3)), and a transition is said to be forbidden if, because of the symmetry of the electronic wave functions of the combining states,† the transition moment $R_{k'k}(Q)_0$ is zero. If weak bands arise, their intensity results from instantaneous nonzero values of $R_{k'k}(Q)$ because of displacements of the nuclei from the equilibrium configuration of the initial state by molecular vibrations with proper symmetry.*

We shall follow through, briefly, the development of the equations employed in the calculation of the intensity of these transitions and

†See Sponer and Teller, Ref. 56, p. 79.

*See Sponer and Teller,[56] p. 98.

arrive at equations that give the order of magnitude of the change in intensity to be expected upon isotopic substitution.

In the following treatment, the theory as presented by Murrel and Pople[58] is used. For the sake of simplicity, we consider absorption from only the zero vibration level of the ground state to the appropriate vibronic levels (the usual case for absorption at low temperatures). No great difficulties are expected, however, in the determination of the isotope effect from other initial levels.

Let us start with Eqs. (A-I-3) and (A-I-4) as they would apply for the case under consideration,

$$R_{ko}(Q) = \int \Theta_o\,(Q,X)\; M(X)\; \Theta_k(Q,X) \qquad \text{(A-II-1)}$$

and

$$f_{kl\leftarrow\!\!-\infty} = C\, E_{kl\leftarrow\!\!-\infty} \left| \int \Phi_\infty(Q) R_{ko}(Q) \Phi_{kl}(Q)\, dQ \right|^2 \qquad \text{(A-II-2)}$$

Here, C contains the constants of (A-I-4), and the excited state is represented by the quantum numbers k and l. For the transitions with which we are concerned, $R_{ko}(Q)$ is zero when evaluated at the equilibrium configuration $(Q)_o$, and the intensity of the transition results from the instantaneous nonzero values of the variable transition moment $R_{ko}(Q)$.

The intensity of the whole electronic band is given approximately by

$$f_{ko} = \Sigma_l f_{kl\leftarrow\!\!-\infty} = C\, E_{ko}\, (R_{ko})^2 \qquad \text{(A-II-3)}$$

The expression is obtained from (A-II-2) by substitution of an average energy of the transition for $E_{kl\leftarrow\!\!-\infty}$ and summing over l. $(R_{ko})^2$ is the mean square of the variable transition moment $R_{ko}(Q)$, evaluated

for the ground state. It is important to recognize the difference between Expressions (A-I-5) and (A-II-3). The square of the average value of $R_{k'k}(Q)$ in Expression (A-I-5) has been replaced by the mean square of $R_{ko}(Q)$ to give Expression (A-II-3).

The details of the evaluation of the mean square of the transition moment are readily available in the paper by Murrel and Pople.[58] Here, it will be sufficient only to point out the part of the expression for $(R_{ko})^2$ which depends on the mass of the nuclei in the molecule. In the expression

$$(R_{ko})^2 = \Sigma_a (dR_{ko}(Q)/dQ_a) \overline{Q_a^2} , \qquad \text{(A-II-4)}$$

Q_a is the normal coordinate of the ath normal mode of motion and $\overline{Q_a^2}$ is the zero-point mean square displacements of the nuclei in the ath zero-point vibration. The quantity $(dR_{ko}(Q)/dQ)$, which gives, in essence, the change of the electronic transition moment during vibration a, is evaluated for the equilibrium nuclear configuration of the initial state. Since the equilibrium nuclear configuration and the normal modes are expected to remain unchanged upon isotopic substitution,[55] the value of $(dR_{ko}(Q)/dQ)$ for each mode a remains unchanged for the various isotopic derivatives of a molecule.

The quantity $\overline{Q_a^2}$ in (A-II-4) may be evaluated,[55] if the oscillators are assumed to be harmonic, by

$$\overline{Q_a^2} = (v + 1/2)\ h\ \nu_a/k_a, \qquad \text{(A-II-5)}$$

where v, the number of quanta of excitation in the ath mode, is zero for the transitions being considered, and ν_a and k_a are the frequency and force constant, respectively, for the ath normal mode in the initial

electronic state (here, the ground state). The force constant, k_a, remains unchanged when an isotopic substitution is made in the molecule.

The individual terms of the summation (A-II-4) express the effectiveness of each mode a in making the transition allowed. For a forbidden electronic transition, where the majority of the intensity results from interactions produced by displacements in a single vibrational mode a the ratio of the oscillator strengths for the two isotopic species I and II is given by

$$(f_{ko})_I/(f_{ko})_{II} = (E_{ko}\nu_a)_I/(E_{ko}\nu_a)_{II} \cong (\nu_a)_I/(\nu_a)_{II} \, . \qquad \text{(A-II-6)}$$

If the theories are correct and the assumptions involved are valid, the experimentally observed ratio of the f-values for derivatives I and II will be equal to the ratio of the frequencies of the mode a, obtained from the vibrational (infrared or Raman) spectra of the two derivatives. Examples of this type are given later in this Appendix.

When more than one mormal mode and possibly more than one perturbing state are involved in the intensity borrowing for the forbidden transition, the ratios of the total intensities of the electronic band for the isotopic derivatives of a molecule cannot be given by the simple expression (A-II-6), but each term in the summation (A-II-4) must be evaluated for each derivative and then the ratio of the summations gives the desired ratio of total intensities,

$$\frac{(f_{ko})_I}{(f_{ko})_{II}} = \frac{(E_{ko}\sum_a (\partial R_{ko}(Q)/(\partial Q_a)\ \overline{Q_a^2})_I}{(E_{ko}\sum_a (\partial R_{ko}(Q)/\partial Q_a)\ \overline{Q_a^2})_{II}} \qquad \text{(A-II-7)}$$

If it should be possible to separate the bands in such an electronic transition, and by use of the selection rules assign them as allowed by a

particular mode a, then the ratio of the sum of the intensities of separated band systems for different isotopic species would be given by Expression (A-II-6).

Application to a Few Specific Molecules

The n-π* Transitions of Aldehydes and Ketones

In the main body of the thesis, the theoretical work for formaldehyde[16] has been extrapolated to the higher aldehydes, and the isotope effects calculated as proposed in this Appendix are in agreement with experimental values for the n-π* transitions in the normal and monodeuteroaldehydes. The oscillator strength of the transition in each aldehyde is expected to decrease further as the aldehydes are more highly deuterated. This is expected because the CH and CD out-of-plane mode is not a pure H or D motion but is a group motion involving other nuclei in the molecule. The ratio of the oscillator strengths for acetaldehyde and acetaldehyde-d_4 is given in Table XVII.

No f-values for the n-π* transition in deuteroformaldehydes are available, but the frequencies of the fundamental mode ν_6, the mode predicted[16] to be most active in the intensity-borrowing mechanism, are available.[55,66] Therefore it is possible to predict the ratio of the oscillator strengths for the n-π* transition in H_2CO and HDCO, and H_2CO and D_2CO. The values of these ratios are given in Table XVII.

The intensity of the forbidden n-π* transition in acetone is undoubtedly derived in the same manner as for the aldehydes. By analogy, the mode of motion responsible for the greater part of the intensity is the mode ν_6 in which the two carbon atoms and the oxygen atom bonded to the central carbon atom are displaced out of the plane

Table XVII

Some predicted f-value ratios for vibrationally allowed transitions

Compound		Transition	ν_a Frequency	f_I/f_{II}
H_2CO	(I)	n-π*	1165[a]	
HDCO	(II)	"	1074[b]	1.08
D_2CO	(II)	"	938[a]	1.24
CH_3CHO	(I)	"	763[c]	
CD_3CDO	(II)	"	570 or 650[c]	1.34 or 1.17
$(CH_3)_2CO$	(I)	"	391[d]	
$(CD_3)_2CO$	(II)	"	335[d]	1.17
C_6H_6	(I)	$^1B_{2u} \leftarrow {}^1A_{1g}$	606.5[e]	
C_6H_5D	(II)	"	603	< 1.01
$C_6H_3D_3$	(II)	"	593	1.02
C_6D_6	(II)	"	577	1.06
C_6H_6	(I)	$^1B_{1u} \leftarrow {}^1A_{1g}$	1596	
$C_6H_3D_3$	(II)	"	1573	~ 1.01
C_6D_6	(II)	"	1552	1.03

[a] Frequencies from Halverson.[31]

[b] Frequencies from Davidson et al.[66]

[c] See Table II.

[d] Frequencies from Lawson and Duncan.[67]

[e] All benzene frequencies from Ingold and co-workers.[63]

of symmetry in one direction and the central carbon in the opposite direction. In this mode, the methyl groups move as a unit and the frequency is dependent on the mass of the methyl groups. The frequencies assigned to this vibration in acetone and acetone-d_6 are available,[67] and the ratio expected for the experimentally determined oscillator strengths for the n-π^* transition in the two molecules is given in Table XVII.

Benzene

The λ2650-A and λ2000-A bands of benzene have been assigned as $^1B_{2u} \leftarrow {}^1A_{1g}$ and $^1B_{1u} \leftarrow {}^1A_{1g}$, respectively. Both are symmetry-forbidden, but the e_{2g} vibrations of the benzene framework at 606 cm^{-1} and 1595 cm^{-1} are capable of producing intensity through interaction with the allowed λ1800A $^1E_{1u} \leftarrow {}^1A_{1g}$ transition. The greater part of the intensity of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition results from the influence of the 606 cm^{-1} vibration,[56,60,65,68] which in benzene-d_6 has the frequency 577 cm^{-1}, giving an expected ratio of oscillator strengths of 1.06. Values for various other deuterobenzenes are included in Table XVII. The $^1B_{1u} \leftarrow {}^1A_{1g}$ transition, according to theory,[58] derives the greater part of its intensity from interactions brought about by the 1595-cm^{-1} vibration in benzene. Values of the expected oscillator-strength ratio for this transition are given in Table XVII.

There are undoubtedly many other cases in which forbidden transitions in molecules are made "allowed" by vibrations in which the reduced mass of the vibrating system may be changed by isotopic substitution. Of course, the magnitude of the change in oscillator strength is proportional to the change in the reduced mass of the

vibrating system. Therefore, measurable effects can be expected only when the reduced mass of the vibrating system undergoes a considerable change upon isotopic substitution.

Studies of isotope effects on forbidden transitions for which the spectrum is too complex to permit analysis may be useful in determining what mode of vibration is active in the intensity-borrowing mechanism. A knowledge of the ground-state vibrational frequencies of all the modes suspect as active must be available for each isotopic derivative, the information being available from Raman and (or) infrared studies.

Agreement between the experimental isotope effects and those calculated by using the theory for the intensity of forbidden transitions[57,58] as outlined in this Appendix should serve to confirm the methods of calculation and support the general theory.[57]

APPENDIX A-III

THE ELECTRONIC SELECTION RULES

The selection rules as obtained from molecular symmetry, that is, from the symmetry of the nuclear configuration, are discussed quite thoroughly by Sponer and Teller.[56] The symmetry types of species of the combining electronic wave functions of a molecule are determined, in general, from the point-group symmetry of the nuclear configuration of the initial electronic state, usually the equilibrium configuration.

The species of the electronic wave functions are perhaps better obtained from the point-group symmetry of the potential field of the nuclear array. That is, the species of combining electronic wave functions should not be determined explicitly from the nuclear symmetry of the molecule, but rather by the symmetry of the potential field of the nuclear array with which the electrons are interacting, the nuclear array being the equilibrium configuration of the initial state.

These statements are valid within the Born-Oppenheimer approximation and the Frank principle.[69] The electronic wave functions are solutions of the Schrödinger equation with the nuclei held at fixed position, therefore the masses of the nuclei are ineffectual in the determination, but the effective potential field of the nuclear array is important. In an electronic transition, the nuclei, according to the Frank principle, remain fixed in position for the duration of the electronic rearrangement.[69] For this reason, the species of the electronic wave functions are determined essentially by the potential field of the equilibrium nuclear array of the initial electronic state.

Since the equilibrium configuration of a molecule is, in general, unaffected by isotopic substitution (especially the vibrational ground-level array of an electronic state), the symmetry of the potential field and consequently the species of the electronic wave functions remain unaltered. Thus, the electronic selection rules remain unchanged when the nuclear symmetry of a polyatomic molecule is destroyed or changed by isotopic substitution.

The selection rules for vibrational transitions will, of course, be altered upon isotopic substitution,[55] since the vibrational wave functions of the molecule depend on the mass of the nuclei.

Extending the suggestion that the species of combining wave functions be determined from the potential field symmetry of the molecule to cover atom or group substitution as well as isotopic substitution may be helpful in understanding the forbidden character of some transitions. This may be similar to or incorporated in the suggestion that local symmetry be used for the electronic-transition selection rules.[70] Transitions like the n-π^* transitions in the aldehydes and ketones can be explained as follows. Simply, the nuclear C_{2v} symmetry may be destroyed by substitution, making the transition allowed, but the potential field symmetry of the molecule or of the group where electronic changes occur during the transition remains essentially unchanged, and the transition retains most of the forbidden characteristics.

When the principle is more exactly applied to the n-π^* transition in aldehydes and ketones,* one arrives at the results shown in Table

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*Sklar[60] has treated the substituted benzenes in an analogous manner. The method used here serves for qualitative understanding.

XVIII. For symmetrical ketones and formaldehyde, the 0-0 band is expected to be missing and the low-temperature spectrum (no v" vibrations excited) to be made up of one or more $n_a v'_a$-0 origins with the complete vibrational system of an allowed transition superimposed on each of these origins. As the temperature is raised 0-$n_a v''_a$ origins can be expected as well as various sequences $\Delta v_1 = 0$. A spectrum of this type will be very complex, especially when the molecule has many normal modes and the separations between the v_a levels in the combining electronic states are small. The n-π^* transition in acetone does have a spectrum (room temperature, vapor phase) which has many overlapping bands and a continuous appearance.

In the higher aldehydes at low temperatures, the 0-0 band origin and the complete vibrational system is expected as well as the origins $n_a v'_a$-0 with their respective complete vibrational systems. Therefore even with no "hot" bands, the spectrum of the aldehydes can be expected to be very complicated because of the possibility of several, at least two, band system origins for the same electronic transition. The spectrum from the n-π^* transition in any aliphatic aldehyde obtained at liquid helium temperatures, although it may be much simpler than the room temperature spectrum, will be very complicated, but a vibrational assignment may be possible with the understanding that more than one origin is possible.[56,68,71] The vapor-phase, room temperature spectra of the aliphatic aldehydes are complex, as expected from the above arguments as well as from the reasons set forth in the Discussion of the Ultraviolet Spectra.

The relative strengths of the allowed portion (0-0 origin and vibrational system) and forbidden portion (nv'_a-0 and 0-nv''_a origins

and their vibrational systems) of the spectrum may well vary with R_2 where R_1 is hydrogen. In the aliphatic aldehydes the allowed portion, with reference to the oscillator strengths of formaldehyde[16] and the symmetrical ketones (see Table XIII), is expected to have an oscillator strength less than or at most equal to that of the forbidden system.

Since the allowed portion of the absorption is not affected by isotopic substitution (see Appendix A-I), a ratio calculated from Eq. (A-II-6) on the assumption that the intensity of the transition results only from the vibrationally induced mixing of excited states may be too high. Some of the values in Table XVII are subject to this criticism.

Table XVIII

Some characteristics of the n-π^* transition in R_1R_2>CO compounds

Characteristic	$R_1 = R_2$	$R_1 \neq R_2$
Symmetry[a]	C_{2v}	$C_{2v}^*(R_1 \cong R_2) \longrightarrow$ C_s as $(R_1 \neq R_2)$ increases[b]
Transition	$^1A_2 \leftarrow {}^1A_1$	$^1A_2^* \leftarrow {}^1A_1^*$ becoming increasingly $^1A'' \leftarrow {}^1A'$ as the potential field from R_1 and R_2 becomes more unsymmetrical and R_1 and (or) R_2 interact more with C = O.
Selection Rule	Forbidden	$^1A_2^* \leftarrow {}^1A_1^*$ weakly allowed; intensity increasing as $^1A'' \leftarrow {}^1A'$ character increases.
Vibrational transition moment produced by:	Vibrations v_a of b_2 species distorting the planar $\overset{A}{A}$> CO group.[c]	Vibrations v_a of b_2^* or a" species distorting the planar $\overset{A}{B}$> CO group.[c]
Band system origins (no hot bands)	$n_a v'_a$-0 ; n_a = 1,3,5, °,°	0-0 and $n_a v'_a$ - 0 ; n_a = 1,3,5,
Intensity	Will change with R group; dependent on interaction with the >CO group.	of 0-0 to $n_a v'_a$-0 will depend on interaction of R_1 relative to R_2 and the total intensity will depend on the interaction of both with >CO.

[a] See Fig. 10.

[b] The asterisk indicates the inexactness of the point-group symmetry.

[c] A and B are atoms bonded directly to the CO group.

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